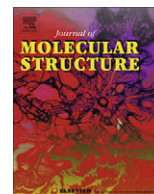




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Experimental (FT-IR and FT-Raman spectra) and theoretical (ab initio HF, DFT) study of 2-chloro-5-methylaniline

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ABSTRACT

In this work, the experimental and theoretical vibrational spectra of 2-chloro-5-methylaniline (2Cl5MA, C₇H₈NCl) were studied. FT-IR and FT-Raman spectra of 2Cl5MA 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 Hartree–Fock and density functional method (B3LYP) with the 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets. 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. The optimized geometric parameters (bond lengths and bond angles) were compared with experimental values of aniline and *p*-methyl aniline molecules.

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1. Introduction

Aniline and its derivatives, which have been used in commercial purposes and industrial, including pesticide, pharmaceuticals manufacturing and chemical dye industries, have been studied extensively [1]. Some of *para*-substituted derivatives of aniline are commonly used local anesthetics and among these molecules the amino group plays an important role in the interactions with the receptor. Molecular geometry 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]. 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 were studied extensively by spectroscopic and theoretical methods. Vibrational assignment based FT-IR in the vapor, solution and liquid phases and the Raman spectra in the liquid state were reported for aniline [4]. Its structure was studied experimentally, in the gas phase by microwave spectroscopy [5,6], in the solid state by X-ray crystallography [7] and electron diffraction [8]. Theoretically, its structure was reported

using semi-empirical [9,10] and ab initio methods [9,11,12]. The complete vibrational mode assignments and frequency analyses on vibrational spectra of substituted anilines were studied [13–17]. Assignments of some bands observed in the infrared (IR) spectrum of *p*-methylaniline are given in literature [3,18–22]. Vibrational modes and frequencies analyses of *m*-methylaniline and fluoro methylaniline were reported [23–25]. Shanker et al. [26] studied of 2-chloro-6-methylaniline (2Cl6MA) with polarized Raman and Infrared spectra.

Literature survey reveals that to the best of our knowledge, no experimental vibrational assignment for 2Cl5MA (also known as 3-amino-4-chloro toluene) molecule has been performed yet. Molecular structure and analysis of the vibrational modes of this molecule using quantum chemical methods (ab initio Hartree–Fock (HF) and density functional theory (DFT)) have not been performed and published in the literature so far. The purpose of the present study is to show FT-IR and FT-Raman spectra and to calculate optimal molecular geometry, minimum energy and vibrational frequencies of 2Cl5MA.

In this study, we recorded FT-IR and FT-Raman spectra of compound and calculated the vibrational frequencies of 2Cl5MA in the ground state to distinguish fundamentals from experimental vibrational frequencies and geometric parameters using HF and DFT/B3LYP (Becke 3-Lee–Yang–Parr) methods. A detailed quantum chemical study will aid in making definite assignments to fundamental normal modes of 2Cl5MA and in clarifying the experimental data for this important molecule.

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2. Experimental

The compound 2Cl5MA molecule in liquid state was purchased from Acros Organics Company with a stated purity of 99%. The FT-IR spectrum of 2Cl5MA molecule was recorded between 4000 cm^{-1} 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 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 .

3. Calculations

The molecular structure of 2Cl5MA in the ground state (*in vacuo*) is determined by HF and B3LYP employing the 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets. The optimized structural parameters were used in the vibrational frequency calculations at HF and DFT levels. The minimum energy was calculated by using level B3LYP/6-311++G(d,p) basis set. Because of this reason we take into account B3LYP/6-311++G(d,p) basis set for all calculations in the present discussion. The all calculated vibrational frequencies are scaled by 0.9050 for HF [27] and 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 [28] for B3LYP with 6-311++G(d,p) basis set. The total energy distribution (TED) was calculated by using the SQM program and the fundamental vibrational modes were characterized by their TED.

The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of 2Cl5MA molecule. All the calculations are performed by using GaussView molecular visualisation program [29] and GAUSSIAN 03 program package on the personal computer [30].

4. Results and discussion

The molecule of 2Cl5MA consists of 17 atoms, so it has 45 normal vibrational modes. Its molecular structure has not been studied by any diffraction technique; therefore we have taken into account two different symmetries depending on the conformation of the NH_2 and CH_3 groups. In previous studies [22,31] of *p*-methylaniline, the existence of different rotational isomers with respect to torsion around C– CH_3 bond is possible due to small energy barrier between such rotational isomers, so two geometries have been completely optimized at the different level of calculations, two methyl hydrogen on the same side that the lone pair electrons of

the N (staggered form) and two methyl hydrogens on the same side that amino hydrogens (eclipsed form). The energy difference was found negligible as well as other geometry differences. Recently, Tzeng and Narayanan [3] and Ballesteros et al. [31] have studied the conformations of aniline derivatives and they have concluded that the amino group has negligible effect on the relative stability among the rotational isomers in the ground state. But our results are not similar this conclusion due to chloro substitution. In the staggered and eclipsed form of 2Cl5MA molecule has imaginary frequencies.

On the basis of C_s symmetry the 45 fundamental vibrations of 2Cl5MA can be distributed as $30A' + 15A''$. The vibrations of the A' species are in-plane and those of the A'' species are out-of-plane. If we take into account C_s symmetry of this molecule, there are two imaginary frequencies correspond to NH_2 wagging and methyl rotation perpendicular to the ring plane. NH_2 plane is also parallel to the ring plane. The structure at any level was not a minimum energy structure. Two possessed imaginary frequencies of irreducible representation belong to A'' . But if the molecule were C_1 there would not be any relevant distribution and molecule has minimum energy (for example, $E(\text{HF}) = -783.77485436\text{ a.u.}$, $E(\text{B3LYP}) = -786.63855331\text{ a.u.}$ for C_s symmetry and $E(\text{HF}) = -783.77630603\text{ a.u.}$, $E(\text{B3LYP}) = -786.63879765\text{ a.u.}$ for C_1 symmetry by using 6-311++G(d,p)). The C_1 symmetry structure was the lowest in energy at all levels. Calculated energies and energy difference for 2Cl5MA molecule, determined by HF and B3LYP at eight basis sets mentioned above, are presented in Table 1 which on the calculated energies, there is a little difference between basis sets, use of the basis sets of larger sizes give rise to increases in the differences between the calculated energies of the 2Cl5MA molecule. However, when we compared the 6-31 and 6-311 basis sets the difference is large.

The molecular structure and numbering of the atoms of 2Cl5MA is shown in Fig. 1. The geometric parameters compared with the aniline and *p*-methylaniline [3,6,17,22,32] bond lengths and bond angles. The calculated vibrational frequencies are compared with the experimental FT-IR and FT-Raman spectra of 2Cl5MA molecule. Comparison of the theoretical parameters calculated at HF and DFT (B3LYP) with the experimental values reveal the overestimation of the calculated theoretical parameters due to neglect of anharmonicity in real system [33].

4.1. Geometrical structure

The first task for a computational work was to determine the optimized geometry of 2Cl5MA. The optimized structure parameters calculated ab initio HF and DFT (B3LYP) with the 6-31++G(d,p) and 6-311++G(d,p) basis sets are listed in Table 2 in accordance with the atom numbering scheme given in Fig. 1. As seen from the values given in Table 2, the increase of the basis set leads to a slight shortening of their values. Our calculated re-

Table 1
Calculated energies and energy difference for 2Cl5MA by HF and DFT (B3LYP) methods

Basis set levels	HF		B3LYP	
	Energy (Hartree)	Energy differences ^a (kcal/mol)	Energy (Hartree)	Energy differences ^a (kcal/mol)
6-311++G(d,p)	-783.77630603	0.000	-786.63879765	0.000
6-311+G(d,p)	-783.77616370	0.089	-786.63870212	0.060
6-311G(d,p)	-783.76936468	4.356	-786.63162460	4.501
6-311G(d)	-783.75271929	14.801	-786.61586653	14.389
6-31++G(d,p)	-783.69615161	50.298	-786.54705884	57.567
6-31+G(d,p)	-783.69599125	50.398	-786.54687328	57.683
6-31G(d,p)	-783.68693569	56.081	-786.53231647	66.818
6-31G(d)	-783.66878929	67.468	-786.51647091	76.761

^a Energies of the other basis sets.

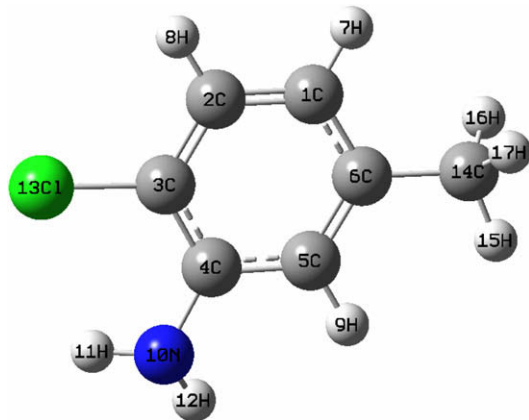


Fig. 1. Optimized geometry of 2Cl5MA structure and atoms numbering.

sults show that the aromatic ring in 2Cl5MA is distorted from regular hexagon due to steric and electronic effects of electron donating and electron withdrawing substituted aniline.

As discussed in our previous paper [34,35], it is well known that HF methods underestimate and DFT method overestimate bond lengths, particularly the CH bond lengths. This theoretical pattern also found for 2Cl5MA molecule. Since large deviation from experimental C–H bond lengths may arise from the low scattering factors of hydrogen atoms in the X-ray diffraction experiment we did not discuss C–H bond lengths.

Several authors [36,37] 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 (Cl, F and Br, etc.) or electron donating type (CH₃, C₂H₅, etc.). 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 well on substitution with electron donating groups. The actual change in the C–H bond length would be influenced by the combined effects of the

Table 2

Optimized geometry of 2Cl5MA in the ground state

Parameters	Exp. [3] <i>p</i> -methylaniline	Exp. ^{a,b} aniline	6-31++G(d,p)		6-311++G(d,p)	
			HF	B3LYP	HF	B3LYP
<i>Bond lengths</i> (Å)						
C1–C2	1.40	1.386, 1.396	1.379	1.393	1.377	1.389
C1–C6	1.39	1.386, 1.396	1.396	1.405	1.395	1.402
C2–C3	1.39	1.380, 1.394	1.386	1.393	1.384	1.389
C3–C4	1.36	1.404, 1.397	1.389	1.406	1.387	1.402
C3–Cl13			1.750	1.766	1.752	1.767
C4–C5	1.39	1.404, 1.397	1.401	1.409	1.399	1.407
C4–N10	1.43	1.398, 1.402	1.384	1.389	1.385	1.387
C5–C6	1.40	1.380, 1.394	1.382	1.395	1.380	1.391
C6–C14	1.55		1.511	1.512	1.510	1.510
C–H (ring) ^c	1.08	1.03, 1.082	1.076	1.086	1.075	1.084
N–H (amino) ^c	1.02	1.07, 1.001	0.995	1.010	0.995	1.009
C–H (methyl) ^c	1.09		1.085	1.095	1.085	1.093
<i>Bond angles</i> (°)						
C2–C1–C6	119.2	119.7, 120.12	119.95	120.22	119.95	120.21
C2–C1–H7			119.72	119.58	119.71	119.56
C6–C1–H7			120.33	120.21	120.34	120.23
C1–C2–C3	120.5		120.46	120.14	120.43	120.12
C1–C2–H8			120.49	120.67	120.51	120.68
C3–C2–H8			119.05	119.19	119.06	119.20
C2–C3–C4	120.5		121.07	121.38	121.13	121.45
C2–C3–Cl13			118.94	119.33	118.89	119.28
C4–C3–Cl13			119.99	119.29	119.98	119.27
C3–C4–C5	120.3	117.9, 119.43	117.48	117.20	117.43	117.13
C3–C4–N10		124.0, 120.28	122.41	121.99	122.47	122.05
C5–C4–N10		124.0, 120.28	120.06	120.76	120.05	120.78
C4–C5–C6	121.5	122.1, 120.70	122.20	122.36	122.23	122.38
C4–C5–H9			118.14	118.13	118.11	118.09
C6–C5–H9			119.66	119.50	119.67	119.53
C1–C6–C5	117.8	117.6, 118.92	118.83	118.70	118.83	118.71
C1–C6–C14			120.28	120.58	120.28	120.48
C5–C6–C14			120.89	120.71	120.90	120.81
C4–N10–H11		119.0, 115.94	116.27	116.42	115.98	116.38
C4–N10–H12		119.0, 115.94	115.33	116.20	115.01	116.15
H–N–H (amino)	113	113.1, –	113.01	113.87	112.76	113.86
C–C–H (methyl) ^c			111.00	111.29	110.97	111.24
H–C–H (methyl) ^c	109.5		107.90	107.60	107.93	107.64
C6–C5–C4–N10			–177.61	–177.35	–177.61	–177.34
C2–C3–C4–N10			177.53	177.40	177.50	177.28
C5–C4–N10–H12			–25.13	–23.81	–25.72	–24.02
C3–C4–N10–H11			21.73	20.36	22.20	20.35

^a From Ref. [7].

^b From Ref. [6].

^c Averaged value.

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 amino group, the nitrogen atom is slightly out-of-plane, with a torsional angle C2–C3–C4–N10 and C6–C5–C4–N10 in the ca. 177 (or ca. 3°). A measure of this displacement is defined the tilt angle [17]. Existence of this angle has been interpreted to be caused by asymmetric interaction between the NH₂ group and benzene ring plane. This interaction is common to all aniline derivatives [3,16]. C4–N10 distance (1.389 Å) is similar to the measured in aniline (1.402 Å and calculated 1.407 Å) [38] and *p*-methylaniline (1.43 Å and calculated 1.414 Å) [22,32].

The optimized NH (amino group) bond length were calculated 0.995 Å by HF and 1.009 Å by DFT with 6-311++G(d,p) method. By comparing these values with experimental value of 1.02 Å for *p*-methylaniline (1.07, 1.001 Å for aniline), it is observed that B3LYP estimate the NH bond length better than HF, which underestimate this bond than experimental values.

The optimized bond lengths of CC in ring in the range from 1.377 to 1.399 Å for HF, 1.389 to 1.407 Å for B3LYP with 6-311++G(d,p) methods which are in good agreement with *p*-methylaniline (1.36–1.40 Å) and 1.380–1.404 Å for aniline. The CCH₃ bond length is calculated underestimate for experimental value for *p*-methylaniline by all the levels.

The C–Cl bond length indicates a considerable increase when substituted in place of C–H. This has been observed even in benzene derivatives [39]. The C–Cl bond length are found 1.767 Å (B3LYP) and 1.752 Å (HF) by using 6-311++G(d,p). Bakiler et al. calculated this bond length 1.746 Å for 3-Cl-pyridine and 1.748 Å for 2-Cl-pyridine [40] by using force field calculations. Kurt et al. [35] calculated C–Cl bond length at 1.767 Å (B3LYP), 1.75 Å (HF) and 1.789 Å (BLYP) for 3-Cl-4MA. This bond length was also observed 1.735–1.744 Å range for similar molecules [34,41–43].

The asymmetry of the benzene ring is also evident from the negative deviation of C1–C6–C5 and C3–C4–C5 angles which are calculated ca. 117° and 118° (HF and B3LYP) and positive deviation of the remaining angles from the normal value of 120° (for example the C4–C5–C6 angle found to be bigger than ca. 2° hexagonal angles). Similar values found to be other aniline derivatives which are *m*-methylaniline [23], *o*-methylaniline [44], *p*-methylaniline [3] and 3-Cl-4MA [35]. As discussed Ballesteros et al. [31] for *p*-methylaniline C1–C6–C14 is equal to the C5–C6–C14 angle, and C5–C4–N10 is equal to C3–C4–N10, and therefore exists no significant interaction between the methyl group and amino group as it occurs in the *m*-methylaniline and contrary to *o*-methylaniline

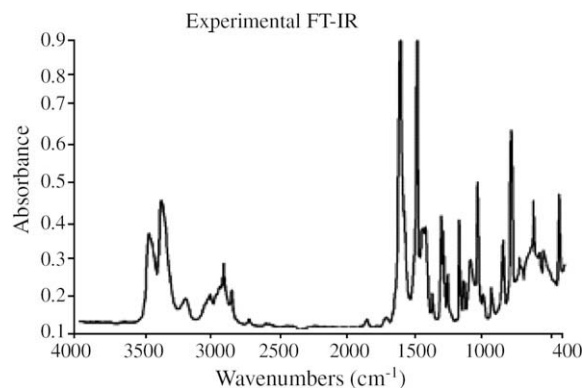


Fig. 2. Experimental FT-IR spectra of 2Cl5MA.

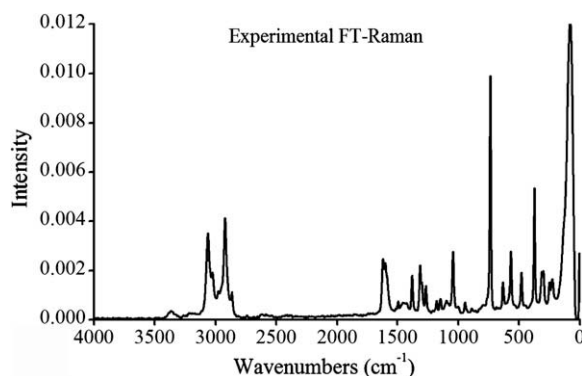


Fig. 3. Experimental FT-Raman spectra of 2Cl5MA.

where exists interaction between both groups. Our calculated values are 120.5° and 120.8° for C1–C6–C14 and C5–C6–C14, or 120.8° and 122.0° for C5–C4–N10 and C3–C4–N10, by using B3LYP/6-311++G(d,p), respectively. This clearly shows that the substitution of Cl group in place of hydrogen appreciably affect the C1–C6–C14, C5–C6–C14, C5–C4–N10 and C3–C4–N10 bond angles. Similar values found to be 3-Cl-4MA by Kurt et al. [35].

4.2. Vibrational spectra

In order to obtain the spectroscopic signature of 2Cl5MA molecule, we performed a frequency calculation analysis. Calculations

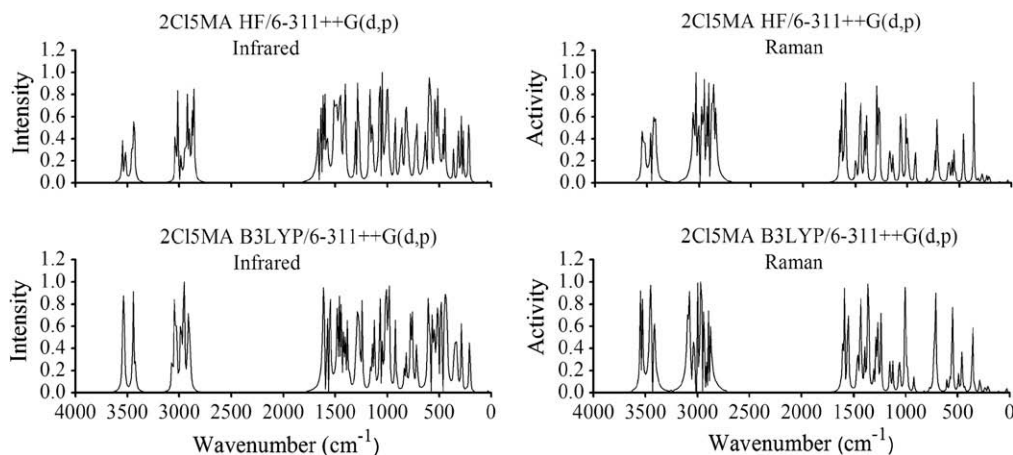


Fig. 4. Comparison of calculated frequencies in cm⁻¹ normalized IR intensities and Raman activities at each level of theory considered for 2Cl5MA. These theoretical spectrum were obtained by using HF and DFT (B3LYP) methods with 6-311++G(d,p).

Table 3
Comparison of the calculated and experimental (FT-IR and FT-Raman) vibrational spectra of 2C15MA

Mode No.	HF/6311++G(d,p)				B3LYP/6311++G(d,p)				Experimental		TED ^c (%)
	Unscaled freq.	Scaled freq. ^a	<i>I</i> ^{Infrared}	<i>S</i> ^{Raman}	Unscaled freq.	Scaled freq. ^b	<i>I</i> ^{Infrared}	<i>S</i> ^{Raman}	FT-IR	FT-Raman	
v1	3907	3536	31.6	35.0	3680	3526	28.6	41.8	3471		vNH(100) asym.
v2	3804	3442	36.7	120.9	3576	3426	30.8	171.8	3381	3355	vNH(100) sym.
v3	3357	3038	5.9	112.8	3196	3062	3.8	130.4		3060	vCH(99) ring
v4	3328	3012	8.2	67.2	3170	3037	6.8	81.0			vCH(100) ring
v5	3315	3000	18.3	83.4	3152	3019	16.5	93.9	3019	3021	vCH(99) ring
v6	3245	2937	24.0	55.2	3102	2972	17.5	58.0			vCH ₃ (100) asym.
v7	3221	2915	22.8	80.0	3074	2945	15.7	96.1	2921	2919	vCH ₂ of CH ₃ (100) asym.
v8	3169	2868	34.8	197.2	3025	2898	32.0	270.0	2860	2861	vCH ₃ (100) sym.
v9	1810	1638	179.0	21.8	1658	1630	184.2	26.4	1616	1615	ρ NH ₂ (41) + δ CNH(23) + vCC(14) ring + vNH(6)
v10	1785	1615	12.7	21.4	1635	1607	6.5	19.4			vCC(49) ring + ρ NH ₂ (15) + δ CNH(10) + δ CCH(8)
v11	1756	1590	31.4	11.4	1613	1586	8.0	8.1	1584	1595	vCC(67) ring + δ CNH(6) + δ CCH(4) + δ NH(4)
v12	1656	1499	61.4	2.8	1525	1499	68.3	5.2	1492	1490	δ CCH(40) ring + vCC(31) ring + vCN(4)
v13	1615	1461	28.3	3.2	1501	1475	24.1	3.7	1476		CH of CH ₃ asym. bend(44) + τ HCCC(20) + δ CCH(12) + vCC(4)
v14	1604	1451	6.6	8.8	1487	1462	7.3	9.9	1450		CH of CH ₃ asym. bend(57) + τ HCCC(20) + δ CCH(12)
v15	1558	1410	29.5	4.6	1449	1424	22.9	3.7	1428		vCC(30) ring + vC-NH ₂ (13) + δ CCH(9) + δ CNH(5)
v16	1538	1392	0.5	5.6	1416	1392	1.2	16.5	1380	1379	CH ₃ sym. bend(51) + δ CCH(44)
v17	1429	1293	32.7	8.2	1347	1324	17.7	13.7	1314	1314	vCC(60) ring + vCN(10) + δ CCH(7) + δ CNH(5)
v18	1405	1272	7.1	11.7	1322	1300	18.1	6.8	1297	1297	δ CH(46) ring + vCC(15) ring + vC-NH ₂ (9) + δ CNH(6)
v19	1294	1171	10.5	4.2	1290	1268	7.5	6.9	1266	1265	vCC(39) ring + δ CCH(31) + vC-NH ₂ (11) + vC-CH ₃ (3)
v20	1278	1156	14.4	1.2	1198	1178	13.3	3.1	1178	1177	δ CCH(41) + vC-CH ₃ (26) + vCC(11) ring + vC-NH ₂ (7)
v21	1258	1138	3.4	2.6	1170	1150	5.7	2.7	1145	1145	δ CCH(58) + vCC(23) ring + NH ₂ (7) rock
v22	1176	1064	68.0	10.1	1105	1086	38.3	4.8	1096		NH ₂ (50) rock + vCC(25) ring + vCC(16) + δ CCH(5)
v23	1158	1048	3.5	0.1	1060	1042	3.7	0.1	1044	1043	CH ₃ (53) rock + γ CCC(27) + γ CH(4)
v24	1117	1011	18.7	7.6	1046	1028	31.5	16.6			vCC(26) ring + δ CCC(18) ring + vCC(13) + δ CCH(6) + vCN(4)
v25	1097	993	8.9	4.1	1023	1006	11.8	2.4			CH ₃ (60) rock + vCC(12) ring + δ CCC(4) ring + NH ₂ (4) rock + δ CCH(3)
v26	1077	974	1.2	0.5	961	944	6.1	1.4	944	942	vCC(22) ring + vC-CH ₃ (14) + vC-NH ₂ (12) + CH ₃ (9) rock + δ CCC(9) ring
v27	1023	926	8.0	3.7	946	930	1.0	0.2			γ CH(66) + γ CCC(20)
v28	959	868	15.9	0.1	858	844	12.2	0.1	856		γ CH(75) + γ CCC(10)
v29	897	812	46.2	0.7	800	786	34.5	0.3	794		γ CH(80) + γ CCC(15)
v30	814	737	3.3	0.9	746	734	5.6	23.4	735	738	δ CCC(32) ring + vCC(22) ring + vC-CH ₃ (12) + vC-NH ₂ (8)
v31	794	719	8.2	26.0	731	719	0.5	0.9			τ CCCC(42) ring + γ CH(24) + γ CCN(8)
v32	680	615	54.3	0.8	629	619	17.7	1.0	630	626	vCCl(36) + δ CCC(23) ring + vC-CH ₃ (16)
v33	663	600	47.4	2.9	598	588	20.4	1.2	585		γ CCC(33) ring + ω NH ₂ (11) + ω CH ₃ (10) + τ CCCH(8)
v34	618	560	45.0	11.0	573	564	4.4	10.8	557	564	δ CCC(33) ring + vCC(11) ring + δ CCN(9) + vC-NH ₂ (7)
v35	591	535	160.1	0.7	512	503	236.8	1.7			ω NH ₂ (70) + δ CNH(13) + vCN(5)
v36	512	463	0.6	4.5	478	470	4.1	4.3	475	475	δ CCN(43) + δ CCC(20) + δ CCCl(9)
v37	498	451	24.0	0.5	451	443	27.1	0.4	442		τ CCCC(48) ring + τ CCCH(11) + τ CCCN(8)
v38	401	363	2.9	8.9	373	367	3.1	8.0		373	vCl(33) + δ CCC(26) ring + δ CC-CH ₃ (12) + δ CCCl(8)
v39	352	318	5.6	0.4	351	345	14.8	0.3			τ CCNH(84) (NH ₂ twist)
v40	351	318	8.3	0.6	299	294	5.0	0.7		296	τ CCNH(12) + τ CCCl(23) + τ CCCC(17) + τ CCCH(8) + τ HCCCl(8)
v41	307	278	10.4	0.7	294	289	2.3	0.9			δ CCC(42) (CH ₃ wagg) + δ CCN(12) (NH ₂ wagg)
v42	262	237	0.1	0.7	246	242	0.2	0.7			δ CCCl(72) + δ CCC(13) (CH ₃ wagg)
v43	236	213	8.6	0.9	216	212	7.2	0.9		219	τ CCCN(37) + τ CCCC(18) ring + τ CCCC(17)
v44	124	112	0.0	0.2	114	112	0.0	0.2		76	τ CCCC(31) + τ CCC-CH ₃ (15) + τ CCCC(14) ring + τ NCCCl(12)
v45	20	18	0.2	0.2	33	32	0.2	0.5			τ CH ₃ (97)
σ		30.559				25.112					

v, stretching; δ , in-plane bending; γ , out-of-plane bending; ρ , scissoring; ω , wagging. [Frequency (cm⁻¹), IR intensities; *I*^{Infrared} (k mmol⁻¹), Raman scattering activities; *S*^{Raman} (Å amu⁻¹)]

^a Scale factor of 0.9050 was used for HF/6-311++G(d,p) basis set [27].

^b 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, respectively [28].

^c Total energy distribution.

were made for a free molecule in vacuum, while experiments were performed for liquid sample, so there are disagreements between calculated and observed vibrational wavenumbers.

Experimental FT-IR and FT-Raman spectra are shown in Figs. 2 and 3, respectively. The calculated IR and Raman spectra are shown in Fig. 4 for comparative purposes, where the calculated intensity and activity is plotted against the harmonic vibrational frequencies. The experimental wavenumbers are tabulated in Table 3 together with the calculated wavenumbers of studied molecule. The resulting vibrational frequencies for the optimized geometry and the proposed vibrational assignments as well as IR intensities and Raman scattering activities are given in Table 3. All of the calculated modes are numbered from the biggest to the smallest frequency within each fundamental wave numbers, ν_n , in the first column of the table. In the last column is given a detailed description of the normal modes based on the total energy distribution (TED).

For 2Cl5MA, the vibrational modes are N–H stretching, C–H stretching, C–Cl stretching, C–N stretching, C–C–H bending, C–C–C bending, C–C–N bending, C–N–H bending, ring bending, NH₂ scissoring, NH₂ wagging, NH₂ rocking and ring torsion modes.

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 [45,46]. In this region, the bands are not affected appreciably by the nature of the substituents. As seen in Table 3, five peaks observed for the 2Cl5MA in the 2800–3500 cm⁻¹ range experimentally in the high frequency region which are 2860, 2921, 3019, 3381 and 3471 cm⁻¹ (FT-IR), 2861, 2919, 3021, 3060 and 3355 cm⁻¹ (FT-Raman). These are usual range of appearance for NH₂, CH₃ and ring C–H stretching vibrations. Accordingly, in the present study, the three adjacent hydrogen atoms left around the ring the 2Cl5MA give rise to three C–H stretching modes (ν_3 – ν_5), three C–H in-plane bending (ν_{18} , ν_{20} and ν_{21}) and three C–H out-of-plane bending (ν_{27} – ν_{29}) vibrations which corresponds to modes of C1–H7, C2–H8 and C5–H9 units. The vibrations ν_3 – ν_5 assigned to C–H stretching are in agreement with the literature [46]. The C–H stretching band was assigned 3015 and 3034 cm⁻¹ for *m*-methylaniline [23] and 3008, 3020 and 3056 cm⁻¹ for *p*-methylaniline [22]. In this work, we calculated frequencies at 3019, 3037 and 3062 cm⁻¹ (ring C–H str.) for benzene ring with B3LYP. 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 [47]. The CH in-plane bends are assigned to the FT-IR bands at 1297, 1178 and 1145 cm⁻¹, respectively. The CH out-of-plane bends are assigned to the FT-IR bands in the range from 944 to 794 cm⁻¹. Both the in-plane and out-of-plane bending vibrations are described as mixed modes. The above conclusions are in very good agreement with literature values [21–24,46–49].

A major coincidence of theoretical values with that of experimental evaluations is found in the symmetric and asymmetric vibrations of the CH₃ moiety (ν_8 and ν_7). The asymmetric stretching for the NH₂, CH₂ and CH₃ has magnitude higher than the symmetric stretching [48]. For benzene derivatives containing a CH₃ group two bands which antisymmetrical and symmetrical stretching occurs about 2900 and 2850 cm⁻¹, respectively [26]. The symmetric stretching of CH₃ observed in FT-IR at 2860 cm⁻¹ (2861 cm⁻¹ FT-Raman) was calculated (ν_8) about at 2868 cm⁻¹ at HF level, while DFT estimated it 2898 cm⁻¹. The asymmetric CH₃ stretch (ν_7) calculated at HF after scaling down gives the value of 2915 cm⁻¹ is nearer to the observed value of 2921 cm⁻¹ FT-IR (2919 cm⁻¹ FT-Raman). But DFT gives high estimate of this frequency in the 2945 cm⁻¹ region. The TED of these modes is 100%. Altun et al. [23] 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 2Cl6MA by Shanker et al.

[26]. In this study, the methyl CH₃ bending modes observed at 1450 and 1476 cm⁻¹. These vibration frequencies calculated (1462 and 1475 cm⁻¹) and assigned modes ν_{13} and ν_{14} , respectively. The CH₃ rocking mode is observed 1045 and 1059 cm⁻¹ for 2Cl6MA by Shanker et al. [26]. We assigned this band at 1044 cm⁻¹ FT-IR (1043 cm⁻¹ FT-Raman). The mode ν_{23} calculated at 1042 cm⁻¹ with DFT method is agreement with experimental value. The methyl group assignments proposed in this study is also in agreement with literature values [6,22,23,26,35,46,48,49].

In Ref. [21], it is expressed that the frequencies of the amino group appear around 3500–3300 cm⁻¹ for the NH₂ stretching, 1630–1610 cm⁻¹ for the scissoring deformation and 1090–1060 cm⁻¹ for rocking deformation. The mode $\nu_{as}(\text{NH}_2)$ has higher frequency compared to the $\nu_s(\text{NH}_2)$ mode. In addition, the $\nu_s(\text{NH}_2)$ mode occurs with greater infrared intensity compared to the $\nu_{as}(\text{NH}_2)$ mode (see Fig. 2). In this study, the NH₂ asymmetric and symmetric stretches (ν_1 and ν_2) at 3471 and 3381 cm⁻¹ FT-IR (3355 cm⁻¹ FT-Raman) are in agreement with calculated values. As expected these two modes are pure stretching modes as it is evident from TED column, they are almost contributing 100%. The NH₂ stretching modes are assigned 3435 and 3354 cm⁻¹ for *m*-methylaniline [23] and 3416 and 3333 cm⁻¹ for *p*-methylaniline [22]. These bands are assigned 3485 and 3396 cm⁻¹ $\nu_{as}(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ modes for 2Cl6MA, respectively [26]. About 1625 cm⁻¹ value is assigned the amino scissoring band for aniline [25], *o*-methylaniline [44], *m*-methylaniline [23] and *p*-methylaniline [3,22]. We observed this band at 1616 (FT-IR) and 1615 cm⁻¹ (FT-Raman). The amino rocking band is observed 1077 cm⁻¹ for *m*-methylaniline [23], 1074 cm⁻¹ for *p*-methylaniline [22] and 1079 for 2Cl6MA [26]. In this study, the amino rocking band (ν_{22}) is assigned at 1096 cm⁻¹ which calculated 1096 cm⁻¹ with DFT.

Because of the mixing of several bands, the identification of C–N vibrations is a very difficult task. Silverstein [46] assigned C–N stretching absorption in the region 1382–1266 cm⁻¹ for aromatic amines. In the present work, the band observed at 1314 cm⁻¹ in FT-IR (and FT-Raman) spectrum has been assigned to C–N stretching vibration. The computed value (ν_{17}) of C–N stretching vibration also is 1324 cm⁻¹. The TED for this mode suggests that this is a mixed mode with out-of-plane C–C stretching mode.

The ring stretching vibrations are very much important in the spectrum of benzene and its derivatives are highly characteristic of the aromatic ring itself. The ring carbon–carbon stretching vibrations occur in the region 1430–1625 cm⁻¹. In this study, the CC stretching mode is expected and the highest one is observed at 1584 cm⁻¹ (ν_{11}) in the FT-IR spectrum (1595 cm⁻¹ FT-Raman). The CC vibration is calculated at 1586 cm⁻¹ is in excellent agreement with experimental value. The calculated C–C–C out-of-plane and in-plane bending modes have been found to be consistent with the recorded spectral values.

Some vibrational modes were shown to be Cl-sensitive modes whereas others were calculated in a narrow frequency range for methyl anilines. Involving the ring-halogen modes are related partially to Cl–C stretching and bending modes. In benzene derivatives containing a Cl group, the Cl–C stretching frequency occurs in the region 600–800 cm⁻¹ [20]. Shanker et al. [26] observed 631 cm⁻¹ with strong infrared and Raman intensities for 2Cl6MA. We assigned this mode (ν_{32}) at 630 cm⁻¹ FT-IR (626 cm⁻¹ FT-Raman). Our calculations show that there is a $\nu(\text{C–Cl})$ band at 691 cm⁻¹ and 615 cm⁻¹ with HF and B3LYP methods, respectively. Other $\nu(\text{C–Cl})$ character mode are 200–400 cm⁻¹ frequency range. We observed this mode (ν_{38} at 373 cm⁻¹ FT-Raman and calculated at 367 cm⁻¹). The bending C–Cl mode was located at 280–294 cm⁻¹ for chloro derivatives [42]. The calculated bending modes are 294 (o.o.p.) and 242 (i.p.) cm⁻¹ for B3LYP. The remainder of the observed and calculated frequencies accounted in Table 3.

The infrared intensity for title molecule from experimental fundamentals at 1616 cm^{-1} is very strong, theoretical intensity of these fundamentals is on the same order for HF method; however it is second strongest fundamentals for B3LYP method. While experimental intensity is very strong for this mode, calculated intensity is 179 and 184.2 km mol^{-1} and the other fundamental's intensity is 160.1 and 236.8 km mol^{-1} for HF and B3LYP methods, respectively (see Table 3). These modes correspond to NH_2 scissoring (ν_9) and wagging (ν_{35}).

We present rms (σ) values to make comparison with experimental data, based on the calculations bottom of Table 3. After scaling, the RMS errors between the observed and scaled frequencies of the molecule are found to be 30.559 and 25.112 for HF and B3LYP methods, respectively. When we summarize, the experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for B3LYP than HF method.

5. Conclusion

In the present work, we have performed the experimental and theoretical vibrational analysis of 2Cl5MA, for the first time. The molecular geometry, vibrational frequencies, infrared intensities and Raman scattering activities of the molecule in the ground state have been calculated by using ab initio HF and DFT (B3LYP) methods with 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets. The vibrational frequencies were calculated and scaled values (6-311++G(d,p) basis set) have been compared with experimental FT-IR and FT-Raman spectra. The observed and the calculated frequencies are found to be in good agreement.

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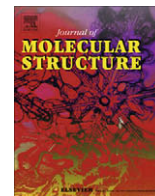
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Update

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Erratum

Erratum to “Experimental (FT-IR and FT-Raman spectra) and theoretical (ab initio HF, DFT) study of 2-chloro-5-methylaniline” [Journal of Molecular Structure 892 (2008) 25–31]

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The authors regret that in the above article Fig. 4 was printed incorrectly. Fig. 4 should be presented as given below:

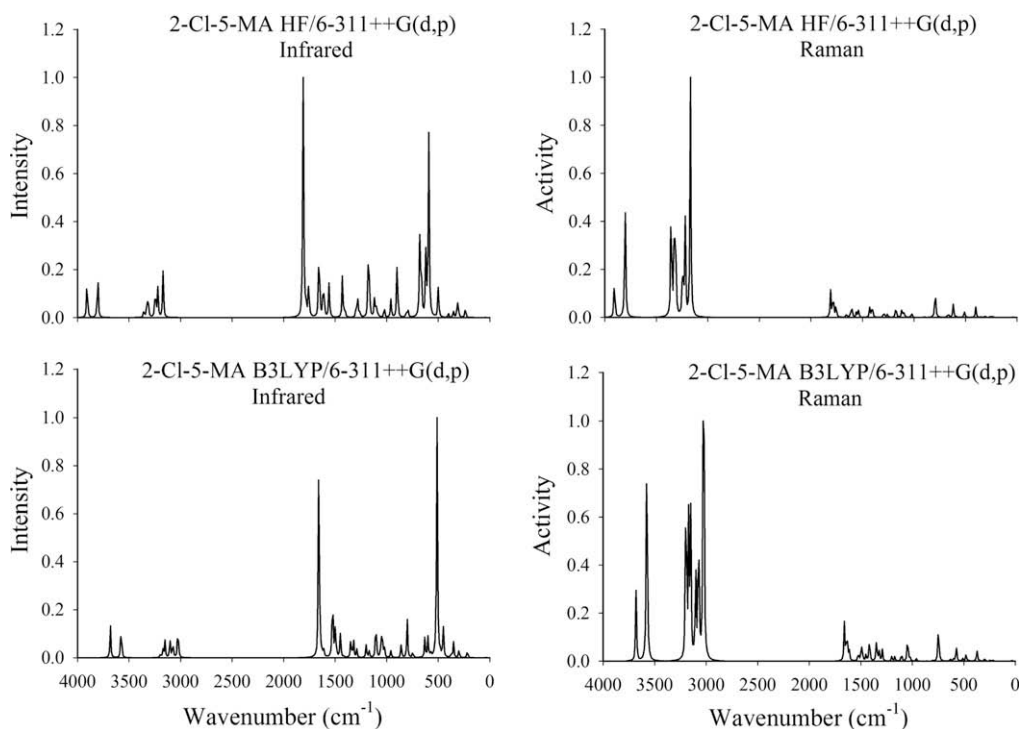


Fig. 4. Comparison of calculated frequencies in cm^{-1} normalized IR intensities and Raman activities at each level of theory considered for 2-Cl-5-MA. These theoretical spectra were obtained by using HF and DFT (B3LYP) methods with 6-311++G(d,p).

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