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# Spectroscopic investigations and computational study of 2-[acetyl(4-bromophenyl)carbamoyl]-4-chlorophenyl acetate

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The Fourier transform Raman (FT-Raman) and Fourier transform infrared (FT-IR) spectra of 2-[acetyl(4-bromophenyl)carbamoyl]-4-chlorophenyl acetate were studied. The vibrational wavenumbers were examined theoretically using the Gaussian03 set of quantum chemistry codes, and the normal modes were assigned by potential energy distribution (PED) calculations. The simultaneous Raman and infrared (IR) activations of the C=O stretching mode in the carbamoyl moiety show a charge transfer interaction through a  $\pi$ -conjugated path. From the optimized structure, it is clear that the hydrogen bonding decreases the double bond character of the C=O bond and increases the double bond character of the C-N bonds. The first hyperpolarizability and predicted IR intensities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar structures, which makes this compound an attractive object for future studies of nonlinear optics. Optimized geometrical parameters of the compound are in agreement with similar reported structures. Copyright © 2009 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: salicylanilide; acetate; carbamoyl; FT-IR spectra; FT-Raman spectra; DFT and PED calculations

## Introduction

Salicylanilides have been the subject of intense interest in medicinal chemistry, because of their ability to serve as inhibitors of the protein tyrosine kinase epidermal growth factor receptor relating to cancer, psoriasis and restenosis.<sup>[1,2]</sup> Salicylanilides (2-hydroxy-N-phenylbenzamides) have been reported as a class of compounds with a wide variety of interesting biological activities, including antimycobacterial and antifungal effects.<sup>[1,3-9]</sup> They act as inhibitors of the two-component regulatory system (TCS) in bacteria.<sup>[10,11]</sup> The importance of electron-attracting substituents in the salicyloyl ring and hydrophobic groups in the anilide moiety for optimal activity has been noted, and the removal of the 2-OH group has been reported to result in the loss of activity.<sup>[10]</sup> Imramovsky et al.<sup>[12]</sup> reported the synthesis and characterization of a series of novel, highly antimicrobial salicylanilide esters of Nprotected amino acids. Anion-triggered, substituent-dependent conformational switching of salicylanilides was reported by Guo et al.<sup>[13]</sup> The synthesis and antimicrobial evaluation of a series of variously ring-substituted salicylanilide acetates were reported by Vinsova et al.<sup>[5]</sup> Boyce et al.<sup>[14]</sup> described the structure-activity-relationship-guided conversion of bioactive salicylanilides into a comparably bioactive derivative, which was utilized as a tool for protein identification. Dahlgren et al.<sup>[6]</sup> reported the design, synthesis and multivariate guantitative structure-activity relationship of salicylanilides, and Singh et al.<sup>[15]</sup> reported the synthesis of 5-chloro-3'-nitro-4' substituted salicylanilides. Arslan et al.<sup>[16]</sup> reported the molecular structure and vibrational spectra of 2-chloro-N-(diethylcarbamothioyl) benzamide by Hartree-Fock (HF) and density functional theory

(DFT) methods. Biagi *et al.*<sup>[17]</sup> reported the synthesis and biological activity of novel, substituted benzanilides as potassium channel activators. The spin-trapping behavior of carbamoyl substituted derivatives toward different oxygen- and carbon-centered radicals has been reported.<sup>[18]</sup> Kinetics and mechanism for the reactions of *N*-methyl-*N*-phenylcarbamoyl chlorides with benzylamines in acetonitrile were reported by Koh *et al.*<sup>[19]</sup> Matyk *et al.*<sup>[20]</sup> reported the synthesis of a series of 64 derivatives of substituted heterocyclic analogues of salicylanilides, and the compounds were evaluated

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for invitro antimycobacterial activity against Mycobacterium tuberculosis, M. avium and two strains of M. kansasii. Methylene group modifications of the N-(isothiazol-5-yl)phenylacetamides synthesis and insecticidal activity were reported by Samaritoni et al.<sup>[21]</sup> Several works have reported on the antimycobacterial benzylsalicylamides,<sup>[22,23]</sup> and the activity of isoesters of salicylanilides: 2-sulfanylbenzanilides, N-benzylsulfanylbenzamides 3-hydroxy picolinanilides, N-benzyl-3-hydroxypicolinamides.<sup>[24]</sup> Vibrational spectroscopic study of acetate group was reported by Ibrahim and Koglin.<sup>[25]</sup> Computational study of the IR spectrum of acetic acid, its cyclic dimer and its methyl ester was reported by Lewandowski et al.<sup>[26]</sup> The molecular structure of acetic acid has been studied in the gas phase by both microwave spectroscopy<sup>[27,28]</sup> and electron diffraction.<sup>[29]</sup> The assessment of solid-state composition of an active salicylanilide compound (N-[5-chloro-4-[(4-chlorophenyl)cyanomethyl]-2-methylphenyl]-2-hydroxy-3,5-diiodobenzamide by FT-Raman spectroscopy was reported by Spiegeleer et al.<sup>[30]</sup> Diclofenac sodium, which consists of a phenylacetate group, a secondary amino group and a dichlorophenyl ring, is a well-known representative of nonsteroidal antiinflammatory drugs.<sup>[31]</sup> The present study is

on the analysis of FT-IR and FT-Raman spectra of 2-[acetyl(4bromophenyl)carbamoyl]-4-chlorophenylacetate; using the computational method, theoretical wavenumbers have also been calculated. This work is a part of our investigations of substituted salicylanilide derivatives. The authors have reported the spectroscopic studies of 4-chloro-2-(4-bromophenylcarbamoyl)phenyl acetate<sup>[32]</sup> and 4-chloro-2-(3,4-dichloro phenyl carbamoyl) phenyl acetate.<sup>[33]</sup> To our knowledge, no theoretical HF or DFT calculations, or detailed vibrational IR and Raman analyses, have been performed on the title compound. A detailed quantum chemical study will aid in understanding the vibrational modes of the title compound and clarifying the experimental data available for this molecule. DFT calculations are known to provide excellent vibrational wavenumbers of organic compounds if the calculated wavenumbers are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity effects.<sup>[34-39]</sup> DFT is now accepted as a popular post-HF approach for the computation of molecular structure, vibrational wavenumbers and energies of molecules by the ab initio community.<sup>[40]</sup> In this work, by using HF, B3PW91 and B3LYP methods we calculated the vibrational wavenumbers of the title compound in the ground state to distinguish the fundamentals from the many experimental vibrational wavenumbers and geometric parameters. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.

# **Experimental**

The chemicals were purchased from Aldrich, USA. Melting point (uncorrected) was determined on a Kofler block. Elemental analyses were performed on an automatic microanalyser CHNS-O CE instrument (FISONS EA 1110, Milano, Italy). Nuclear magnetic resonance (NMR) spectra were measured in CDCl<sub>3</sub> solution at ambient temperature on a Varian Mercury-VxBB 300 spectrometer (299.95 MHz for <sup>1</sup>H and 75.43 MHz for <sup>13</sup>C; Varian, Palo Alto, CA, USA). The chemical shifts  $\delta$  are given in ppm referenced to tetramethylsilane (TMS) as internal standard. The coupling constants (J) are reported in hertz. Mass spectra were measured on ABI/MSD SCIEX API 3000 LC/MS/MS system (MSD SCIEX, Concord, ON, Canada). The reaction was monitored and the purity of the products checked by thin layer chromatography (TLC) (Silufol UV 254, Kavalier Votice, Czech Republic and Merck TLC plate Silica gel 60 F<sub>254</sub>). The plates were visualized using UV light.

The FT-IR spectrum (Fig. 1) was recorded on a DR/Jasco FT-IR-6300 spectrometer in KBr pellets. The spectral resolution was 4 cm<sup>-1</sup>. The FT-Raman spectrum (Fig. 2) was obtained on a Bruker RFS 100/S, Germany. For excitation of the spectrum, the emission of a Nd : YAG laser was used, with excitation wavelength 1064 nm and maximal power 150 mW. The measurements were on solid samples. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2 cm<sup>-1</sup>. The expanded IR and Raman spectra in the region 500–2000 and 200–1800 cm<sup>-1</sup> are given in Figs S1 and S2 (Supporting Information).

*N*-(4-Bromophenyl)-5-chloro-2-hydroxyl benzamide (5 mmol) was dissolved in chlorobenzene (15 ml), and acetyl chloride was added (20 mmol). The mixture was refluxed for 5 h, and concentrated to dryness in a vacuum evaporator. The crude product was purified by crystallization from ethyl acetate.

Yield 45%; m.p. 114–116 °C; Anal./Calc. for  $C_{17}H_{13}BrCINO_4$  (410.65): 49.72% C, 3.19% H, 3.41% N; found: 50.09% C, 3.55% H, 3.42% N; MS: 411.7(M + 1)<sup>+</sup>; <sup>1</sup>H-NMR  $\delta$ : 7.55–7.47(m, AA' BB', 2H, H3', H5'), 7.38–7.32 (m, 2H, H4, H6), 7.08–6.99 (m, 3H, H3, H2', H6'), 2.39 (s, 3H, CH<sub>3</sub>), 2.3 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C-NMR  $\delta$ : 172.5, 168.5, 167.6, 145.8, 136.9, 132.8, 131.8, 131.3, 130.1, 128.7, 126.2, 124.5, 122.9, 25.9, 20.9.



Figure 1. FT-IR spectrum of 2-[acetyl(4-bromophenyl)carbamoyl]-4-chlorophenyl acetate.





Figure 2. FT-Raman spectrum of 2-[acetyl(4-bromophenyl)carbamoyl]-4- chlorophenyl acetate.

# **Computational Details**

Calculations of the title compound were carried out with Gaussian03 software program<sup>[41]</sup> using the HF/6-31G\*, B3PW91/6-31G\* and B3LYP/6-31G\* basis sets to predict the molecular structure and vibrational wavenumbers. Calculations were carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface. At the optimized structure (Fig. 3) of the examined species, no imaginary wavenumbers were obtained, proving that a true minimum on the potential surface was found. Parameters corresponding to optimized geometries of the title compound are given in Table S1 (Supporting Information). The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with the experimental data. Therefore, scaling factors of 0.9613 and 0.8929 were uniformly applied to the DFT and HF calculated wavenumbers.<sup>[42]</sup> The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the guantum chemical methods to overestimate the force constants at the exact equilibrium geometry. The potential energy distribution (PED) was calculated with the help of GAR2PED software package.<sup>[43]</sup>

# **Results and Discussion**

### **IR and Raman spectra**

The observed IR and Raman bands with their relative intensities and calculated scaled wavenumbers and assignments are given in Table 1.



Figure 3. Optimized geometry of the molecule.

#### C-Cl and C-Br vibrations

The vibrations belonging to the bond between the ring and chlorine atoms are worth discussing here since mixing of vibrations is possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule.<sup>[44]</sup> Mooney<sup>[45,46]</sup> assigned vibrations of C-Cl, C-Br and C-I in the wavenumber range of 1129–480 cm<sup>-1</sup>. The C–Cl stretching gives generally strong bands in the region 710-505 cm<sup>-1</sup>. For simple organic chlorine compounds, C-Cl absorptions are in the region 750-700 cm<sup>-1</sup>. Sundaraganesan et al.<sup>[47]</sup> reported C-Cl stretching at 704 (IR), 705 (Raman) and 715 (DFT) and the deformation bands at 250 and 160 cm<sup>-1</sup>. The aliphatic C–Cl bands absorb<sup>[48]</sup> at  $830-560 \text{ cm}^{-1}$ , and putting more than one chlorine on a carbon atom raises the C-Cl wavenumber. The C-Cl<sub>2</sub> stretching mode is reported at around 738 cm<sup>-1</sup> for dichloromethane and the scissoring mode  $\delta$ CCl<sub>2</sub> at around 284 cm<sup>-1</sup>.<sup>[48,49]</sup> Pazdera et al.[50,51] reported the C-Cl stretching mode at 890 cm<sup>-1</sup>. For 2-cyanophenylisocyanide dichloride, the C-Cl stretching mode is reported at 870 (IR), 877 (Raman) and 882 cm<sup>-1</sup> (theoretical).<sup>[52]</sup> Arslan et al.[16] reported the C-Cl stretching mode at 683 
 Table 1.
 Calculated vibrational wavenumbers (scaled), measured infrared and Raman bands positions and assignments of 2-[acetyl(4-bromophenyl)carbamoyl]-4-chlorophenylacetate

HF/6-31G*		B3PW91/6-31G*		B3LYP/6-31G*				
v (cm <sup>-1</sup> )	IR intensitv	$\frac{\upsilon}{(\text{cm}^{-1})}$	IR intensity	$\frac{\upsilon}{(\text{cm}^{-1})}$	IR intensity	IR $v(cm^{-1})$	Raman $v(cm^{-1})$	Assignments <sup>a</sup>
2077	0.47	2155	0.14	2145	0.10	2150	2151	C 11 (01)
3077	0.47	3155	0.14	3145	0.19	3158 W	3151 W	$vC_2H_8(91)$
3056	3.23	3135	2.52	3128	2.17	-	3136 W	$vC_5H_9(99)$
3049	0.72	3133	0.17	3122	0.40	-	_	$U C_{28} \Pi_{30}$ (58) $U C_{23} \Pi_{26}$ (21) $U C_{27} \Pi_{29}$ (14)
2040	5.95	2120	4.55	2120	0.44	_	_	$U \subset_1 \Pi_7 (91)$
2020	0.29	2129	0.50	2102	4.94	_	_	$UC_{23}\Pi_{26}(00) UC_{28}\Pi_{30}(23) UC_{22}\Pi_{21}(12)$
3029	5.59	2112	1.00	2100	5.49 4.05	2000	2002	$v C_{22} \Pi_{21} (80) v C_{28} \Pi_{30} (18)$
2020	4.91	2006	3.72	2060	4.0J	2070 m	2071 vc	$U \subset_{22} \Pi_{21} (80) U \subset_{23} \Pi_{26} (16)$
2905	9.56	3077	7.46	3062	2.20	5070 III	50/1 V5	$U_{as}$ Me II (97)
2900	9.50 2.46	3042	7.40 2.10	3025	2 2 2 2	_	_	$U_{as}$ MeI (70) $U_{as}$ MeII (15)
2950	3.06	3042	1 3 2	3025	2.55	3012 sh	_	$v_{as} Me H(84) v_{as} Me H(13)$
2886	2 27	2964	1.52	2957	1 72	2952 w	2963 w	$v_{as}$ Me II (100)
2879	3.01	2959	2 74	2949	2.76	2937 w	2937 s	1. Me I (99)
1714	247.39	1704	170.63	1689	165.47	1753 vs	1733 m	$v(1_{12}O_{12}(78))$
1682	94.15	1649	58.32	1632	55.95	1685 vs	1686 vs	$v C_{12} O_{13} (50)$
1639	538.84	1609	304.44	1592	280.31	_	1602 s	$v C_{12} O_{10} (42) v C_{22} O_{22} (20)$
1612	20.73	1599	23.29	1584	29.67	1586 w	1589 s	vPh I (69)
1610	3.14	1598	11.31	1584	23.27	_	_	vPh II (60)
1593	0.30	1591	6.82	1577	5.68	_	_	vPh I (72)
1587	20.56	1573	32.31	1558	35.00	1559 w	_	$v$ Ph II (54) $\delta$ CHC II (11)
1502	127.00	1492	109.83	1487	98.30	1490 s	1488 w	δCHC I (60) υPh I (33)
1492	110.51	1476	80.78	1471	55.51	-	1472 w	$\delta$ CHC II (36) $\delta_{as}$ Me II (14) $\upsilon$ Ph II (23)
1469	14.76	1466	15.83	1470	37.10	-	-	$\delta_{as}$ Me II (76)
1458	15.13	1457	15.31	1461	16.16	-	-	$\delta_{as}$ Me I (96)
1455	25.94	1452	10.81	1456	10.40	-	1453 w	$\delta_{as}$ Me II (71)
1451	25.59	1451	38.67	1455	29.98	1428 w	1433 wbr	$\delta_{as}$ Me I (80)
1417	30.29	1400	13.78	1403	26.20	-	-	$\delta_{s}$ Me I (92)
1415	44.65	1399	24.93	1397	43.52	1397 s	-	$\delta_{s}$ Me II (90)
1399	84.43	1397	115.15	1394	3.11	1393 w	-	υPh I (39) δCHC I (45)
1399	78.94	1394	85.00	1388	117.26	1369 s	1385 w	$\delta$ CHC II (19) $\upsilon$ Ph II (39)
1324	403.83	1336	49.95	1312	81.54	-	-	υPh II (81)
1322	1.86	1334	8.49	1311	2.35	-	-	δCHC I (90)
1287	317.35	1309	56.58	1309	7.65	1304 s	1305 m	vPh I (94)
1276	291.48	1309	249.87	1292	291.12	-	1282 w	$\upsilon N_{20}C_{24}$ (14) $\upsilon C_{18}N_{20}$ (11) $\upsilon N_{20}C_{32}$ (30)
1223	193.75	1267	56.23	1267	28.45	-	1270 w	$\delta$ CHC II (56) $\upsilon$ Ph II (14)
1206	366.44	1251	471.37	1234	504.41	1237 w	1222 m	$vN_{20}C_{32}$ (31) $vC_{18}N_{20}$ (24)
1199	6.41	1213	19.17	1200	12.60	1219 vs	-	$vN_{20}C_{24}$ (46) $vC_4C_{18}$ (19)
1191	9.20	1198	10.16	1188	9.84	1195 W	1192 W	$vC_3O_{11}$ (19) $\delta$ CHC II (14) $v$ Ph II (22)
1187	2.84	1183	5.50	1150	10.14	-	1168 W	$\partial CHCI(68)$
1160	4.71	1171	572.00	1120	510.15	1102 111	1102 111	(10) $UC_{11}C_{12}(12) UC_{3}UC_{11}(13) UC_{12}C_{14}(12) Mile 1$
1142	10.21	1148	7.08	1142	33.75	1138 m	1128 w	δCHC II (31) $\nu$ C <sub>18</sub> N <sub>20</sub> (10) $\nu$ Ph II (13)
1111	73.81	1110	20.43	1107	10.83	1110 s	1101w	δCHC I(57) υPh I (28)
1098	1.47	1103	91.52	1096	100.78	1100 m	-	δCHC II (63)
1091	7.82	1088	2.69	1081	4.22	-	-	vPh II (52) δCHC II (16) $v$ C <sub>6</sub> Cl <sub>10</sub> (30)
1084	1.60	1071	38.60	1063	4.14	-	1073 m	δMe I(36) δCHC II (28)
10/8	25.92	1059	5.56	1061	39.78	1062 w	-	$v_{PNI}(55) v_{25} Br_{31}(14)$
1065	22.81	1052	16.91	1056	11.06	-	-	∂Me II (68)
1061	14.24	1027	10.03	1027	22.08	1026 W	1031 WDr	0/VIE II (5U) SPh L (72)Ph L (16)
1054	0.94	1013	00.70	1012	07.84	1012 m	1022 Sh	0 = 11 (72) 0 = 0 = 0 = 0 = 0 = 0 = 0 = 0 = 0 = 0
1043	20.96	1005	/8.29	1001	0 50	1005 W	-	OWELT (39) $U \subset 12 \subset 14$ (21) $U \cup 11 \subset 12$ (10) $\pi CCCC(1/22)$ SCHC(1/25) $U \subset 1/21$ )
1030	56.25	994	9.44 0.40	990 QQ1	0.50	- 070 VV	983 11	$\gamma$ CHC I (22) of the t (33) $\gamma$ CHC I (31) $\gamma$ CHC I (90)
1020	67 70	965	0.00	960	0.10	_	-	γ CHC II (82)
1020	07.70	200	0.00	200	0.01	_	-	y Circ II (02)



Table 1.	(Continued)							
HF/6	-31G*	B3PW91/6-31G*		B3LYP/6-31G*				
$v \over (cm^{-1})$	IR intensity	v(cm <sup>-1</sup> )	IR intensity	υ (cm <sup>-1</sup> )	IR intensity	$^{ m IR}_{ m \upsilon(cm^{-1})}$	Raman $v$ (cm <sup>-1</sup> )	Assignments <sup>a</sup>
997	18.42	962	21.10	955	22.98	952 w	948 w	$vC_{32}C_{34}$ (22) δC <sub>4</sub> O <sub>19</sub> C <sub>18</sub> (11) δN <sub>20</sub> O <sub>19</sub> C <sub>18</sub> (11) δCCC II (11)
972	27.96	922	21.18	919	20.36	-	910 w	γCHC II (64) τPh II (17)
904	33.35	888	19.65	878	17.48	886 m	887 m	υC <sub>12</sub> C <sub>14</sub> (40) υO <sub>11</sub> C <sub>12</sub> (16) δCCC II (16)
887	5.31	858	66.96	850	70.40	844 s	-	γ CHC I (59)
880	22.52	839	1.34	837	1.25	840 w	-	γ CHC I (77)
877	36.49	837	7.14	834	4.24	-	826 w	γ CHC I (51)
852	34.64	829	35.50	825	31.14	807 m	822 w	γCHC II (57) γO <sub>11</sub> C <sub>2</sub> C <sub>4</sub> C <sub>3</sub> (11)
818	24.52	791	29.58	786	28.97	778 m	787 w	γO <sub>19</sub> C <sub>4</sub> N <sub>20</sub> C <sub>18</sub> (14) τCCCC II (14) γC <sub>18</sub> CCC II (12) γO <sub>11</sub> C <sub>2</sub> C <sub>4</sub> C <sub>3</sub> (10)
777	28.15	761	46.48	755	55.73	-	759 w	γO <sub>19</sub> C <sub>4</sub> N <sub>20</sub> C <sub>18</sub> (19) υO <sub>11</sub> C <sub>12</sub> (12) δCCC II (18) δCCC I (12) τCCCC I (12)
758	2.44	736	1.78	732	1.69	737 w	734 w	$\tau$ CCCC I(67) $\gamma$ N <sub>20</sub> C <sub>22</sub> C <sub>27</sub> C <sub>24</sub> (12) $\gamma$ Br <sub>31</sub> CCC (10)
733	53.00	717	68.36	712	68.33	713 m	711 m	τ CCCC II (12) δC <sub>3</sub> C <sub>12</sub> O <sub>11</sub> (12) γO <sub>11</sub> C <sub>2</sub> C <sub>4</sub> C <sub>3</sub> (10) δCCC I (18)
712	52.51	699	5.44	695	6.45	688 w	681 m	τCCCC II (42) γO <sub>11</sub> C <sub>2</sub> C <sub>4</sub> C <sub>3</sub> (14)
683	32.52	682	22.24	678	22.29	680 m	-	δCCC I (16) δCCC II (18) δC <sub>4</sub> N <sub>20</sub> C <sub>18</sub> (16) δCO Me I(12)
660	6.36	651	1.34	650	2.50	-	659 w	δCCC II (47) δCCC I (17)
651	21.75	644	12.59	644	8.31	638 w	-	$\delta$ CCC I (47) $\tau$ CCCC II (19)
635	22.21	628	15.98	625	18.47	621 w	631 m	$\delta$ CCC I (28) γO <sub>33</sub> C <sub>34</sub> N <sub>20</sub> C <sub>32</sub> (13) τ CCCC II (10)
609	13.51	600	8.50	596	9.35	599 m	599 w	γO <sub>33</sub> C <sub>34</sub> N <sub>20</sub> C <sub>32</sub> (34) δCC <sub>18</sub> C II (5)
581	4.68	572	4.65	568	4.54	566 m	-	$\gamma O_{13}C_{14}O_{11}C_{12}$ (24) $\delta C_{14}O_{13}C_{12}$ (16)
570	16.09	564	2.02	560	3.35	-	-	τCCCC II (9) γCl <sub>10</sub> C <sub>1</sub> C <sub>5</sub> C <sub>6</sub> (9) δC <sub>34</sub> O <sub>33</sub> C <sub>32</sub> (18) δCOMe II (16)
565	6.33	554	4.45	550	4.09	-	-	γO <sub>13</sub> C <sub>14</sub> O <sub>11</sub> C <sub>12</sub> (41) υC <sub>25</sub> Br <sub>31</sub> (42) τCCCC II (16)
541	17.23	519	18.77	518	15.73	521 m	521 w	$\gamma N_{20}C_{22}C_{27}C_{24}$ (41) $\gamma Br_{31}C_{28}C_{23}C_{25}$ (20)
524	16.83	511	12.75	509	10.95	-	-	τCCCC II (23) γO <sub>11</sub> C <sub>2</sub> C <sub>4</sub> C <sub>3</sub> (23) γCI <sub>11</sub> C <sub>1</sub> C <sub>5</sub> C <sub>6</sub> (22)
480	0.61	468	1.06	466	1.22	-	470 w	τCCCC II (23) γO <sub>11</sub> C <sub>2</sub> C <sub>4</sub> C <sub>3</sub> (12) γC <sub>18</sub> C <sub>3</sub> C <sub>5</sub> C <sub>4</sub> (18) δC <sub>22</sub> N <sub>20</sub> C <sub>24</sub> (14)
458	3.30	457	2.17	455	1.73	448 w	448 w	δC <sub>22</sub> N <sub>20</sub> C <sub>24</sub> (15) δC <sub>27</sub> N <sub>20</sub> C <sub>24</sub> (15) δCO <sub>11</sub> C (26) δC <sub>34</sub> O <sub>33</sub> C <sub>32</sub> (16)
436	0.09	424	0.08	425	0.05	-	430 w	$\tau$ CCCCI(86)
428	5.41	421	5.80	421	3./6	418 w	_	$\tau$ CCCC II (36) $\delta$ C <sub>22</sub> N <sub>20</sub> C <sub>24</sub> (16) $\delta$ COMe II (12) $\delta$ CO <sub>11</sub> C (12)
416	9.74	419	4.99	415	8.52	-	407 w	δMe I (27) δCCC II (10) δCO <sub>11</sub> C (18) δC=O Me I (18)
377	26.14	382	21.13	377	20.86	-	374 w	$vC_{25}Br_{31}$ (23) $\delta$ COMe II (33)
372	0.93	366	2.13	366	2.57	368 W	359 w	$\tau$ CCCC II (23.) $\delta$ CO <sub>11</sub> C (18) $\delta$ C <sub>4</sub> O <sub>19</sub> C <sub>18</sub> (16)
357	7.56	346	5.06	344	4.65	-	343 m	$\gamma Br_{31}CCC (29) \tau CCCC \Gamma (22) \delta C_{18} C_{24} N_{20} (11) \\ \delta C_{32} C_{24} N_{20} (11)$
340	6.88	335	4.16	333	3.96	-	337 W	$\delta CCIC(30) \gamma CICCCC(19)$
308	6.63	311	7.46	308	8.12	-	296 m	$\delta$ MeII CO (19) $\delta$ C <sub>4</sub> N <sub>20</sub> C <sub>18</sub> (24) $\delta$ CO <sub>11</sub> C (20)
2/9	7.28	281	6.89	2/9	7.02	-	279 w	
253	2.44	254	1.74	253	1.79	_	242 m	$\tau C_3 O_{11} C_{12} O_{13} (12)$
234	2.72	234	1.62	231	1.81	-	-	$\delta \text{LBrC}$ (41) $\gamma \text{C}_{24} \text{C}_{18} \text{C}_{32} \text{N}_{20}$ (15)
191	2.87	189	2.16	188	2.14	_	197 s	$τ_{\rm CCC_{18}O_{19}}$ (13) $τ_{\rm CCC_{18}N_{20}}$ (13) $γ_{\rm CICCC}$ (11) $\delta C_{18}C_{32}N_{20}$ (18)
169	1.90	174	3.11	171	3.09	-	174 w	δCCN <sub>20</sub> (14) τCCCC I (13) γN <sub>20</sub> CCC (12) δCC <sub>18</sub> C (11)
164	5.75	164	3.31	164	2.96	-	-	$\delta C_3 C_{12} O_{11}$ (26) $\tau CCCC \parallel$ (19) $\delta C=O ME \parallel$ (13)
156	1.40	159	0.43	156	0.87	-	156 vs	τCNC <sub>32</sub> O <sub>33</sub> (20) τCNC <sub>32</sub> C <sub>34</sub> (50)
153	1.58	153	2.13	151	1.89	-	-	τ Me II (32) δCCN <sub>20</sub> (34)
142	0.26	132	0.19	138	0.23	-	-	τMe I (81)

Table 1. (Continued)								
HF/6-31G*		B3PW91/6-31G*		B3LYP/6-31G*				
$v$ (cm $^{-1}$ )	IR intensity	υ (cm <sup>-1</sup> )	IR intensity	v(cm <sup>-1</sup> )	IR intensity	$IR$ $v(cm^{-1})$	Raman $v$ (cm $^{-1}$ )	Assignments <sup>a</sup>
126	0.87	126	0.91	125	0.80	-	_	δCC <sub>18</sub> C II (19) τO <sub>19</sub> C <sub>18</sub> N <sub>20</sub> C <sub>24</sub> (15) δCCIC (11) τCCC <sub>18</sub> O <sub>19</sub> (10)
116	9.62	117	8.30	117	9.79	-	-	τCCC <sub>18</sub> N <sub>20</sub> (30) τCNC <sub>32</sub> O <sub>33</sub> (16) τCNC <sub>32</sub> C <sub>34</sub> (16) γC <sub>18</sub> CCC (14) τC <sub>4</sub> C <sub>18</sub> N <sub>20</sub> C <sub>24</sub> (14)
108	2.24	109	2.03	107	2.37	-	105 s	$ \begin{aligned} \tau C_{4}C_{18}N_{20}C_{24}(25)\tauO_{19}C_{18}N_{20}C_{32}(25) \\ \gamma C_{24}C_{18}C_{32}N_{20}(22)\tauCCC_{18}O_{19}(19) \end{aligned} $
95	1.16	94	0.93	97	1.10	-	-	τC <sub>3</sub> O <sub>11</sub> C <sub>12</sub> C <sub>14</sub> (34) τCCC <sub>18</sub> O <sub>19</sub> (17) τCCC <sub>18</sub> N <sub>20</sub> (17)
86	10.63	85	6.87	89	5.65	-	-	τCNC <sub>32</sub> O <sub>33</sub> (41) τMe II(20)
67	0.48	65	0.28	65	0.29	-	-	τCCCC II (31) τCNC <sub>32</sub> O <sub>33</sub> (18) τCNC <sub>32</sub> C <sub>34</sub> (18)
51	0.21	53	0.29	52	0.34	-	-	τC <sub>3</sub> C <sub>4</sub> C <sub>18</sub> O <sub>19</sub> (54) τC <sub>3</sub> O <sub>11</sub> C <sub>12</sub> C <sub>14</sub> (10)
35	1.14	36	3.53	37	2.95	-	-	τC <sub>3</sub> O <sub>11</sub> C <sub>12</sub> O <sub>13</sub> (60) δCO <sub>11</sub> C (13) δC <sub>3</sub> C <sub>12</sub> O <sub>11</sub> (12)
33	2.61	30	0.08	27	0.10	-	-	τC <sub>18</sub> N <sub>20</sub> C <sub>24</sub> C <sub>22</sub> (55) τO <sub>19</sub> C <sub>18</sub> N <sub>20</sub> C <sub>24</sub> (14) τCNC <sub>32</sub> O <sub>33</sub> (13)
23	0.23	24	0.11	23	0.09	-	-	τC <sub>3</sub> C <sub>4</sub> C <sub>18</sub> O <sub>19</sub> (56) τC <sub>4</sub> C <sub>18</sub> N <sub>20</sub> C <sub>24</sub> (17)
18	0.45	19	0.13	18	0.24	-	-	τC <sub>4</sub> C <sub>18</sub> N <sub>20</sub> C <sub>24</sub> (62) τCNC <sub>32</sub> O <sub>33</sub> (16)

v, stretching;  $\delta$ , in-plane bending;  $\gamma$ , out-of-plane bending;  $\tau$ , torsion; s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; para and tri substituted phenyl rings are designated as Phl, Phll ring; subscript; as, asymmetric; s, symmetric.

<sup>a</sup> PED, potential energy distribution, only contribution larger than 10% were given.

(experimental) and at 711, 736, 687, 697 cm<sup>-1</sup> (theoretical). The deformation bands<sup>[16]</sup> of CCl are reported at 431, 435 and 441 cm<sup>-1</sup>. For the title compound, the band at 1081 cm<sup>-1</sup> is assigned as C–Cl stretching mode. The deformation bands of CCl are also identified. This is in agreement with the literature data.<sup>[49,53,54]</sup> For 4-chlorophenylboronic acid, the CCl stretching and deformation bands are reported at 571 (DFT) and at 287 and 236 cm<sup>-1</sup>, respectively.<sup>[55]</sup> Bromine compounds<sup>[56]</sup> show stretching vibrations in the region 750–485 cm<sup>-1</sup> due to C–Br. The CBr deformations<sup>[56]</sup> are found in the region 400–140 cm<sup>-1</sup>. For *p*-bromoacetanilide, the stretching vibration of C–Br is reported at 515 (DFT) and 504 cm<sup>-1</sup> (IR) by Jothy *et al.*<sup>[57]</sup> In the present case, the band at 550 cm<sup>-1</sup> is assigned as the C–Br stretching mode.

#### Acetate group vibrations

Methyl groups are generally referred to as electron-donating substituents in the aromatic ring system.<sup>[58]</sup> The methyl group attached to the acetate group is designated as Me I. In acetates, the asymmetric vibrations of the methyl group are expected in the region 2940–3040 cm<sup>-1</sup> and symmetric vibrations in the region 2910–2930 cm<sup>-1</sup>, and usually the bands are weak.<sup>[59]</sup> Aromatic acetyl substituents absorb in a narrow range 3000–3020 cm<sup>-1</sup>, which sometimes coincides with a CH stretching mode of the ring.<sup>[59]</sup> In the present case, the asymmetric methyl bands are calculated to be at 3068, 3025 (B3LYP), and experimentally a band is observed in the Raman spectrum at 3071 cm<sup>-1</sup> and at 3070 cm<sup>-1</sup> in the IR spectrum. The symmetric methyl stretching vibration is observed at 2937 cm<sup>-1</sup> in both spectra and at 2949 cm<sup>-1</sup> theoretically.

In contrasted to the weak absorptions of methyl stretching vibrations, the methyl symmetric deformation absorb moderately to strongly in the range 1365  $\pm$  25 cm $^{-1}$  and asymmetric deformations in the region<sup>[59]</sup> 1390–1480 cm $^{-1}$ . The B3LYP calculations give 1461, 1455 and 1403 cm $^{-1}$  as asymmetric and symmetric deformation bands.

According to Colthup et al., [48] in acetates the methyl next to the C=O absorbs near  $1374 \text{ cm}^{-1}$  due to symmetric deformation; the asymmetric methyl deformation absorbs weakly near 1430 cm<sup>-1</sup>. The methyl rocking generally appears in the regions  $1050 \pm 30$ and 975  $\pm$  45  $\rm cm^{-1}$  as a weak, moderate or sometimes strong band, the wavenumber of which is coupled to the C-C stretching vibrations, which occurs in the neighborhood of 900 cm<sup>-1</sup>. With acetates, the rocking modes are clearly separated and show weak to medium activity in the region^{[59]} 1050  $\pm$  30 and 980  $\pm$  45  $cm^{-1}$ . The band at 1005  $cm^{-1}$  in IR and 1073  $cm^{-1}$  in Raman spectrum is assigned to the rocking modes of the methyl group. B3LYP calculations give these modes as 1001 and  $1063 \text{ cm}^{-1}$ . In O-bonded-C(=O)Me group,<sup>[59]</sup> the C=O stretching vibration exhibits a strong band at 1750  $\pm$  20 cm<sup>-1</sup>. Esters and lactones have two characteristically strong absorption bands arising from C=O and C-O stretchings. The intense C=O stretching vibration occurs at higher wavenumbers than that in normal lactones. The force constant of the carbonyl bond is increased by the electronattracting nature of the adjacent oxygen atom due to inductive effect.<sup>[48]</sup> In the present case, the stretching mode  $C_{12}=O_{13}$  is observed at 1753 cm<sup>-1</sup> in IR spectra and 1733 cm<sup>-1</sup> in Raman spectra and the calculated value for this mode is  $1689 \, \text{cm}^{-1}$ . The C-O next to the carbonyl is stiffer than the other bonds due to resonance that tends to localize the high vibration in the C-O bond. Acetates show a strong vibration in the region 1260–1320 cm<sup>-1</sup>, as vC–O band.<sup>[48]</sup> For phenyl acetate,<sup>[60]</sup> the vCC(=O)O stretching band is observed at 1215 cm<sup>-1</sup>. The band at 1162 cm<sup>-1</sup> in the Raman spectrum and 1158 cm<sup>-1</sup> theoretically (B3LYP) is assigned as vCC(=0)O for the title compound. This mode is not pure but contains significant contribution from other modes. The deformation bands of C<sub>12</sub>-O<sub>13</sub> are also identified (Table 1). For the acetate group<sup>[25,61]</sup> the deformation bands of C=O are reported at 642 and 581  $cm^{-1}$  experimentally. In the present case, the C-C stretching mode of the acetate group is observed at 886 (IR), 887 (Raman) and 878  $cm^{-1}$  (theoretical).

According to literature, the C–C stretching mode is reported at 847 cm<sup>-1</sup> experimentally and at 866 cm<sup>-1</sup> theoretically.<sup>[25]</sup>

#### **Carbamoyl group vibrations**

The carbonyl stretching vibration<sup>[59,62]</sup> C=O is expected in the region 1715-1680 cm<sup>-1</sup>, and in the present study the bands observed at 1685 cm<sup>-1</sup> in the IR spectrum and at 1686, 1602 cm<sup>-1</sup> in the Raman spectrum are assigned as C<sub>32</sub>=O<sub>33</sub> and C<sub>18</sub>=O<sub>19</sub> stretching modes. B3LYP calculations give these modes at 1632 and 1592 cm<sup>-1</sup>. The intensity of the carbonyl group can increase because of conjugation or formation of hydrogen bonds. The increase in conjugation, therefore, leads to intensification of Raman lines as well as increase in IR intensities. The mode  $\nu C_{32} = O_{33}$  is simultaneously active in IR and Raman spectra, which clearly explains a charge transfer between the donor and acceptor through a  $\pi$ -conjugated path.<sup>[63,64]</sup> Methyl groups are generally referred to as electron-donating substituents in the aromatic ring system<sup>[58]</sup> and the methyl group attached to the carbamoyl moiety is designated as Me II. The observed bands at 3012 and 2952  $cm^{-1}$  in the IR and 2963  $cm^{-1}$  in the Raman spectrum are assigned to the stretching modes of the methyl group II.<sup>[56,65]</sup> Absorption intensities in the IR spectrum provide much information on the nature of chemical bonds and the effects due to intramolecular environment. The electronic effect, hyperconjugation, usually means the interaction of the orbitals of a methyl group with the  $\pi$  orbitals of an adjacent C–C bond. In the present case, the methyl group II hydrogen atoms are subjected simultaneously to hyperconjugation and induction, which causes the decrease of IR intensity as reported in the literature.<sup>[66]</sup> Thus hyperconjugation and induction of the methyl group II, causing changes in intensity in the IR spectrum, clearly indicate that the methyl group II hydrogen atoms are directly involved in the donation of electronic charges. The asymmetric and symmetric bending modes of the methyl group II are normally expected in the region 1465-1440 and 1390-1370 cm<sup>-1</sup>, respectively. The B3LYP calculations give bands of Me II at 1470, 1456 and  $1397 \text{ cm}^{-1}$ . The enhancement of intensity of the symmetric bending mode at 1397 cm<sup>-1</sup> in the IR spectrum is due to the presence of C=O adjacent to the methyl group,<sup>[67]</sup> which is in good agreement with the calculated value. The strong IR intensity of the symmetric mode suggests a large positive charge localized on the hydrogen atoms, which further supports the occurrance of hyperconjugation. A weak band is observed in the Raman spectrum at 1451 cm<sup>-1</sup> corresponding to the asymmetric deformation of methyl group II.

The C–N stretching vibration<sup>[59]</sup> is moderately to strongly active in the region 1275 ± 55 cm<sup>-1</sup>. El-Shahawy *et al.*<sup>[68]</sup> observed a band at 1320 cm<sup>-1</sup> in the IR spectrum as the vC–N mode. Primary aromatic amines with nitrogen directly on the ring absorb at 1330–1260 cm<sup>-1</sup> due to stretching of the phenyl carbon–nitrogen bond.<sup>[16,48]</sup> Sandhyarani *et al.*<sup>[69]</sup> reported vC–N at ~1318 cm<sup>-1</sup>, and Anto *et al.*<sup>[70]</sup> and Ambujakshan *et al.*<sup>[71]</sup> reported vC–N at 1332, 1331 (IR), 1315 (Raman), 1315 and 1323 cm<sup>-1</sup> (HF). For the title compound, the C–N stretching modes are observed at 1219, 1237 (IR), 1222 cm<sup>-1</sup> (Raman) and at 1292, 1234, 1200 cm<sup>-1</sup> (theoretical). All these modes are not pure but contain significant contribution from other modes.

#### Phenyl ring vibrations

As the identification of all the normal modes of vibration of large molecules is not easy, we tried to simplify the problem by

considering each molecule as a substituted benzene. Such an idea has already been successfully utilized by several workers for the vibrational assignment of molecules containing multiple homoand hetero-aromatic rings.<sup>[70,72-76]</sup> In the following discussion, the di- and tri-substituted phenyl rings are designated as Ph I and Ph II, respectively. The modes of the two phenyl rings will differ in wavenumber, and the magnitude of splitting will depend on the strength of interaction between different parts (internal coordinates) of the two rings. For some modes, this splitting is so small that they may be considered as guasidegenerate, whereas for other modes a significant amount of splitting is observed.<sup>[72-74,77]</sup> The benzene ring possesses six ring-stretching vibrations of which the four with the highest wavenumbers occurring near 1600, 1580, 1490 and 1440  $\rm cm^{-1}$ are good group vibrations.<sup>[59]</sup> With heavy substituents, the bands tend to shift to somewhat lower wavenumbers, and the greater the number of substituents on the ring, the broader the absorption regions.<sup>[59]</sup> In the case of C=O substitution, the band near 1490 cm<sup>-1</sup> can be very weak.<sup>[59]</sup> The fifth ring-stretching vibration is active near  $1315 \pm 65$  cm<sup>-1</sup>, a region that overlaps strongly with that of the CH in-plane deformation.<sup>[59]</sup> The sixth ring-stretching vibration, the ring breathing mode, appears as a weak band near 1000 cm<sup>-1</sup> in mono, 1,3-di and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the other modes.

In asymmetric trisubstituted benzenes, when all the three substituents are light, the wavenumber interval of the breathing mode<sup>[49]</sup> is between 500 and 600 cm<sup>-1</sup>. When all the three substituents are heavy, the wavenumber appears above  $1100 \text{ cm}^{-1}$ . In the case of mixed substituents,<sup>[49]</sup> the wavenumber is expected to appear between 600 and 750 cm<sup>-1</sup>. The band calculated at 1081 cm<sup>-1</sup> is assigned as the ring-breathing mode of the phenyl ring Ph II. According to Varsanyi,<sup>[49]</sup> for para substituted benzene, the ring-breathing mode is expected in the interval 1050-1100 cm<sup>-1</sup>, and in the present case the band at 1062 cm<sup>-1</sup> in IR and 1061  $\text{cm}^{-1}$  by theory (B3LYP) is assigned the ring-breathing mode of Ph I. For the phenyl ring Ph II, the  $\delta$ CH in-plane bending vibrations are expected in the region 1090-1265 cm<sup>-1</sup>.<sup>[40,44,59]</sup> The CH out-of-plane deformations<sup>[59]</sup> are observed between 1000 and 700  $\text{cm}^{-1}$ . Generally, the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. In the case of trisubstituted benzenes, two  $\gamma$  CH bands are observed at 890  $\pm$  50 and 815  $\pm$  45 cm<sup>-1</sup> in the IR spectrum, and thebands at 910, 822 cm<sup>-1</sup> in Raman, 807 cm<sup>-1</sup> IR and 919, 825 cm<sup>-1</sup> (B3LYP) are assigned to these modes. The strong CH out-of-plane deformation band occurring at 840  $\pm$  50 cm<sup>-1</sup> is typical for para-substituted benzene.<sup>[59]</sup> For the title compound, a band is observed at 844 cm<sup>-1</sup> in the IR spectrum, which finds support from computational results. The IR bands in the  $2880-1936 \text{ cm}^{-1}$  region and their broadening support intramolecular hydrogen bonding.<sup>[32]</sup>

#### Geometrical parameters and first hyperpolarizability

To the best of our knowledge, no X-ray crystallographic data of this molecule has yet been established. However, the theoretical results obtained are almost comparable with the reported structural parameters of the parent molecules. The bonds of length  $C_{18}=O_{19}=1.2439$  Å,  $C_{32}=O_{33}=1.2438$  Å,  $C_{12}=O_{13}=1.2267$  Å show typical double bond characteristics. However, the C–N bond lengths  $C_{18}-N_{20}$  (1.4149 Å),  $C_{24}-N_{20}$  (1.4529 Å) and  $C_{32}-N_{20}$ 

(1.4170 Å) are shorter than the normal C-N single bond length of about 1.48 Å. The shortening of these C-N bonds reveals the effect of resonance in this part of the molecule.<sup>[16]</sup> For a phenylcarbamoyl derivative, Kubicki<sup>[78]</sup> reported C<sub>phenyl</sub>-N bond length as 1.414 Å and that of the N-C(=O) as 1.352 Å. The C=O and C-N bond lengths in benzamide, acetamide, formamide are, respectively, 1.2253, 1.2203, 1.2123 and 1.3801, 1.3804, 1.3683 Å.<sup>[79]</sup> The C=O bonds C<sub>18</sub>=O<sub>19</sub>, C<sub>32</sub>=O<sub>33</sub>, C<sub>12</sub>=O<sub>13</sub> and C-N bonds C<sub>24</sub>-N<sub>20</sub>,  $C_{18}-N_{20}, C_{32}-N_{20}$  are 1.2439, 1.2438, 1.2267, 1.4529, 1.4149, 1.4170 Å respectively, in the present case. According to the literature,<sup>[80-83]</sup> the changes in bond lengths in C=O and C-N are consistent with the following interpretation: hydrogen bond decreases the double bond character of the C=O bond and increases the double bond character on C-N bond. The angles  $O_{11}-C_{12}-O_{13}$  and  $O_{13}-C_{12}-C_{14}$  are increased by 2.2° and 7.8° and the angle  $O_{11}-C_{12}-C_{14}$  is reduced by  $10^{\circ}$  at  $C_{12}$  position from 120°, revealing the repulsion between the methyl group MeI and O<sub>13</sub>.

The C-C bond lengths in the phenyl rings I and II lie in the range 1.3930-1.3987 Å and 1.3875-1.4080 Å, respectively, while the C-C bond length of benzene  $^{[84]}$  is 1.399 Å and of benzaldehyde  $^{[85]}$ is 1.3973Å. In contrast, the value of angles  $C_5 - C_4 - C_{18}$  (116.5°) and  $C_4 - C_{18} - O_{19}$  (119.7°) are smaller than those of benzaldehyde,<sup>[85]</sup>  $121.0^{\circ}$  and  $123.6^{\circ}$ . These differences are ascribed to the steric repulsion between the  $H_{9}$  and methyl group MeII hydrogen atoms. The dihedral angle C<sub>5</sub>-C<sub>4</sub>-C<sub>18</sub>-N<sub>20</sub> was determined to be  $-145.7^{\circ}$  by the B3LYP method. On the contrary, the equilibrium structure of benzaldehyde is planar.<sup>[85]</sup> The steric repulsion in the present case is also considered to cause a nonplanar skeleton. The  $C_4-C_{18}$  bond length (1.4964 Å) is larger than the corresponding length in benzaldehyde<sup>[85]</sup> (1.4794 Å) by about 0.017Å. The C-Cl bond length (1.8206) given by B3LYP calculations is in agreement with the value obtained by Arslan et al.[16] The substitution of chlorine in the phenyl ring shortens the C–C bond lengths  $C_1-C_6$ ,  $C_5 - C_6$  of the benzene ring. Chlorine is highly electronegative and tries to obtain additional electron density. It attempts to draw it from the neighboring atoms, which move closer in order to share the electrons more easily as a result. Due to this, the bond angle  $C_1 - C_6 - C_5$  is found to be 121.6° in the present calculation, which is 120° for normal benzene. Kurt<sup>[55]</sup> reported the bond lengths and angles as follows: C-CI = 1.757 Å,  $C_1-C_6 = 1.391 \text{ Å}$ ,  $C_5-C_6 = 1.391 \text{ Å}, C_1-C_6-C_5 = 121.2^\circ, C_1-C_6-CI_{10} = 119.4^\circ.$ The experimental values<sup>[86]</sup> are 1.736 Å, 1.365 Å, 1.369Å, 121.2° and 119.7°.

For acetate group, Ibrahim and Koglin<sup>[25]</sup> reported  $C_{12}-C_{14}$ , C<sub>14</sub>-H<sub>15-17</sub>, C<sub>12</sub>-O<sub>11</sub>, C<sub>12</sub>=O<sub>13</sub> bond lengths as 1.52, 1.102, 1.364 and 1.214 Å respectively, whereas in the present case the corresponding values are 1.4949, 1.0902-1.0968, 1.416 and 1.2267Å. For the title compound, the bond angles of the acetate group are:  $C_{14}-C_{12}-O_{11} = 110.0$ ,  $C_{14}-C_{12}-O_{13} = 127.8^{\circ}$  and  $C_{12}-C_{14}-H_{15-17} = 108.7-110.8^{\circ}$ , which are in agreement with the reported values<sup>[25]</sup> 113.0, 126.6, 122.0 and 107°. The strong steric repulsion between the phenyl ring II and the amide group is confirmed by the nonplanarity of the benzamide, where the amide group is turned by  $-136.3^{\circ}$  (C<sub>3</sub>-C<sub>4</sub>-C<sub>18</sub>-O<sub>19</sub>) with respect to the benzene ring.<sup>[83]</sup> Siddiqui et al.<sup>[87]</sup> reported the bond lengths for phenylcarbamoyl groups as follows:  $N_{20} - C_{18} = 1.3314 - 1.3384$  Å,  $N_{20}-C_{24} = 1.4294-1.4404 \text{ Å}, C_{18}-O_{19} = 1.2363-1.2413 \text{ Å},$  $C_4-C_3 = 1.3893$  Å,  $C_4-C_5 = 1.4033$  Å,  $C_4-C_{18} = 1.5053$  Å,  $C_{24}-C_{22} = 1.4034$  Å and  $C_{24}-C_{27} = 1.4038$  Å. For the title compound, the corresponding values are 1.4149, 1.4529, 1.2439, 1.4080, 1.4068, 1.4964, 1.3987 and 1.3976 Å. In the present study, the bond angles for the carbamoyl group are  $C_{18}\text{-}N_{20}\text{-}C_{24}~=$  $116.6^{\circ}$ ,  $C_{18}-N_{20}-C_{32}$  =  $125.9^{\circ}$ ,  $C_{24}-N_{20}-C_{32}$  =  $117.5^{\circ}$ ,  $C_3 - C_4 - C_5 = 118.5^{\circ}, C_5 - C_4 - C_{18} = 116.5^{\circ}, O_{19} - C_{18} - N_{20} =$  $120.2^{\circ}$ ,  $C_4 - C_{18} - O_{19} = 119.7^{\circ}$ ,  $C_4 - C_{18} - N_{20} = 120.0^{\circ}$ ,  $C_{22}-C_{24}-C_{27}~=~120.5^{\circ}$  and  $N_{20}-C_{24}-C_{27}~=~120.1^{\circ}.$  The corresponding values reported for a similar compound<sup>[87]</sup> are 117.0, 123.7, 118.5, 119.0, 124.2, 122.6, 120.6, 115.1, 122.2 and 119.1°. The B3LYP calculations give the dihedral angles  $C_{28}-C_{27}-C_{24}-N_{20} =$  $180.0^{\circ}, O_{19}-C_{18}-C_4-C_3 = -136.3^{\circ}, N_{20}-C_{18}-C_4-C_3 = 40.9^{\circ}, N_{20}-C_{18}-C_4-C_3 = -10.9^{\circ}, N_{20}-C_{$  $O_{19}-C_{18}-C_4-C_5 = 37.1^\circ$ , and  $N_{20}-C_{18}-C_4-C_5 = -145.7^\circ$ around the benzamide group, whereas the corresponding reported values<sup>[88]</sup> for a similar derivative are 178.5, -16.8, 163.8, 161.6 and  $-17.8^{\circ}$ . The deviations are due to the presence of COCH<sub>3</sub> group attached with  $N_{29}$ . The  $C_{18}$ - $N_{29}$  bond is twisted from the phenyl rings I and II as is evident from the torsion angles  $C_{27} - C_{24} - N_{20} - C_{18} = -112.5^{\circ}, C_{22} - C_{24} - N_{20} - C_{18} = 67.3^{\circ},$  $N_{20}-C_{18}-C_4-C_3 = 40.9^{\circ}$  and  $N_{20}-C_{18}-C_4-C_5 = -145.7^{\circ}$ . At  $C_4$ position, the angles  $C_5 - C_4 - C_{18}$  is reduced by 3.5° and  $C_3 - C_4 - C_{18}$ is increased by  $4.7^{\circ}$  from  $120^{\circ}$ , and this asymmetry of exocyclic angles reveals the interaction between  $O_{19}$  and the phenyl ring II.

Analysis of organic molecules having conjugated  $\pi$ -electron systems and large hyperpolarizability using IR and Raman spectroscopy has evolved as a subject of research.<sup>[89]</sup> The potential application of the title compound in the field of nonlinear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectra. The ring-stretching bands at 1586, 1369, 1304, 1195, 1138, 1110 and 1012 cm<sup>-1</sup> observed in the IR spectrum have their counterparts in the Raman spectrum at 1589, 1385, 1305, 1192, 1128, 1101 and 1022 cm<sup>-1</sup>, respectively, and their relative intensities in IR and Raman spectrum are comparable.

The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system is calculated using the DFT method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components because of Kleinman symmetry.<sup>[90]</sup>

The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_{i} \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \dots$$
(1)

where  $E_0$  is the energy of the unperturbed molecule,  $F^i$  is the field at the origin,  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are the components of dipole moment, polarizability, the first hyper polarizabilities and second hyperpolarizibilites, respectively. The calculated first hyperpolarizability of the title compound is  $1.62 \times 10^{-30}$  esu, which is comparable with the **r**eported values of similar derivatives,<sup>[32]</sup> but experimental data are not readily available. We conclude that the title compound is an attractive object for future studies of its nonlinear optical properties.

The calculated (B3LYP) results give the following thermodynamic parameters: self consistent field (SCF) energy is -4042.77 a.u.; zero point vibrational energy is 693.12 kJ/mol; entropy is



Figure 4. Correlation graph.

166.94 cal/mol-K; specific heat capacity at constant volume is 82.08 cal/mol-K; *E* (thermal) is 183.16 kcal/mol; and the dipole moment is 2.41 debye.

In order to investigate the performance and vibrational wavenumbers of the title compound, root mean-square (RMS) value and correlation coefficients between calculated and observed wavenumbers were calculated (Fig. 4). RMS values of wavenumbers were evaluated using the following expression.<sup>[91]</sup>

$$RMS = \sqrt{\frac{1}{n-1} \sum_{i}^{n} \left(\upsilon_{i}^{\text{calc}} - \upsilon_{i}^{\text{exp}}\right)^{2}}$$
(2)

The RMS error of the observed Raman and IR bands are found to be 32.12 and 35.01 for HF, 12.37 and 14.42 for B3PW91 and 12.03 and 14.01 for B3LYP methods, respectively. Small differences between experimental and calculated vibrational modes are observed. It must be due to the fact that hydrogen-bond vibrations present in the crystal lead to strong perturbation of the IR wavenumbers and intensities of many other modes. Also, we state that experimental results pertain to the solid phase whereas the theoretical calculations to gaseous phase.

## Conclusion

The FT-IR and FT-Raman spectra of 2-[acetyl(4-bromophenyl)carbamoyl]-4-chlorophenyl acetate were studied. The molecular geometry and the wavenumbers were calculated using different basis sets and the normal modes assigned by PED calculations. The simultaneous IR and Raman activations of the C==O stretching mode in the carbamoyl moiety shows the charge transfer interaction through a  $\pi$ -conjugated path. Optimized geometrical parameters of the title compound are in agreement with the reported values. Analysis of the phenyl ring modes shows that C-C stretching mode is equally active as strong bands in both IR and Raman spectra, which can be interpreted as the evidence of intramolecular charge transfer via conjugated ring path and is responsible for hyperpolarizability enhancement leading to nonlinear optical activity.

#### **Supporting information**

Supporting information may be found in the online version of this article.

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