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Synthesis, FT-IR, FT-Raman and quantum chemical investigations of *N*-(3-methylphenyl)-2,2-dichloroacetamide

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ABSTRACT

N-(3-methylphenyl)-2,2-dichloroacetamide of the configuration $X_yC_6H_{5-y}$-NHCO-$CHCl_2$ (where, X = CH_3 and y =1) was synthesized and an extensive spectroscopic investigations have been carried out by recording the Fourier transform infrared (FT-IR) and FT-Raman spectra in an effort to provide the complete analysis of the fundamental modes of the compound. The *ab initio* and DFT studies were carried out with 6-311++G(d,p) and 6-31G(d,p) basis set to determine the structural, thermodynamical and vibrational characteristics of the compound. The steric influence of methyl group on the characteristic frequencies of amide (-CONH-) group has been analysed.

1. Introduction

Amides are of fundamental interest since conjugation between nitrogen lone-pair electrons and the carbonyl π-bond, results in distinct physical and chemical properties. As a result of conjugation between the carbonyl bond and the nitrogen lone pair, the C-N bond in amides possesses considerable double bond character thus; one can expect restricted rotation about this bond and a planar configuration for the amide group. This planar structure has been confirmed by measurement with X-rays and the *trans*- configuration is the most stable and it has been shown that protein chains involve this structure [1-9]. *N*-phenylacetamide is an interesting system because the nearly planar amide group display bond distances, which are close to those found in polypeptides. Spectroscopic and crystal structural studies give valuable informations on bond properties. The –CO-NH- group adopts a planar 'peptide-like' conformation, as in the case of formamide [10], methyl hydrazinocarboxylate [11], *N*-methylformamide [12], *o*-methyl acetanilide [13] and formanilide [14,15].

Many *N*-phenylacetamide derivatives exhibit fungicidal, herbicidal and pharmacological activities which further stimulated the recent interest in their chemistry. Anilide herbicides such as alachlor, acetochlor, metolachlor, pretilachlor and butachlor are promising weed control agents for a wide variety of economically important crops including rice, cotton, potatoes and corns [16-21]. *N*-phenylacetamide is used in medicine under the name antifebrin, as a febrifuge and it has pain relieving properties [22]. Acetanilide is a useful intermediate in various reactions of aniline in which it is desirable to protect the amino group.

As amides are the simplest model for peptides and also due to the fungicidal, herbicidal and several pharmacological activities of many acetanilide derivatives, their exact structure has been the subject of many experimental and theoretical studies [23-28]. The vibrational spectroscopic analysis of *N*-(3-methylphenyl)-2,2-dichloroacetamide has not been studied. Thus, in continuation of earlier studies on *N*-(chloro substituted phenyl)-2,2-dichloroacetamides [1] and *N*-(2-methylphenyl)-, and *N*-(4-methylphenyl)-2,2-dichloroacetamides [29], the *N*-(3-methylphenyl)-2,2-dichloroacetamide (3MPA) of the configuration $X_yC_6H_{5-y}$-NHCO-$CHCl_2$ (where, X = CH_3 and y = 1) has been synthesised. Spectroscopic and quantum chemical studies were carried out on 3MPA in an effort to provide possible explanations for vibrational frequencies and to understand the effect of methyl group on the characteristic frequencies of amide group.

2. Experimental

2.1. Synthesis

The compound *N*-(3-methylphenyl)-2,2-dichloroacetamide was synthesized from methylaniline, dichloroacetic acid and phosphorus oxychloride based on the procedure reported [1,29]. The pure samples of 3-methylaniline, dichloroacetic acid and phosphorus oxychloride were purchased from Aldrich chemicals, USA and are used as such without further purification. All other chemicals used are of analar (AR) grade. The synthesized crude compound was recrystallised from ethanol several times. The yield of the product is about 65%. The melting point of the recrystallised sample is 99 °C. The

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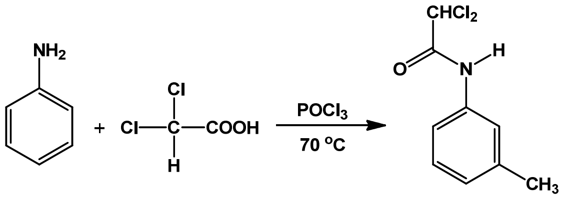
purity of the compound was confirmed by chemical analysis for C, H and N. The % found (calculated) C 49.59 (49.57), H 4.15 (4.16) and N 6.39 (6.42). The simple reaction is shown in Scheme 1.



Scheme 1

2.2. Instrumentation

The FT-IR spectrum of the compound was recorded by KBr disc method in the range of 4000 to 400 cm^{-1} with Shimadzu FTIR-8400 spectrometer, features a temperature stabilized DLATGS detector, 30 degree Michelson interferometer and a high-energy ceramic globar source. The spectral resolution is 2 cm^{-1}. The FT-Raman spectrum of the compound was recorded in the Bruker IFS 66V spectrometer with FRA 106 Raman module. The Raman spectrum was obtained in the wavenumber range 3500–100 cm^{-1}. The light scattering was excited using a low-noise diode pumped Nd:YAG laser source operating at 1.064 μm with 200 mW power. A special (enhanced) liquid nitrogen cooled germanium detector was used. The frequencies of all sharp bands are accurate to 2 cm^{-1}.

2.3. Computational details

The gradient corrected density functional theory (DFT) [30] with the three-parameter hybrid functional Becke3 (B3) [31] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [32], level of calculations have been carried out in the present investigation, using 6-311++G(d,p) basis sets with Gaussian 03 [33] program package. Following geometry optimisations with HF and B3LYP method using 6-311++G(d,p) and 6-31G(d,p) basis sets to characterise all stationary points as minima, the vibrational frequencies resulting in IR and Raman frequencies together with intensities, Raman depolarization ratios and thermodynamical parameters were determined. Owing to the complexity of the molecule, the potential energy distribution of the vibrational modes of the compounds are also calculated through normal coordinate analysis [34-36] using the force constants obtained from the B3LYP/6-311++G(d,p) method utilising the program of Fuhrer *et al.* [37].

3. Results and discussion

3.1. Molecular geometry

The molecular structure and atom numbering scheme of the compound 3MPA under investigation is shown in Figure 1. The geometry of the molecule is considered by possessing C_S point group symmetry. The 60 fundamental vibrations of 3MPA span the irreducible representations 39A′ + 21A″. All the vibrations are active in both IR and Raman.

3.2. Structural properties

The optimized structural parameters bond lengths and the bond angles for the thermodynamically preferred geometry of 3MPA at HF and B3LYP levels with 6-31G(d,p) and 6-311++G(d,p) basis sets are presented in Table 1 in accordance with the atom numbering scheme of the molecules shown in Figure 1. The bond lengths between the amide nitrogen and the aromatic ring, C6-N7 and between the amide nitrogen and the carbonyl carbon atom, N7-C8 given in Table 1 reflect the changes in conjugation. The adjacent methyl group influence on the rotation of acylamino group. The steric interaction of methyl substituent on the ring is of great importance in determining its structural and vibrational properties. As the steric hindrance increases and the plane of acylamino group rotates, the C6-N7 bond becomes longer and the N7-C8 bond becomes shorter. The thermodynamic parameters of the compound has also been computed at HF and B3LYP methods with 6-311++G(d,p) basis sets and are presented in Table 2. The calculated SCF energy and entropy of the compounds clearly indicates that 3MPA is more stable than 2MPA [29]. The bond length of the compounds 3MPA determined at the DFT level of theory is in good agreement with the structural parameters of *N*-phenylacetamide [38].

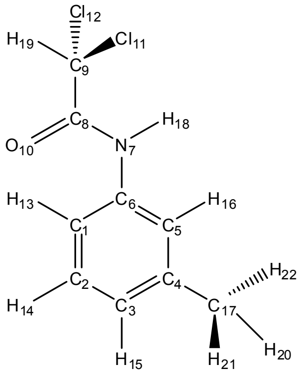


Figure 1. Molecular structure and atom numbering of *N*-(3-methylphenyl)-2,2-dichloroacetamide.

3.3. Vibrational analysis

The FT-IR and FT-Raman spectra of *N*-(3-methylphenyl)-2,2-dichloroacetamide are shown in Figures 2 and 3. All the observed wavenumbers are assigned in terms of fundamentals, overtones and combination bands. The observed and calculated frequencies by *ab initio* and DFT methods along with their relative intensities, probable assignments, depolarization ratios and potential energy distributions (PED) of 3MPA are summarized in Tables 3 and 4.

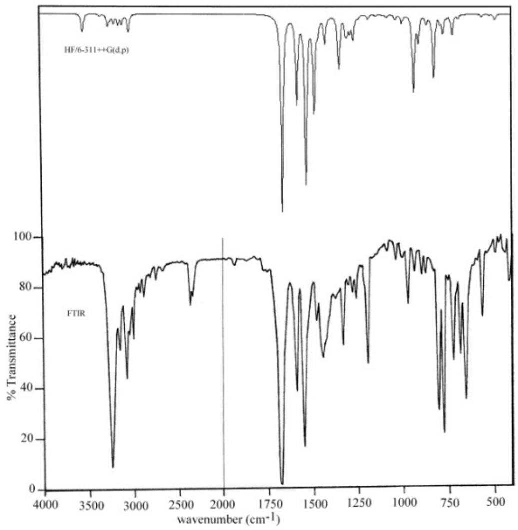


Figure 2. FT-IR and theoretical spectra of *N*-(3-methylphenyl)-2,2-dichloroacetamide.

Table 1. Structural parameters calculated for *N*-(3-methylphenyl)-2,2-dichloroacetamide employing HF and B3LYP methods with 6–311++G(d,p) and 6–31G(d,p) basis sets.

Structural parameters	*N*-(3-methylphenyl)-2,2-dichloroacetamide				
	HF 6–311++G(d,p)	B3LYP 6–311++G(d,p)	HF 6–31G(d,p)	B3LYP 6–31G(d,p)	Experimental [b]
Internuclear distance (Å)					
C1-C2	1.384	1.392	1.383	1.393	1.384
C2-C3	1.384	1.393	1.384	1.395	1.376
C3-C4	1.388	1.398	1.388	1.400	1.391
C4-C5	1.387	1.395	1.388	1.398	1.379
C5-C6	1.389	1.399	1.389	1.401	1.397
C6-C1	1.389	1.400	1.390	1.402	1.391
C6-N7	1.413	1.415	1.413	1.415	1.413
N7-C8	1.346	1.359	1.346	1.360	1.354
C8-C9	1.537	1.542	1.537	1.544	1.495
C8-O10	1.189	1.216	1.194	1.221	1.219
C4-C17	1.511	1.510	1.511	1.511	
C9-Cl[a]	1.778	1.804	1.776	1.806	
C-H (Ring)[a]	1.075	1.084	1.075	1.085	
C17-H (Methyl)[a]	1.085	1.093	1.084	1.093	
N7-H18	0.994	1.011	0.994	1.012	
C9-H19	1.072	1.083	1.073	1.086	
Bond angle (°)					
C2-C1-C6	118.515	118.573	118.525	118.539	
C2-C1-H13	120.684	121.207	120.812	121.477	
C6-C1-H13	120.801	120.220	120.662	119.984	
C1-C2-C3	121.620	121.392	121.605	121.386	
C1-C2-H14	118.787	118.908	118.791	118.927	
C3-C2-H14	119.595	119.701	119.605	119.687	
C2-C3-C4	120.047	120.382	120.058	120.386	
C2-C3-H15	119.914	119.959	119.944	120.020	
C4-C3-H15	120.039	119.659	120.999	119.594	
C3-C4-C5	118.488	118.319	118.522	118.365	
C3-C4-C17	121.442	121.383	121.448	121.374	
C5-C4-C17	120.070	120.298	120.030	120.261	
C4-C5-C6	121.414	121.357	121.356	121.267	
C4-C5-H16	119.218	119.322	119.213	119.338	
C6-C5-H16	119.369	119.321	119.431	119.395	
C1-C6-C5	119.918	119.977	119.935	120.057	
C1-C6-N7	123.591	123.198	123.531	123.055	
C5-C6-N7	116.491	116.825	116.534	116.888	
C6-N7-H18	114.908	115.086	115.020	115.266	
C6-N7-C8	128.813	129.006	128.633	128.717	
H18-N7-C8	116.279	115.908	116.348	116.017	
O10-C8-N7	126.956	126.867	127.031	127.038	
O10-C8-C9	117.842	118.222	117.702	118.095	
N7-C8-C9	115.202	114.911	115.267	114.867	
C8-C9-Cl11	111.513	111.701	111.571	111.642	
C8-C9-Cl12	111.510	111.697	111.566	111.639	
C8-C9-H19	107.290	107.642	106.983	107.460	
Cl11-C9-Cl12	111.029	110.955	111.098	110.967	
Cl11-C9-H19	107.635	107.293	107.690	107.443	
Cl12-C9-H19	107.635	107.292	107.689	107.443	
C4-C17-H20	111.071	111.190	111.172	111.278	
C4-C17-H22	110.961	111.243	111.074	111.364	
C4-C17-H21	110.967	111.250	111.080	111.369	
H20-C17-H22	107.985	107.890	107.894	107.754	
H20-C17-H21	107.989	107.826	107.898	107.762	
H21-C17-H21	107.727	107.332	107.563	107.112	
Dihedral angle (°)					
C2-C1-C6-N7	-179.998	-180.000	-179.999	-179.998	
C4-C5-C6-N7	180.000	180.000	180.000	180.000	
C1-C6-N7-H18	179.998	180.000	179.998	180.000	
C1-C6-N7-C8	0.004	0.004	0.005	0.002	
C5-C6-N7-H18	0.004	0.003	0.003	0.002	
C5-C6-N7-C8	-179.994	-179.994	-179.994	-179.997	
C6-N7-C8-O10	0.007	0.001	0.002	0.002	
C6-N7-C8-C9	-180.000	-180.000	-179.995	-179.997	
H18-N7-C8-O10	-180.000	-180.000	-179.995	-179.996	

[a] Mean value; [b] values taken from Ref. [38].

3.3.1. Carbon-carbon vibrations

The C-C stretching modes of 3MPA are assigned to the bands observed at 1595, 1432, 1410 and 1357 cm^{-1} in the Raman spectrum. The C-C stretching modes of 3MPA is observed in the range 1595-1357 cm^{-1} while in the case of 2MPA and 4MPA these are obtained in the range 1644-1382 cm^{-1} and 1642-1307 cm^{-1}, respectively [29]. The vibrational frequencies observed in the Raman spectrum of 3MPA at 1217 cm^{-1} is attributed to C-C(HCl_2) stretching mode. The in-plane and out of plane bending vibrations are assigned and presented in Tables 3 and 4. All these assignments are agreed well with the reported literature values [39]. The CCC in-plane bending and out of plane vibrations are described as mixed modes as there are about 10-20% PED contributions mainly from C-H in-plane and out of plane bending vibrations, respectively. In 3MPA the ring breathing mode corresponding to the a_{1g} mode of benzene is assigned to the wavenumber observed in the infrared spectrum at 878 cm^{-1} and in the Raman at 875 cm^{-1} [29].

Table 2. The calculated thermodynamic parameters of *N*-(3-methylphenyl)-2,2-dichloroacetamide employing HF and B3LYP methods with 6–311++G(d,p) and 6–31G(d,p) basis sets.

	***N*-(3-methylphenyl)-2,2-dichloroacetamide**			
Thermodynamic parameters (298 K)	**HF 6–311++G(d,p)**	**B3LYP 6–311++G(d,p)**	**HF 6–31G(d,p)**	**B3LYP 6–31G(d,p)**
SCF Energy (a.u)	-1394.511	–1398.952	–1394.359	–1399.776
Total Energy (thermal), E_{total} (kcal.mol^{-1})	117.447	109.876	118.145	110.439
Heat Capacity at const. volume, C_v (cal.mol^{-1}.K^{-1})	41.241	42.274	41.043	42.148
Entropy, S (cal.mol^{-1}.K^{-1})	112.073	107.445	112.464	107.309
Vibrational Energy, E_{vib} (kcal.mol^{-1})	115.669	108.098	116.368	108.661
Zero-point vibrational Energy, E_0 (kcal.mol^{-1})	110.272	102.844	110.989	103.428
Rotational Constants (GHz)				
A	1.187	1.161	1.189	1.159
B	0.290	0.286	0.289	0.286
C	0.271	0.267	0.270	0.267
Dipole moment (Debye)				
μ_x	1.297	1.699	1.340	1.641
μ_y	-2.212	-2.176	-2.019	-1.907
μ_z	0.001	0.001	0.000	0.001
μ_{total}	2.564	2.761	2.423	2.516

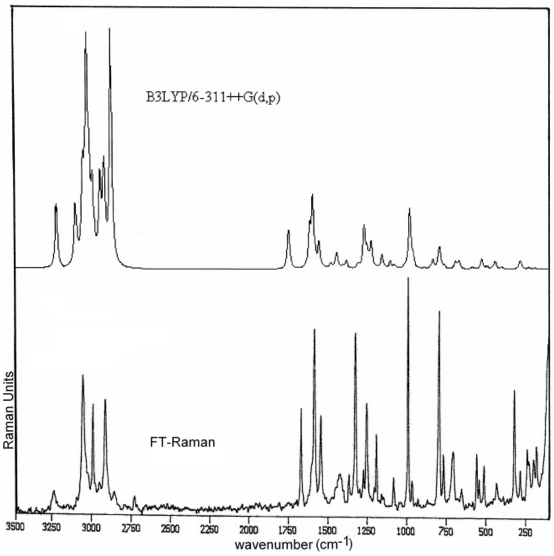


Figure 3. FT-Raman and theoretical spectra of *N*-(3-methylphenyl)-2,2-dichloroacetamide.

3.3.2. C-H vibrations

The aromatic C-H stretching vibrations are normally found between 3100 and 3000 cm^{-1}. In this region the bands are not affected appreciably by the nature of substituents. The aromatic C-H stretching frequencies arise from the modes observed at 3062 (a_{1g}), 3047 (e_{2g}), 3060 (b_{1u}) and 3080 (e_{1u}) cm^{-1} of benzene and its derivatives [40]. The C-H present in the benzene ring of 3MPA gives strong to weak bands at 3104, 3043 and 3014 cm^{-1}. The vibrational modes observed at 3073 and 3063 cm^{-1} in the infrared and Raman spectra are attributed to the C-H stretching of -$CHCl_2$ group. The aromatic C-H in-plane bending modes of 3MPA are observed at 1163, 1138, 1042 and 975 cm^{-1}. The C-H out of plane bending mode the compound are observed in the region 1100 to 600 cm^{-1} and are presented in Tables 3 and 4. The aromatic C-H in-plane and out of plane bending vibrations have substantial contribution from the ring CCC in-plane and out of plane bending, respectively. The C-H(Cl_2) in-plane and out of plane bending vibrations are significantly mixed with CC in-plane and out of plane modes, respectively.

3.3.3. Amide group vibrations

The amide (–CONH–) group vibrations of the compounds investigated are correlated with *N*-(phenyl)-2,2-dichloro acetamide (NPA), *N*-(2-methylphenyl)-2,2-dichloroacetamide (2MPA) and *N*-(4-methylphenyl)-2,2-dichloroacetamide (4MPA) vibrations [1,29]. Amide-I band, the C=O stretching mode is the strongest band in the infrared spectrum and appears with diminished intensity in the Raman spectrum. In *N*-phenylacetamide structure there is competition between the phenyl ring and the C=O for the lone pair of electrons of the nitrogen. The strong IR band observed at 1680 cm^{-1} is assigned to the amide-I band of 3MPA while the Raman counterpart is obtained as very strong band at 1678 cm^{-1}. The comparison of C=O stretching of 3MPA with that of NPA molecule reveals that the C=O stretching frequencies of the compound under investigation does not show significant variation from that of the parent compound *N*-phenyl-2,2-dichloroacetamide.

The N-H stretching band of secondary amides seen in the infrared spectrum between 3370 and 3170 cm^{-1}. A weaker band may appear at about 3100 cm^{-1} in secondary amides due to Fermi resonance of 1550 cm^{-1}. Thus the very strong band observed at 3245 cm^{-1} in infrared spectrum and 3247 cm^{-1} in Raman is attributed to the N-H stretching of 3MPA molecule. The 4MPA shows the characteristic very strong N-H stretching band at 3240 in the IR and at 3236 cm^{-1} in Raman spectrum. In comparison with NPA, the N-H stretching frequency of 3MPA is lowered by 20-30 cm^{-1} while between 2MPA and 3MPA there is no significant changes.

The dipole moment measurements, X-ray and neutron diffraction studies demonstrated that the trans conformer of *N*-phenylacetamide is the predominant and most stable [14,15,39,41-42]. The influence of the ring substituent on N-H stretching frequency of *N*-phenylacetamide and its derivatives may be the resultant steric effect, direct field effects, hydrogen bonding and bond polarisation effects [43]. The steric effect of methyl substituent must be considered in conjunction with the conformations. The increase in N-H stretching frequency may be expected in introduction of an *o*-methyl group into the phenyl ring of *N*-phenylacetamide. In the present investigation, it is observed that there is no increase in the N-H stretching frequencies of 3MPA than that of NPA. This clearly confirms that the steric effect due to methyl group is not significantly operating on the N-H stretching.

The frequencies observed at 1554 and 1555 cm^{-1} in 3MPA are ascribed to the amide-II band, N-H in-plane bending mode. Shift in the lower frequency side with that of 2MPA (1588 and 1590 cm^{-1}) shows that the methyl group in 3MPA exerts less steric influence on the N-H bond. The C-N stretching mode, the amide-III band, of 3MPA is assigned at 1335 cm^{-1} in IR and Raman spectra, respectively. The spectral data indicates that no rise in C-N stretching frequencies of 3MPA and there is no hyper conjugative influence of the methyl group towards the C-N bond.

Table 3. The observed FT-IR, FT-Raman and calculated frequencies using HF/6–311++G(d,p) and B3LYP/6–311++G(d,p) force field along with their relative intensities, probable assignments and potential energy distribution (PED) *N*-(3-methylphenyl)-2,2-dichloroacetamide[a].

Species	Observed wavenumber (cm^{-1})		HF/6–311++G(d,p) Calculated wavenumber				B3LYP/6–311++G(d,p) Calculated wavenumber			DPR	Assign.	%PED
	FT-IR	FT-R	Unscaled (cm^{-1})	Scaled (cm^{-1})	IR intensity	Raman Activity	Unscaled (cm^{-1})	Scaled (cm^{-1})	IR intensity			
A′	3245 vs	3247 w	3863	3245	44.64	49.66	3594	3235	29.33	0.13	νNH	$95\nu_{NH}$
A′	3104 m		3419	3111	2.65	46.47	3242	3112	4.19	0.21	νCH	$92\nu_{CH}$
A′	3075 s		3368	3065	2.40	62.64	3186	3059	1.57	0.22	νCH	$93\nu_{CH}$
A′		3060 s	3342	3041	21.29	160.39	3183	3056	16.80	0.21	νC-H(Cl$_2$)	$94\nu_{CH}$
A′	3043 m		3323	3024	7.43	60.32	3165	3038	6.29	0.75	νCH	$92\nu_{CH}$
A′		3014 vw	3299	3002	17.04	54.84	3139	3013	12.93	0.28	νCH	$94\nu_{CH}$
A′	2998 m	2999 s	3247	2955	23.25	61.83	3106	2982	16.07	0.71	ν_aCH$_3$	$93\nu_{CH}$
A″	2955 vw	2956 vw	3219	2929	23.33	72.52	3075	2952	14.93	0.75	ν_aCH$_3$	$96\nu_{CH}$
A′	2922 vw	2923 s	3168	2883	35.18	184.68	3026	2905	29.16	0.03	ν_sCH$_3$	$92\nu_{CH}$
A′	1680 s	1678 vs	1951	1678	379.46	30.32	1761	1691	339.16	0.18	νC=O	$96\nu_{C=O}$
A′			1801	1639	238.01	29.75	1651	1634	134.39	0.57	νC=C	$92\nu_{C=C}$
A′	1594 s	1595 vs	1778	1618	5.72	53.82	1632	1616	2.47	0.54	νC=C	$91\nu_{C=C}$
A′	1554 vs	1555 s	1732	1576	389.06	19.71	1584	1568	259.16	0.43	βN-H	$93\beta_{NH}$
A′			1650	1502	159.81	4.28	1523	1508	145.34	0.22	νC=C	$88\nu_{C=C}$
A″	1482 m		1615	1470	12.42	4.60	1498	1483	14.41	0.74	δ_aCH$_3$	$91\delta_{CH3}$
A′	1447 m	1447 vw	1605	1461	6.99	9.82	1488	1473	7.95	0.75	δ_aCH$_3$	$93\delta_{CH3}$
A′		1432 w	1562	1421	43.17	2.52	1443	1429	42.11	0.66	νC-C	$85\nu_{CC}$
A′		1410 vw	1538	1400	3.55	6.16	1417	1403	1.30	0.29	νC-C	$87\nu_{CC}$
A′		1357 s	1456	1325	47.04	3.08	1348	1335	7.38	0.17	νC-C	$82\nu_{CC}$
A′	1335 m	1335 m	1411	1284	215.28	32.94	1337	1324	80.19	0.10	νC-N	$84\nu_{CN}$
A′	1283 w	1283 vw	1389	1264	22.57	8.97	1285	1272	22.29	0.17	δ_sCH$_3$	$90\delta_{CH3}$
A′	1260 w	1262 s	1381	1257	30.49	5.62	1273	1260	19.33	0.75	βC-H(Cl$_2$)	$83\beta_{CH} + 12\beta_{CC}$
A′			1358	1236	11.18	19.36	1253	1240	21.66	0.17	νN-(C$_6$H$_5$)	$87\nu_{NC}$
A′		1217 vw	1315	1197	3.78	0.26	1229	1217	35.54	0.13	νC-C	$84\nu_{CC}$
A″	1199 s	1200 m	1281	1166	13.60	11.47	1197	1185	3.32	0.34	γC-H(Cl$_2$)	$77\gamma_{CH} + 16\gamma_{CC}$
A′		1163 vw	1224	1114	3.93	5.87	1185	1173	1.92	0.75	βC-H	$75\beta_{CH} + 15\beta_{CCC}$
A′	1138 vw		1193	1086	3.57	3.08	1119	1108	8.05	0.32	βC-H	$73\beta_{CH} + 18\beta_{CCC}$
A″	1094 w	1092 w	1160	1056	2.47	0.17	1062	1051	2.89	0.75	ωCH$_3$	$66\omega_{CH3} +21\gamma_{CH}$
A′	1042 w		1112	1012	0.70	0.08	1038	1028	0.17	0.75	βC-H	$71\beta_{CH} + 16\beta_{CCC}$
A′	1005 vw	1001 vs	1112	1012	2.27	1.65	1015	1005	0.99	0.57	ρCH$_3$	$77\rho_{CH3} + 14\beta_{CH}$
A′	975 m	976 w	1083	986	2.62	47.51	998	988	0.64	0.07	βC-H	$70\beta_{CH} + 20\beta_{CCC}$
A″			1061	966	2.59	5.59	981	971	5.03	0.02	γC-H	$72\gamma_{CH} + 18\gamma_{CCC}$
A″	938 w	942 vw	1017	925	5.30	0.38	920	911	2.98	0.75	γC-H	$74\gamma_{CH} + 20\gamma_{CCC}$
A″	900 w	894 vw	980	892	5.67	1.14	916	907	4.85	0.57	γC-H	$70\gamma_{CH} + 22\gamma_{CCC}$
A′	878 w	875 vw	965	878	14.72	0.11	868	859	11.80	0.75	βCCC	$72\beta_{CCC} + 18\beta_{CH}$
A″			918	835	52.76	7.35	802	794	0.38	0.75	γC-H	$69\gamma_{CH} + 21\gamma_{CCC}$
A′	806 vs	804 vs	880	801	76.04	0.73	802	794	111.85	0.75	βC=O	$85\beta_{C=O} + 12\beta_{NH}$
A′	780 vs	777 m	870	792	46.40	17.25	796	788	14.15	0.07	ν_aCCl$_2$	$84\nu_{CCl} + 12\beta_{CH}$
A″	726 s	730 m	837	762	16.72	2.52	760	752	40.15	0.73	γN-H	$77\gamma_{NH} + 18\gamma_{CO}$
A′		715 m	765	696	5.65	0.17	704	697	13.91	0.75	βCCC	$74\beta_{CCC} + 14\beta_{CH}$
A′	687 s		757	689	98.83	5.70	685	678	100.19	0.16	ν_sCCl$_2$	$82\nu_{CCl} + 12\beta_{CH}$
A″	658 vs	658 vw	733	667	2.16	6.25	648	642	1.88	0.75	γC=O	$82\gamma_{C=O} + 14\gamma_{NH}$
A′	566 m	567 m	634	577	1.81	1.77	584	578	12.27	0.75	βC-C	$65\beta_{CC} + 22\beta_{CH}$
A′	542 vw	542 w	572	521	53.90	0.22	560	554	27.83	0.75	βCCC	$68\beta_{CCC} + 18\beta_{CH}$
A′	512 vw	521 m	568	517	2.81	8.07	534	529	1.48	0.18	βC-N	$72\beta_{CN} + 16\beta_{CO}$
A′			531	483	31.16	2.08	492	487	31.46	0.57	βN-C$_6$H$_5$	$67\beta_{NC} + 19\beta_{CCC}$
A″	462 vw		492	448	5.18	0.23	449	445	6.05	0.75	γC-N	$74\gamma_{CN} + 18\gamma_{C=O}$
A″	430 vw	433 w	474	431	0.49	7.01	433	429	0.44	0.04	γN-C$_6$H$_5$	$68\gamma_{NC} + 16\gamma_{CCC}$
A′	417 m	422 m	428	389	0.20	1.38	395	391	0.35	0.36	βC-C(H$_3$)	$65\beta_{CC} + 21\beta_{CH}$
A′		330 s	297	270	3.75	3.13	273	270	0.79	0.33	δCCl$_2$	$79\delta_{CCl2} + 15\beta_{CH}$
A″		293 w	295	268	0.18	1.89	273	270	3.28	0.75	γCCC	$64\gamma_{CCC} + 20\gamma_{CH}$
A″		248 m	289	263	1.50	2.23	267	264	0.60	0.56	γC-C(H$_3$)	$62\gamma_{CC} + 18\gamma_{CH}$
A″		231 vw	231	210	1.55	1.36	214	212	1.86	0.75	τCCl$_2$	$64\tau_{CCl2} + 24\omega_{CCl2}$
A″		188 m	191	174	5.86	1.14	175	173	6.38	0.32	ωCCl$_2$	$62\omega_{CCl2} + 24\tau_{CCl2}$
A′		101 vs	185	168	5.79	0.02	169	167	3.57	0.75	ρCCl$_2$	$70\rho_{CCl2} + 18\beta_{CH}$
A″			102	93	0.10	0.48	93	93	0.14	0.74	γCCC	$65\gamma_{CCC} + 24\gamma_{CH}$
A″			50	50	0.06	3.59	55	55	4.96	0.75	γCCC	$61\gamma_{CCC} + 21\gamma_{CH}$
A″			49	49	7.76	0.21	46	46	0.45	0.75	γCCC	$63\gamma_{CCC} + 24\gamma_{CH}$
A″			35	35	0.68	3.89	32	32	1.58	0.75	γCCC	$62\gamma_{CCC} + 22\gamma_{CH}$
A″			15	15	0.08	0.09	14	14	0.02	0.75	τCH$_3$	90τCH$_3$

[a] ν-stretching; β-in-plane bending; δ-deformation; ρ-rocking; γ-out of plane bending; ω-wagging; τ-twisting/torsion; IR intensities, KM/mole; Raman scattering activities, (A^o)^4/(a.m.u); DPR: Depolarization ratio.

The amide-IV, C=O in-plane bending of 3MPA is found at 806 and 804 cm^{-1} in the IR and Raman, respectively. There is no significant shift in the C=O in-plane bending, frequencies of 3MPA than that of NPA, 2MPA and 4MPA. The amide-V, the N-H out of plane bending is observed as strong and medium bands at 726 and 730 cm^{-1} in 3MPA. The C=O out of plane bending of 3MPA is seen at 658 cm^{-1}. Both the amide-V and amide-VI out of plane bending modes of 2MPA, 3MPA and 4MPA is significantly raised than that of NPA. The PED calculations determine that the amide-IV and amide-VI bands possessing the character of N-H vibrations by mixing. The amide-V bands of 3MPA is significantly overlapped C=O out of plane bending vibrations.

3.3.4. Methyl group (–CH$_3$) vibrations

The symmetric, ν_s(CH$_3$) frequency of 3MPA is established at 2922 and 2923 cm^{-1}. The asymmetric stretching of 3MPA, ν_a(CH$_3$) is assigned at 2998 cm^{-1} under A' species. The depolarized frequencies seen at 2955and 2956 cm^{-1} in the spectra of 3MPA are attributed to the ν_a(CH$_3$) under A" species. The asymmetrical methyl deformation mode, δ_a(CH$_3$) of 3MPA are observed at 1482 cm^{-1} under A" species while the band at 1447 cm^{-1} in the infrared spectrum is attributed to the methyl asymmetric deformational modes δ_a(CH$_3$) in the A' species.

Table 4. The observed FT-IR, FT-Raman and calculated frequencies using HF/6–31G(d,p) and B3LYP/6–31G(d,p) force field along with their relative intensities, probable assignments and potential energy distribution (PED) of *N*-(3-methylphenyl)-2,2-choroacetamide[a].

Species	Observed wavenumber (cm^{-1})		HF/6–31G(d,p) Calculated wavenumber				B3LYP/6–31G(d,p) Calculated wavenumber			DPR	Assign.	%PED
	FT-IR	FT-R	Unscaled (cm^{-1})	Scaled (cm^{-1})	IR intensity	Raman Activity	Unscaled (cm^{-1})	Scaled (cm^{-1})	IR intensity			
A′	3245 vs	3247 w	3880	3259	45.55	42.16	3610	3285	27.71	0.14	νNH	94ν_{NH}
A′	3104 m		3446	3136	2.23	49.81	3266	3135	3.75	0.21	νCH	95ν_{CH}
A′	3073 s		3381	3077	2.37	69.75	3200	3072	20.90	0.28	νCH	92ν_{CH}
A′		3060 s	3364	3061	26.72	165.61	3198	3070	1.08	0.19	νC-H(Cl$_2$)	93ν_{CH}
A′	3043 m		3344	3043	9.11	64.85	3183	3056	7.44	0.75	νCH	94ν_{CH}
A′		3014 vw	3320	3021	18.87	55.22	3156	3030	14.57	0.28	νCH	92ν_{CH}
A′	2998 m	2999 s	3271	2977	22.67	63.84	3130	3005	14.89	0.73	ν_aCH$_3$	93ν_{CH}
A″	2955 vw	2956 vw	3242	2950	28.44	84.53	3098	2974	18.11	0.75	ν_aCH$_3$	94ν_{CH}
A′	2922 vw	2923 s	3186	2899	35.27	147.37	3042	2920	28.24	0.03	ν_sCH$_3$	93ν_{CH}
A′	1680 s	1678 vs	1983	1686	333.70	24.09	1796	1688	280.47	0.16	νC=O	95$\nu_{C=O}$
A′			1819	1655	189.05	29.89	1668	1651	103.31	0.59	νC=C	90$\nu_{C=C}$
A′	1594 s	1595 vs	1794	1633	8.30	42.05	1647	1631	4.54	0.54	νC=C	91$\nu_{C=C}$
A′	1554 vs	1555 s	1745	1588	397.63	15.99	1594	1578	259.58	0.38	βN-H	92β_{NH}
A′			1666	1516	170.85	4.11	1537	1522	149.69	0.24	νC=C	89$\nu_{C=C}$
A″	1482 m		1626	1480	11.94	9.31	1510	1495	13.30	0.74	δ_aCH$_3$	93δ_{CH3}
A′	1447 m	1447 vw	1615	1470	5.16	19.90	1500	1485	5.76	0.75	δ_aCH$_3$	91δ_{CH3}
A′		1432 w	1577	1435	43.66	4.81	1456	1441	41.02	0.73	νC-C	89ν_{CC}
A′		1410 vw	1551	1411	3.74	12.30	1429	1415	1.10	0.41	νC-C	88ν_{CC}
A′		1357 s	1465	1333	42.42	1.77	1364	1350	20.98	0.23	νC-C	90ν_{CC}
A′	1335 m	1335 m	1421	1293	198.61	20.61	1344	1331	52.17	0.16	νC-N	89ν_{CN}
A′	1283 w	1283 vw	1391	1266	14.08	7.04	1296	1283	17.35	0.24	δ_sCH$_3$	92δ_{CH3}
A′	1260 w	1262 s	1383	1259	34.48	8.94	1272	1259	28.74	0.75	βC-H(Cl$_2$)	81β_{CH} + 14β_{CC}
A′			1367	1244	14.90	13.43	1254	1241	27.46	0.32	νN-C$_6$H$_5$	85ν_{NC}
A′		1217 vw	1325	1206	2.41	0.13	1232	1220	24.74	0.70	νC-C	88ν_{CC}
A″	1199 s	1200 m	1291	1175	11.29	11.05	1202	1190	2.56	0.42	γC-H(Cl$_2$)	77γ_{CH} + 16γ_{CC}
A′		1163 vw	1237	1126	4.03	7.28	1194	1182	1.94	0.74	βC-H	75β_{CH} + 15β_{CCC}
A′	1138 vw		1204	1096	3.78	2.71	1126	1115	7.83	0.52	βC-H	74β_{CH} + 14β_{CCC}
A″	1094 w	1092 w	1165	1060	3.77	0.51	1066	1055	4.26	0.75	ωCH$_3$	69ω_{CH3} +21γ_{CH}
A′	1042 w		1120	1019	1.63	0.42	1043	1033	0.10	0.75	βC-H	70β_{CH} + 15β_{CCC}
A′	1005 vw	1001 vs	1118	1017	1.43	2.21	1016	1006	0.59	0.65	ρCH$_3$	77ρ_{CH3} + 15β_{CH}
A′	975 m	976 w	1090	992	1.66	33.14	991	981	1.12	0.13	βC-H	72β_{CH} + 18β_{CCC}
A″			1067	971	1.98	2.53	986	976	3.63	0.04	γC-H	74γ_{CH} + 16γ_{CCC}
A″	938 w	942 vw	1024	932	7.41	1.32	920	911	4.28	0.75	γC-H	72γ_{CH} + 21γ_{CCC}
A″	900 w	894 vw	986	897	5.19	0.68	916	907	3.22	0.44	γC-H	70γ_{CH} + 22γ_{CCC}
A″	878 w	875 vw	974	886	15.45	2.23	870	861	9.62	0.75	γC-H	65γ_{CH} + 24γ_{CCC}
A′			917	834	53.35	8.06	805	797	15.24	0.75	βCCC	67β_{CCC} + 18β_{CH}
A′	806 vs	804 vs	889	809	68.96	1.36	804	796	89.83	0.75	βC=O	80$\beta_{C=O}$ + 14β_{NH}
A′	780 vs	777 m	873	794	47.50	14.06	794	786	14.74	0.10	ν_aCCl$_2$	78ν_{CCl} + 12β_{CH}
A″	726 s	730 m	840	764	18.57	3.27	760	752	44.55	0.71	γN-H	77γ_{NH} + 16γ_{CO}
A′		715 m	770	701	2.38	0.40	706	699	4.55	0.75	βCCC	74β_{CCC} + 12β_{CH}
A′	687 s		756	688	100.69	5.26	687	680	102.91	0.22	ν_sCCl$_2$	82ν_{CCl} + 12β_{CH}
A″	658 vs	658 vw	737	671	2.39	5.62	649	643	2.55	0.75	γC=O	80$\gamma_{C=O}$ + 14γ_{NH}
A′	566 m	567 m	635	578	5.08	2.28	588	582	21.56	0.75	βC-C	67β_{CC} + 20β_{CH}
A′	542 vw	542 w	578	526	66.20	0.88	563	557	29.29	0.75	βCCC	70β_{CCC} + 14β_{CH}
A′	512 vw	521 m	571	520	2.80	6.70	534	529	1.74	0.27	βC-N	71β_{CN} + 15β_{CO}
A′			533	485	32.81	1.47	492	487	33.88	0.61	βN-C$_6$H$_5$	67β_{NC} + 14β_{CCC}
A″	462 vw		492	448	2.90	0.47	450	446	3.33	0.75	γC-N	76γ_{CN} + 16$\gamma_{C=O}$
A″	430 vw	433 w	477	434	0.62	6.87	435	431	0.50	0.06	γN-C$_6$H$_5$	69γ_{NC} + 18γ_{CCC}
A′	417 m	422 m	430	391	0.37	1.72	395	391	0.42	0.42	βC-C(H$_3$)	65β_{CC} + 21β_{CH}
A′		330 s	299	272	0.03	2.95	277	274	0.36	0.75	δCCl$_2$	77δ_{CCl2} + 18β_{CH}
A″		293 w	299	272	4.01	3.76	275	272	3.53	0.38	γCCC	65γ_{CCC} + 24γ_{CH}
A″		248 m	290	264	1.33	2.51	267	264	0.64	0.60	γC-C(H$_3$)	62γ_{CC} + 18γ_{CH}
A″		231 vw	232	211	0.85	2.21	216	214	1.13	0.75	τCCl$_2$	67τ_{CCl2} + 22ω_{CCl2}
A″		188 m	193	176	6.14	1.27	177	175	6.93	0.40	ωCCl$_2$	65ω_{CCl2} + 24τ_{CCl2}
A′		101 vs	188	171	5.81	0.08	172	170	3.33	0.75	ρCCl$_2$	71ρ_{CCl2} + 16β_{CH}
A″			103	94	0.08	0.52	95	95	0.16	0.74	γCCC	63γ_{CCC} + 22γ_{CH}
A″			50	50	0.01	5.35	54	54	4.45	0.75	γCCC	65γ_{CCC} + 21γ_{CH}
A″			42	42	8.25	0.58	45	45	0.29	0.75	γCCC	64γ_{CCC} + 24γ_{CH}
A″			38	38	0.22	5.14	42	42	1.55	0.75	γCCC	66γ_{CCC} + 22γ_{CH}
A″			13	13	0.08	0.07	17	17	0.08	0.75	τCH$_3$	90τCH$_3$

[a] ν-stretching; β-in-plane bending; δ-deformation; ρ-rocking; γ-out of plane bending; ω-wagging; τ-twisting/torsion; IR intensities, KM/mole; Raman scattering activities, (A^o)^4/(a.m.u); DPR: Depolarization ratio.

3.3.5. CCl$_2$ group vibrations

When several chlorine atoms are attached to one carbon atom, the band is usually more intense and at high frequency end of the assigned limits. The C-Cl absorption is observed in the broad region between 850 and 550 cm^{-1}. Thus, the strong and medium bands in IR at 780 and 777 cm^{-1} cm^{-1} are assigned to the asymmetric CCl$_2$ stretching wavenumber of 3MPA. The symmetric CCl$_2$ stretching is observed at 687 cm^{-1} in 3MPA. The CCl$_2$ asymmetric and symmetric stretching frequency of 3MPA does not show any appreciable variation from that of the corresponding frequencies in NPA, 2MPA and 4MPA. The in-plane CCl$_2$ deformation vibrations and the out of plane CCl$_2$ twisting and wagging modes are obtained in the low frequency region of the Raman spectra as medium to strong bands. These assignments are in good agreement with the literature values [1,44] and well supported by normal coordinate analysis. The CCl$_2$ wagging mode significantly overlaps with CCl$_2$ twisting mode and vice versa and also the in-plane C-H bending vibrations contributed to CCl$_2$ deformation and rocking modes.

Computed harmonic frequencies typically overestimate vibrational fundamentals due to basis set truncation and neglect of electron correlation and mechanical anharmonicity [45]. To compensate these shortcomings and to correlate the experimentally observed and theoretically computed frequencies for each vibrational modes of the compounds under HF and DFT-B3LYP methods, scale factors are introduced [46-54]. Initially, all scaling factors have been kept fixed at a value of 1.0 to produce the pure HF and DFT calculated vibrational frequencies which are given in Tables 3 and 4. Subsequently, in HF method the scaling factors 0.84 and 0.91 used for N–H and all other vibrations, respectively, except for C=O stretching. For C=O stretching, 0.86 and 0.85 were used with 6-311++G(d,p) and 6-31G(d,p) basis sets, respectively. In B3LYP level the correction factors 0.90, 0.96 and 0.99 for N-H, C-H and all other frequencies of 3MPA while for C=O, 0.96 and 0.94 with 6-311++G(d,p) and 6-31G(d,p) basis sets are the scale factors. The resultant scaled frequencies are also listed in Table 3 and 4. These are much closer to unity and thus the vibrational frequencies calculated by using the B3LYP functional with 6-311++G(d,p) basis set can be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra.

4. Conclusion

The molecular structural parameters, thermodynamic properties and vibrational frequencies of the fundamental modes of the optimized geometry of 3MPA have been determined from HF and DFT-B3LYP methods. The FT-IR and FT-Raman vibrational frequencies of the compounds under investigations revealed close similarities in the magnitudes of the frequencies when compared with 2MPA and 3MPA, in spite of the fact that the methyl substituent in the phenyl ring are at different positions. The comparison of the fundamental vibrations, the following observations are made: The magnitude of C=O frequency variation is also not significantly influenced by the position of methyl group. In the present investigation, there is no increase in the N-H stretching frequency of 3MPA than that of *N*-phenyl-2,2-dichloro-acetamide, clearly confirms that the steric effect due to *m*-methyl group is not significantly operating on the N-H. The comparison of other amide group frequencies did not show any appreciable variation in the respective wave numbers except the amide IV band, C=O in-plane bending and the amide-VI band, C=O out of plane bending mode of the compounds. The basis set 6-311++G(d,p) is reliable for the determination of the electronic structure by quantum chemical investigations of such complex compounds.

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