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# Synthesis, FTIR and FT-Raman spectral analysis and structure–activity relations of *N*-(4-bromophenyl)-2,2-dichloroacetamide by DFT studies



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# HIGHLIGHTS

• The structural, vibrational and reactivity characteristics have been determined.

• The molecule has great electronegativity difference and charge is highly polarized.

• The atoms C2, C3, C5, C6, N7, O9 and C10 are more prone to nucleophilic attack.

• The LUMO of the molecule feature a larger number of nodes than the HOMO.

• The  $n_{\rm N} \rightarrow \pi^*_{\rm CO}$  interaction possess a strong stabilization of 64.21 kcal mol<sup>-1</sup>.

#### ARTICLE INFO

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# ABSTRACT

The FTIR and FT-Raman vibrational spectra of *N*-(4-bromophenyl)-2,2-dichloroacetamide molecule has been recorded and analysed the complete vibrational fundamental modes of the most stable geometry of the compound using the experimental FTIR and FT-Raman data on the basis of peak positions, relative intensities and quantum chemical studies. The observed vibrational frequencies were compared with the theoretical wavenumbers of the optimised geometry of the compound obtained from the DFT-B3LYP gradient calculations employing the high level 6-311++G<sup>\*\*</sup> and cc-pVTZ basis sets. The effect of substituent —Br in the amide moiety have been analysed and compared. The kinetic and thermodynamic stability and chemical reactivity descriptors of the molecule have been determined. The reactive centres are found from the molecular electrostatic potential and the atomic charges. The limits of electrostatic potential are  $-9.617e \times 10^{-3}$  and  $+9.617e \times 10^{-3}$ . The molecule has great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. The lone pair donor orbital,  $n_N \to \pi^*_{CO}$  interaction possess a strong stabilisation of 64.21 kcal mol<sup>-1</sup>.

# 1. Introduction

Amides are of fundamental chemical interest as conjugation between nitrogen lone-pair electrons and the carbonyl  $\pi$ -bond which possess distinct physical and chemical properties. A planar structure of amide group has been confirmed by measurement with X-rays and the *trans*-configuration is the most stable [1–8]. 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 [9,10] which is in agreement with the reports of other experimental investigators [11–14]. Substituted 2-arylacetamides are very

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interesting compounds because of their structural similarity to the lateral chain of natural benzyl penicillin [15,16]. Amides are also used as ligands due to their excellent coordination abilities [17,18].

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 [19– 22]. The choloroacetanilde herbicide alachlor is one of the most extensively used agro chemical [23,24]. 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

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and it has pain relieving properties [25]. 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 [26– 34]. The room-temperature structure of *N*-(4-bromophenyl)acetamide was reported to crystallise in the orthorhombic space group Pna2<sub>1</sub> by Andreetti et al. [35] and recently a new polymorph of the same compound has been determined at 173 K in the space group *P*2<sub>1</sub>/*c* by Jasinski et al. [36].

The vibrational spectroscopic analysis of acetanilide derivative N-(4-bromophenyl)-2,2-dichloroacetamide (4BNPA) has not been studied. Thus, in continuation of earlier studies on N-(chloro substituted phenyl)-2,2-dichloroacetamides [37] and N-(methyl-phenyl)-2,2-dichloroacetamides [38,39], N-(dimethyl substituted phenyl)-2,2-dichloroacetamides [40] and owing to the significance of the N-arylacetamides in biological systems and in industries, the compound N-(4-bromophenyl)-2,2-dichloroacetamide has been prepared and an extensive spectroscopic and quantum chemical studies are carried out in an effort to provide possible explanations for vibrational frequencies, to understand the effect of bromine on the characteristic amide group frequencies and to provide clear information on the structure-reactivity relations of the molecule.

#### 2. Experimental

The compound *N*-(4-bromophenyl)-2,2-dichloroacetamide (4BNPA) was prepared from the respective 4-bromoaniline, dichloroacetic acid and phosphorus oxychloride based on the procedure reported [37]. The pure samples of 4-bromoaniline, 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 synthesised crude compound was recrystallised from ethanol several times. The yield of the product is about 70%. The purity of the compound was confirmed by chemical analysis (found/calculated) for C (33.82/33.96), H (2.07/2.14) and N (4.90/4.95). The Scheme I depicts the preparation of the compound under investigation.

The FTIR spectrum of the compound was 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 2 cm<sup>-1</sup>. The FT-Raman spectrum of the compound was also recorded with the same instrument with FRA 106 Raman module. The Raman spectrum was obtained in the wavenumber range 4000– 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 powers. A special (enhanced) liquid nitrogen cooled germanium detector was used. The frequencies of all sharp bands are accurate to 2 cm<sup>-1</sup>.

# 3. Computational details

The gradient corrected density functional theory (DFT) [41] with the three-parameter hybrid functional Becke3 (B3) [42] for



the exchange part and the Lee-Yang-Parr (LYP) correlation functional [43], calculations have been carried out using 6-311++G<sup>\*\*</sup> and cc-pVTZ basis sets with Gaussian-09 [44] program, invoking gradient geometry optimisation [45]. Following geometry optimisations with B3LYP method, 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 4BNPA resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The dipole moment derivatives and polarizability derivatives were computed analytically. The force constants obtained from the B3LYP/6-311++G\*\* method have been utilised in the normal coordinate analysis by Wilson's FG matrix method [46–48]. The potential energy distributions corresponding to each of the observed frequencies were calculated with the program of Fuhrer et al. [49].

The Raman scattering activities ( $S_i$ ) of the fundamental modes were suitably converted to relative Raman intensities ( $I_i$ ) using the following relationship derived from the basic theory of Raman scattering [50].

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i [1 - \exp(-hcv_i/kT)]}$$

where  $v_0$  is the exciting frequency (cm<sup>-1</sup>),  $v_i$  is the vibrational wavenumber of the *i*th normal mode, *h*, *c* and *k* are universal constants, and *f* is the suitably chosen common scaling factor for all the peak intensities.

Isoelectronic molecular electrostatic potential surfaces (MEP) and electron density surfaces [51] were calculated using 6- $311++G^{**}$  basis set. The molecular electrostatic potential at a point 'r' in the space around a molecule (in atomic units) can be expressed as:

$$V(r) = \sum_{A} \frac{Z_{A}}{|\vec{R_{A}} - \vec{r}|} - \int \frac{\rho(\vec{r'})dr'}{|\vec{r'} - \vec{r}|}$$

where  $Z_A$  is the charge on nucleus A, located at  $R_A$  and  $\rho(r')$  is the electronic density function for the molecule. The first and second terms represent the contributions to the potential due to nuclei and electrons, respectively. V(r) is the resultant electrical potential at each point r, which is the net electrostatic effect produced at the point r by both the electrons and nuclei of the molecule. The molecular electrostatic potential (MEP) serves as a useful quantity to explain hydrogen bonding, reactivity and structure–activity relationship of molecules including biomolecules and drugs [52]. Structures resulting from the plot of electron density surface mapped with electrostatic potential surface depict the shape, size, charge density distribution and the site of chemical reactivity of a molecule. GaussView 5.0.8 visualisation program [53] has been utilised to construct the MEP surface, the shape of highest frontier molecular orbitals.

The stabilisation energy  $E^{(2)}$  associated with i (donor)  $\rightarrow j$  (acceptor) delocalisation is estimated from the second-order perturbation approach [54] as given below

$$E^{(2)} = q_i rac{F^2(i,j)}{arepsilon_i - arepsilon_i}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$  and  $\varepsilon_j$  are diagonal elements (orbital energies) and F(i,j) is the off-diagonal Fock matrix element.

Various reactivity and selectivity descriptors such as chemical hardness, chemical potential, softness, electrophilicity, nucleophilicity and the appropriate local quantities employing natural population analysis (NPA) scheme are calculated. Both the global and local reactivity descriptors are determined using finite difference approximation to reveal the intramolecular reactivity of the molecule. The vertical ionization potential (*I*), electron affinity (*A*) and the electron populations are determined on the basis of B3LYP/6-311++G<sup>\*\*</sup> method. The energy of the *N* electron species of the NCEP has been determined by restricted B3LYP method while N - 1 and N + 1 electronic species were done by restricted open B3LYP method using the optimised geometry by B3LYP/6-311++G<sup>\*\*</sup> method. The site-selectivity of a chemical system can be determined by using Fukui functions [55,56] which can be interpreted either as the change of electron density  $\rho(r)$  at each point *r* when the total number of electrons are changed or as the sensitivity of chemical potential ( $\mu$ ) of a system to an external perturbation at a particular point *r*.

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{N}}\right)_{\nu(\mathbf{r})} = \left(\frac{\delta \mu}{\delta \nu(\mathbf{r})}\right)_{\mathbf{N}}$$

Yang and Parr introduced local softness s(r) to predict the reactivity [56]. The s(r) describes the sensitivity of the chemical potential of the system to the local external perturbation and is obtained by simply multiplying Fukui function f(r) with global softness *S*. The local softness values are generally used in predicting electrophilic, nucleophilic and free radical reactions, regioselectivity etc.

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{\nu(r)}$$
 and  $s(r) = f(r)S$ 

where *S* is the global softness which is inversely related to global hardness ( $\eta$ ).

The generalised philicity descriptor,  $\omega(r)$  contains almost all informations about hitherto known different global and local reactivity and selectivity descriptors, in addition to the information regarding electrophilic/nucleophilic power of a given atomic site in a molecule [57]. The local quantity called philicity associated with a site *k* in a molecule can be calculated as  $\omega_k^a = \omega f_k^a$ , where  $\omega = \mu^2/2\eta$  and a = +, - and 0 represents local philic quantities describing nucleophilic, electrophilic and radical attacks respectively. The condensed philicity summed over a group of relevant atoms which is defined as the group philicity [58] can also be determined by using the relation  $\omega_g^a = \sum_{k=1}^n \omega_k^a$  where, *n* is the number of atoms coordinated to the reactive atom and  $\omega_k^a$  is the local electrophilicity of the atom *k*.

# 4. Results and discussion

#### 4.1. Structural properties

The optimised molecular geometry and atom numbering scheme of 4BNPA is shown in Fig. 1. The steric interaction of bromo 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 4BNPA at B3LYP levels with  $6-311++G^{**}$  and cc-pVTZ basis sets are presented in Table 1. The theoretical values determined by B3LYP/6-311++G\*\* method are used for comparison purposes unless otherwise stated. It is observed that the mean C-C bond distance calculated between the ring carbon atoms of 4BNPA is 1.393 Å, and the C–C and C–H bond lengths are found to be not significantly deviated with the -Br substitution. The bond length of the compound 4BNPA determined at the DFT level of theory are in good agreement with the structural parameters of N-phenylacetamide [13] where the mean bond distance of C–C (ring) is found to be 1.386 Å and N-(4-bromophenyl)acetamide [36] where the mean bond distance of C–C (ring) is 1.385 Å. The equal bond distances of C3-C4 and C4-C5 reveals that the bromine atom lie



**Fig. 1.** The stable geometry and atom numbering of *N*-(4-bromophenyl)-2,2-dichloroacetamide.

in the plane of the ring. The —CO—NH— group also adopts a planar 'peptide-like' conformation, as in the case of formamide [59], *N*-methylformamide [60], *o*-methylacetanilide [61] and formanilide [11,12], *N*-(methylphenyl)-2,2-dichloroacetamides [38,39], *N*-(dimethyl substituted phenyl)-2,2-dichloroacetamides [40]. The theoretical amide group bond distances are very well agreed with the experimental bond distances of *N*-(4-bromophenyl)acetamide [36]. The bond lengths between the amide nitrogen and the aromatic ring, C1—N7 and between the amide nitrogen and the carbonyl group, N7—C8 given in Table 1 reflect the changes in conjugation. The mesomeric effect (+M) of —Br group on the C1—N7 bond distances is also having some significance.

With the electron donating substituents on the benzene ring, the symmetry of the ring is distorted, yielding ring angles smaller than 120° at the point of substitution and slightly larger than 120° at the ortho and meta positions [62]. An opposite trend is observed in 4BNPA due to the predominance of inductive (-I) effect of the bromine. The angle at the point of substitution C3-C4-C5 in 4BNPA is 120.6°. Similarly the ortho bond angles C2-C3-C4 and C4-C5-C6 in 4BNPA are 119.2° and 120.2°, respectively. In the amide group region the bond angles C1-N7-C8 (128.7°/ (127.5°)), N7-C8-O9 (126.6°/(123.8°)) and O9-C8-C10 (118.4°/ (121.6°)) differ significantly from the experimental values given in parenthesis of N-(4-bromophenyl)acetamide. The dihedral angles determined theoretically are agreed well with the experimental values except C2–C1–N7–C8 (179.5°/(164.5°)) and C6–C1–N7–C8  $(0.5^{\circ}/(-18.6^{\circ}))$ . These are due the role of intermolecular hydrogen bonding present in the solid state. In the crystal, molecules are linked by N-H···O hydrogen bonds forming chains. Weak C—H $\cdots$  $\pi$  interactions are also present and contribute to the crystal packing stability [36].

The energy and thermodynamic parameters of the compound have also been computed at B3LYP methods with 6-311++G<sup>\*\*</sup> and cc-pVTZ basis sets and are presented in Table 2. The frequency

#### Table 1

Structural parameters calculated for N-(4-bromophenyl)-2,2-dichloroacetamide (4BNPA) employing B3LYP methods with 6-311++G\*\* and cc-pVTZ basic sets.

-				
Structural parameters	B3LYP / 6-311++G**	B3LYP/cc-pVTZ	Expt. <sup>a</sup>	Expt. <sup>b</sup>
Internuclear distance (Å)				
	1.40	1.40	1 207	1 204
	1.40	1.40	1.597	1.594
CI = C6	1.40	1.40	1.391	1.390
C1—N7	1.41	1.41	1.413	1.401
C2-C3	1.39	1.39	1.379	1.380
C2—H13	1.09	1.08		0.950
C3–C4	1.39	1.39	1.391	1.384
C3-H14	1.08	1.08		0.950
C4-C5	1 39	1 39	1 384	1 384
$C_{4}$ Pr10	1.02	1.01	1.501	1 901
C4-B119	1.92	1.20	1.276	1.091
05-06	1.39	1.39	1.376	1.377
C5—H15	1.08	1.08		0.950
C6—H16	1.08	1.08		0.950
N7—C8	1.36	1.36	1.354	1.347
N7—H17	1.01	1.01		0.892
68-09	1 22	121	1 219	1 2 2 6
$C_{8}$ – $C_{10}$	1 54	1 54	1 495	1 501
	1.54	1.90	1.455	1.501
	1.80	1.80		
C10-C112	1.80	1.80		
C10–H18	1.08	1.08		0.98
Bond angle (°)				
$C_{2}$ $C_{1}$ $C_{6}$	110 5	110.4		110.4
$C_2 = C_1 = C_0$	119.5	119.4		119.4
$C_2 = C_1 = N_7$	117.2	117.2		117.1
C6-C1-N7	123.3	123.4		123.5
C1–C2–C3	120.8	120.8		120.5
C1-C2-H13	120.0	119.9		119.7
C3-C2-H13	119.2	119.3		119.7
(2-(3-(4)))	119.2	119.3		119.2
$C_2 = C_3 = H_1 A$	120.1	120.2		120.4
	120.1	120.2		120.4
C4-C3-H14	120.6	120.6		120.4
C3-C4-C5	120.6	120.6		121.2
C3-C4-Br19	119.6	119.6		119.1
C5-C4-Br19	119.8	119.8		119.7
C4–C5–C6	120.2	120.2		119.3
C4-C5-H15	120.3	120.2		120.3
C6-C5-H15	119.5	119.5		120.3
	110.7	110.7		120.5
	119.7	119.7		120.4
CI-C6-H16	120.1	120.0		119.8
C5-C6-H16	120.2	120.3		119.8
C1-N7-C8	128.7	128.8		127.5
C1-N7-H17	115.3	115.5		115.1
C8-N7-H17	116.0	115.7		117.0
N7-C8-09	126.6	126.8		123.8
N7_C8_C10	115.0	115.2		114.5
00-00-010	110 /	119.0		114.5
	110.4	110.0		121.0
C8-C10-C111	112.3	113.5		
C8–C10–Cl12	110.9	109.6		
C8-C10-H18	107.7	108.1		109.5
Cl11-C10-Cl12	111.0	110.9		
Cl11-C10-H18	107.4	107.2		
C112-C10-H18	107 3	107 3		
	107.5	107.5		
Dihedral angle (°)				
Cl—N7—C8—O9	0.1	1.1		-3.1
Cl-N7-C8-C10	-179.2	-177.0		176.7
$C_{2}$ $C_{1}$ $N_{7}$ $C_{8}$	_179.5	_1794		16/ 1
$C_{2} = C_{1} = N_{7} = C_{2}$	-175.5	-175.4		104.1
$C_0 = C_1 = C_1 = C_2$	0.5	0.0		-10.0
	0.1	0.0		0.8
N7-C1-C2-C3	-179.9	-180.0		178.2
C1-C2-C3-C4	0.1	0.0		0.3
C2-C3-C4-C5	-0.0	-0.0		-0.7
C2-C3-C4-Br19	180.0	180.0		179.9
C3-C4-C5-C6	0.0	0.0		0.0
$C_{-}C_{-}C_{-}C_{-}D_{r}10$	190.0	190.0		170.2
CO-CO-C4-BI19	-180.0	- 180.0		1/9.3
C4-C5-C6-C1	0.04	0.1		1.2
C2-C1-C6-C5	-0.1	-0.1		-1.6
C5-C6-C1-N7	179.9	179.9		-178.8

<sup>a</sup> Values taken from Ref. [13].
<sup>b</sup> Values taken from Ref. [36].

calculations compute the zero point energies, thermal correction to internal energy, enthalpy, Gibbs free energy and entropy as well as the heat capacity for a molecular system. The larger total dipole moment (2.106 D) is due to more charge separation.

#### Table 2

The calculated thermodynamic parameters of *N*-(4-bromophenyl)-2,2-dichloroacetamide (4BNPA) employing B3LYP/6-311++G<sup>\*\*</sup> and B3LYP/cc-pVTZ methods.

Thermodynamic parameters (298 K)	4BNPA					
	B3LYP/6- 311++G**	B3LYP/cc-pVTZ				
SCF energy, (Hartrees) Total energy (thermal), $E_{\text{total}}$ (kcal mol <sup>-1</sup> )	-3933.1656429 87.358	–3933.3037306 87.474				
Vibrational energy, <i>E</i> <sub>vib</sub> (kcal mol <sup>-1</sup> ) Zeropoint vibrational energy (kcal mol <sup>-1</sup> )	85.580 79.447	85.696 79.60				
Heat capacity ( $C_{\nu}$ ), (cal mol <sup>-1</sup> k <sup>-1</sup> )	44.45	44.302				
Entropy, S (cal mol <sup>-1</sup> $k^{-1}$ )	120.75	119.71				
Rotational constants (GHz)						
X	1.467	1.474				
Y	0.137	0.138				
Ζ	0.135	0.135				
Dipolemoment (Debye)						
$\mu_x$	-0.808	-0.950				
$\mu_y$	-1.931	-1.943				
$\mu_z$	-0.230	0.260				
$\mu_{ m total}$	2.106	2.178				
E <sub>HOMO</sub> (eV)	-6.6775					
$E_{\text{LUMO}}$ (eV)	-1.8243					
$E_{\text{HOMO}-1}$ (eV)	-7.7970					
$E_{LUMO+1}$ (eV)	-1.1725					
$E_{\rm LUMO} - E_{\rm HOMO} (\rm eV)$	4.8532					
Ionization potential (I)	8.4188					
Electron affinity (A)	0.24					
Chemical potential $(\mu)$	-4.3294					
Hardness $(\eta)$	4.0894					
Global softness (S)	0.1223					
Electrophilicity ( $\omega$ )	2.2917					
Electronegativity $(\chi)$	4.3294					
Electrofugality ( $\Delta E_e$ )	10.7105					
Nucleofugality $(\Delta E_n)$	2.05					

#### 4.2. Thermodynamic analysis

The temperature dependence of the thermodynamic properties heat capacity at constant pressure ( $C_p$ ), entropy (S) and enthalpy change ( $\Delta H_{0 \rightarrow T}$ ) for 4BNPA are also determined by B3LYP/6-311++G<sup>\*\*</sup> method and listed in Table 3. The anharmonicity effects have been eliminated by scaling the thermodynamic properties by 0.97. The Fig. 2 depicts the correlation of heat capacity at constant

#### Table 3

Temperature dependence of the thermodynamic properties of *N*-(4-bromophenyl)-2,2-dichloroacetamide (4BNPA) determined by B3LYP/6-311++G\*\* method.

T (K)	N-(4-bromophenyl)-2,2-dichloroacetamide									
	$C_p$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	S (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H$ (kcal mol <sup>-1</sup> )							
50	70.27	301.12	2.67							
100	97.12	358.18	6.87							
150	123.09	402.48	12.37							
200	149.04	441.44	19.18							
250	174.76	477.47	27.27							
298.15	198.63	510.31	36.27							
300	199.52	511.54	36.64							
350	222.63	544.06	47.20							
400	243.67	575.19	58.86							
450	262.49	604.99	71.53							
500	279.17	633.53	85.08							
550	293.91	660.84	99.41							
600	306.94	686.99	114.44							
650	318.50	712.02	130.08							
700	328.80	736.01	146.27							
750	338.02	759.01	162.94							
800	346.32	781.10	180.05							
850	353.82	802.32	197.56							
900	360.63	822.74	215.43							
950	366.83	842.41	233.61							
1000	372.49	861.37	252.10							



**Fig. 2.** Temperature dependence of entropy, heat capacity at constant pressure ( $C_P$ ) and enthalpy change ( $\Delta H$ ) of *N*-(4-bromophenyl)-2,2-dichloroacetamide.

pressure ( $C_p$ ), entropy (*S*) and enthalpy change ( $\Delta H_{0-T}$ ) with temperature along with the correlation equations. From Table 3, one can find that the entropies, heat capacities, and enthalpy changes are increasing with temperature ranging from 50 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature [63]. The observed relations of the thermodynamic functions vs. temperatures with the regression factors ( $R^2$ ) not less than 0.9995 for 4BNPA are given by

$$\begin{split} S &= 274.3973 + 0.8609T - 2.7997 \times 10^{-4}T^2 \\ C_p &= 38.4778 + 0.6235T - 2.9382 \times 10^{-4}T^2 \\ \Delta H &= -6.9551 + 0.1058T + 1.5688 \times 10^{-4}T^2 \end{split}$$

# 4.3. Analysis of molecular electrostatic potential

The molecular electrostatic potential surface (MEP) which is a method of mapping electrostatic potential onto the iso-electron density surface simultaneously displays electrostatic potential (electron + nuclei) distribution, molecular shape, size and dipole moments of the molecule and it provides a visual method to understand the relative polarity [64,65]. Electrostatic potential maps illustrate the charge distributions of the molecules three dimensionally. One of the purposes of finding the electrostatic potential is to find the reactive sites of a molecule. The reactive site is a particularly charged region of a molecule that has an affinity for interacting with charged particles. The total electron density surface mapped with electrostatic potential of 4BNPA constructed by B3LYP/6-311++G\*\* method is shown in Fig. 3. The extreme limits of the total electron density are  $-5.709e \times 10^{-2}$  to +5.709e  $\times$  10<sup>-2</sup>. The electrostatic potential contour map for positive and negative potentials and electrostatic potential surface of the compound are shown in Fig. 4 and in the Supplementary Fig. S1, respectively. The colour scheme for the MEP surface is red, electron rich, partially negative charge; blue, electron deficient, partially positive charge; light blue, slightly electron deficient region; yellow, slightly electron rich region; green, neutral; respectively. It is obviously from the Figs. 3 and 4 that the region around oxygen atoms linked with carbon through double bond represents the most negative potential region (red<sup>1</sup>). The hydrogen

<sup>&</sup>lt;sup>1</sup> For interpretation of colour in Figs. 3 and 4, the reader is referred to the web version of this article.

atoms attached to the ends of methyl group posses the maximum positive charge (blue). The predominance of green region in the MEP surfaces corresponds to a potential halfway between the two extremes red and dark blue colour. In other words, red indicates the lowest electrostatic potential energy, and blue indicates the highest electrostatic potential energy. Intermediary colours represent intermediary electrostatic potentials. Areas of low potential, red, are characterised by an abundance of electrons. Areas of high potential, blue, are characterised by a relative absence of electrons. In both the compounds the total electron density surface mapped with electrostatic potential clearly reveals the presence of high negative charge on the carbonyl oxygen and in part of the ring while more positive charge around the N–H region. The region of electrostatic potential is  $-9.617e \times 10^{-3}$  to  $+9.617e \times 10^{-3}$ . Electrostatic potential maps (Figs. 4 and 5) can also be used to determine the nature of the bonds of the molecules. The molecule 4BNPA has great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electronegativity difference leads to regions that are almost entirely red and almost entirely blue. Thus, a high electrostatic potential indicates the relative absence of electrons and a low electrostatic potential indicates an abundance of electrons. The electrostatic potential maps also illustrate the reactive sites of molecules whose polarity is not easy to intuitively deduce.

#### 4.4. Analysis of frontier molecular orbitals

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters



**Fig. 3.** The total electron density surface mapped with electrostatic potential of *N*-(4-bromophenyl)-2,2-dichloroacetamide.



**Fig. 4.** The contour map of electrostatic potential of the total density of *N*-(4-bromophenyl)-2,2-dichloroacetamide.

for quantum chemistry [63]. The energies of HOMO LUMO, LUMO+1 and HOMO-1 and their orbital energy gaps are calculated using B3LYP/6-311++G\*\* method and the pictorial illustration of the frontier molecular orbitals are shown in Fig. 5. Molecular orbitals, when viewed in a qualitative graphical representation, can provide insight into the nature of reactivity, and some of the structural and physical properties of molecules. Well known concepts such as conjugation, aromaticity and lone pairs are well illustrated by molecular orbitals. Visual analysis of the molecular orbitals allows concepts of structural symmetry to be extended to frontier electron symmetry. It is actually possible to predict reactivity by examining the molecular orbitals. The positive and negative phases are represented in red and green colours, respectively. The LUMO orbitals of the molecule feature a larger number of nodes than the HOMO orbitals. A large extent of localisation of the  $\pi$ -type wavefunction on C=O double bond is observed. The HOMO of the molecule speared out over the ring and the amide parts of the molecule while the LUMO does spread over the entire parts. This clearly indicates the  $n \rightarrow \pi$  and  $\pi \rightarrow \pi^*$  transitions are the most probable. The calculated energy gap (4.8532 eV) of HOMO-LUMO's explains the ultimate charge transfer interface within the molecule.

# 4.5. Natural bond orbital (NBO) analysis

NBO analyses of molecules illustrate the Lewis structure, charge, bond order, bond type, hybridization, resonance, donor-acceptor interactions, etc. The bonding concepts such as type of bond orbital, their occupancies, the natural atomic hybrids of which the NBO is composed, giving the percentage of the NBO on each hybrid, the atom label, and a hybrid label showing the hybrid orbital ( $sp^x$ ) composition (the amount of *s*-character, *p*-character, etc.) of 4BNPA molecule determined by B3LYP/6-311++G<sup>\*\*</sup> method are depicted in the Supplementary Table T1. The occupancies of NBOs reflect their exquisite dependence on the chemical environment of the molecule. The NBO energy values show the corresponding spatial symmetry breaking in the direction of unpaired spin. The Lewis structure that is closest to the optimized structure is determined.



**Fig. 5.** The frontier molecular orbitals and their energy gap of *N*-(4-bromophenyl)-2,2-dichloroacetamide.

For example, the bonding orbital for N7–C8 with 1.99 electrons has 62.65% N7 character in a  $sp^{1.73}$  hybrid and has 37.35% C8 character in a  $sp^{2.03}$  hybrid orbital. In the case of C8–O9 bonding orbital with 1.992 electrons has 35.66% C8 character in a  $sp^{1.95}$  hybrid and has 64.34% O9 character in a  $sp^{1.46}$  hybrid orbital. A bonding orbital for N7–H17 with 1.9821 electrons has 70.68% N7 character in a  $sp^{2.84}$  hybrid and has 29.32% H17 character in an *s* orbital. The C–C bonds of the aromatic ring posses more *p* character than s character. This is clearly indicates the delocalization of  $\pi$  electrons among all the carbon atoms. Similarly C1–N7 bond has also posses more *p* character.

# 4.6. Donor–acceptor interactions

The NBO method demonstrates the bonding concepts like atomic charge, Lewis structure, bond type, hybridization, bond order, charge transfer and resonance possibility. Strong electron delocalisation in the Lewis structure also shows up as donor–acceptor interactions. This calculation is done by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating their energetic importance by 2nd order perturbation theory. The stabilisation of orbital interaction is proportional to the energy difference between interacting orbitals. Therefore, the interaction having strongest stabilisation takes place between effective donors and effective acceptors. This bonding–anti bonding interactions can be quantitatively described in terms of the NBO approach that is expressed by means of second-order perturbation interaction energy  $E^{(2)}$ [54,64,66]. This energy represents the estimate of the off-diagonal NBO Fock matrix element. The stabilization energy  $E^{(2)}$  associated with *i* (donor)  $\rightarrow$  *j* (acceptor) delocalisation is estimated from the second-order perturbation approach [67] as given below

$$E^{(2)} = q_i \frac{F^2(i,j)}{\varepsilon_i - \varepsilon_i}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$  and  $\varepsilon_j$  are diagonal elements (orbital energies) and F(i,j) is the off-diagonal Fock matrix element.

All lone pair-bond pair interactions and only bond pair-bond pair interactions with stabilization energy greater than 3.0 kcal mol<sup>-1</sup> are listed in the Supplementary Table T2. In 4BNPA molecule, the lone pair donor orbital,  $n_{\rm N} \rightarrow \pi^*_{\rm CO}$  interaction between the nitrogen (N7) lone pair and the C8-O9 antibonding orbital possess a strong stabilization of 64.21 kcal mol<sup>-1</sup>. The lone pair donor orbital,  $n_N \rightarrow \pi^*_{CC}$  interaction between the nitrogen (N7) lone pair and the C1-C6 antibonding orbital has a stabilization energy 32.63 kcal mol<sup>-1</sup>. The  $n \rightarrow \pi^*$  stabilization energy of lone pair of electrons present in the oxygen atom (09) to the antibonding orbital ( $\sigma^*$ ) of (N7–C8) and (C8–C10) are 24.08 and 21.97 kcal mol^-1, respectively. The bond pair donor orbital,  $\pi_{CC} \rightarrow$  $\pi^*_{CC}$  interaction between the C1–C6 bond pair and the C4–C5 antibonding orbital give stabilization of 22.34 kcal mol<sup>-1</sup> while between the C4–C5 bond pair and the C2–C3 antibonding orbital has stabilized by 21.28 kcal mol<sup>-1</sup>.

#### 5. Vibrational analysis

The FTIR and FT-Raman spectra of N-(4-bromophenyl)- 2,2dichloroacetamides are shown in Figs. 6 and 7. All the observed wavenumbers are assigned in terms of fundamentals, overtones and combination bands. The observed and calculated frequencies along with their relative intensities and probable assignments are presented in Table 4. The geometry of the molecules is considered by possessing  $C_1$  point group symmetry. All the vibrations are active in both IR and Raman. The theoretical spectra of the compound given in Figs. 6 and 7 are simulated by using Lorentzian functions.

# 5.1. Carbon-carbon vibrations

The carbon–carbon stretching of 4BNPA molecule is found in the IR spectrum at 1616, 1590, 1490, 1402 and 1298 cm<sup>-1</sup> as medium to very strong bands and at 1631, 1595, 1501, 1412, 1310 and 1192 cm<sup>-1</sup> in Raman. These frequencies appear in the respective range [31–34]. The CCC in-plane and out of plane bending modes of 4BNPA have been found and presented in Table 4. In 4BNPA the ring breathing mode is observed at 866 and 880 cm<sup>-1</sup> while the CCC trigonal bending is seen at 1011 and 1009 cm<sup>-1</sup>, respectively in IR and Raman spectra. All these assignments agree well with the reported literatures [37–40,68].

#### 5.2. C-H vibrations

The C—H bond present in the phenyl group of 4BNPA gives very strong to very weak stretching bands at 3091 and 3008 cm<sup>-1</sup> in IR spectrum. The band observed in the Raman spectrum at 3020 cm<sup>-1</sup> is attributed to the C—H stretching vibration of —CHCl<sub>2</sub> group. The aromatic C—H in-plane bending modes are observed in 4BNPA at 1119, 1074, 979 and 968 cm<sup>-1</sup> in the IR and Raman spectra. The C—H out of plane bending modes of the present compound are



**Fig. 6.** (a) FTIR spectrum and Theoretical (b) B3LYP/6-311++G<sup>\*\*</sup>, and (c) B3LYP/ccpVTZ spectra of *N*-(4-bromophenyl)-2,2-dichloroacetamide.

observed in the said region [38–40,68] and presented in the Table 4. The alkyl C—H in–plane bending modes are observed in the same region of C—C stretching. The alkyl C—H in–plane bending modes are assigned to the frequencies at 1242 and 1256 cm<sup>-1</sup> in IR and Raman spectra, respectively.

# 5.3. Amide group vibrations

The characteristic vibrations of the amide (-CONH-) group of *N*-(4-bromophenyl)-2,2-dichloroacetamide are analysed and the correlation of (-CONH-) group vibrations of some acetanilide are presented in Table 5. The strong band observed at 3276 cm<sup>-1</sup> in IR is attributed to the N–H stretching. By comparison with NPA, the N-H stretching of 4BNPA does not vary significantly with the N-(4-chlorophenyl)-2,2-dichloroacetamide (4CNPA). But it is blue shifted by 21 and 77 cm<sup>-1</sup> from that of N-(2-chlorophenyl)-2,2dichloroacetamide (2CNPA) and N-(2,4-dichlorophenyl)-2,2dichloroacetamide (24CNPA) molecules, respectively. Similarly the 4BNPA has 25–36 cm<sup>-1</sup> higher N–H stretching frequency than that of the N-(methyl substituted phenyl)-2,2-dichloroacetamides. 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. 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 *t*butyl group into the phenyl ring of N-phenylacetamide. This clearly confirms that the steric effect due to o-methyl and o-chloro groups is not significantly operating on the N-H stretching vibration and the electronic effects predominates [37-40,68].

The very strong IR bands observed at 1678 and 1685 cm<sup>-1</sup> are assigned to the amide-I, the C=O stretching band of 4BNPA molecule. The comparison of the wavenumber of C=O stretching in



**Fig. 7.** (a) FT-Raman spectrum and (b) Theoretical B3LYP/6-311++G<sup>\*\*</sup>, (c) B3LYP/ccpVTZ spectra of *N*-(4-bromophenyl)-2,2-dichloroacetamide.

4BNPA with that of chloro and methyl substituted *N*-phenylacetamide (NPA) molecules reveals that the substitution of bromine in the phenyl ring does not make the molecule effectively compete with the carbonyl oxygen for the electrons of the nitrogen, thus increasing the force constants of the C=O bond. From Table 5, it is evident 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-dichloroaetamide, *N*-(chloro substituted phenyl)- and *N*-(methyl substituted phenyl)-2,2dichloroacetamides [13,37–40,68].

The very strong vibration observed at 1553 and 1563 cm<sup>-1</sup> in IR/Raman spectra are ascribed to the amide-II band, N—H in-plane bending of 4BNPA. The amide-II bands of NPA, 4CNPAand 4BNPA does not show any significant variation. By comparing with the amide-II bands of 2MPA and 24DMPA, a red shift is observed in 4BNPA mode. This shows that the methyl groups excerts more steric influence on the N—H bond properties.

The C–N stretching mode, the amide-III band, of 4NPA is assigned to the wave number observed at 1335 and 1346 cm<sup>-1</sup> in the infrared and Raman spectra, respectively. The fundamental modes 1338 cm<sup>-1</sup> in IR and 1350 cm<sup>-1</sup> in Raman are assigned to the C–N stretching of 4CNA. The amide-III band of NPA is observed at 1344 cm<sup>-1</sup> in the infrared while in Raman it is observed at 1355 cm<sup>-1</sup>. The spectral data indicates that no appreciable rise in C–N stretching frequency of 4BNPA and also there is no mesomeric influence of the bromine towards the C–N bond.

The amide-IV, C=O in-plane bending of 4BNPA is found at 799 and 789 cm<sup>-1</sup> in the IR and Raman spectra, respectively. For NPA compound this mode is assigned to 811 and 810 cm<sup>-1</sup>. There is a significant blue shift is observed in the C=O in-plane bending

#### Table 4

The observed FTIR, FT-Raman and calculated frequencies using B3LYP/6-311++G<sup>\*\*</sup> and B3LYP/cc-pVTZ force field along with their relative intensities, probable assignments and potential energy distribution (PED) of *N*-(4-bromophenyl)-2,2-dichloroacetamide (4BNPA)<sup>a</sup>.

Observed wavenumber	erved B3LYP/6-311++G** Calculated wavenumber Depo enumber ratio			Depolarisation ratio	1 B3LYP/cc-pVTZ Calculated wavenumber				Depolarisation Assignment %PED ratio		%PED		
(cm <sup>-</sup> ) FTIR	FTR	Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity	Raman intensity		Unscaled (cm <sup>-1</sup> )	Scaled (cm <sup>-1</sup> )	IR intensity	Raman intensity			
3276 s 3203 m 3134 m		3594	3271	35.32	31.07	0.15	3593	3270	39.64	32.97	0.17	vN—H 2 × 1616 2 × 1563	$95\nu_{\rm NH}$
3091 s	3096 VS	3242	3080	5.86	17.20	0.16	3247	3085	5.82	16.83	0.19	vC—Н	92v <sub>CH</sub>
	•••	3204	3044	0.74	29.12	0.22	3206	3046	0.92	28.65	0.24	vC—Н	93ν <sub>CH</sub>
		3200	3040	0.63	19.73	0.36	3203	3043	0.81	19.57	0.38	vC—Н	90v <sub>CH</sub>
	3020 m	3182	3023	2.01	23.30	0.18	3179	3020	2.01	25.22	0.18	$vC-H(Cl_2)$	94v <sub>CH</sub>
3008 vw		3162	3004	9.12	20.36	0.36	3164	3006	9.25	20.21	0.37	vC—H	92ν <sub>CH</sub>
2948 w 2793 vw	2948 w											$2 \times 1490$ $2 \times 1501$ $2 \times 1402$	
2362 w												2 × 1177	
1894 w	1005	1700	1074	222 51	20 5 4	0.20	1705	1077	204.22	25.00	0.20	2 × 968	06.
1678 VS	1685 m	1/62 1622	16/4	332.51	30.54	0.20	1/65 1624	16//	294.32	25.69	0.20	v = 0	$96V_{C=0}$
1500 m	VW 1505	1621	1508	1 02	100.00	0.35	1622	1600	5.06	100.00	0.41	VCC	90v
1550 11	VS	1051	1550	1.05	100.00	0.44	1055	1000	5.50	100.00	0.50		89V <sub>CC</sub>
1553 vs	1563 m	1564	1533	359.11	43.62	0.34	1563	1532	393.10	47.29	0.33	βN—H	87β <sub>NH</sub>
1490 VS	1501 W	1518	1488	123.95	5.52 4 91	0.19	1526	1495	114.75	3.52 5.12	0.26	VCC	92V <sub>CC</sub>
1335 s	1346 s	1338	1358	38.32 80.14	36 73	0.24	1341	1402	60.85	22.88	0.26	vce vc-N	87 V <sub>CC</sub> 85 V <sub>CN</sub>
1298 m	1310 w	1323	1297	12.36	10.43	0.26	1326	1299	26.92	16.28	0.25	VCC	84V <sub>CC</sub>
1242 s	1256 s	1275	1250	43.72	16.09	0.25	1271	1246	59.30	27.55	0.27	$\beta CH(Cl_2)$	87β <sub>CH</sub> + 10β <sub>CC</sub>
		1261	1236	33.20	33.78	0.25	1258	1233	12.45	13.62	0.26	$vN-(C_6H_5)$	80v <sub>NC</sub>
1210 w		1252	1227	21.23	2.24	0.69	1234	1209	18.52	2.44	0.65	$\gamma CH(Cl_2)$	$72\gamma_{CH} + 18\gamma_{CC}$
	1192 m	1218	1194	7.73	0.69	0.72	1215	1191	7.12	0.72	0.75	vCC	$91v_{CC}$
1177 m		1207	1183	7.14	19.06	0.20	1209	1185	9.06	16.87	0.21	$\nu C - C(HCl_2)$	89v <sub>cc</sub>
1119 w		1142	1119	12.35	0.37	0.20	1143	1120	11.93	0.39	0.19	βСН	70β <sub>CH</sub> + 12β <sub>CCC</sub>
1074 s	1089 m	1087	1065	33.76	11.06	0.13	1091	1069	33.44	10.52	0.16	βCH	$67\beta_{CH} + 21\beta_{CCC}$
1011 m	1009 w	1022	1002	31.75	3.23	0.11	1029	1008	26.88	2.92	0.15	TB	$7/\beta_{CCC} + 18\beta_{CH}$
069 m	9/9 m	988	968	0.64	0.05	0.74	996	9/6	0.52	0.05	0.75	βCH	$70\beta_{CH} + 14\beta_{CCC}$
908 111	905 VW	972	953	0.62	3.78 0.11	0.18	972	953	0.41	3.22 0.10	0.23	pCH	$67p_{CH} + 15p_{CCC}$
940 VW 866 s	937 III 880 s	868	952 851	0.14	3.96	0.75	902 870	943 853	0.02	3 90	0.74	RB	$78\beta_{CCC} + 14\beta_{CCC}$
825 s	000 3	851	834	36.25	0.03	0.75	860	843	36.58	0.18	0.73	γCH	$63\gamma_{CH} + 22\gamma_{CCC}$
	802 m	821	805	32.78	0.03	0.73	828	811	22.05	0.21	0.74	γCH	$62\gamma_{CH} + 24\gamma_{CCC}$
799 s	789 w	798	782	57.62	1.56	0.75	795	779	45.55	1.51	0.74	βC==0	$82\beta_{C=0} + 15\beta_{NH}$
765 s	756 m	766	751	60.12	4.54	0.08	762	747	62.52	3.43	0.09	$v_aCCl_2$	$80v_{CCl}$ + $10\beta_{CH}$
743 s	738 m	712	698	27.02	2.59	0.04	724	710	0.12	0.07	0.70	γΝ—Η	$61\gamma_{\rm NH}$ + $21\gamma_{\rm CO}$
712 vw	718 m	709	695	0.38	0.31	0.73	715	701	32.15	1.99	0.10	үСН	62γ <sub>CH</sub> + 20γ <sub>CCC</sub>
642 m	641 s	649	636	95.03	2.13	0.59	648	635	74.87	2.43	0.36	v <sub>s</sub> CCl <sub>2</sub>	$78v_{CCI} + 14\beta_{CH}$
	627 S	643	630	0.20	1.59	0.66	645 580	632	7.02	2.04	0.54	γ <b>C=</b> 0	$68\gamma_{C=0} + 12\gamma_{NH}$
		536 541	530	54.27 6.98	0.15	0.55	541	530	55.51 7.02	0.55	0.51	BCCC	$60\beta_{CN} + 10\beta_{CO}$
506 s	511 m	511	501	29.84	0.08	0.71	518	508	27.99	0.31	0.40	vC—Br	87Vc p
428 w	431 w	425	417	0.75	4.39	0.05	423	415	1.26	3.67	0.06	$\beta N - (C_c H_s)$	$62\beta_{NC} + 16\beta_{CCC}$
406 w	403 vw	421	413	0.05	0.01	0.36	422	414	0.03	0.05	0.17	γCN	$59\gamma_{CN} + 22\gamma_{CO}$
	378 m	379	371	12.09	0.72	0.57	379	371	13.09	0.60	0.62	βCCC	60β <sub>CCC</sub> + 17β <sub>CH</sub>
	344 m	334	327	0.06	0.53	0.72	339	332	0.30	0.47	0.66	δCCl <sub>2</sub>	$72\delta_{CC12} + 12\beta_{CH}$
	302 m	312	306	18.25	0.30	0.71	312	306	18.01	0.37	0.73	$\tau CCl_2$	$62\tau_{CC12}$ + $24\omega_{CC12}$
	256 w	257	252	0.61	0.96	0.38	255	250	0.45	1.04	0.36	$\omega$ CCl <sub>2</sub>	$60\omega_{CC12} + 20\tau_{CC12}$
	240 w	230	225	0.05	0.41	0.21	232	227	0.12	0.34	0.23	ρCCl <sub>2</sub>	64ρ <sub>CCl2</sub> + 18β <sub>CH</sub>
	208 s	204	200	0.26	0.09	0.61	203	199	0.22	0.17	0.47	βC—Br	$69\beta_{C-Br} + 12\beta_{CCC}$
	146 W	130	133	2.97	0.53	0.30	139	136	3.02	0.43	0.31	$\gamma N - C_6 H_5$	$55\gamma_{NC} + 21\gamma_{CCC}$
		111 84	109	2.07	0.26	0.75	114 83	112 81	2.04	0.23	0.72	γC—Br	$50\gamma_{C-Br} + 20\gamma_{CCC}$
		56	02 55	5.07	0.19	0.75	54	53	436	0.19	0.75	VCC	$5 - \gamma_{CCC} - 15 \gamma_{CH}$
		31	30	0.04	0.53	0.75	32	31	0.11	0.55	0.75	γCCC	$50 \gamma_{CC} + 20 \gamma_{CH}$
		10	10	2.46	1.78	0.75	15	15	1.69	2.04	0.75	γCCC	$51\gamma_{CCC} + 18\gamma_{CH}$

<sup>a</sup> v – stretching;  $\beta$  – in-plane bending;  $\delta$  – deformation;  $\rho$  – rocking;  $\gamma$  – out of plane bending;  $\omega$  – wagging and  $\tau$  – twisting; TB-trigonal bending and RB-ring breathing. Raman intensity is normalised to 100.

frequency of 4BNPA when compared with the N-(chloro/methyl substituted phenyl)-2,2-dichloroacetamide compounds.

The amide-V, the N–H out of plane bending is observed at 743 and 738  $\rm cm^{-1}$  in 4BNPA. This mode in NPA is seen at 712 and

715 cm<sup>-1</sup>. Thus, the bromo substitution raised the N—H out of plane bending. The C=O out of plane bending of 4BNPA is observed at 627 cm<sup>-1</sup> in Raman spectrum. In NPA this amide-VI band is observed in IR at 558 and 568 cm<sup>-1</sup>. The amide-VI out of plane

bending mode of 4BNPA is significantly raised than that of NPA. The *o*-methyl group in 2MPA excerts more blue shift on the amide-VI frequency than other compounds.

#### 5.4. C—Br vibrations

Bromine compounds absorb strongly in the region 650–485 cm<sup>-1</sup> due to C—Br stretching vibrations. The in-plane bending vibrations are identified at 325-140 cm<sup>-1</sup>. Thus, the strong intensity bands observed at 506 in the infrared spectrum and 208 cm<sup>-1</sup> in Raman spectrum are attributed to the C—Br stretching and in-plane bending modes, respectively. These assignments are in good agreement with the literature [69].

# 5.5. 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. The very strong and medium bands in IR at 765 and having the Raman counterpart at 765 cm<sup>-1</sup> are assigned to the asymmetric CCl<sub>2</sub> stretching vibration of 4BNPA. The medium to strong symmetric CCl<sub>2</sub> stretching in 4BNPA is observed at 642 cm<sup>-1</sup> in IR and 641 cm<sup>-1</sup> in Raman spectra. The CCl<sub>2</sub> asymmetric and symmetric stretching frequency does not show any appreciable variation from that of the corresponding frequencies in NPA. The in-plane CCl<sub>2</sub> deformation vibration of 4BNPA is obtained at a low frequency region of the Raman spectra as medium band corresponding to  $344 \text{ cm}^{-1}$ . The out of plane CCl<sub>2</sub> twisting and wagging modes are assigned and given in the Table 4. These assignments are in good agreement with the literature values [38–40]. In the low frequency region the fundamental modes of acetanilide [68] differ from the compound under investigation because of the observation of the vibrations of heavy atoms.

# 6. Scale factors

Computed harmonic frequencies typically overestimate vibrational fundamentals due to basis set truncation and neglect of electron correlation and anharmonicity [70]. To compensate these shortcomings and to correlate the experimentally observed and theoretically computed frequencies for each vibrational modes of the compound scale factors are introduced. A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different types of fundamental vibrations. To determine the scale factors, the procedure used previously [71–77] have been followed that minimises the residual separating the experimental and theoretically predicted vibrational frequencies. The optimum scale factors for vibrational frequencies were determined by minimising the residual

$$\Delta = \sum_{i}^{N} \left( \lambda \omega_{i}^{\text{Theor}} - v_{i}^{\text{Expt}} \right)^{2}$$

where  $\omega_i^{\text{Theo}}$  and  $v_i^{\text{Expt}}$  are the *i*th theoretical harmonic frequency and *i*th experimental fundamental frequency (in cm<sup>-1</sup>), respectively and *N* is the number of frequencies included in the optimisation which leads to

$$\text{RMS} = \sqrt{\frac{\Delta}{N}}$$

A uniform scaling factor is recommended for all frequencies <1800 cm<sup>-1</sup> at the B3LYP method with 6-311++G<sup>\*\*</sup> basis set and is adopted in this study. Due to the large anharmonicities of C—H and N—H stretching frequencies >2700 cm<sup>-1</sup> were scaled by two different scale factors [75,76].

Initially, all scaling factors have been kept fixed at a value of 1.0 to produce the pure DFT calculated vibrational frequencies (unscaled) which are given in Table 4. Subsequently, the scale factors 0.91, 0.95 and 0.98 for N–H, C–H/C=O and all other vibrations, respectively, were used with 6-311++G<sup>\*\*</sup> and cc-pVTZ basis sets. The resultant scaled frequencies are also listed in Table 4. The RMS value using the with 6-311++G<sup>\*\*</sup> and cc-pVTZ basis sets are 9.9 and 8.4, respectively. The correlation diagram for the calculated and the experimental frequencies are shown in the Supplementary Fig. S2.

# 7. Topological charge distribution

The atomic charges of the neutral, cationic and anionic species of 4BNPA determined by natural population analysis (NPA) and the local reactivity properties of N-(4-bromophenyl)-2.2-dichloroacetamide using B3LYP/6-311++G\*\* method are presented in Table 6. Among the ring carbon atoms C1 has a positive charge while others have negative charge. The positive charge of C1 is due to the attachment of highly electronegative nitrogen atom (N7) to it. The carbon attached with the bromo group has less negative charge than that of others. This is due to the electron attracting nature of the bromine by means of inductive effect. The very high positive charge on the amide carbon C8 is due to the partial polar nature of C=O group. This also leads to a high negative charge on the oxygen atom O9. The bromine atom has small positive charge because of the mesomeric (+M) effect. The correlation of the atomic charges of the neutral, anion and cation of N-(4-bromophenyl)-2,2-dichloroacetamide is shown in the Supplementary Fig. S3.

#### 8. Analysis of structure-activity descriptors

In studying the importance of nucleophilicity excess descriptor, a careful analysis on the electronic structure, property and reactivity of 4BNPA compound is performed. The complete molecule is considered as a single unit. This unit can easily take part in charge transfer process within the coordinating atoms in the molecule. Table 6 and Supplementary Table T3 presents the philicity values of the 4BNPA compound. The understanding of chemical reactivity and site selectivity of the molecular systems has been effectively handled by the conceptual density functional theory (DFT) [78]. Chemical potential, global hardness, global softness, electronegativity and electrophilicity are global reactivity descriptors, highly successful in predicting global chemical reactivity trends. The global parameters like ionization potential (I), electron affinity (A), electrophilicity ( $\omega$ ), electronegativity ( $\chi$ ), hardness  $(\eta)$ , and softness (S) of the molecule are determined and displayed in Table 2. The site-selectivity of a chemical system, cannot, however, be studied using the global descriptors of reactivity.

Fukui functions and local softness are extensively applied to probe the local reactivity and site selectivity. The formal definitions of all these descriptors and working equations for their computation have been described [78–80]. The Fukui functions of the individual atoms of the neutral, cationic and anionic species of 4BNPA calculated by B3LYP/6-311++G\*\* method are presented in the Supplementary Table T3. It is clearly understood that the atoms C2, C3, C5, C6, N7, O9 and C10 are favourable for nucleophilic attack. The other atoms of 4BNPA are favourable for electrophilic attack. The molecule under investigation mainly gives substitution reactions.

The local softness, relative electrophilicity  $(s_k^+/s_k^-)$  and relative nucleophilicity  $(s_k^-/s_k^+)$  indices, the dual local softness  $\Delta s_k$  and the multiphilicity descriptors  $(\Delta \omega_k)$  have also been determined

Table 5
Correlation of amide (-CONH-) group vibrations of the compounds investigated.

Compounds name	$v_{C=0}$	$\beta_{N-H}$ $\nu_{C-N}$		β <sub>C=0</sub>		$\gamma_{N-H}$		γc=o		$v_{N-H}$				
	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR	FTIR	FTR
<sup>a</sup> NPA	1672	1680	1555	1568	1344	1355	811	810	712	715	558	568	3270	3275
<sup>a</sup> 2CNPA	1678	1685	1545	1551	1340	1346	807	804	739	742	574	-	3255	3253
<sup>a</sup> 4CNPA	1676	1682	1555	1558	1338	1350	801	800	745	749	574	584	3277	3269
<sup>a</sup> 24CPA	1682	1685	1569	1567	-	1342	812	815	-	752	570	567	3199	3201
<sup>b</sup> 2MPA	1677	1674	1588	1590	1341	1350	807	800	717	725	667	675	3250	3247
<sup>c</sup> 3MPA	1680	1678	1554	1555	1335	1335	806	804	726	730	658	658	3245	3247
<sup>b</sup> 4MPA	1669	1669	1551	1546	1348	1340	810	809	745	744	636	638	3240	3236
<sup>d</sup> 24DMPA	1692	1691	1591	1595	1345	1350	822	820	-	-	661	-	3266	-
<sup>d</sup> 35DMPA	1670	1668	1567	1570	1340	1341	805	807	-	-	601	602	3296	-
<sup>e</sup> 4BNPA	1678	1685	1553	1563	1335	1346	799	789	743	738	-	627	3276	-

<sup>a</sup> Values taken from Ref. [13].

<sup>b</sup> Values taken from Ref. [37].

<sup>c</sup> Values taken from Ref. [38].

<sup>d</sup> Values taken from Ref. [39].

<sup>e</sup> Values from the present investigation.

 Table 6

 The partial charges of the atoms determined by natural population analysis (NPA) and the local reactivity properties of N-(4-bromophenyl)-2,2-dichloroacetamide using B3LYP/6-311++G<sup>\*\*</sup> method.

Atom	Neutral	Anion	Cation	$\Delta f_{(k)}$	$\Delta s_k$	$\Delta \omega_k$	Electrophilicity	Nucleophilicity
C1	0.1517	0.0491	0.1134	-0.1409	-0.0172	-0.3229	-2.6789	-0.3733
C2	-0.2092	-0.1155	-0.2561	0.0468	0.0057	0.1073	1.9979	0.5005
C3	-0.2105	-0.1108	-0.2319	0.0783	0.0096	0.1794	4.6589	0.2146
C4	-0.1142	-0.0996	-0.1987	-0.0699	-0.0085	-0.1602	0.1728	5.7877
C5	-0.2036	-0.1084	-0.2382	0.0606	0.0074	0.1389	2.7514	0.3634
C6	-0.2101	-0.1161	-0.2369	0.0672	0.0082	0.1540	3.5075	0.2851
N7	-0.5963	-0.3353	-0.5993	0.2580	0.0315	0.5913	87.0000	0.0115
C8	0.6447	0.3217	0.5195	-0.4482	-0.0548	-1.0271	-2.5799	-0.3876
09	-0.5838	-0.2775	-0.7074	0.1827	0.0223	0.4187	2.4782	0.4035
C10	-0.2820	-0.1514	-0.3105	0.1021	0.0125	0.2340	4.5825	0.2182
Cl11	-0.0046	0.0139	-0.1197	-0.0966	-0.0118	-0.2214	0.1607	6.2216
Cl12	0.0042	0.0193	-0.1484	-0.1375	-0.0168	-0.3151	0.0990	10.1060
H13	0.2075	0.1196	0.1905	-0.1049	-0.0128	-0.2404	-5.1706	-0.1934
H14	0.2246	0.1280	0.2019	-0.1193	-0.0146	-0.2734	-4.2555	-0.2350
H15	0.2245	0.1278	0.2025	-0.1187	-0.0145	-0.2720	-4.3955	-0.2275
H16	0.2503	0.1375	0.2460	-0.1171	-0.0143	-0.2684	-26.2326	-0.0381
H17	0.4029	0.2139	0.3860	-0.2059	-0.0252	-0.4719	-11.1834	-0.0894
H18	0.2356	0.1260	0.2099	-0.1353	-0.0165	-0.3101	-4.2646	-0.2345
Br19	0.0684	0.0577	-0.0228	-0.1019	-0.0125	-0.2335	-0.1173	-8.5234

to predict the reactive sites of the molecule and are summarised in Table 6. From the dual local softness  $\Delta s_k$  and the multiphilicity descriptors ( $\Delta \omega_k$ ) one can confirm that the atoms C2, C3, C5, C6, N7, O9 and C10 are favourable for nucleophilic attack. The other atoms of 4BNPA are favourable for electrophilic attack. The local reactivity descriptors of the individual atoms of the molecule  $s_k^a = f_k^a S$ ,  $\omega_k^a = \omega f_k^a$  and  $f_k^a$  where, a = +, – and 0 represents local philicity quantities describing for nucleophilic, electrophilic and free radical attack, respectively presented in Tables 6 and T3 are clearly express the nature of activity of the individual atoms.

# 9. Conclusion

The FTIR and FT-Raman vibrational spectra of *N*-(4-bromophenyl)-2,2-dichloroacetamide molecule has been recorded and analysed the complete vibrational fundamental modes of the most stable geometry of the compound using the experimental FTIR and FT-Raman data on the basis of peak positions, relative intensities and quantum chemical studies. The following observations are made

(i) The reactive centres are found from the molecular electrostatic potential and the atomic charges. The limits of electrostatic potential are  $-9.617e \times 10^{-3}$  and  $+9.617e \times 10^{-3}$ .

- (ii) The molecule has great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule.
- (iii) The lone pair donor orbital,  $n_N \rightarrow \pi^*_{CO}$  interaction possess a strong stabilization of 64.21 kcal mol<sup>-1</sup>.
- (iv) There is no systematic variation in C—C stretching vibrations with the bromine substitution in the ring. The effect of substituent —Br in the amide moiety have been analysed and compared.
- (v) The kinetic and thermodynamic stability and chemical reactivity descriptors of the molecule have been determined. The atoms C2, C3, C5, C6, N7, O9 and C10 are favourable for nucleophilic attack while others are favourable for electrophilic attack.
- (vi) There is no significant shift in the amide-I, C=O stretching; amide-II, N-H in-plane bending and amide-III, the C-N stretching vibrational frequencies of *N*-(4-bromophenyl)-2,2-dichloroacetamide
- (vii) There is a significant blue shift is observed in the amide-IV, C=O in-plane bending frequency when compared with the *N*-(chloro/methyl substituted phenyl)-2,2-dichloroacetamide compounds.
- (viii) The bromo substitution raised the N—H out of plane bending.

- (ix) The amide-VI, C=O out of plane bending mode of 4BNPA is significantly raised than that of NPA. The o-methyl group in 2MPA excerts more blue shift on the amide-VI frequency than other compounds.
- (x) The observed N-H stretching frequencies are found lowering in the case of methyl substituted compounds except 35DMPA than that of NPA. But bromine does not affect this mode.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.01. 091.

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