

Contents lists available at ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

# Synthesis, structural, vibrational and quantum chemical investigations of *N*-(2-methylphenyl)-2,2-dichloroacetamide and *N*-(4-methylphenyl)-2,2-dichloroacetamide

# V. Arjunan<sup>a,\*</sup>, P. Ravindran<sup>b</sup>, K. Subhalakshmi<sup>a</sup>, S. Mohan<sup>c</sup>

<sup>a</sup> Department of Chemistry, Kanchi Mamunivar Centre for Post-Graduate Studies, Puducherry – 605 008, India

<sup>b</sup> Department of Chemistry, Mahatma Gandhi Government Arts College, Mahe – 673 311, India

<sup>c</sup> Centre for Research and Development, PRIST University, Thanjavur – 613 403, India

## ARTICLE INFO

Article history: Received 22 February 2009 Received in revised form 25 June 2009 Accepted 7 July 2009

Keywords: FTIR FT-Raman N-(Methylphenyl)-2,2-dichloroacetamide DFT Ab initio

#### 1. Introduction

*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. Amides are of fundamental chemical interest as conjugation between nitrogen lone-pair electrons and the carbonyl  $\pi$ -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 and 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]. According to literature data, three different conformational forms of the amide group are possible: trans, cis (planar) and non-planar. Ab initio calculations and the rotational spectrum of acetanilide confirmed that the planar conformer with the CH<sub>3</sub> group anti to the ring is the most stable [10,11], in agreement with the reports of other experimental investigations [12-15]. The -CO-NH- group adopts a planar 'peptide-like' conformation, as in the case of formamide [16], methyl hydrazinocarboxylate [17], N-

# ABSTRACT

*N*-(2-Methylphenyl)-2,2-dichloroacetamide (2MPA) and *N*-(4-methylphenyl)-2,2-dichloroacetamide (4MPA) of the configuration  $X_yC_6H_{5-y}$ -NHCO-CHCl<sub>2</sub> (where, X = CH<sub>3</sub> and y = 1) were synthesised and an extensive spectroscopic investigations have been carried out by recording the Fourier transform infrared (FTIR) and FT-Raman spectra and subjecting them to normal co-ordinate analysis, in an effort to provide mixing of the fundamental modes with the help of potential energy distribution (PED). The *ab initio* and DFT studies were carried out with 6-311++G(d,p) basis set to determine the structural, thermodynamical and vibrational characteristics of the compounds and also to understand the steric influence of methyl group on the characteristic frequencies of amide (–CONH–) group.

© 2009 Elsevier B.V. All rights reserved.

methylformamide [18], *o*-methylacetanilide [19] and formanilide [12,13]. The influence by intermolecular hydrogen bonding and crystal packing on the conformation of the acylamino group relative to the aromatic ring were discussed [20,21].

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 [22–25]. The choloroacetanilde herbicide alachlor is one of the most extensively used agro chemical [26,27]. Propanil (3,4-dichloropropioanilide) is a selective contact anilide herbicide commonly used for the control of broad leveled and grass weeds. *N*-Phenylacetamide is used in medicine under the name antifebrin, as a febrifuge and it has pain relieving properties [28]. Acetanilide is an useful intermediate in various reactions of aniline in which it is desirable to protect the amino group.

Many researches have been carried out the nonlinear properties of molecular crystals of acetanilide [29–32]. *Ab initio* molecular orbital calculations and infrared spectroscopic data for the frequencies are applied to analyse the grouping in a series model aromatic secondary amides: formanilide; acetanilide; *o*-methylacetanilide; 2,6-dimethylformanilide, 2,6-dimethylacetanilide; *N*-benzylacetamide and *N*-benzylformamide [19,33,34]. The temperature dependence of the Raman scattering from a single crystal of acetanilide and fully deuterated acetanilide

<sup>\*</sup> Corresponding author. Tel.: +91 413 2211111; fax: +91 413 2251613. *E-mail address:* varjunftir@yahoo.com (V. Arjunan).

<sup>1386-1425/\$ –</sup> see front matter  $\ensuremath{\mathbb{C}}$  2009 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2009.07.008

Melting point and elemental analysis of the prepared compounds.

Name of the compound	Melting point (°C)	% found/(calculate	ed)	
		C	Н	Ν
N-(2-Methylphenyl)-2,2-dichloroacetamide N-(4-Methylphenyl)-2,2-dichloroacetamide	130 152	49.52(49.57) 49.50(49.57)	4.12 (4.16) 4.17 (4.16)	6.41 (6.42) 6.43 (6.42)

in the low frequency (phonon) and C=O stretching regions was studied by Sauvajol et al. [35].

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 [19,36–39]. The vibrational spectroscopic analysis of acetanilide derivatives particularly the *N*-(methyl substituted phenyl)-2,2-dichloroacetamides have not been studied. Thus, in continuation of earlier studies on *N*-(chloro substituted phenyl)-2,2-dichloroacetamides [1], we have prepared *N*-(2-methylphenyl)- and *N*-(4-methylphenyl)-2,2dichloroacetamides of the configuration  $X_yC_6H_{5-y}$ -NHCO-CHCl<sub>2</sub> (where, X = CH<sub>3</sub> and y = 1) and an extensive spectroscopic and quantum chemical studies were carried out 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

The compounds *N*-(2-methylphenyl)-, and *N*-(4-methylphenyl)-2,2-dichloroacetamides were prepared from the respective methylaniline, dichloroacetic acid and phosphorus oxychloride based on the procedure reported [1]. The pure samples of 2-methylaniline, 4-methylaniline, dichloroacetic acid and phosphorus oxychloride were purchased from Aldrich chemicals, U.S.A. and are used as such without further purification. All other chemicals used are of analar (AR) grade. The synthesised crude compounds were recrystallised from ethanol several times. The melting points of the recrystallised samples were determined. The purity of the compounds were confirmed by chemical analysis for C, H and N. The compounds prepared, the melting point and elemental analysis of the compounds are presented in Table 1.

The FTIR spectra of the compounds were recorded in the solid phase by KBr disc method in a Bruker IFS 66 V spectrometer in the range of 4000–400 cm<sup>-1</sup>. The spectral resolution was  $\pm 2$  cm<sup>-1</sup>. The FT-Raman spectra of these compounds were also recorded with the same instrument with FRA 106 Raman module. The Raman spectrum was obtained in the wavenumber range 3500–100 cm<sup>-1</sup>. The light scattering was excited using a low-noise diode pumped Nd:YAG laser source operating at 1.064  $\mu$ m with 200 mW power. A special (enhanced) liquid nitrogen cooled germanium detector was used. The frequencies of all sharp bands are accurate to  $\pm 2$  cm<sup>-1</sup>.

#### 3. Computational details

The gradient corrected density functional theory (DFT) [40] with the three-parameter hybrid functional Becke3 (B3) [41] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [42], level of calculations have been carried out in the present investigation, using 6-311++G(d,p) basis sets with Gaussian-03 [43] program package, invoking gradient geometry optimisation [44] on a Pentium-IV/1.6 GHz processor. Following geometry optimisations with HF and B3LYP method using 6-311++G(d,p) basis sets, the optimised structural parameters were used in the vibrational frequency calculations to characterise all stationary points as minima. The harmonic vibrational frequency calculations were carried out for 2MPA and 4MPA resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The dipole moment derivatives and polarizability derivatives were computed analytically. The Raman intensities were computed in the double harmonic approximation [45], ignoring cubic and higher force constants and omitting second and higher polarizability derivatives. 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 [46-48] using the force constants obtained from the HF and DFT methods utilising the program of Fuhrer et al. [49]. The force constants were refined by damped least square fitting technique to achieve a close agreement between the observed and calculated frequencies.



Fig. 1. Molecular structure and atom numbering of (a) N-(2-methylphenyl)- and (b) N-(4-methylphenyl)-2,2-dichloroacetamides.

Computed harmonic frequencies typically overestimate vibrational fundamentals due to basis set truncation and neglect of electron correlation and mechanical anharmonicity [50]. 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 [51–58]. 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 4 and 5. Subsequently, in the HF/6-311++G(d,p) method the empirical scaling factors 0.85, 0.86 and 0.91 for N–H, C=O and other vibrations, respectively, for both 2MPA and 4MPA are used as suggested by

Table 2

Structural parameters calculated for N-(2-methylphenyl)-2, 2-dichloroacetamide and N-(4-methylphenyl)-2, 2-dichloroacetamide employing HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods.

Structural parameters	N-(2-Methylphenyl)-2,	2-dichloroacetamide	N-(4-Methylphenyl)-2,	N-Phenylacetamide	
	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	Experimental <sup>b</sup>
Internuclear distance (Å)					
C1-C2	1.386	1.392	1.378	1.387	1.384
C2-C3	1.380	1.391	1.392	1.401	1.376
C3-C4	1.385	1.393	1.384	1.396	1.391
C4–C5	1.385	1.395	1.390	1.395	1.379
C5-C6	1.401	1.412	1.384	1.397	1.397
C6-C1	1 388	1 399	1 392	1 401	1 391
C6-N7	1 416	1 417	1 414	1 415	1 413
N7-C8	1 347	1 359	1 345	1 358	1 354
C8-C9	1.517	1 542	1 537	1 542	1 495
C8-010	1 180	1.342	1 190	1.342	1 210
	1.105	1.210	1.150	1.210	1.215
dC U(ring)	1.778	1.004	1.776	1.004	
<sup>a</sup> C-H (filig)	1.074	1.083	1.075	1.082	
<sup>a</sup> C–C (methyl)	1.513	1.511	1.510	1.509	
N/-H18	0.992	1.010	0.994	1.011	
C9-H19	1.072	1.083	1.072	1.083	
<sup>a</sup> C17–H (methyl)	1.086	1.094	1.086	1.094	
Bond angle (° )					
C2-C1-C6	119.806	119.719	120.567	120.451	
C2-C1-H13	120.102	120.683	119.506	119.716	
C6-C1-H13	120.092	119.598	119.927	119.833	
C1-C2-C3	120.599	120.551	121.256	121.223	
C1-C2-H14	119.028	119.113	118.918	119.036	
C3-C2-H14	120.374	120.337	119.826	119.741	
C2-C3-C4	119.140	119.330	117.350	117.493	
C2-C3-H15	120 696	120 580			
C4-C3-H15	120.164	120,000			
C3-C4-C5	120.101	120.031	122 321	122 262	
C3-C4-H	110 /61	110 668	110 5/3	110 333	
	119.401	119,000	119.345	119,555	
	110.779	110.017	110.150	110.400	
C4-C5-C6	110.232	110.115	119.505	119.501	
C4-C5-C17	119.994	120.341			
6-65-617	121./54	121.545	100.010		
(2-(3-(1/			120.810	120.878	
C4-C3-C17			121.840	121.629	
C1-C6-C5	120.445	120.572	119.141	119.270	
C1-C6-N7	122.416	122.195	116.799	117.159	
C5-C6-N7	117.140	117.233	124.060	123.571	
<sup>a</sup> C–C17–H (methyl)	111.331	111.574	111.093	111.282	
<sup>a</sup> H–C17–H (methyl)	107.544	107.283	107.802	107.602	
C6-N7-H18	115.494	115.383	115.011	115.078	
C6-N7-C8	128.949	129.161	128.619	128.841	
H18-N7-C8	115.556	115.457	116.370	116.081	
N7-C8-O10	127.239	127.084	128.847	126.764	
N7-C8-C9	115.129	114.869	115.310	115.004	
010-C8-C9	117.632	118.048	117.843	118.232	
C8-C9-H19	107.269	107.625	107.285	107.638	
<sup>a</sup> C8–C9–C1	111 564	111 752	111 526	111 723	
<sup>a</sup> Cl_C9_H	107 601	107 256	107.628	107 287	
<sup>a</sup> Cl=C9=Cl	111 005	110 931	111 016	110 921	
	111.005	110.551	111.010	110.521	
Dihedral angle (°)					
C2-C1-C6-N7	-179.997	-179.999	-179.996	-179.997	
C4-C5-C6-N7	179.997	179.999	179.996	179.997	
C1-C6-N7-H18	179.965	179.987	0.023	0.033	
C1-C6-N7-C8	-0.039	-0.015	-179.964	-179.944	
C5-C6-N7-H18	-0.033	-0.012	-179.974	-179.9649	
C5-C6-N7-C8	179.963	179.985	0.039	0.057	
C6-N7-C8-O10	0.002	0.004	-0.004	-0.01	
C6-N7-C8-C9	180.0	-179.997	179.996	-179.993	
U10 N7 C0 010	190.0	190.0	170.001	170.099	

<sup>a</sup> Mean value.

<sup>b</sup> Values taken from Ref. no. [50].

The calculated thermodynamic parameters of N-(2-methylphenyl)-2,2-dichloroacetamide and N-(4-methylphenyl)-2,2-dichloroacetamide employing HF/6-31++G(d,p) and B3LYP/6-311++G(d,p) methods.

Thermodynamic parameters (298 K)	N-(2-Methylphenyl)-2,	2-dichloroacetamide	N-(4-Methylphenyl)-2,2-dichloroacetami		
	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)	
SCF energy (a.u.)	-1394.509	-1398.951	-1394.511	-1398.952	
Total energy (thermal), $E_{\text{total}}$ (kcal mol <sup>-1</sup> )	118.216	111.175	118.032	109.840	
Heat capacity at const. volume, $C_v$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	42.987	46.064	43.253	42.337	
Entropy, $S$ (cal mol <sup>-1</sup> $K^{-1}$ )	114.713	118.146	118.808	107.955	
Vibrational energy, <i>E</i> <sub>vib</sub> (kcal mol <sup>-1</sup> )	116.438	109.397	116.255	108.062	
Zero-point vibrational energy, $E_0$ (kcal mol <sup>-1</sup> )	110.707	103.199	110.274	102.780	
Rotational constants (GHz)					
Α	1.158	1.132	1.498	1.459	
В	0.335	0.331	0.259	0.256	
С	0.308	0.304	0.254	0.251	
Dipolemoment (Debye)					
$\mu_x$	0.772	1.127	1.294	1.724	
$\mu_{v}$	2.377	2.391	-2.049	-2.043	
$\mu_z$	0.002	0.001	0.004	0.008	
$\mu_{ ext{total}}$	2.50	2.643	2.424	2.673	

Scott and Radom [59], and Wong [60]. In B3LYP/6-311++G(d,p) level the correction factors 0.91 for N–H, 0.96 up to  $1762 \text{ cm}^{-1}$  and 0.99 for other frequencies of 2MPA while for 4MPA 0.98 is the scale factor for other vibrations less than  $1759 \text{ cm}^{-1}$ . The resultant scaled frequencies are also listed in Tables 4 and 5. 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 utilised to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra [61].

# 4. Results and discussion

#### 4.1. Molecular geometry

The molecular structure and atom numbering scheme of the compounds under investigation is shown in Fig. 1. The geometry of the molecules are considered by possessing  $C_S$  point group symmetry. Under  $C_S$  symmetry the 60 fundamental vibrations of 2MPA and 4MPA span the irreducible representations 39A' + 21A". All the vibrations are active in both IR and Raman.

#### 4.2. Structural properties

The steric interaction of methyl substituent on the ring is of great importance in determining its structural and vibrational properties. The steric crowding by adjacent substituents on an aromatic ring may be reduced by the rotation of one of the substituents around its bond to the aromatic ring. The optimised structural parameters bond lengths and the bond angles for the thermodynamically preferred geometry of 2MPA and 4MPA at HF and B3LYP levels with 6-311++G(d,p) basis sets are presented in Table 2 in accordance with the atom numbering scheme of the molecules shown in Fig. 1(a) and (b). The bond lengths between the amide nitrogen and the aromatic ring, C6-N7 and between the amide nitrogen and the carbonyl group, N7-C8 given in Table 2 reflect the changes in conjugation. The adjacent methyl group influence on the rotation of acylamino group. 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 3. The calculated SCF energy and entropy of the compounds clearly indicates that 4MPA is more stable than 2MPA. The bond length of the compounds 2MPA and 4MPA determined at the DFT level

of theory are in good agreement with the structural parameters of *N*-phenylacetamide [62].

#### 4.3. Vibrational analysis

The FTIR and FT-Raman spectra of *N*-(2-methylphenyl)and *N*-(4-methylphenyl)-2,2-dichloroacetamides are shown in Figs. 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 2MPA and 4MPA are summarised in Tables 4 and 5.

#### 4.3.1. Carbon-carbon vibrations

The carbon–carbon stretching modes of the phenyl group are expected in the range from 1650 to  $1400 \, \text{cm}^{-1}$ . Benzene has two degenerate modes at  $1596 \, \text{cm}^{-1}$  ( $e_{2g}$ ) and  $1485 \, \text{cm}^{-1}$  ( $e_{1u}$ ).





The observed FTIR, 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) of  $N-(2-methylphenyl)-2,2-dichloroacetamide^a$ .

Species	Observed wavenum (cm <sup>-1</sup> )	ber	HF/6-311++G(d,p)	calculated wavenu	mber		B3LYP/6-311++G(d	l,p) calculated wave	enumber	Depolarization ratio	Assignment	%PED
	FTIR	FTR	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity	Raman activity	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity			
A′	3250 vs	3247 w	3891	3307	50.52	43.90	3608	3283	38.64	0.12	νNH	$94\nu_{\rm NH}$
A′	3110 s		3420	3112	2.91	46.73	3241	3111	4.31	0.20	νCH	$97\nu_{CH}$
A′			3368	3065	2.37	62.55	3191	3063	17.70	0.22	νCH	$95\nu_{CH}$
A′	3059 vs	3065 s	3350	3049	22.28	200.90	3184	3057	1.75	0.16	$\nu C-H(Cl_2)$	$93\nu_{CH}$
A′	3026 s		3333	3033	18.91	77.06	3175	3048	11.76	0.73	νCH	$92\nu_{CH}$
A′			3320	3021	3.65	61.44	3162	3036	6.39	0.55	νCH	$92\nu_{CH}$
A′	3006 vs	3010 vw	3256	2963	21.72	62.64	3111	2987	13.93	0.54	$\nu_a CH_3$	$95\nu_{CH}$
Α″		2992 s	3197	2909	22.19	56.45	3051	2929	13.53	0.75	$\nu_a CH_3$	$97\nu_{CH}$
A′	2925 w	2923 s	3152	2868	32.24	151.46	3007	2887	22.76	0.03	$\nu_{s}CH_{3}$	$96\nu_{CH}$
A′	1677 vs	1674 s	1951	1678	373.88	30.47	1762	1692	328.90	0.19	νC=0	$95\nu_{C=0}$
A′	1644 s		1802	1640	51.23	27.71	1651	1634	16.55	0.74	$\nu C = C$	$92\nu_{C=C}$
A′	1611 m		1778	1618	195.35	71.21	1631	1615	108.24	0.49	$\nu C = C$	$91\nu_{C=C}$
A′	1588 s	1590 vs	1724	1569	365.94	4.11	1578	1562	284.36	0.63	βΝ–Η	90β <sub>NH</sub>
A′	1549 vs	1555 s	1644	1496	27.34	7.05	1519	1504	29.00	0.52	$\nu C = C$	$89\nu_{C=C}$
Α″	1487 m		1615	1470	79.16	5.54	1494	1479	9.29	0.70	$\delta_a CH_3$	93δ <sub>CH3</sub>
A′			1614	1469	8.23	8.35	1492	1477	92.54	0.75	vC-C	$87\nu_{CC}$
A′	1458 vs	1450 w	1597	1453	34.66	2.28	1477	1462	16.10	0.07	$\delta_a CH_3$	91δ <sub>CH3</sub>
A′	1428 m	1430 w	1540	1401	1.29	4.09	1418	1404	3.64	0.46	νC-C	85ν <sub>CC</sub>
A′	1382 m	1385 w	1435	1306	125.45	15.22	1341	1328	60.01	0.09	νC-C	87ν <sub>CC</sub>
A′	1341 s	1350 s	1413	1286	155.20	22.52	1323	1310	19.93	0.12	νC-N	88v <sub>cn</sub>
A′	1328 s	1330 m	1386	1261	25.89	6.68	1282	1269	60.58	0.22	$\delta_s CH_3$	92δ <sub>CH3</sub>
A′	1286 m	1285 vw	1381	1257	29.17	5.36	1264	1251	11.64	0.75	$\beta C - H(Cl_2)$	$85\beta_{CH} + 12\beta_{CC}$
A′		1267 s	1334	1214	0.65	34.55	1252	1239	20.57	0.16	$\nu N - C_6 H_5$	88v <sub>NC</sub>
A′	1247 s		1319	1200	2.36	2.86	1221	1209	15.17	0.22	vC-C	89ν <sub>CC</sub>
A″	1223 m	1220 vw	1288	1172	3.08	0.04	1208	1196	1.82	0.45	$\gamma C-H(Cl_2)$	79γ <sub>CH</sub> + 15γ <sub>CC</sub>
A′		1195 m	1232	1121	3.82	11.35	1188	1176	0.04	0.43	βС–Н	$75\beta_{CH} + 15\beta_{CCC}$
A′	1115 m	1112 w	1198	1090	1.68	8.93	1137	1126	4.23	0.67	βC–Η	$77\beta_{CH} + 12\beta_{CCC}$
A″		1085 w	1158	1054	1.12	0.21	1073	1062	11.42	0.75	ωCH <sub>3</sub>	$69\omega_{CH_2} + 18\gamma_{CH}$
A′	1037 m	1040 vw	1142	1039	10.55	10.55	1059	1048	1.68	0.07	βC–H	$71\beta_{CH} + 15\beta_{CCC}$
A′		1010 s	1112	1012	0.55	0.29	1006	996	3.61	0.75	ρCH <sub>3</sub>	$79\rho_{CH_2} + 16\beta_{CH_2}$
A′			1082	985	4.36	3.12	998	988	0.58	0.11	βC–H	$72\beta_{CH} + 20\beta_{CCC}$
A″	975 s	976 w	1070	974	3.37	0.09	972	962	0.43	0.75	νC-Η	76 <sub>7</sub> CH + 18 <sub>7</sub> CCC
A″	938 m		1058	963	1.13	1.38	959	949	2.26	0.49	γC-H	$72\gamma_{CH} + 21\gamma_{CCC}$
Α″	873 s	875 w	981	893	1.28	0.31	882	873	1.05	0.75	νC-H	70 <sub>γCH</sub> + 22 <sub>γCCC</sub>
A″	858 m	852 w	926	843	14.99	4.80	867	858	6.47	0.23	γC-H	$68\gamma_{CH} + 24\gamma_{CCC}$
A′			917	834	57.52	6.64	803	795	7.06	0.75	βccc	70β <sub>CCC</sub> + 18β <sub>CH</sub>
A′	807 vs	800 s	866	788	34.93	21.77	799	791	50.21	0.01	βC=0	$82\beta_{C=0} + 12\beta_{NH}$
A′	769 vs	777 m	848	772	99.29	1.21	770	762	82.92	0.75	$v_{a}CCl_{2}$	$82\nu_{CC1} + 12\beta_{CH}$
A″	717 s	725 m	838	763	17.38	6.05	762	754	43.34	0.46	νN-H	$79\gamma_{NH} + 15\gamma_{CO}$
A′			798	726	1.10	0.82	733	726	3.58	0.75	вссс	74Вссс + 12Всн
A′	703 s		757	689	82.55	5.41	674	667	3.31	0.75	v <sub>s</sub> CCl <sub>2</sub>	84иссі + 10Всн
A″	667 vs	675 vw	721	656	4.88	7.38	647	641	94.97	0.15	νC=0	$79\gamma_{C=0} + 14\gamma_{NH}$
A′	570 s	560 m	603	549	6.43	8.94	566	560	16.11	0.29	βC–C	698сс + 228сн
A'	543 m	545 w	601	547	0.74	0.34	565	559	5.87	0.75	вссс	70Bccc + 18Bcu
A′	515 vw	525 m	555	505	49.63	0.04	539	534	22.41	0.75	BC-N	$71\beta_{CN} + 15\beta_{CO}$
A'			525	478	21.53	2.05	490	485	21.52	0.50	BN-CeHs	$67B_{NC} + 19B_{CCC}$
A″	446 s	443 w	492	448	7 27	0.21	451	446	5.86	0.75	$\gamma C - N$	$72_{VCN} + 14_{VC-2}$
Α″	412 w	410 w	469	427	3.10	5.83	432	428	6.16	0.01	VN-CeH	$69 \gamma_{\rm NC} + 14 \gamma_{\rm CCC}$
A'	T12 VV	395 vw	450	410	3 38	3.03	411	407	0.59	0.26	$\beta C - C(H_2)$	65Bcc + 21Bcu
Δ/		332 m	326	297	2.05	1.95	200	296	2.89	0.75	accla	$80\delta_{car} \pm 180$
Δ″		295 147	304	237	0.35	1.55	283	230	0.65	0.63	2000	$67_{2}$ + $22_{2}$
Δ″		255 W	202	277	3.26	2.74	200	267	2.05	0.32	$\gamma C = C(\mathbf{H})$	682/ + 192/
n		230 111	230	271	5.20	2.74	270	207	2.22	0.32	$\gamma C - C(\Pi_3)$	00 YCC + 10 YCH

Species	Observed	HF/6-311++G(d,p)	calculated wavenun	nber		B3LYP/6-311++G(d,	p) calculated wave	number	Depolarization ratio	Assignment	%PED
	wavenumber (cm <sup>-1</sup> )										
	FTIR FTR	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity	Raman activity	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity			
A"		227	207	3.65	0.27	207	205	2.26	0.75	±CCl <sub>2</sub>	$64\tau_{ccl}, + 26\omega_{ccl},$
Α″		215	196	0.50	0.10	178	176	5.63	0.75	ωCCl <sub>2</sub>	$65\omega_{\text{ccl}}^{2} + 22\tau_{\text{ccl}}^{2}$
A'		194	177	5.35	1.41	178	176	0.25	0.41	pCC12	$73\rho_{CCL}$ + $15\beta_{CH}$
Α″		166	151	06.0	1.51	151	149	0.44	0.75	yccc	$67\gamma_{\rm CCC}^{2} + 22\gamma_{\rm CH}$
Α″		106	96	0.18	0.17	98	98	0.27	0.68	yccc	$65\gamma_{CCC} + 18\gamma_{CH}$
Α″		50	50	0.11	3.82	50	50	3.15	0.75	yccc	$63\gamma_{\rm CCC} + 21\gamma_{\rm CH}$
Α″		38	38	8.69	0.61	42	42	2.60	0.75	yccc	$62\gamma_{CCC} + 24\gamma_{CH}$
Α″		12	12	0.02	2.95	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	00	1.41	0.75	$\tau CH_3$ (torsion)	

mass (a.m.u.); and force constant (mdyne/Å)



**Fig. 3.** FT-Raman spectrum of (a) *N*-(2-methylphenyl)-2,2-dichloroacetamide and (b) *N*-(4-methylphenyl)-2,2-dichloroacetamide.

Similarly the frequency of two non-degenerate modes observed at  $1310 \text{ cm}^{-1}$  (b<sub>2u</sub>) and  $995 \text{ cm}^{-1}$  (a<sub>1g</sub>) in benzene [63], are not very sensitive to substitution, although heavy halogens and bulky methyl groups cause undoubtedly slightly alter the frequency [64]. Under C<sub>5</sub> symmetry, the C=C stretching of 2MPA molecule is found in the IR spectrum at 1644, 1611 and  $1549 \,\mathrm{cm}^{-1}$  as medium to very strong bands and strong band at 1555 cm<sup>-1</sup> in Raman, while in the case of 4MPA these vibrations are observed in IR spectra at 1642, 1601 and 1513 cm<sup>-1</sup>. The corresponding bands in Raman spectrum are seen at 1611 and 1517 cm<sup>-1</sup>. The C-C stretching modes of 2MPA are assigned to the bands observed at 1428, 1382 and 1247 cm<sup>-1</sup> in the IR while the respective Raman bands are observed at 1430 and 1385 cm<sup>-1</sup>. The vibrational frequencies observed in the infrared spectrum of 4MPA at 1410, 1385 and 1243 cm<sup>-1</sup> and at 1409, 1381 and 1241 cm<sup>-1</sup> in the Raman spectrum are attributed to C-C stretching modes. The in-plane carbon and out of plane bending vibrations are assigned and presented in Tables 4 and 5. All these assignments are agree well with the reported literature values [65]. 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 2MPA the ring breathing mode corresponding to the  $a_{1g}$ mode of benzene is determined at 834 cm<sup>-1</sup> by HF and 795 cm<sup>-</sup> by B3LYP methods. The ring breathing mode of 4MPA is observed in the infrared spectrum at 868 cm<sup>-1</sup> and in the Raman at 871 cm<sup>-1</sup> [66].

## 4.3.2. C-H vibrations

The aromatic C–H stretching vibrations are normally found between 3150 and 3000 cm<sup>-1</sup>. 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<sup>-1</sup> of benzene and its derivatives. The C–H present in the benzene ring of 2MPA gives very strong to strong bands at 3110 and 3026 cm<sup>-1</sup> in IR. The vibrational modes observed at 3109, 3079 and 3040 cm<sup>-1</sup> are assigned to the ring C–H stretching modes of 4MPA. The frequencies at 3059, 3065 and 3061, 3060 cm<sup>-1</sup>, respectively is attributed to the C–H stretching of –CHCl<sub>2</sub> group. The aromatic C–H in-plane bending modes of 2MPA and 4MPA corresponding to the benzene

The observed FTIR, 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) of N-(4-methylphenyl)-2,2-dichloroacetamide.

Species	Observed (cm <sup>-1</sup> )	wavenumber	HF/6-311++G(d,p)	calculated wavenu	mber		B3LYP/6-311++G(d,p) calculated wavenumber		Depolarization ratio	% PED		
	FTIR	FTR	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity	Raman activity	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity			
A′	3240 vs	3236 w	3864	3284	46.74	53.93	3595	3271	31.09	0.14	νNH	92v <sub>NH</sub>
A′	3109 m		3415	3108	1.76	45.56	3241	3111	3.13	0.22	νCH	94v <sub>CH</sub>
A′		3079 w	3367	3064	2.34	62.36	3183	3056	1.67	0.22	νCH	91v <sub>CH</sub>
A′	3061 s	3060 s	3328	3028	8.68	168.34	3169	3042	9.08	0.17	$\nu C-H(Cl_2)$	93v <sub>CH</sub>
A′		3040 w	3325	3026	25.63	50.45	3165	3038	18.16	0.58	νCH	90v <sub>CH</sub>
A′			3307	3009	16.37	46.29	3151	3025	13.17	0.74	νCH	92v <sub>CH</sub>
A″	3002 m	3003 s	3242	2950	23.71	61.90	3103	2979	16.15	0.75	$\nu_{a}CH_{3}$	93v <sub>CH</sub>
A′	2936 vw		3214	2925	26.24	91.72	3071	2948	16.35	0.75	$\nu_{a}CH_{3}$	95v <sub>CH</sub>
A′	2919 vw	2920 s	3165	2880	45.98	236.19	3023	2902	37.27	0.05	v <sub>s</sub> CH <sub>3</sub>	92VCH
A′	1669 vs	1669 s	1947	1674	380.63	37.68	1759	1689	348.79	0.20	νC=0	$95\nu_{C=0}$
A'	1642 w		1806	1643	33.01	125.65	1655	1622	5.80	0.50	νC=C	$90\nu_{C=C}$
A'	1601 m	1611 s	1786	1625	147.81	4.45	1636	1603	81.14	0.70	$\nu C = C$	$89\nu_{C-C}$
A′	1551 s	1546 s	1718	1563	489.43	19.40	1568	1537	359.74	0.38	BN(H	91BNH
A′	1513 s	1517 vw	1673	1522	47.95	5.70	1544	1513	42.20	0.32	$\nu C = C$	$88\nu_{c-c}$
A″		1475 vw	1613	1468	20.46	8.10	1495	1465	27.23	0.73	δ <sub>2</sub> CH <sub>2</sub>	91δ <sub>CH</sub>
A'	1446 vw	1450 w	1605	1461	6.27	10.58	1487	1457	7 20	0.75	δ.CH2	88ôcu
A'	1410 m	1409 w	1549	1410	47 17	0.04	1438	1409	32.09	0.48	$\nu C(C)$	87 <sub>Vcc</sub>
A'	1385 m	1381 w	1540	1401	4 99	9.38	1414	1386	0.07	0.41	$\nu C(C)$	86vcc
A'	1348 m	1340 vs	1456	1325	64.66	5 50	1346	1319	63.64	0.19	$\nu C(N)$	89VCN
A'	1307 w	1308 m	1409	1282	187.87	31 57	1338	1311	6 32	0.13	δ <sub>e</sub> CH <sub>2</sub>	908cu
A′	1507 11	1900 111	1386	1261	34 34	9.22	1274	1249	45.26	0.19	vC(C	85Vcc
A'	1283 vw	1284 vw	1381	1257	30.69	5.65	1259	1234	29.02	0.75	BC(H(Cl <sub>2</sub> )	83Bcu + 12Bcc
A'	1264 m	1201 000	1336	1216	1 43	21 72	1252	1227	21.81	0.23	vN(C <sub>c</sub> H <sub>5</sub>	861/hc
Α′	1201 m	1241 vs	1316	1198	4 35	20.66	1232	1209	0.59	0.06	$\nu C(C)$	87 <sub>Vcc</sub>
Α″	12.15 m 1220 w	1211 vs	1303	1186	0.60	10.10	1216	1192	13 27	0.16	$\gamma C(H(Cl_{2}))$	80ycu + 14ycc
A'	1178 w	1179 m	1277	1162	6.16	14 34	1208	1184	0.05	0.10	BC(H	76Bcu + 14Bccc
Α′	1119 vw	1175 111	1187	1080	12.95	0.99	1148	1125	11.83	0.75	BC(H	77Bau + 16Baaa
Δ″	1043 yw		1163	1058	2 37	0.02	1061	1040	3 35	0.75	wCH <sub>2</sub>	$70\omega_{\rm eff} \pm 18\gamma$
Δ′	1045 VW		1105	1008	2.37	0.34	1036	1015	3 3 8	0.13	BC(H	$73B_{cH} + 14B_{cH}$
Δ/	1021 104		1008	000	0.85	0.06	1000	088	5.68	0.75	oCH <sub>2</sub>	780 116B
Λ/	020 14	091 147	1093	090	1.65	2.45	084	064	1 15	0.75	BC(H	$70P_{CH_3} + 10P_{CH}$
A	980 W	901 W	1067	969 065	1.05	2.45	060	904	1.15	0.44	pc(II	72pcH + 18pccc
A"	944 VW	012	1050	903	1.90	0.10	909	930	2.55	0.75	YC(H	$73^{\circ}\gamma_{CH} + 14^{\circ}\gamma_{CCC}$
A'	000	912 W	1053	958	5.39	1.28	950	931	0.89	0.38	γC(H	$72\gamma_{CH} + 20\gamma_{CCC}$
A"	808 W	871 VS	943	858	12.03	0.83	873	828	5.30	0.75	pece	76рссс + 16рсн
A'	010	000	934	850	13.22	20.86	849	832	17.10	0.05	γC(H	$69\gamma_{CH} + 22\gamma_{CCC}$
A'	8 10 VS	809 m	917	834	105.30	6.39	821	805	43.38	0.75	pc=0	$85\beta_{C=0} + 10\beta_{NH}$
A"	792 s	793 W	914	832	18.60	0.48	798	782	61.81	0.75	$\nu_a CCI_2$	$74\nu_{CCI} + 14\beta_{CH}$
A''	745	744	838	781	40.32	0.24	794	778	5.60	0.75	γC(H	$71\gamma_{CH} + 18\gamma_{CCC}$
A"	745 W	744 m	842	766	1.//	26.43	763	748	47.76	0.02	γΝ(Η	$70\gamma_{\rm NH} + 16\gamma_{\rm CO}$
A'	710 W	703 s	778	708	0.41	1.84	/19	705	0.06	0.75	pett	$74\beta_{CCC} + 12\beta_{CH}$
A'	668 VS	620	/5/	689	86.55	6.21	654	641	80.0	0.75	$\nu_s CCI_2$	$74\nu_{CC1} + 14\beta_{CH}$
A''	636 W	638 m	698	635	0.29	5.98	647	634	98.23	0.71	γC=0	$/8\gamma_{C=0} + 12\gamma_{NH}$
A	615 VW		6//	616	10.85	1.79	634	621	8.85	0.68	BC(C	6/β <sub>CC</sub> + 24β <sub>CH</sub>
A'	532 w	517.	5/2	521	1.46	0.43	556	545	31.21	0.75	BCCC	$6/\beta_{CCC} + 18\beta_{CH}$
A'	515 m	51/ W	563	512	81.76	0.04	517	507	33.87	0.75	BC(N	$75\beta_{CN} + 16\beta_{CO}$
A'	490 m	491 W	492	448	24.81	6.61	457	448	24.89	0.16	$\beta N(C_6H_5)$	$69\beta_{NC} + 19\beta_{CCC}$
A″	466 W		467	425	1.28	5.39	425	417	1.72	0.05	γC(N	$72\gamma_{CN} + 12\gamma_{C=0}$
A″	420 vw	411 w	457	416	0.65	0.06	419	411	0.19	0.75	$\gamma N(C_6H_5)$	$65\gamma_{NC} + 18\gamma_{CCC}$
A'		358 m	408	371	0.25	0.99	378	370	0.18	0.55	$\beta C(C(H_3))$	66β <sub>CC</sub> + 20β <sub>CH</sub>
A'		332 s	378	344	0.22	3.63	349	342	0.06	0.75	occl <sub>2</sub>	$82\delta_{CCl_2} + 18\beta_{CH}$
A″		316 m	317	288	2.36	1.57	297	291	1.60	0.13	γССС	65γссс + 22γсн
A″		260 w	293	267	1.45	2.74	265	260	1.18	0.52	$\gamma C(C(H_3))$	$64\gamma_{CC} + 20\gamma_{CH}$

Species	Observed wavenumber (cm <sup>-1</sup> )	HF/b-311++G(d,p)	רפורחופובת אפאבווחו	nber			.p) calculated wave				
	FTIR FTR	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity	Raman activity	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity			
Α″	233 vw	234	213	0.13	0.12	214	210	0.02	0.75	±CCl <sub>2</sub>	$65 \tau_{ccl}, + 25 \omega_{ccl},$
Α″	195 s	179	163	5.99	1.27	164	161	6.43	0.27	ωCCl <sub>2</sub>	$63 \omega_{ccl}, + 26 \tau_{ccl},$
A'	111 vs	146	133	4.62	0.40	133	130	3.74	0.75	pCCl <sub>2</sub>	$71\rho_{\text{CCI},} + 15\beta_{\text{CH}}$
Α″		105	96	0.07	0.60	97	97	0.09	0.75	λαα	$65\gamma_{\rm CCC}^2 + 22\gamma_{\rm CH}$
A"		48	48	7.51	0.33	55	55	4.65	0.75	yccc	$63\gamma_{CCC} + 23\gamma_{CH}$
A"		42	42	0.19	2.27	38	38	0.10	0.75	yccc	$61\gamma_{ccc} + 22\gamma_{cH}$
Α″		25	25	60.0	0.81	22	22	2.57	0.75	yccc	$62\gamma_{CCC} + 24\gamma_{CH}$
A″		15	15	1.06	4.88	14	14	0.04	0.75	$\tau CH_3$ (torsion)	

( Pointino) 2 older

degenerate  $e_{2g}$  (1178 cm<sup>-1</sup>) and  $e_{1u}$  (1037 cm<sup>-1</sup>) and two nondegenerate  $b_{2u}$  (1152 cm<sup>-1</sup>) and  $a_{2g}$  (1340 cm<sup>-1</sup>) vibrations, are observed in the region 1300–1000 cm<sup>-1</sup>. The C–H out of plane bending mode the compounds similar to the  $b_{2g}$  (985 cm<sup>-1</sup>),  $e_{2u}$ (970 cm<sup>-1</sup>),  $e_{1g}$  (850 cm<sup>-1</sup>) and  $a_{2u}$  (671 cm<sup>-1</sup>) modes of benzene derivatives are observed in the region 1100–600 cm<sup>-1</sup> [63] and are presented in Tables 4 and 5. 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<sub>2</sub>) in-plane and out of plane bending vibrations are significantly mixed with CC in-plane and out of plane modes, respectively.

#### 4.3.3. Amide group vibrations

The amide (-CONH-) group vibrations of the compounds investigated are correlated with the unsubstituted N-phenyl-2,2dichloroacetamide (NPA) vibrations [1] and presented in Table 6. In *N*-phenylacetamide structure there is competition between the phenyl ring and the C=O for the lone pair of electrons of the nitrogen. 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. Hence the very strong IR bands observed at 1677 and 1669 cm<sup>-1</sup> is assigned to the amide-I band of 2MPA and 4MPA molecules, respectively. The Raman counterpart are obtained as strong band at 1674 and 1669 cm<sup>-1</sup>, respectively. The comparison of the wavenumber of C=O stretching in 2MPA and 4MPA with that of NPA molecule reveals that the substitution of methyl group in the phenyl ring does not makes the molecule effectively compete with the carbonyl oxygen for the electrons of the nitrogen, thus increasing the force constants of the C=O bond. It is evident from the infrared and Raman vibrational frequencies of 2MPA and 4MPA, that the C=O stretching frequencies of the compounds under investigation does not show significant variation from that of the parent compound N-phenyl-2,2-dichloroaetamide.

Secondary amides shows only one N-H stretching band in the infrared spectrum between 3370 and 3170 cm<sup>-1</sup>. A weaker band may appear at about  $3100 \,\mathrm{cm}^{-1}$  in secondary amides due to Fermi resonance of 1550 cm<sup>-1</sup>. The exact location of the N-H stretching mode depends upon the other groups adjacent to the -CONHskeleton [1]. Thus the very strong band observed at 3250 cm<sup>-1</sup> in IR and 3247 cm<sup>-1</sup> in Raman is attributed to the N-H stretching of 2MPA molecule. The 4MPA shows the characteristic very strong N–H stretching band at 3240 in the IR and at 3236 cm<sup>-1</sup> in Raman spectrum. In comparison with NPA, the N-H stretching frequencies of 2MPA and 4MPA compounds are invariably lowered by  $20-30 \text{ cm}^{-1}$ . In N-phenylacetamide, the C=O and N-H bonds may be either cis or trans to each other. But the dipole moment measurements, X-ray and neutron diffraction studies demonstrated that the trans conformer is the predominant and most stable [11-15,65]. 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. It has been shown that the mesomeric and inductive effects of para substituents have little influence on the N-H stretching frequencies, and it is reasonable to assume that polarisation interactions of ortho substituents likewise have little effect on N-H stretching frequency [67].

The steric effect of ortho 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. It is not due to the direct field effect but because of the steric interactions. If the most intense N–H stretching band is assigned to the trans conformer-II, then N–H stretching frequency is increased by about 15 cm<sup>-1</sup> on introduction of an ortho-methyl substituent into N-phenylacetamide. The alkyl

Compounds name	$\nu_{C=0}$		$\beta_{N-H}$		$\nu_{C-N}$		β <sub>c=0</sub>		$\gamma_{N-H}$		γc=o		$\nu_{N-H}$	
	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR
NPAª	1672	1680	1555	1568	1344	1355	811	810	712	715	558	568	3270	3275
2MPA	1677	1674	1588	1590	1341	1350	807	800	717	725	667	675	3250	3247
4MPA	1669	1669	1551	1546	1348	1340	810	809	745	744	636	638	3240	3236

 Table 6

 Correlation of amide (-CONH-) group vibrations of the compounds investigated.

<sup>a</sup> Values are taken from Ref. [1].

substituents should not exert sizable direct field effects and the observed frequency increases are therefore an appropriate measure of the steric interactions.

In the present investigation, it is observed that there is no increase in the N–H stretching frequencies of 2MPA and 4MPA than that of *N*-phenyl-2,2-dichloroacetamide. This clearly confirms that the steric effect due to *o*-methyl group is not significantly operating on the N–H stretching and it also reveals that the compound 2MPA exist in the favoured trans configuration–I. The calculated energies of the conformers ( $E_I$  = –1398.74663396 a.u.) and ( $E_{II}$  = –1398.73065843 a.u.) also favourable.



The frequencies observed at 1588 and  $1551 \text{ cm}^{-1}$  in IR are ascribed to the amide-II band, N–H in-plane bending mode of 2MPA and 4MPA, respectively. The corresponding Raman counterparts are obtained at 1590 and  $1546 \text{ cm}^{-1}$ . The C–N stretching mode, the amide-III band, of 2MPA is assigned at 1341 and  $1350 \text{ cm}^{-1}$  in IR and Raman spectra, respectively. The fundamental mode seen at  $1348 \text{ cm}^{-1}$  in IR and  $1340 \text{ cm}^{-1}$  in Raman are assigned to the C–N stretching of 4MPA. The amide-III band of NPA is observed at  $1344 \text{ cm}^{-1}$  in the infrared while in Raman it is observed at  $1355 \text{ cm}^{-1}$ . The spectral data indicates that no rise in C–N stretching frequencies of 2MPA and 4MPA and there is no hyper conjugative influence of the methyl group towards the C–N bond.

The amide-IV, C=O in-plane bending of 2MPA is found at 807 and 800 cm<sup>-1</sup> in the IR and Raman, respectively. For 4MPA compound this mode is seen at 810 and 809 cm<sup>-1</sup>. There is no significant shift in the C=O in-plane bending, frequencies of 2MPA and 4MPA compounds than that of NPA. The amide-V, the N-H out of plane bending is observed as strong and medium bands at 717 and 725 cm<sup>-1</sup> in 2MPA and this mode is seen at 745 and 744 cm<sup>-1</sup> in 4MPA. The C=O out of plane bending of 2MPA is seen at 667 and 675 cm<sup>-1</sup> in IR and Raman, respectively. In 4MPA this amide-VI band is observed at 636 and 638 cm<sup>-1</sup>. Both the amide-V and amide-VI out of plane bending modes of 2MPA and 4MPA is significantly raised than that of NPA. The PED calculations determine that the amide-IV and amide-VI bands of 2MPA and 4MPA are significantly overlapped C=O out of plane bending vibrations.

#### 4.3.4. Methyl group (-CH<sub>3</sub>) vibrations

Considering the assignments of  $-CH_3$  group frequencies, the asymmetric stretching and asymmetric deformation modes of the  $-CH_3$  group would be expected to be depolarised for A" symmetry species. The symmetric,  $\nu_s(CH_3)$  frequencies are established at 2925, 2923 and 2919, 2920 cm<sup>-1</sup> in the spectra of 2MPA and

4MPA, respectively. The asymmetric stretching of 2MPA,  $\nu_a(CH_3)$  is assigned at 3006 and 3010 cm<sup>-1</sup>, while in the case of 4MPA the mode is observed at 2936 cm<sup>-1</sup> under A' species. The strong depolarised frequencies seen at 2992, 3002 and 3003 cm<sup>-1</sup> in the spectra of 2MPA and 4MPA are attributed to the  $\nu_a(CH_3)$  under A" species. The asymmetrical methyl deformation mode,  $\delta_a(CH_3)$  of 2MPA and 4MPA are observed at 1487 and 1475 cm<sup>-1</sup> under A" species corresponding to 2MPA and 4MPA, respectively. The very strong to medium bands at 1328 and 1307 cm<sup>-1</sup> in the infrared spectra and at 1330 and 1308 cm<sup>-1</sup> in Raman spectra of 2MPA and 4MPA, respectively are attributed to the methyl symmetric deformational modes  $\delta_s(CH_3)$  in the A' species [36,44,68]. The other bending vibrational frequencies of methyl group are clearly indicated in Tables 4 and 5. The normal co-ordinate analysis shows that the methyl wagging mode is effectively mixed with the out of plane C–H mode.

#### 4.3.5. CCl<sub>2</sub> group vibrations

The C-Cl absorption is observed in the broad region between 850 and 550 cm<sup>-1</sup>. 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. In view of this, the strong and medium bands in IR at 769 and 792 cm<sup>-1</sup> having the Raman counterpart at 777 and 793 cm<sup>-1</sup> are assigned to the asymmetric CCl<sub>2</sub> stretching wavenumber of 2MPA and 4MPA molecules, respectively. The symmetric  $CCl_2$  stretching is observed at 703 and 668 cm<sup>-1</sup> in 2MPA and 4MPA, respectively. The CCl<sub>2</sub> asymmetric and symmetric stretching frequencies of 2MPA and 4MPA does not show any appreciable variation from that of the corresponding frequencies in NPA. The in-plane CCl<sub>2</sub> deformation vibrations and the out of plane CCl<sub>2</sub> 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 [1,69] and well supported by normal coordinate analysis. The CCl<sub>2</sub> wagging mode significantly overlaps with CCl<sub>2</sub> twisting mode and vice versa and also the in-plane C-H bending vibrations contributed to CCl<sub>2</sub> deformation and rocking modes.

# 5. Conclusion

The molecular structural parameters, thermodynamic properties and vibrational frequencies of the fundamental modes of the optimised geometry of 2MPA and 4MPA have been determined from HF and DFT-B3LYP methods. The FTIR and FT-Raman vibrational frequencies of the compounds under investigations revealed close similarities in the magnitudes of the frequencies in spite of the fact that the substituents 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 groups present. In the present investigation, there is no increase in the N-H stretching frequency of 2MPA and 4MPA than that of N-phenyl-2,2-dichloroacetamide, clearly confirms that the steric effect due to o-methyl group is not significantly operating on the N-H stretching and it also reveals that the compounds under investigations takes the favoured trans configuration-I, predominantly. The comparison of other amide group frequencies did not show any appreciable variation in the respective wavenumbers 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.

#### References

- [1] V. Arjunan, S. Mohan, S. Subramanian, B. Thimme Gowda, Spectrochim. Acta 60A (2004) 1141
- A.C. Scott, Physica D 51 (1990) 333.
- A.C. Scott, I.J. Bigio, C.T. Johnson, Phys. Rev. B 39 (1989) 12883. [3]
- [4] T. Benkui, P.P. John, Phys. Lett. A 240 (1998) 282.
- [5] Y. Xiao, Phys. Lett. A 243 (1998) 174.
- [6] J. Tekec, Z. Iric, Z. Przulj, J. Phys. Condens. Mat. 10 (1998) 1487.
- [7] G. Kalosakas, S. Aubry, G.P. Tsironis, Phys. Lett. A 247 (1998) 413.
- [8] X. Pang, X. Chen, J. Phys. Chem. Solids 62 (2001) 793.
- [9] O.F. Nielson, Asian J. Phys. 9 (2000) 139.
- [10] J.F. Olsen, S. Kang, Theoret. Chim. Acta (Berl.) 17 (1970) 329.
- [11] W. Caminati, A. Maris, A. Millemaggi, New J. Chem. 24 (2000) 821.
- [12] V.P. Manea, K.J. Wilson, J.R. Cable, J. Am. Chem. Soc. 119 (1997) 2033.
- [13] J.A. Dickinson, M.R. Hockridge, E.G. Robertson, J.P. Simons, J. Phys. Chem. 103A (1999) 6938.
- [14] H.J. Wasserman, R.R. Ryan, S.P. Layne, Acta Crystallogr. 41C (1985) 783.
- [15] S.W. Johnson, J. Eckert, M. Barthes, R.K. McMullan, M. Muller, J. Phys. Chem. 99 (1995) 16253.
- [16] E. Hirota, R. Sugisaki, C.J. Nielsen, O. Sôrensen, J. Mol. Spectrosc. 119 (1974) 251.
- [17] W. Caminati, A.C. Fantoni, L. Schafer, K. Siam, C. Van Alsenoy, J. Am. Chem. Soc. 108 (1986) 4364.
- [18] A.C. Fantoni, W. Caminati, J. Chem. Soc., Faraday Trans. 92 (1996) 343.
- [19] S. Ilieva, B. Hadjieva, B. Galabov, J. Mol. Struct. 508 (1999) 73.
- [20] M. Sakai, N. Kuroda, Y. Nishina, Phys. Rev. 47B (1993) 150.
- [21] S. Kashino, T. Matsushita, T. Iwamoto, K. Yamaguchi, M. Haisa, Acta Crystallogr. C42 (1986) 457.
- [22] R. Bartha, J. Agric. Food Chem. 16 (1968) 602.
- [23] M.A. Alawi, Fresenius'z, Anal. Chem. 312 (1982) 53.
- [24] Q. Wang, W. Yang, W. Liu, Pestic. Sci. 55 (1999) 1103.
- [25] I.B. Vasilakoglou, I.G. Eleftherohorinos, K.B. Dhima, Weed Res. 41 (2001) 535.
- [26] D.M. Tessier, J. Marshall Clark, Anal. Chem. Acta 376 (1998) 103.
- [27] C. Eckermann, B. Matthes, M. Nimtz, V. Reiser, B. Lederer, P. Böger, J. Schröder, Phytochemistry 64 (2003) 1045.
- [28] J. Binoy, N.B. Prathima, C. Murali Krishna, C. Santhosh, I. Hubert Joe, V.S. Jayakumar, J. Phys. Chem. 103A (1999) 6872.
- [29] D. Sajan, I. Hubert Joe, V.S. Jayakumar, Curr. Sci. 77 (1999) 915.
- [30] D.A. Weitz, S. Garoff, J.I. Gersten, A. Nitzam, J. Chem. Phys. 78 (1983) 524.
- [31] M.J. Frisch, J.A. Pople, Gaussian 98, Gaussian Inc., Pittsburgh, PA, 1998.
- [32] D. Sajan, I. Hubert Joe, V.S. Jayakumar, J. Phys.: Conf. Series 28 (2006) 123.
- [33] D. Kaur, R. Preet Kaur, J. Mol. Struct.: Theochem. 757 (2005) 53.
- [34] C. Decoret, B. Tinland, J. Mol. Struct. 12 (1972) 485
- [35] J.L. Sauvajol, R. Almairac, J. Moret, M. Barthes, J.L. Ribet, J. Raman Spectrosc. 20 (1989) 517.
- [36] K.-W. Lei, W.-S. Liu, M.-Y. Tan, Spectrochim. Acta 66A (2007) 590.
- [37] K.-W. Lei, W.-S. Liu, M.-Y. Tan, Spectrochim. Acta 66A (2007) 377.

- [38] W.-N. Wu, W.-B. Yuan, N. Tang, R.-D. Yang, L. Yan, Z.-H. Xu, Spectrochim. Acta 65A (2006) 912.
- [39] D. Cheshmedzhieva, S. Ilieva, B. Galabov, J. Mol. Struct.: Theochem. 681 (2004) 105.
- [40] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864.
- [41] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [42] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [43] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W.Wong, C. Gonzalez, J.A. Pople, Gaussian Inc., Wallingford, CT, 2004.
- [44] H.B. Schlegel, J. Comput. Chem. 3 (1982) 214.
- [45] G. Zerbi, in: Person, Zerbi (Eds.), Vibrational Intensities in Infrared and Raman Spectroscopy, Elsevier, New York, 1982.
- [46] E.B. Wilson Jr., J. Chem. Phys. 7 (1939) 1047.
- [47] E.B. Wilson Jr., J. Chem. Phys. 9 (1941) 76.
- [48] E.B. Wilson Jr., J.C. Decius, P.C. Cross, Molecular Vibrations, McGraw Hill, New York. 1955.
- [49] H. Fuhrer, V.B. Kartha, K.L. Kidd, P.J. Kruger, H.H. Mantsch, Computer Program for Infrared and Spectrometry. Normal Coordinate Analysis, vol. 5, National Research Council, Ottawa, Canada, 1976.
- [50] J.A. Pople, H.B. Schlegel, R. Krishnan, J.S. Defrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, Int. J. Quantum Chem. Quantum Chem. Symp. 15 (1981) 269.
- [51] H.F. Hameka, J.O. Jensen, J. Mol. Struct.: Theochem. 362 (1996) 325.
- C.P. Vlahacos, H.F. Hameka, J.O. Jensen, Chem. Phys. Lett. 259 (1996) 283. [52]
- [53] D. Zeroka, J.O. Jensen, J. Mol. Struct.: Theochem. 425 (1998) 181.
- [54] K.K. Ong, J.O. Jensen, H.F. Hameka, J. Mol. Struct.: Theochem. 459 (1999) 131.
- [55] J.O. Jensen, A. Banerjee, C.N. Merrow, D. Zeroka, J.M. Lochner, J. Mol. Struct.: Theochem. 531 (2000) 323.
- [56] J.O. Jensen, D. Zeroka, J. Mol. Struct.: Theochem. 487 (1999) 267.
- [57] H.F. Hameka, J.O. Jensen, J. Mol. Struct.: Theorem. 331 (1995) 203.
   [58] M.W. Ellzy, J.O. Jensen, H.F. Hameka, J.G. Kay, D. Zeroka, Spectrochim. Acta 57A (2001)2417
- [59] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.
- [60] M.W. Wong, Chem. Phys. Lett. 256 (1996) 391.
- [61] S.Y. Lee, B.H. Boo, Bull. Korean Chem. Soc. 17 (1996) 760.
- [62] H.J. Wasserman, R.R. Ryan, S.P. Layne, Acta Crystallogr. C41 (1985) 783.
- [63] L.J. Bellamy, The Infrared Spectra of Complex Molecules, 3rd ed., Wiley, New York, 1975.
- [64] G. Varsanyi, Assignments for Vibrational Spectra of Seven Hundred Benzene Derivaties, vol. I, Adam Hilger, London, 1974.
- [65] V. Arjunan, S. Subramanian, S. Mohan, Spectrochim. Acta 60A (2004) 995.
- [66] N. Puviarasan, V. Arjunan, S. Mohan, Turk. J. Chem. 26 (2002) 323.
- [67] L.K. Dyall, J.E. Kemp, Spectrochim. Acta 22 (1966) 483.
- [68] E. Krishnamoorthy, G. Ramana Rao, J. Raman Spectrosc. 20 (1989) 409.
- [69] J.R. Durig, M.M. Bergana, H.V. Phan, J. Raman Spectrosc. 22 (1991) 141.