

Experimental and theoretical FT-IR and FT-Raman spectroscopic analysis of N1-methyl-2-chloroaniline

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In this work, the experimental and theoretical vibrational spectra of N1-methyl-2-chloroaniline (C₇H₈NCl) were studied. FT-IR and FT-Raman spectra of the title molecule 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 by using density functional method (B3LYP) with 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 are 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. ¹³C and ¹H NMR chemical shifts results were compared with the experimental values. The optimized geometric parameters (bond lengths and bond angles) were given and are in agreement with the corresponding experimental values of aniline and *p*-methyl aniline. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: FT-IR and FT-Raman spectra; DFT; N1-methyl-2-chloroaniline; vibrational frequencies; ¹³C and ¹H NMR chemical shifts

INTRODUCTION

The molecular archetype of the aromatic amines is aniline. It and its derivatives have been widely used in pharmaceuticals manufacturing. Electro-optical, chemical dye industries and other commercial and industrial purposes have also been used them extensively.^[1–3] Some *para*-substituted derivatives of aniline are commonly used as local anesthetics, and among these molecules the amino group plays an important role in the interactions with the receptor. Therefore, in the view of understanding the properties of aniline and its derivatives, as well as their reaction mechanisms, extensive experimental^[4] and theoretical investigations have focused on the elucidation of the structure from the normal vibrations of aniline and its methyl derivatives.^[1–7] The inclusion of a substituent in aniline leads to variation in the molecular charge distribution, and consequently greatly affects the electronic, structural and vibrational parameters.^[8]

Vibrational assignments based on FT-IR in the vapor, solution and liquid phases and the Raman spectra in the liquid state were reported for aniline.^[9] They were also obtained in the gas phase from microwave spectroscopy^[10,11] and in the solid state from X-ray crystallography.^[12] Its structure was calculated using semi-empirical^[13,14] and *ab initio* methods.^[13,15,16] Recent studies on vibrational spectra of substituted anilines assigned^[1,5,17–20] complete vibrational modes and frequencies. Vibrational modes and frequencies analyses of *m*-methylaniline were studied by Altun *et al.*^[1] Assignments of some bands observed in the Infrared spectrum of *p*-methylaniline are given in the literature.^[4,21–25] The vibrational spectra of fluoromethyl aniline^[26,27] and chloromethyl aniline^[28] were reported. Shanker *et al.*^[29] studied of 2-chloro-

6-methylaniline (2Cl6MA) with polarized Raman and Infrared spectra. Barluenga^[30] synthesized and studied ¹H and ¹³C NMR spectra of 2-chloro-*N*-methylaniline (2-Cl-*N*-MA).

In spite of recent studies on vibrational spectra of aniline and a number of substituted anilines, neither IR and Raman spectra nor the quantum mechanical calculations for N1-methyl-2-chloroaniline (also known as 2-Cl-*N*-MA) have been reported, yet. Therefore, we have undertaken the detailed theoretical and experimental investigation of the vibrational spectra of this molecule. Density functional B3LYP calculations have been performed to support our assignment. A detailed interpretation of the vibrational spectra of 2-Cl-*N*-MA has been made on the basis of the calculated total energy distribution (TED). In addition, the gauge-including atomic orbital (GIAO) ¹³C and ¹H chemical shifts calculations of the title compound have been carried out by using B3LYP method with 6-311++G(d,p) basis set.

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EXPERIMENTAL

2-Cl-N-MA, 97%, was purchased from Acros Organics Company. The FT-IR spectrum of the title molecule, which is liquid at room temperature, was recorded between 4000 and 400 cm^{-1} on a Perkin Elmer FT-IR System Spectrum BX spectrometer calibrated using polystyrene bands. The spectrum was recorded with a scanning speed of 10 $\text{cm}^{-1} \text{min}^{-1}$ and the spectral resolution of 4.0 cm^{-1} . FT-Raman spectrum of the sample was recorded on a Bruker RFS 100/S FT-Raman 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.

CALCULATIONS

The molecular structure of 2-Cl-N-MA in the ground state (*in vacuo*) is computed by performing DFT/B3LYP methods with 6-311++G(d,p) basis set. The optimized structural parameters were used in the vibrational frequencies calculations at DFT level. For B3LYP with 6-311++G(d,p) basis set, the wavenumbers in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983, respectively.^[31] The theoretical results enabled us to make the detailed assignments of the experimental IR and Raman spectra. The TED was calculated by using the scaled quantum mechanics (SQM) program^[32] and the fundamental vibrational modes were characterized by their TED.

For NMR calculations, ^1H and ^{13}C NMR chemical shifts (δ_{H} and δ_{C}) were calculated using the GIAO method^[33] in chloroform (CDCl_3) at B3LYP method with 6-311++G(d,p) basis set. Relative chemical shifts were then estimated by using the corresponding TMS shielding calculated in advance at the same theoretical level as the reference. ^{13}C and ^1H isotropic magnetic shielding (IMS) of any X carbon (or hydrogen) atom was made according to the value ^{13}C IMS of TMS: $\text{CS}_x = \text{IMS}_{\text{TMS}} - \text{IMS}_x$ (^1H IMS of TMS: $\text{HS}_x = \text{IMS}_{\text{TMS}} - \text{IMS}_x$). The experimental values for ^1H and ^{13}C isotropic chemical shifts for TMS were 30.84 and 188.1 ppm, respectively.^[34]

All calculations are performed by using GaussView molecular visualization program^[35] and GAUSSIAN 03 program package on the personal computer^[36] and TED by using the SQM program.^[32]

RESULTS AND DISCUSSION

2-Cl-N-MA, with two substituents, chloro and *N*-methyl amino groups attached to a planar benzene ring, consists of 17 atoms, so it has 45 normal vibrational modes. On the basis of a C_s symmetry the 45 fundamental vibrations of 2-Cl-N-MA can be distributed as $30\text{A}' + 15\text{A}''$. The vibrations of the A' species are in plane and those of the A'' species are out of plane. If we take into account the C_s symmetry of this molecule, there are two imaginary frequencies correspond to $\text{CN}-\text{CH}_3$ out of bending and methyl rotation perpendicular to the ring plane (CH_3 torsion). The structure at any level was not a minimum energy structure. Two imaginary frequencies of irreducible representation belong to A'' . But if the molecule were C_1 , there would not be any relevant distribution whereas the molecule has a true minimum energy (e.g. $E(\text{B3LYP}) = -493613.3767 \text{ kcal mol}^{-1}$ for C_s symmetry and $E(\text{B3LYP}) = -493615.8048 \text{ kcal mol}^{-1}$ a.u. for C_1 symmetry by

using 6-311++G(d,p)). By using the same method and basis set, it was seen that all the vibrational frequencies were positive. Therefore, we were confident that a definite absolute minimum energy in the potential energy was found. The C_1 symmetry structure was the lowest in energy at all levels.

The molecular structure and numbering of the atoms of 2-Cl-N-MA is shown in Fig. 1. The geometric parameters (bond lengths and bond angles) were compared with those of aniline and *p*-methylaniline.^[4,11,20,25,37] The calculated vibrational frequencies are compared with the experimental FT-IR, FT-Raman spectra of title molecule.

Geometrical structure

The first task for a computational work was to determine the optimized geometry of 2-Cl-N-MA. The optimized structure parameters calculated with DFT (B3LYP) method and 6-311++G(d,p) basis set are listed in Table 1 in accordance with the atom numbering scheme given in Fig. 1. Our calculated results show that the aromatic ring in 2-Cl-N-MA is distorted from regular hexagon due to steric and electronic effects of the electron donating and electron withdrawing substituents.

To the best of our knowledge, experimental data on the geometric structure of 2-Cl-N-MA are not available in the literature. Therefore, we could not compare the calculation results given in Table 1 with the experimental data. The optimized geometric parameters of 2-Cl-N-MA are compared only to those of aniline and *p*-methylaniline.^[4,11,20,25,37]

Several authors^[38,39] have been explained the changes in frequency or bond length of the C—H bond, due to substitution, by 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 and Br...) or electron donating type (CH_3 , C_2H_5 ...). The carbon atoms are bonded to the hydrogen atoms with a 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 for substitution by electron donating groups. The actual change in the C—H bond length would be influenced by the combined

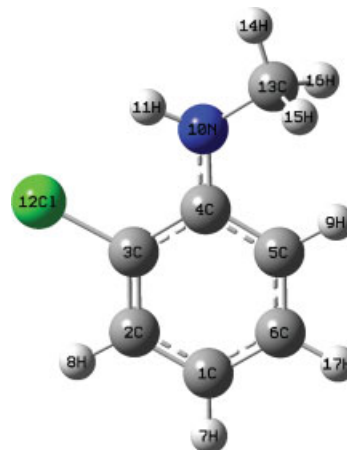


Figure 1. Optimized geometry of 2-Cl-N-MA structure and atoms numbering

Table 1. Optimized geometry of 2-Cl-N-MA in the ground state

Parameters	Exp ^[3]	Exp ^{abc}	
	<i>p</i> -methylaniline	Aniline	B3LYP
Bond lengths (Å)			
C1–C2	1.39	1.380, 1.394, 1.3933	1.395
C1–C6	1.39	1.404, 1.397, 1.403	1.392
C1–H7	1.08		1.083
C2–C3	1.40	1.386, 1.396, 1.3955	1.385
C2–H8	1.08	1.03, 1.082, 1.099	1.083
C3–C4			1.412
C3–Cl12		1.744, 1.745, 1.739 ^d	1.769
C4–C5	1.40	1.404, 1.397, 1.403	1.409
C4–N10	1.43	1.398, 1.402, 1.4057	1.376
C5–C6	1.39	1.380, 1.394, 1.3933	1.391
C5–H9	1.08	1.05, 1.08, 1.099	1.082
C6–H17	1.08	0.95, 1.083, 1.099	1.084
N10–H11	1.02	1.07, 1.001, 1.021	1.007
N10–C13			1.448
C13–H14	1.09		1.090
C13–H15	1.09		1.099
C13–H16	1.09		1.095
Bond angles (°)			
C2–C1–C6	117.8	117.6, 118.92, 119.03	119.00
C2–C1–H7			120.02
C6–C1–H7			120.98
C1–C2–C3	120.5		120.00
C1–C2–H8			120.85
C3–C2–H8			119.15
C2–C3–C4			122.30
C2–C3–Cl12	121.5	122.1, 120.70, 120.69	118.83
C4–C3–Cl12			118.87
C3–C4–C5	120.3	117.9, 119.43, 119.01	116.54
C3–C4–N10			121.20
C5–C4–N10		124.0, 120.28, 120.45	122.25
C4–C5–C6	120.5		121.25
C4–C5–H9			119.25
C6–C5–H9			119.49
C1–C6–C5	119.2	119.7, 120.12, 120.28	120.90
C1–C6–H17			120.06
C5–C6–H17			119.05
C4–N10–H11		119.0, 115.94, -	115.92
C4–N10–C13			123.07
H11–N10–C13			117.25
N10–C13–H14			108.49
N10–C13–H15			112.74
N10–C13–H16			111.19
H14–C13–H15	109.5		108.38
H14–C13–H16	109.5		107.63
H15–C13–H16	109.5		108.25
C6–C5–C4–N10			–178.28
C2–C3–C4–N10			178.43

^a From Reference [20].
^b From Reference [11].
^c From Reference [25].
^d From Reference [45].

effects of the inductive-mesomeric interaction and the electric dipole field of the polar substituent.

The equilibrium structure for the ground state shows that one of the methyl C—H bonds is parallel to the ring plane. In the *N*-methyl amino group, the nitrogen atom is slightly out of plane, with a torsional angle C2—C3—C4—N10 and C6—C5—C4—N10 of ca. 178° (or ca. 2°). A measure of this displacement is defined the tilt angle.^[20] Existence of this angle has been interpreted to be caused by asymmetric interaction between the *N*-methyl amine group and benzene ring plane. However, the X-ray angle value for this angle in aniline, 4.6°,^[12] is larger than the theoretical one. This interaction is common to all aniline derivatives.^[4,19]

The optimized N—H bond length by DFT with 6-311++G(d,p) method is 1.007 Å. By comparing this value with the experimental value of 1.02 Å for *p*-methylaniline (1.07, 1.001, 1.021 Å for aniline), it is observed that B3LYP estimate the N—H bond length fairly well.

The optimized C—C bond lengths in the ring in the range from 1.385 to 1.412 Å by the B3LYP with 6-311++G(d,p) method are in good agreement with those in *p*-methylaniline (1.39–1.40 Å) and aniline (1.380–1.404 Å). The C4—N10 bond distance of ca. 1.38 Å is just 0.05 Å lower than the reported experimental value of 1.43 Å for *p*-methylaniline.^[4]

The C—Cl bond length indicates a considerable increase as compared to the C—H bond. This has been observed even in benzene derivatives.^[40] The C—Cl bond length is found 1.769 Å. 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.*^[43] calculated C—Cl bond length at 1.767 Å (B3LYP), 1.75 Å (HF) and 1.789 Å (BLYP) for 3-Cl-4MA. In our previous paper,^[44] we calculated a C—Cl value in the range of 1.730–1.751 Å with HF, B3LYP and B3PW91 methods for 2-Cl-nicotinic acid. This bond length was also observed at 1.735–1.744 Å range for similar molecules.^[45–48] The C—H bond lengths in the benzene ring and methyl group are in agreement with experimental and literature values.^[1,3]

The asymmetry of the benzene ring is also evident from the negative deviation of the C3—C4—C5 and C2—C1—C6 angles which are calculated ca. 119° and positive deviation of C2—C3—C4 and C4—C5—C6 angles from the normal value of 120° (e.g. the C2—C3—C4 angle is found to be bigger than the hexagonal angles by ca. 2°. The remaining angles are ca. equal to normal value of 120°. Similar values are found in other aniline derivatives, *m*-methylaniline,^[1] *o*-methylaniline,^[7] *p*-methylaniline^[4] and 3-Cl-4MA.^[43] As discussed by Ballesteros *et al.*^[6] for *p*-methylaniline, C3—C4—N10 equals C5—C4—N10. Our calculated values are 121.20 and 122.25° for C3—C4—N10 and C5—C4—N10, respectively. This clearly shows that the substitution of H for Cl appreciably affects the C3—C4—N10 and C5—C4—N10 bond angles. Similar values were found for 3-Cl-4MA by Kurt *et al.*^[43]

NMR spectra

Initially, the molecular structure of 2-Cl-*N*-MA has been optimized with the 6-311++G(d,p) basis set. Then, GIAO ¹³C and ¹H chemical shift calculations have been made by using B3LYP method with 6-311++G(d,p) basis set. ¹H and ¹³C chemical shift values (with respect to TMS) have been calculated for the optimized structures of the title compound and compared to the experimental chemical shift values. The experimental and calculated values for ¹³C and ¹H NMR are shown in Table 2. As in Fig. 1, the studied molecule shows seven different carbon

Table 2. Theoretical and experimental ¹³C and ¹H NMR isotropic chemical shift (with respect to TMS, all values in ppm) for 2-Cl-*N*-MA

Atom	Experimental ^[30]	B3LYP/6-311++G(d,p)
C1	116.7	120.9
C2	128.7	134.9
C3	118.7	132.1
C4	144.8	151.4
C5	110.4	115.0
C6	127.6	133.7
C13	29.9	30.7
RMS		6.94
H7	6.9 ^a	6.9
H8	6.9 ^a	7.6
H9	6.9 ^a	6.8
H11	4.3	4.2
H14	2.8	3.1
H15	2.8	2.7
H16	2.8	2.9
H17	6.9 ^a	7.5
RMS		0.36
Overall RMS		4.74

^a Average value.

atoms. Taking into account that the range of ¹³C NMR chemical shifts for analogous organic molecules usually is >100 ppm,^[49,50] the accuracy ensures reliable interpretation of spectroscopic parameters. In the present paper, ¹³C NMR chemical shifts in the ring for the title compound are >100 ppm, as they would be expected (in Table 2). Nitrogen atom shows electronegative property. Therefore, the chemical shift value of C4 which is in the ring has been observed at 144.8 ppm^[30] (C=N) and calculated (with respect to TMS) 151.4 ppm. Similarly, five carbons peaks in the ring are observed from 110.4 to 128.7 ppm^[30] are calculated from 115.0 to 134.9 ppm. Besides, another carbon peak is calculated 30.7 ppm, is observed at 29.9 ppm^[30] (N—CH₃). The RMS values for carbon chemical shifts are found to be 6.94 for B3LYP method with the 6-311++G(d,p) basis set.

The studied molecule has four hydrogen atoms in the ring and three hydrogen atoms attached to the carbon atom and one hydrogen atom attached the nitrogen atom. In the ¹H NMR spectrum just one type of protons appears at 2.8 ppm^[30] as a singlet (CH₃), whereas the chemical shift values (with respect to TMS) of 2.7, 2.9 and 3.1 ppm have been determined by using B3LYP method, these values are shown in Table 2. The remainder of the observed and calculated ¹H NMR isotropic chemical shift values listed in Table 2. The RMS values for hydrogen chemical shifts are found to be 0.36 for B3LYP method with the 6-311++G(d,p) basis set.

As can be seen from Table 2, there is a very good agreement between experimental and theoretical chemical shift results for the title compound. The overall RMS values for carbon and hydrogen chemical shifts are found to be 4.74.

Vibrational spectra

In order to obtain the spectroscopic signature of 2-Cl-*N*-MA, we performed a frequency calculation analysis. Calculations were

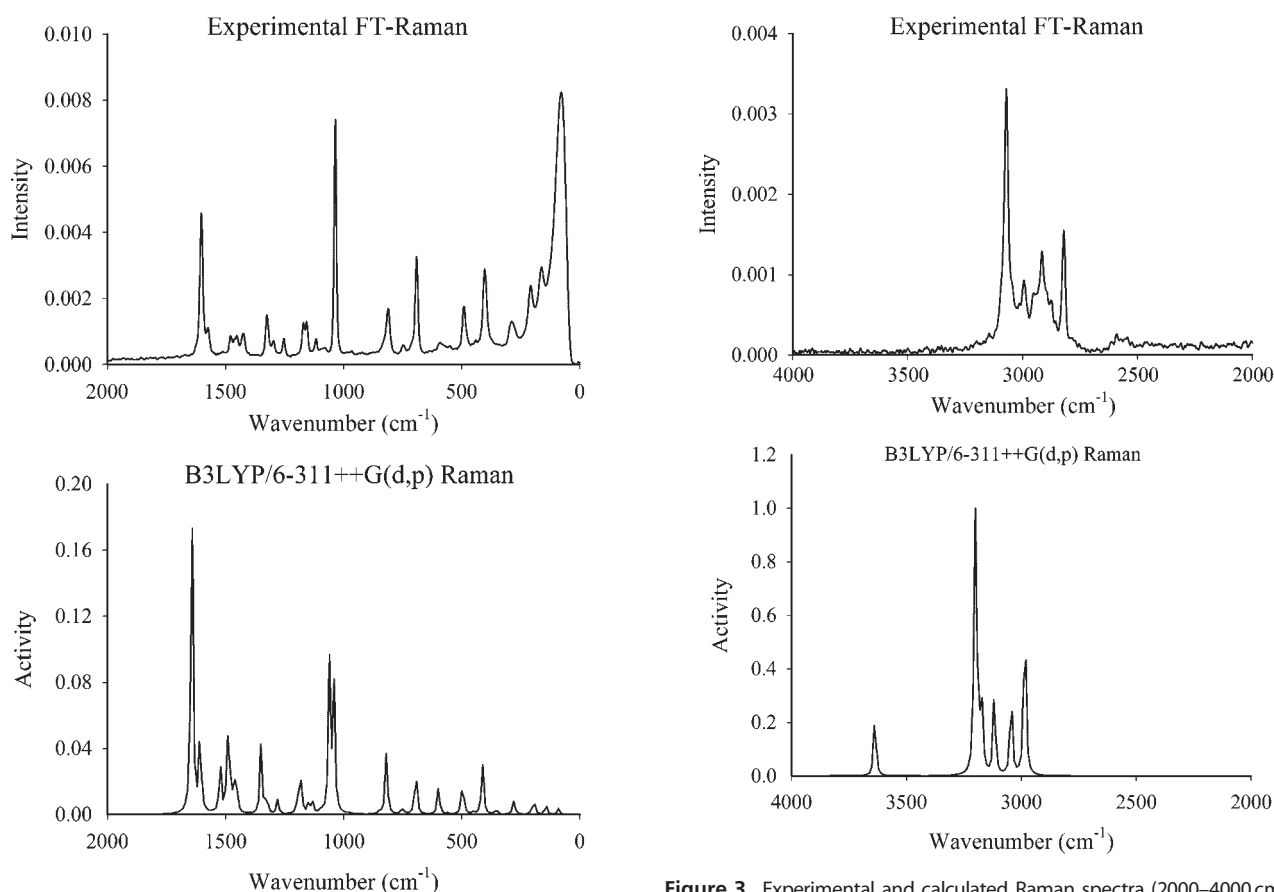


Figure 2. Experimental and calculated Raman spectra (0–2000 cm^{-1}) of 2-Cl-N-MA

made for a free molecule in vacuum, while experiments were performed for liquid sample, so there are disagreements between calculated and observed vibrational wavenumbers, and some calculated frequencies are not observed in the FT-IR and FT-Raman spectra.

The experimental and theoretical IR and Raman spectra are shown in Figs 2–5 for comparative purposes, where the calculated intensity and activity are plotted against the harmonic vibrational frequencies. The experimental wavenumbers, calculated wavenumbers and IR intensities and Raman scattering activities are given in Table 3. In the last column is given a detailed description of the normal modes based on the TED. All of the calculated modes are numbered from the biggest to the smallest frequency within each fundamental wavenumbers, ν_n , in the first column of the table.

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.^[51,52] These are usual ranges for CH_3 , NH_2 and ring C—H stretching vibrations. The N—H stretching vibrations occur in the region 3200–3500 cm^{-1} . The scaled N—H stretch is calculated at 3484 cm^{-1} and the experimental value is observed at 3431 cm^{-1} FT-IR. Accordingly, in the present study, the four adjacent hydrogen atoms left around the ring in 2-Cl-N-MA give rise to four C—H stretching modes (ν_2 – ν_5), four C—H in-plane bending (ν_{19} – ν_{21} , ν_{23}) and four C—H out-of-plane bending (ν_{27} , ν_{28} , ν_{29} , ν_{31}) vibrations which correspond to modes of C1—H7, C2—H8, C5—H9 and C6—H17 units. The vibrations ν_2 – ν_5

Figure 3. Experimental and calculated Raman spectra (2000–4000 cm^{-1}) of 2-Cl-N-MA

assigned to symmetric and asymmetric C—H stretching are in agreement with the literature.^[51] The C—H stretching bands were assigned at 3015 and 3034 cm^{-1} for *m*-methylaniline^[1] and 3008, 3020 and 3056 cm^{-1} for *p*-methylaniline.^[25] In this work, we calculated these vibrations at 3036, 3052, 3062 and 3067 cm^{-1} with B3LYP (ring C—H str.) that are in agreement with the experimental values (3067 and 3043 cm^{-1}). The TED of these modes is 100%. The C—H in-plane bending frequencies appear in the range of 1000–1300 cm^{-1} and C—H out-of-plane bending vibration in the range 750–1000 cm^{-1} .^[53] Hence the CH in-plane bends are assigned to the FT-IR bands at 1251, 1168, 1154 and 1114 cm^{-1} (1249, 1166, 1153 and 1112 cm^{-1} FT-Raman) and the calculated values 1257, 1173, 1159 and 1113 cm^{-1} show excellent agreement with the experimental values. The TED for these modes suggests that these are mixed modes. The CH out-of-plane bends are assigned to the FT-IR bands in the range from 963 to 742 cm^{-1} (modes 27, 28, 29, 31). The calculated values are in agreement with the assigned experimental values (e.g. one of them is 741 and 742 cm^{-1} calculated and assigned, respectively). Both the in-plane and out-of-plane bending vibrations are described as mixed modes. After scaling procedure, the theoretical C—H vibrations are in good agreement with the experimental values and literature.^[1,24–26,51–54] The change in the frequencies of these deformations from the values in benzene is determined mainly by the relative position of the substituents and is almost independent of their nature.^[55]

A major coincidence of the theoretical values with that of experimental evaluations is found in the symmetric and

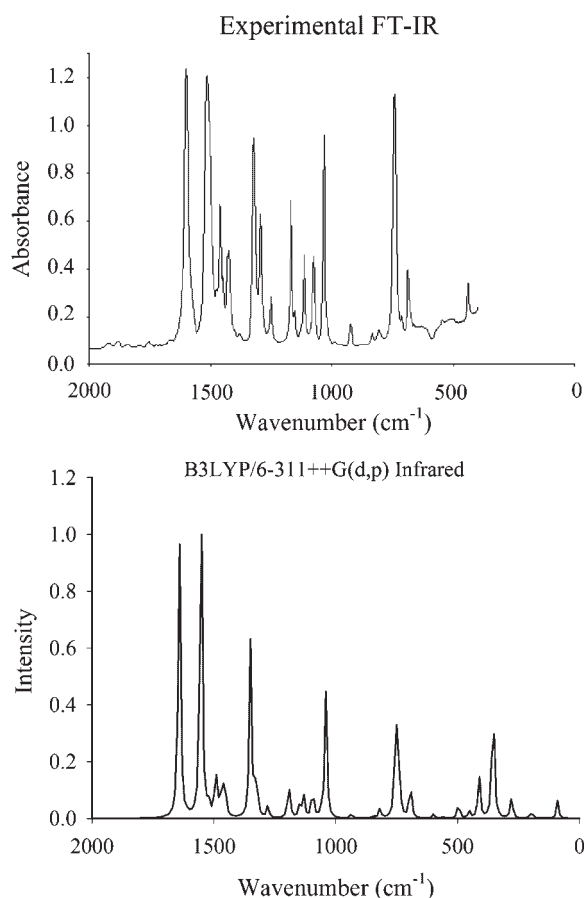


Figure 4. Experimental (400–2000 cm⁻¹) and calculated (0–2000 cm⁻¹) IR spectra of 2-Cl-N-MA

asymmetric vibrations of the CH₃ moiety (ν_8 , ν_7 and ν_6). The asymmetric stretching for the CH₂, NH₂ and CH₃ has a magnitude higher than that of the symmetric stretching.^[54] For benzene derivatives containing a CH₃ group two bands which antisymmetrical and symmetrical stretching occur at about 2900 and 2850 cm⁻¹, respectively.^[29] The symmetric stretching of CH₃ was observed in FT-IR at 2873 cm⁻¹ and calculated (ν_8) at 2859 cm⁻¹. The asymmetric CH₃ stretch (ν_6 and ν_7) calculated at DFT after scaling down gives the values of 2916 and 2986 cm⁻¹, which is nearer the observed values of 2912 and 2989 cm⁻¹ FT-IR (2909 and 2988 cm⁻¹ FT-Raman). The TED of these modes is 100%. Altun *et al.*^[1] assigned these bands at 2919 and 2857 cm⁻¹ for *m*-methylaniline. These bands were observed at 2984 (also 2935) and 2886 cm⁻¹ for 2-Cl-6-MA by Shanker *et al.*^[29] In the present investigation, the methyl CH₃ bending modes are observed at 1450 and 1462 cm⁻¹. These vibration frequencies are calculated (1442 and 1461 cm⁻¹) and assigned with modes ν_{15} and ν_{14} , respectively. The N—CH₃ stretching vibration is calculated at 1076 cm⁻¹. The other observed and calculated CH₃ frequencies are reported in Table 3. The methyl group assignments proposed in this study are also in agreement with literature values.^[1,11,25,29,43,51,54]

The ring stretching vibrations are very important in the spectrum of benzene and its derivatives; they are highly characteristic of the aromatic ring itself. When the ring modes in toluene^[56] and aniline,^[7,20] which contain one substituent attached to an aromatic ring, are compared, it is seen that most

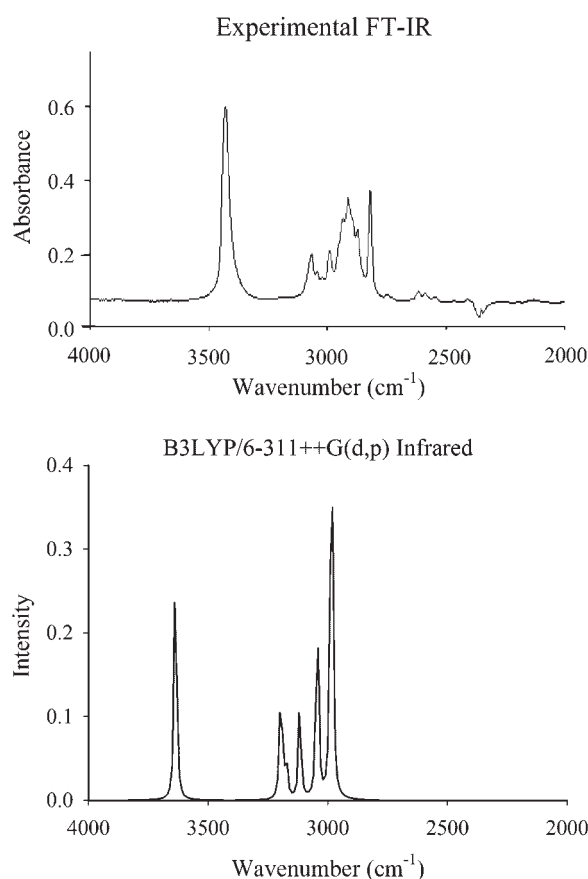


Figure 5. Experimental and calculated IR spectra (2000–4000 cm⁻¹) of 2-Cl-N-MA

of the aniline modes are found slightly higher in frequency than the toluene modes. However, most of the ring modes of toluene or aniline are found at significantly lower frequencies in 2-Cl-N-MA, which is disubstituted benzene. For example, the ring modes labelled ν_2 , ν_{11} , ν_{15} , ν_{26} and ν_{36} downshift, respectively, from 3079 cm⁻¹ (3084 cm⁻¹), 1587 cm⁻¹ (1590 cm⁻¹), 1445 cm⁻¹ (1468 cm⁻¹) and 961 cm⁻¹ (996 cm⁻¹) in toluene^[56] (aniline)^[7,20] to 3067, 1516, 1295, and 923 cm⁻¹ in 2-Cl-N-MA. The frequency changes in the modes ν_{11} , ν_{15} and ν_{26} are due to the changes in the force constant–reduced mass ratio resulting mainly from different extents of mixing between vibrations of the ring and substituent groups. The frequency reduction seen in the pure ring mode (ν_2) with the inclusion of a substituent group to aniline or toluene can be explained from the corresponding changes in the reduced masses and force constants. Vibrations between 1400 and 1650 cm⁻¹ in benzene derivatives are assigned ring carbon–carbon stretching modes. In the present investigation, the CC stretching modes are calculated at 1614 and 1580 cm⁻¹ which observed at 1601 FT-IR and 1600, 1571 cm⁻¹ in the FT-Raman spectrum (ν_9 and ν_{10}). As revealed by TED, the ring-breathing mode which can be described as the ‘trigonal ring breathing’ vibration or the ‘star of David’ vibration of the aromatic ring at 1023 cm⁻¹ coincides satisfactorily with the very strong FT-Raman band at 1035 cm⁻¹ (1033 cm⁻¹ FT-IR).^[57] The ring assignments proposed in this study is also in agreement with literature values.^[7,20,25,56,57]

Table 3. Comparison of the calculated and experimental (FT-IR and FT-Raman) vibrational spectra of 2-Cl-N-MA

Mode no.	B3LYP/6311++G(d,p)				Experimental		TED ^b (%)
	Unscaled freq	Scaled freq ^a	ν_{infrared}	ν_{Raman}	FT-IR	FT-Raman	
ν_1	3637	3484	45.6	75.1	3431 s		$\nu_{\text{NH}}(100)$ sym.
ν_2	3202	3067	4.9	270.4	3067 w	3067 s	$\nu_{\text{CH}}(100)$ ring.
ν_3	3196	3062	12.9	23.4			$\nu_{\text{CH}}(100)$ ring.
ν_4	3186	3052	7.5	93.9	3043 vw		$\nu_{\text{CH}}(100)$ ring.
ν_5	3169	3036	4.2	62.0			$\nu_{\text{CH}}(100)$ ring.
ν_6	3116	2986	18.2	101.3	2989 vw	2988 vw	$\nu_{\text{CH}_3}(100)$ asym.
					2934 vw		Combination
ν_7	3044	2916	37.4	102.4	2912 m	2909 w	$\nu_{\text{CH}_3}(100)$ asym.
ν_8	2985	2859	81.3	207.8	2873 vw		$\nu_{\text{CH}_3}(100)$ sym.
					2818 m	2819 w	Combination
					2745 vw		Combination
					2615 vw		Combination
					2587 vw		Combination
					1882 w		Combination
					1754 w		Combination
ν_9	1642	1614	148.0	54.5	1601 vs	1600 s	$\nu_{\text{CC}}(63)$ ring
ν_{10}	1607	1580	0.6	14.4		1571 vw	$\nu_{\text{CC}}(60)$ ring + $\delta_{\text{CH}}(11)$ + $\delta_{\text{CNH}}(10)$
ν_{11}	1553	1527	171.7	0.2	1516 vs		$\delta_{\text{CNH}}(28)$ + $\nu_{\text{CC}}(17)$ ring + $\delta_{\text{CH}}(17)$ + $\nu_{\text{CN}}(15)$
ν_{12}	1522	1496	5.8	8.4			$\delta_{\text{HCN}}(67)$ + $\tau_{\text{HCNC}}(19)$
ν_{13}	1494	1468	16.9	4.3		1474 vw	$\delta_{\text{CH}}(30)$ ring + $\nu_{\text{CC}}(21)$ ring + $\delta_{\text{HCN}}(14)$ + CH of CH_3 bend(11)
ν_{14}	1486	1461	10.6	14.8	1462 s		CH_3 bend(57) + $\delta_{\text{HCN}}(12)$ + $\tau_{\text{HCNC}}(10)$ + $\tau_{\text{HCNH}}(10)$
ν_{15}	1467	1442	11.6	2.4	1450 vw		CH_3 bend(27) + $\delta_{\text{HCN}}(25)$ + $\delta_{\text{CH}}(18)$ ring + $\delta_{\text{HNC}}(11)$ + $\nu_{\text{CC}}(12)$
ν_{16}	1456	1431	18.7	7.3	1424 m	1420 vw	$\delta_{\text{CH}}(30)$ ring + CH_3 bend(17) + $\nu_{\text{CC}}(15)$ + $\delta_{\text{HCN}}(12)$ + $\delta_{\text{HNC}}(12)$
ν_{17}	1350	1327	82.1	11.4	1323 vs	1322 w	$\nu_{\text{CN}}(33)$ + $\delta_{\text{CH}}(25)$ ring + $\nu_{\text{CC}}(21)$ ring
ν_{18}	1326	1303	22.8	3.1	1295 s	1291 vw	$\nu_{\text{CC}}(64)$ ring + $\delta_{\text{CH}}(21)$ ring
ν_{19}	1278	1257	5.4	2.5	1251 w	1249 vw	$\delta_{\text{CH}}(37)$ ring + $\nu_{\text{CC}}(18)$ ring + $\nu_{\text{CN}}(13)$
ν_{20}	1193	1173	17.5	3.8	1168 s	1166 vw	$\delta_{\text{CH}}(45)$ ring + $\nu_{\text{CC}}(15)$ ring + $\delta_{\text{HCN}}(13)$
ν_{21}	1179	1159	0.9	5.0	1154 w	1153 w	$\delta_{\text{CH}}(62)$ ring + $\nu_{\text{CC}}(12)$ ring
ν_{22}	1148	1128	5.9	1.7			$\text{CH}_3(72)$ rock + $\tau_{\text{HCNH}}(11)$ + $\tau_{\text{HCNC}}(11)$
ν_{23}	1132	1113	12.0	2.1	1114 m	1112 vw	$\delta_{\text{CH}}(33)$ ring + $\nu_{\text{CC}}(33)$ ring + $\text{CH}_3(15)$ rock
ν_{24}	1095	1076	15.5	0.7	1075 m		$\nu_{\text{N-CH}_3}(43)$ + $\nu_{\text{CC}}(20)$ ring + $\text{CH}_3(10)$ rock
ν_{25}	1059	1041	2.6	25.7			$\nu_{\text{CC}}(52)$ ring + $\delta_{\text{CH}}(15)$ ring + $\nu_{\text{N-CH}_3}(10)$
ν_{26}	1041	1023	58.7	20.8	1033 vs	1035 vs	$\delta_{\text{CCC}}(40)$ trigonal ring breathing + $\nu_{\text{CC}}(22)$ + $\nu_{\text{CC}}(13)$
ν_{27}	976	960	0.0	0.2	963 vw		$\gamma_{\text{CH}}(85)$ ring + $\gamma_{\text{CCCC}}(10)$ ring
ν_{28}	936	920	2.3	0.1	923 w		$\gamma_{\text{CH}}(80)$ ring + $\gamma_{\text{CCI}}(14)$

(Continues)

Table 3. (Continued)

Mode no.	B3LYP/6311++G(d,p)				Experimental		TED ^b (%)
	Unscaled freq	Scaled freq ^a	I^{infrared}	S^{Raman}	FT-IR	FT-Raman	
ν_{29}	845	831	1.2	0.6	834 w		$\gamma\text{-CH}(55)$ ring + $\gamma\text{-CCCCC}(29)$ ring
ν_{30}	818	804	4.6	10.9	807 vw	807 w	$\delta\text{-CCC}(24)$ ring + $\nu\text{-CN}(24)$ + $\nu\text{-CC}(20)$ ring + $\delta\text{-CH}(11)$ ring
ν_{31}	753	741	58.1	1.0	742 vs	742 vw	$\gamma\text{-CH}(63)$ ring
ν_{32}	739	726	18.8	0.2	712 vw		$\tau\text{-CCH}(45)$ ring + $\tau\text{-CCCC}(35)$ ring
ν_{33}	694	682	18.5	8.5	687 m	689 m	$\delta\text{-CCC}(34)$ ring def. + $\nu\text{-CCI}(24)$ + $\delta\text{-CCH}(10)$
ν_{34}	598	588	2.1	5.0			$\delta\text{-CCC}(32)$ + $\delta\text{-CCN}(28)$ + $\nu\text{-CC}(13)$
ν_{35}	557	548	0.9	0.2	545 vw		$\tau\text{-CCC}(37)$ ring + $\tau\text{-CCH}(33)$
ν_{36}	496	487	7.6	6.3	499 vw	487 w	$\delta\text{-CCN}(17)$ + $\delta\text{-CCCI}(17)$ + $\delta\text{-CCC}(13)$ + $\nu\text{-CN}(11)$
ν_{37}	452	444	3.6	0.3	439 m		$\tau\text{-CCCC}(41)$ ring + $\tau\text{-CCH}(25)$ + $\tau\text{-CCCN}(10)$
ν_{38}	412	405	20.5	9.2		400 m	$\nu\text{-CCI}(41)$ + $\gamma\text{-NH}(16)$ + $\delta\text{-CCC}(15)$ ring
ν_{39}	353	347	65.2	0.8			$\gamma\text{-NH}(63)$
ν_{40}	280	276	5.9	1.6		280 vw	$\delta\text{-CCC}(33)$ + $\delta\text{-CNC}(22)$
ν_{41}	275	271	4.9	0.9			$\tau\text{-CCCC}(36)$ + $\tau\text{-CCCN}(22)$ + $\gamma\text{-CNC}(18)$
ν_{42}	202	199	1.9	0.9		204 vw	$\tau\text{-CH}_3(58)$ + $\delta\text{-CCI}(12)$ + $\tau\text{-CCCCI}(10)$ + $\gamma\text{-CNC}(10)$
ν_{43}	192	189	1.5	1.7			$\delta\text{-CCN}(30)$ + $\delta\text{-CCCCI}(16)$ + $\delta\text{-CNC}(13)$ + $\tau\text{-CH}_3(12)$
ν_{44}	143	141	0.4	1.7		160 vw	$\tau\text{-CCCCI}(36)$ + $\tau\text{-CCCN}(14)$ + $\tau\text{-CCCC}(12)$
ν_{45}	89	88	8.4	0.9		74 vs	$\tau\text{-CCN-CH}_3(90)$
σ (RMS)	12.062						
R^2		0.9998					

^a Wavenumbers in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983 for B3LYP/6-311++G(d,p) basis set.^[31]

^b Total energy distribution. ν : stretching; δ : in-plane bending; γ : out-of-plane bending; τ : torsion. [I^{infrared} (Frequency (cm^{-1}), IR intensities, I^{infrared} ($\text{K m}^{-1} \text{mol}^{-1}$); Raman scattering activities, S^{Raman} ($\text{\AA} \text{amu}^{-1}$)].

The C—N stretching frequency is a rather difficult task since there are problems in identifying these frequencies from other vibrations. Silverstein^[51] assigned C—N stretching absorption in the region 1382–1266 cm⁻¹ for aromatic amines. The C—N stretching is observed at 1293 cm⁻¹.^[21] Hence the band at 1323 cm⁻¹ in FT-IR (1322 cm⁻¹ FT-Raman) spectrum is assigned to C—N stretching vibration. After scaled down, the computed value (ν_{17}) of C—N stretching vibration also is 1327 cm⁻¹, nearer the observed value. The TED for this mode suggests that this is a mixed mode. For *p*-methylaniline, Altun *et al.*^[25] assigned this band at 1267 cm⁻¹ FT-IR (1271 cm⁻¹ FT-Raman).

Some vibrational modes were shown to be Cl-sensitive modes whereas others were calculated in a narrow frequency range for methyl anilines. The involved ring-halogen modes are related partially to Cl—C stretching and bending modes. These modes are in the 200–600 cm⁻¹ frequency range as reported by Varsanyi.^[24] We may, therefore, assign the band at 400 cm⁻¹ FT-Raman to $\nu(\text{C—Cl})$ and the calculated value of this mode (ν_{38}) is at 405 cm⁻¹. According to the calculated TED, our calculations show that there is no pure $\nu(\text{C—Cl})$ band in this range. The bending C—Cl mode was located at 280–294 cm⁻¹ for chloro derivatives.^[46] This band is assigned at 280 cm⁻¹. The calculated bending mode is 276 cm⁻¹ for B3LYP. The other observed and calculated frequencies are in Table 3.

The Infrared intensity for the title molecule from experimental fundamentals at 1601 cm⁻¹ is very strong; the theoretical intensity of these fundamentals is in the same order by DFT/B3LYP method. This vibration intensity is 148.0 km mol⁻¹ (refer Table 3). This mode corresponds to CC stretching mode. The largest calculated Raman scattering activity (270.4 Å⁻⁴ amu⁻¹) peak corresponds to the C—H stretching.

We present RMS and correlation values to make comparison with experimental data, based on the calculations at the bottom of Table 3. After scaling, the rms error between the observed and scaled frequencies of the molecule is found to be 12.062 cm⁻¹ and the plots are linear with a unit slope and the correlation (R^2)

Table 4. Atomic charges of 2-Cl-*N*-MA and *N*-methylaniline (*N*-MA) calculations performed at the B3LYP method with 6-311++G(d,p) basis set

Atom	2-Cl- <i>N</i> -MA	<i>N</i> -MA
C1	-0.467	-0.299
C2	-0.075	-0.191
C3	1.591	-0.288
C4	-1.918	-0.207
C5	-0.192	0.232
C6	-0.080	-0.143
H7	0.147	0.136
H8	0.175	0.161
H9	0.137	0.129
N10	-0.022	-0.129
H11	0.242	0.246
Cl/H	0.194	0.123
C13/H	-0.357	-0.386
H14	0.148	0.138
H15	0.169	0.167
H16	0.145	0.146
H17	0.163	0.163

Table 5. The calculated thermodynamic parameters of 2-Cl-*N*-MA employing B3LYP/6-311++G(d,p) basis set

Parameters	DFT(B3LYP)
Total energy (thermal) (kcal mol ⁻¹)	90.23
Vibrational energy (thermal) (kcal mol ⁻¹)	88.45
Heat capacity (kcal mol ⁻¹ K ⁻¹)	0.0320
Entropy (Kcal mol ⁻¹ K ⁻¹)	0.0907
Dipole moment (Debye)	2.089
Rotational constants (GHz)	1.5304
	1.5022
	0.7624

values is found to be 0.9998 for B3LYP method. It is to be noticed that this means the experimental fundamentals are in better agreement with the scaled fundamentals and that the B3LYP/6-311++G(d,p) calculation is a very good method for vibrational frequencies.

Other molecular properties

The calculation of effective atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. Atomic charges are calculated by determining the electron population of each atom as defined by the basis functions. In Table 4, are compared the atomic charges of 2-Cl-*N*-MA and *N*-methylaniline calculated by DFT/B3LYP method using the 6-311++G(d,p) basis set. The results show that substitution of the aromatic ring by a Cl atom leads to a redistribution of electron density. The H8 and H11 atoms in *cis* position to Cl accommodate higher positive charge. On the other hand, atomic charges in the methyl group are almost identical in both molecules.

The thermodynamic parameters of the compounds have also been computed at DFT B3LYP/6-311G(d,p) level and are presented in Table 5.

CONCLUSION

In the present work, we have performed the experimental and theoretical vibrational analysis of 2-Cl-*N*-MA, for the first time. The molecular geometry, vibrational frequencies, Infrared intensities, Raman scattering activities, ¹H and ¹³C NMR chemical shifts of the molecule in the ground state have been calculated by using the DFT (B3LYP) method with 6-311++G(d,p) basis set. The vibrational frequencies were calculated and scaled values have been compared with experimental FT-IR and FT-Raman spectra. ¹H and ¹³C NMR chemical shifts have been compared with experimental values. As a result, all theoretical values calculated in B3LYP/6-311++G(d,p) methods are in good agreement with the vibrational frequencies (FT-IR, FT-Raman) and chemical shifts (NMR) observed in the experimental spectra.

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