The spectroscopic (FT-IR and FT-Raman) and theoretical studies of 5-bromo-salicylic acid

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ABSTRACT

The experimental and theoretical study on the structures and vibrations of 5-bromo-salicylic acid (5-BrSA, $C_7H_5BrO_3$) are presented. The Fourier transform infrared spectra (4000–400 cm^{-1}) and the Fourier transform Raman spectra (4000–0 cm^{-1}) of the title molecule in the solid phase have been recorded. The geometrical parameters and energies have been obtained for all eight conformers from DFT (B3LYP) with 6-311++G(d,p) basis set calculations. There are eight conformers, Cn, n = 1–8 for this molecule. The computational results identify the most stable conformer of 5-BrSA as the C1 form. The vibrations of stable and unstable conformers of 5-BrSA are researched with the aid of quantum chemical calculations. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The molecular structures, vibrational frequencies, infrared intensities and Raman scattering activities were calculated a pair of molecules linked by the intermolecular O—H...O hydrogen bond. The spectroscopic and theoretical results are compared to the corresponding properties for 5-BrSA monomers and dimer of C1 conformer. The optimized bond lengths, bond angles and calculated frequencies showed the best agreement with the experimental results.

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1. Introduction

Salicylic acid is also known 2-hydroxybenzoic acid, is widely used as plant growth regulators, as a preservative in food products, and in organic synthesis, antiseptic and anti-fungal agents. It has been shown to regulate a large variety of physiological processes in plants [1,2]. Salicylic acid and its derivatives show anti platelet activity and have strong antiseptic and germicidal properties [3]. They have recently become attractive to experimentalists as well as theoreticians since their structures are of some biological significance particularly in medicinal and enzyme chemistry [4–8]. The effects of the structural features on the physico-chemical properties and on the bioactivity of these compounds were investigated in numerous experimental and theoretical studies [4–6].

Extensive experimental and theoretical investigations have focused on elucidating the structure and normal vibrations of salicylic acid and its derivatives. Far-infrared and low-frequency Raman spectra of salicylic acid were reported [9,10]. Jadrijević et al. [11] researched of salicylic acid and its derivates with FT-IR and NMR spectra. Also, they studied the substituent effect on the spectral properties of salicylic acid derivatives. Vibrational spectra

of jet-cooled salicylic acid were measured by Yahagi et al. [12]. Volvo et al. [13] calculated normal coordinates for salicylic acid molecule and proposed the assignment of the observed Raman and IR spectra. Aqueous solutions of salicylic acid and its derivatives in various pH are studied infrared and Raman spectra by Humbert et al. [14]. The crystal structure of salicylic acid has been studied by X-ray [15,16]. Theoretical model for the infrared spectra in the O—H stretching region of hydrogen-bonded salicylic acid is presented [17]. The DFT calculations in the ground and excited electronic states have been recently reported [18]. Goulet and Aroca [19] presented infrared and Raman spectra of solid salicylic acid and performed DFT B3LYP/6-311+G(d,p) calculations. Chen et al. [20] investigated conformers and intramolecular hydrogen bonding of salicylic acid monomer and its anions. Amino substituted salicylic acid is studied by experimental and theoretical [3]. The molecular structures and the intra-molecular hydrogen bonding for salicylic acid, 2-hydroxythiobenzoic acid, 2-hydroxythionobenzoic acid and 2-hydroxydithiobenzoic acid have been precisely investigated by an ab initio method and density functional theory (DFT) [21]. Infrared and Raman spectra, ab initio calculations vibrational assignment of 4-amino-salicylic acid are studied by Akkaya and Akyüz [22]. Seven stable conformers for 4-amino-salicylic acid are obtained. Nogueira [23] investigated of frequencies of 3-amino-salicylic acid and 2-mercaptonicotinic acid by the infrared and Raman spectra.

The geometric structure of 5-BrSA is studied by X-ray [24]. However, literature survey reveals that to the best of our knowledge, no experimental and computational vibrational spectroscopic study on free 5-BrSA is published in the literature yet. This inadequacy observed in the literature encouraged us to make this theoretical and experimental vibrational spectroscopic research based on the conformers of molecule to give a correct assignment of the fundamental bands in experimental FT-IR and FT-Raman spectra. Therefore, present study aims to give a complete description of the molecular geometry and molecular vibrations of the 5-BrSA.

5-BrSA (also known as 5-bromo-2-hydroxybenzoic acid) is substituted benzene with three different functional groups; an OH, a Br atom and COOH groups. As model system salicylic acid and bromo atom are chosen. The possible stable conformers of 5-BrSA molecule were searched. There are eight conformers for 5-BrSA. The optimized geometry of the conformers and vibrational frequencies for conformers of 5-BrSA were calculated at DFT/B3LYP level of theory using the 6-311++G(d,p) basis set. C1 form is the more stable conformer than the other conformers. The results of the theoretical and spectroscopic studies are reported herein. Also, the vibrational wavenumbers of C1 dimer conformer of 5-BrSA have also been calculated. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters. A detailed interpretation of the vibrational spectra of 5-BrSA has been made on the basis of the calculated total energy distribution (TED).

2. Experimental

The compound 5-BrSA sample was purchased from Acros Organics Company with a stated purity 99% and it was used as such without further purification. 5-BrSA is in solid phase. Therefore, the FT-IR spectrum (4000–400 cm^{-1}) of KBr disc of the sample was recorded on a Perkin Elmer FT-IR System Spectrum BX spectrometer calibrated using polystyrene bands. The spectrum was recorded with a scanning speed of 10 cm^{-1} min^{-1} and the spectral resolution of 4.0 cm^{-1}. FT-Raman spectra of the sample was recorded using 1064 nm line of Nd:YAG laser as excitation wave length in the region 0–4000 cm^{-1} on a Bruker RFS 100/S FT-Raman. The detector is a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 4 cm^{-1} resolution using a laser power of 100 mW.

3. Computational details

The geometry data of title molecule was taken from X-ray structure [24]. In order to obtain stable structures, the geometrical parameters for eight conformers and dimer of 5-BrSA in the ground state (in vacuo) were optimized at DFT by the B3LYP level of theory using the 6-311++G(d,p) basis set. The vibrational wavenumbers of 5-BrSA dimer with H-bonding between carboxyl groups of C1 conformation have also been calculated to improve simulation of the experimental spectra. The vibrational frequencies for the eight conformers are calculated with this method and then wavenumbers in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983, respectively [25]. The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of title molecule. The total energy distribution (TED) was calculated by using the SQM [26] program and the fundamental vibrational modes were characterized by their TED. We tabulated only C1 conformer calculations data because of most stable conformer. All the calculations are performed by using Gaussview molecular visualisation program and Gaussian 03 program package on the personal computer [27]. The Becke's three-parameter hybrid density functional,

B3LYP [28,29], was used to calculate harmonic vibrational wavenumbers with the 6-311++G(d,p) basis set. It is well known in the quantum chemical literature that among available functional the B3LYP functional yields a good description of harmonic vibrational wavenumbers for small and medium sized molecules.

4. Results and discussion

The molecule of 5-BrSA, which has three substituents such that the bromo atom and hydroxyl group (OH) and carboxyl group (COOH) attached to a planar benzene ring. All forms of molecule, hydroxyl group, carboxyl group and benzene ring are in the same plane. All conformers of 5-BrSA and C1 dimer form which contains two intermolecular and two intramolecular hydrogen bonds are shown in Fig. 1. We reported some geometric parameters and vibrational frequencies for 5-BrSA by using DFT (B3LYP) and compared with the experimental crystal geometries (bond lengths, bond angles) [24] and experimental frequencies.

Calculated energies and energy difference for all conformers of the 5-BrSA molecule, determined by B3LYP level 6-311++G(d,p) are presented in Table 1. Intra-hydrogen bonds can be responsible for the geometry and the stability of a predominant conformation; the formation of hydrogen bonding between a hydroxyl group and O=COH cause the structure of the conformer C1 to be the most stable conformer. From DFT calculations with 6-311++G(d,p) basis set, the conformer C1 is predicted to be from 3.494 to 24.914 kcal/mol more stable the other conformers (see Table 1). Two conformers (C1 and C2) are calculated to have higher energies than the other conformers even though there might exist weaker hydrogen bonding either between the O—H group and the O atom which COOH group or between the H atom which COOH group and the O—H group.

4.1. Geometrical structures

The molecular structure of 5-BrSA has been studied by X-ray diffraction [24]. The first task for the computational work was to determine the optimized geometry of 5-BrSA. The atomic numbering scheme of most stable conformer, other conformers and dimer structure of 5-BrSA are shown in Fig. 1. Intermolecular hydrogen bonds can be responsible for the geometry and the stability of a predominant conformation; the formation of hydrogen bonding between a hydroxyl group and O=COH cause the structure of the conformer C1 to be the most stable conformer.

The predicted bond lengths and bond angles for most stable conformer (C1) and dimer of C1 conformer of 5-BrSA are tabulated in Table 2 in comparison to the experimental values obtained from 5-BrSA crystal [24]. Taking into account that the molecular geometry in the vapour phase may be different from in the solid phase, owing to extended hydrogen bonding and stacking interactions there is reasonable agreement between the calculated and experimental geometric parameters. Comparison of the calculated and observed bond lengths, the theoretical parameters are greater than experimental data.

Several authors [30,31] have been explained the changes in frequency or bond length of the C—H bond on substitution due to a change in the charge distribution on the carbon atom of the benzene ring. The substituents may be either of the electron withdrawing type (F, Cl, Br, …). The carbon atoms are bonded to the hydrogen atoms with a σ bond in benzene and the substitution of a halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atoms in substituted benzenes exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C—H force constant and a decrease in the corresponding bond length. The reverse holds well on substitution with electron donating groups. The actual change in
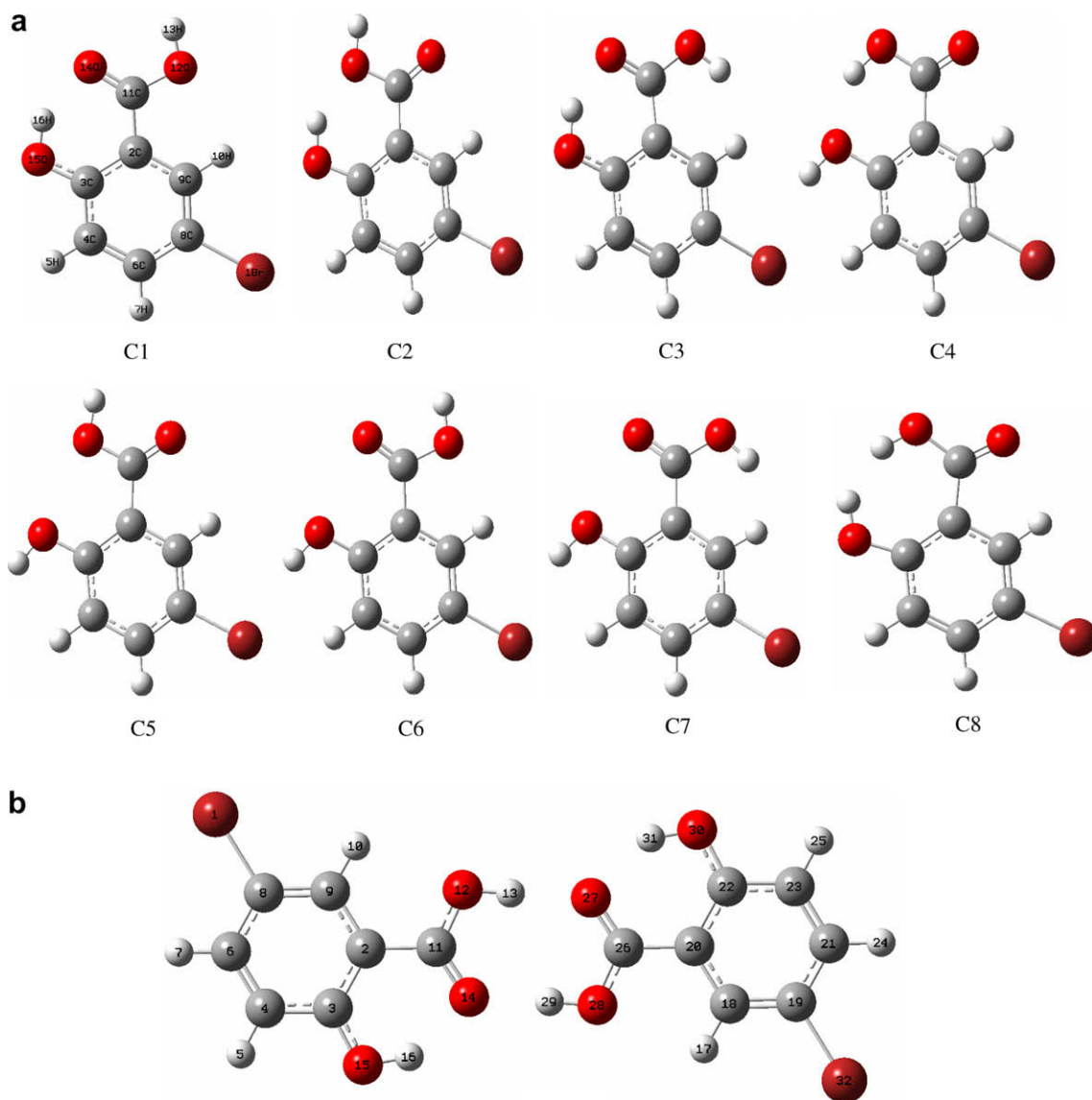
Fig. 1. (a) The theoretical geometric structures of 5-BrSA molecule. (b) C1 dimer conformer of 5-BrSA molecule.

Table 1
Calculated energies and energy difference for eight conformers of 5-BrSA by DFT/B3LYP/6-311++G(d,p) method

Conformers	Energy (hartree)	Relative energy ($E_{rel.}$)[a] (kcal/mol)
C1	−3069.74629263	0.000
C2	−3069.74072459	3.494
C3	−3069.73521537	6.951
C4	−3069.73014453	10.133
C5	−3069.72912230	10.775
C6	−3069.72862099	11.089
C7	−3069.71467834	19.838
C8	−3069.70658980	24.914

[a] Energies of the other seven conformers relative to the most stable C1 conformer.

the C—H bond length would be influenced by the combined effects of the inductive-mesomeric interaction and the electric dipole field of the polar substituent.

Since the large deviation from experimental C—H bond lengths may arise from the low scattering of hydrogen atoms in the X-ray diffraction experiment. The perceivable ones are for the bond distances of C—H among which the biggest difference is 0.123 Å.

These bond lengths were found to be 0.9601 Å in 5-BrSA crystal [24], but theoretically calculated data are greater than 1 Å.

The C—X (X; F, Cl, Br, . . .) bond length indicates a considerable increase when substituted in place of C—H. This has been observed even in benzene derivatives [32]. Atom Br is in the plane of the salicylic acid. The bond distance C—Br is approximately 0.012 Å greater than experimental value (1.904 Å) which is in good agreement with calculated value. In international tables for crystallography [33] the CO bond lengths in the carboxylic acid group conform to the average values are tabulated for an aromatic carboxylic acid in which C=O is 1.226(20) Å and C—O is 1.305(20) Å. The corresponding bond lengths in the 5-BrSA are 1.227(6) and 1.309(6) Å [24] which are calculated 1.225 and 1.347 Å.

The structural parameters are found to be similar for two conformers (C1 and C2). Most of the bond angles and distances are almost the same but there are some differences that should be mentioned. However, there are small differences other conformations that should be touched on. This one is C=O bonds which C1 conformer's data are approximate the experimental data. C1 conformer has the C_{11}—O_{14} bond distance by 1.225 Å, this band obtained 1.227 Å with X-ray [24]. There is the shortest O_{12}—H_{13} bond distance in C8 conformer by 0. 958 Å, however this band obtained

Table 2
Comparison of geometric parameters, bond lengths (Å), and bond angles (°), for the monomer and dimer C1 conformer of 5-BrSA calculated by the B3LYP 6-311++G(d,p) method

Parameters	X-ray[a]	C1	Dimer (C1)[b]
Bond lengths (Å)			
C(1)—Br(8)	1.904(5)	1.917	1.916
C(2)—C(3)	1.404(7)	1.416	1.416
C(2)—C(9)	1.403(7)	1.408	1.409
C(2)—C(11)	1.476(7)	1.467	1.466
C(3)—C(4)	1.386(7)	1.402	1.402
C(3)—O(15)	1.350(6)	1.341	1.342
C(4)—C(6)	1.366(7)	1.383	1.383
C(6)—C(8)	1.387(7)	1.400	1.401
C(8)—C(9)	1.353(7)	1.380	1.379
C(11)—O(12)	1.309(6)	1.347	1.316
C(11)—O(14)	1.227(6)	1.225	1.246
O(12)—H(13)	0.850	0.969	0.998
O(14)—H(16)	1.870	1.765	1.762
O(15)—H(16)	0.850	0.981	0.980
O(14)—O(15)	2.614	2.627	2.622
H(13)...O(27)	1.830		1.676
O(12)...O(27)	2.681(5)		2.674
Bond angles(°)			
C(3)—C(2)—C(9)	118.7(5)	119.8	119.6
C(3)—C(2)—C(11)	120.5(5)	119.0	120.0
C(9)—C(2)—C(11)	120.9(5)	121.3	120.3
C(2)—C(3)—C(4)	119.5(5)	119.0	119.0
C(2)—C(3)—O(15)	122.5(5)	123.3	123.5
C(4)—C(3)—O(15)	118.0(5)	117.7	117.5
C(3)—C(4)—C(6)	121.0(5)	120.6	120.7
H(5)—C(4)—H(6)	119.8	121.0	121.0
C(4)—C(6)—C(8)	119.2(5)	120.0	120.0
Br(1)—C(8)—C(6)	118.4(4)	119.4	119.5
Br(1)—C(8)—C(9)	120.2(4)	119.9	120.0
C(6)—C(8)—C(9)	121.4(5)	120.6	120.5
C(2)—C(9)—C(8)	120.1(5)	119.9	120.0
C(2)—C(11)—O(12)	115.3(5)	114.7	115.9
C(2)—C(11)—O(14)	122.0(5)	124.2	122.0
O(12)—C(11)—O(14)	122.6(5)	121.1	122.1
C(11)—O(12)—H(13)	108.8	107.2	110.6
C(3)—O(15)—H(16)	109.7	108.2	108.0
O(15)—H(16)—O(14)	145.0	144.6	144.4
O(12)—H(13)...O(27)	179.0		179.6

[a] The X-ray data from Ref. [24].
[b] C1 dimer conformer is centrosymmetrical.

0.8499 Å. The bond distance C_2—C_{11} among in C1 conformer is smaller than the other conformers. This bond was found to be 1.476 Å in 5-BrSA crystal and calculated as the biggest in unstable conformers (C7 and C8, 1.505 and 1.512 Å) probably due to effect of intra-hydrogen (H16...O14) on the structure.

In the ring part optimized geometry of the molecule shows very good agreement with experiment. The CC bond lengths of the benzene rings are observed in the range 1.353(7)–1.404(7) Å [24] which calculated in the range 1.380–1.416 Å in the benzene ring. For salicylic acid these bond lengths are observed in the range 1.383–1.416 Å in the benzene ring [34]. The similar correlation was found for similar molecules in the literature [21,22,35,36].

The asymmetry of the benzene ring is also evident from the negative deviation of C3—C2—C9, C2—C3—C4, and C2—C9—C8 angles and positive deviation of C3—C4—C6 and C6—C8—C8 angles from the normal value of 120°. The remaining angle (C4—C6—C8) is equal to normal value of 120°. Similar values found to be salicylic acid and other benzene derivatives [21,35,36]. Other conformers CCC angles are calculated bigger and smaller (ca. 1° or 2°) than hexagonal angle. For 5-BrSA, C3—C2—C11 angle is smaller than C9—C2—C11 because of interaction between the carboxyl acid (COOH) and hydroxyl (OH) group.

The intermolecular hydrogen bonds are almost linear (the O—H···O angle equals 179.0°) and their length is 2.681 Å. We

calculated this angle and length 179.6° and 2.674 Å. The intramolecular hydrogen bonds between the hydroxyl groups and the oxygen atoms of the carbonyl groups are strongly bent (the O—H···O angle equals 145.0°) and the O···O distance is 2.614 Å. The calculated values (144.6° and 2.627 Å) are excellent agreement with experimental values.

The torsional angles C3—C2—C11—O12 and C9—C2—C11—O14 are 179.3° and 178.8°, respectively. The tilt angles are calculated 180°. The dihedral angles are nearly the same among the all conformers.

4.2. Vibrational spectra

In order to obtain the spectroscopic signature of 5-BrSA molecule, we performed a frequency calculation analysis. Calculations were made for a free molecule in vacuum, while experiments were performed for solid samples, so there are disagreements between calculated and observed vibrational wavenumbers, and some frequencies are calculated, however these frequencies are not observed in the FT-IR and FT-Raman spectra. To the best of our knowledge there is no vibrational data for gas phase 5-BrSA. Therefore we have to compare calculated results with those of solid phase vibrational spectrum.

The present molecule 5-BrSA consists of 16 atoms, so it has 42 normal vibrational modes. On the basis of C_s symmetry the 42 fundamental vibrations eight forms of title molecule can be distributed as 29A′ + 13A″. The vibrations of the A′ species are in plane and those of the A″ species are out-of-plane. All vibrations are active in both IR and Raman. But if the molecules were C_1 symmetry there would not be any relevant distribution.

Fig. 2a presents the experimental FT-IR and FT-Raman spectra. The calculated IR and Raman spectra are shown in Fig. 2b for comparative purposes, where the calculated intensity and activity is plotted against the harmonic vibrational frequencies. The experimental wavenumbers are tabulated in Table 3 together with the calculated wavenumbers for monomer and dimer C1 conformer of studied molecule. The resulting vibrational frequencies for the optimized geometries and the proposed vibrational assignments as well as IR intensities and Raman scattering activities are given in Table 3. In the last column is given a detailed description of the normal modes based on the total energy distribution (TED). The symmetry species of all the vibrations are written in the first column of the table. Modes are numbered from biggest to smallest frequency within each fundamental wave numbers, *v*.

Owing to lack of enough detailed experimental data for this molecule, the vibrational spectrum was obtained by molecular orbital calculation using Gaussian 03 [27] program. Vibrational modes of 5-BrSA were researched by harmonic frequency calculations performed at the corresponding energy optimized geometries. The assignment of the vibrational absorptions was made by the comparison with the related molecule and also with the results obtained from the theoretical calculations. As seen in Table 3, there is great mixing of the ring vibrational modes and also between the ring and substituent modes. The descriptions of the modes are very complex because of the low symmetry of the studied molecule. Especially, in plane modes and out-of-plane modes are the most difficult to assigned due to mixing with the ring modes and also with the substituent modes.

It is worth mentioning that, however, in solid 5-BrSA, COOH group and ring OH {(OH)h} group are involved in inter- and intra-hydrogen bonding interactions. In the crystal lattice dimeric molecules, held together by hydrogen bridges between carboxyl groups, are arranged [24]. In order to simulate H-bonding through COOH group we also calculate vibrational wavenumbers of 5-BrSA dimer of C1 conformer (see Table 3).
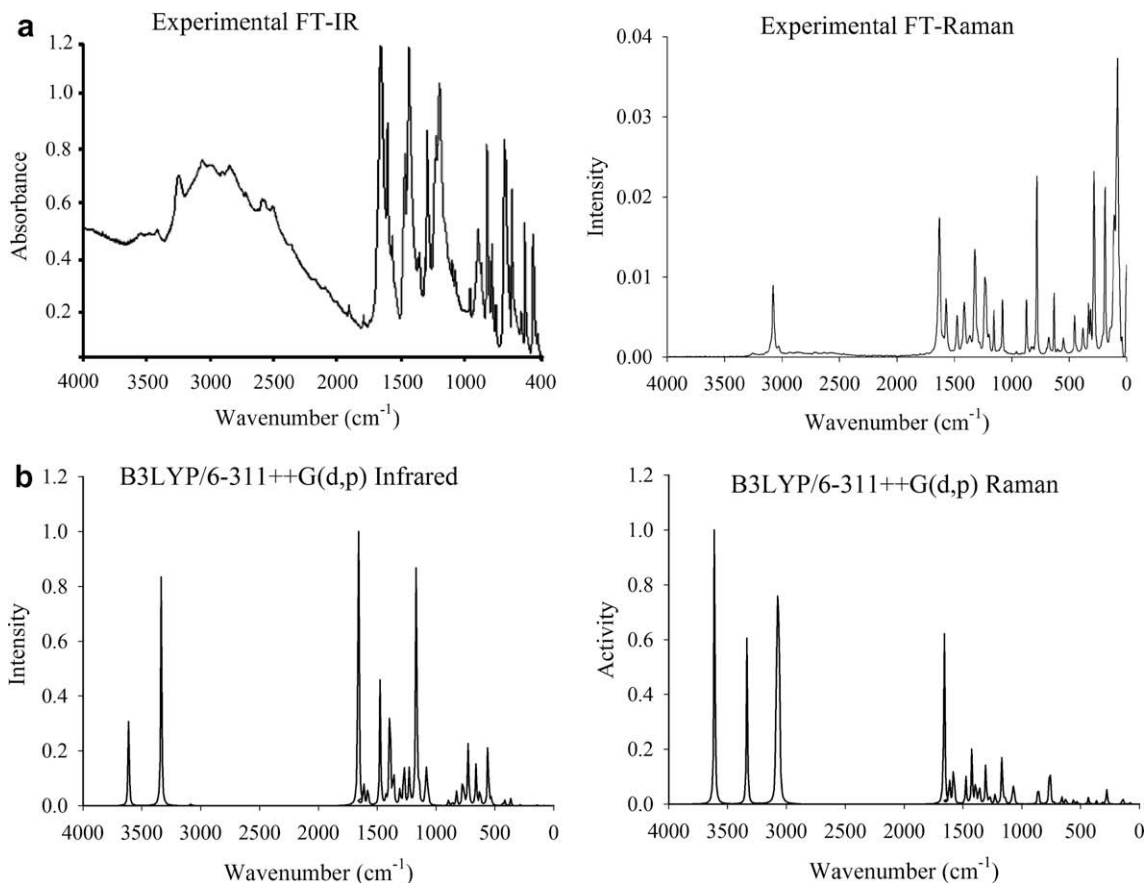
Fig. 2. (a) The experimental FT-IR and FT-Raman spectrum of 5-BrSA molecule. (b) Calculated frequencies in cm^{-1} normalized IR intensities and Raman activities of C1 conformer for 5-BrSA at B3LYP/6-311++G(d,p) level of DFT theory.

For 5-BrSA, group the vibrational modes are CH stretching modes, CO stretching modes, CBr stretching modes, CC stretching modes, OH stretching modes, CCH bending, CCC bending, CCO bending, OCO bending, COH bending, CCBr bending, ring bending and ring torsion. Between 1350 and 400 cm^{-1} several characteristic in plane deformations C—H, out-of-plane C—H vibrations as well as out-of-plane (CCC) deformations observe. Two of mixed modes involving contributions from CC stretching as well as OH in plane deformations are observed in the range 1500–1350 cm^{-1}. In the range of 1800–1500 cm^{-1}, the CC, C=O and COOH group stretching vibrations occur. In the spectral range over 3000 cm^{-1}, O—H and C—H stretching modes take place [37].

The OH vibrations are extremely sensitive to formation of hydrogen bonding. The O—H stretching band is characterized by very broadband appearing near about 3400–3600 cm^{-1}. For salicylic acid, the OH vibration is observed to 3238 cm^{-1} in FT-IR spectra [11]. This band calculated 3610 and 3334 cm^{-1} which modes (v1, v2) of O_{12}—H_{13}, O_{15}—H_{16}, units, respectively. As expected these two modes are pure stretching modes as it is evident from TED column, they are almost contributing 100%. These frequencies are observed at 3551 and 3250 cm^{-1} FT-IR experimentally. In the Raman spectrum this absorption is absent. As discussed in our previous papers [38–40], with the halogen (F, Cl, Br, ...) substitution, OH stretching vibrations shifted to higher wavenumbers region [41]. This means that, the OH vibrations are sensitive due to halogen coordination. This vibration is observed to 3338, 3397 and 3409 cm^{-1} for 3-, 4-, 5-amino-salicylic acid [3]. The O—H in plane bending vibration occurs in the general of 1440–1395 cm^{-1} [42]. In 5-BrSA, the O—H in plane bending is assigned to 1441 cm^{-1} FT-IR and 1411 cm^{-1} FT-Raman which are calculated 1425 and

1392 cm^{-1}. The O—H in plane bending of a motion of a hydroxyl group is calculated 1188 cm^{-1} (unscaled value) which is assigned at 1196 cm^{-1}. For 3-, 4-, 5-amino-salicylic acid, title vibration is observed to 1461, 1450, and 1454 cm^{-1} [3]. Akkaya and Akyüz [22] assigned this vibration at 1294 and 1160 cm^{-1} IR for 4-amino-salicylic acid. For 3-amino-salicylic acid, this band is observed to 1340 and 1171 cm^{-1} which is a motion of hydroxyl group [23]. In this study, the O—H out-of-plane bending (v30) is observed at 554 cm^{-1} in the FT-Raman. For 4-amino-salicylic acid, OH out of bending is assigned to 625 cm^{-1} by Akkaya and Akyüz [22]. The O—H in plane bending and out-of-plane bending vibrations values in dimer conformations are increasing, because of the hydrogen bonding effect through the carboxyl groups (see Table 3).

The heteroaromatic structure shows the presence of the C—H stretching vibrations in the 3000–3100 cm^{-1} range which is the characteristic region for the ready identification of C—H stretching vibrations [43]. Accordingly, in the present study, the three adjacent hydrogen atoms left around the benzene ring, the 5-BrSA give rise three C—H stretching modes (v3–v5), three C—H in plane bending (v13, v15, v17) and three C—H out-of-plane bending (v20, v21, v23) vibrations which corresponds to stretching modes of C_4—H_5, C_6—H_7, C_9—H_{10} units. The vibrations assigned to aromatic C—H stretching in the range 3066–3144 cm^{-1} [44] are in agreement with experimental assignment 3061 cm^{-1} FT-IR (3075 cm^{-1} FT-Raman) [43]. These modes are calculated from 3086 to 3058 cm^{-1} for the most stable C1 conformer. They are very pure modes since their TED contribution are 100%. In aromatic compounds, the C—H in plane bending frequencies appear in the range of 1000–1300 cm^{-1} and the C—H out-of-plane bending vibration in the range 750—1000 cm^{-1} [45,46]. Hence the CH in

Table 3
Comparison of the experimental (FT-IR and FT-Raman) wavenumbers (cm^{-1}) and theoretical harmonic frequencies (cm^{-1}), infrared intensities ($I^{Infrared}$, Km mol^{-1}), Raman scattering activities (Å^{-4} amu^{-1}) of C1 monomer and dimer conformer of 5-BrSA calculated by the B3LYP method using 6-311++G(d,p) basis set

Experimental				Theoretical C1 monomer conformer				Theoretical C1 dimer conformer		
Modes no	Symmetry species	FT-IR	FT-Raman	Unscaled freq.	Scaled freq.[a]	$I^{Infrared}$	S^{Raman}	Unscaled freq.	Scaled freq.[a]	TED[b] (%)
ν1	A′	3551 vw		3769	3610	128.2	137.4	3232, 3149	3096, 3017	νOH (100) (O12—H13)
ν2	A′	3250 w		3480	3334	323.0	77.0	3513, 3511	3366, 3364	νOH (100) (O15—H16)
ν3	A′			3222	3086	2.4	44.5	3223, 3223	3088, 3088	νCH (100)
ν4	A′		3075 m	3205	3071	1.2	154.4	3206, 3206	3071, 3071	νCH (100)
ν5	A′	3061 vw		3192	3058	0.6	58.0	3192, 3192	3058, 3058	νCH (100)
ν6	A′	1660 vs	1629 s	1732	1660	467.2	95.4	1692, 1670	1663, 1642	νC=O (68)
ν7	A′	1606 s		1643	1615	39.6	14.3	1639, 1624	1611, 1596	νCC (63) ring
ν8	A′	1570 vw	1569 w	1606	1579	31.6	23.0	1606, 1602	1579, 1575	νCC (60) ring + δCCH (13) + δCOH (13)
ν9	A′	1471 m	1473 vw	1500	1474	176.7	12.3	1508, 1499	1482, 1474	δCCH (49) + νCC (25) ring
ν10	A′	1441 vs		1449	1425	10.7	25.4	1486, 1475	1461, 1450	νCC (43) + δCOH (23) + νCO (10)
ν11	A′		1411 w	1416	1392	206.1	13.5	1445, 1437	1420, 1412	δCOH (30) + νCC (23) + νCO (15) + δOCO (10)
ν12	A′	1359 vw		1384	1360	63.2	11.2	1395, 1392	1371, 1368	νCC (41) ring + δCOH (19) + δCCH (12)
ν13	A′	1312 vw	1318 s	1328	1305	24.5	20.7	1327, 1325	1304, 1303	δCCH (36) + νCC (27) ring + νCO (21)
ν14	A′	1294 s		1294	1272	80.3	4.4	1265, 1264	1244, 1243	νCC (35) ring + νCO (27) + δCOH (12)
ν15	A′	1222 m	1226 m	1247	1226	64.7	5.3	1247, 1244	1226, 1223	δCCH (45) + νCC (23) ring + δCOH (15)
ν16	A′	1196 s		1188	1168	383.7	24.5	1358, 1352	1335, 1329	δCOH (40) + νCC (28) + νCO (10)
ν17	A′		1152 w	1164	1144	32.0	3.3	1172, 1171	1152, 1151	δCCH (52) + νCC (24) ring + νCO (10)
ν18	A′	1096 vw	1079 w	1103	1084	64.1	3.4	1119, 1117	1100, 1098	δCCC (35) trigonal ring breathing + νCC (25) + νCO (25)
ν19	A′	1078 vw		1086	1067	32.4	13.0	1093, 1093	1074, 1074	νCC (32) + δCCH (26) + νCO (15)
ν20	A″	957 w		973	957	0.3	0.0	975, 975	958, 958	γCH (90)
ν21	A″	898 m		908	892	8.7	0.0	912, 911	896, 895	γCH (87)
ν22	A′	868 vw	869 w	875	860	5.9	11.3	883, 881	868, 866	δCCC (42) + νC—OH (17) + νCBr (10)
ν23	A″	826 s		839	825	20.6	0.1	842, 839	828, 825	γCH (85)
ν24	A″	786 m	780 s	787	773	38.2	0.0	784, 774	771, 761	τCCCO (53) + τOCOH (24)
ν25	A′	755 w		775	762	22.7	25.3	804, 793	790, 779	νCC (48) + νCO (15) + δCOC (12)
ν26	A″			738	725	103.2	0.6	711, 710	699, 698	γOH (97)
ν27	A″	688 s	668 vw	680	669	4.6	0.4	677, 673	666, 662	τCCCC (76) + τOCOH (11)
ν28	A′			670	658	56.9	3.1	701, 691	689, 679	δOCO (61) + δCCC (10)
ν29	A′	628 s	630 w	636	625	28.2	3.4	637, 637	626, 626	δCCC (53) + νCBr (22)
ν30	A″	554 w		567	558	104.9	2.3	933	917	γOH (82)
ν31	A′	527 m	543 vw	540	531	9.7	1.0	562, 555	552, 545	δCCO (50) + δCCC (12) ring + δOCO (12)
ν32	A″			528	519	1.4	0.2	530, 530	521, 521	τCCCH (32) + τCCCC (25) + τCCCO (17)
ν33	A′	461 m	449 vw	442	434	2.4	3.4	475, 460	467, 452	δCCO (58) + δCCC (12) ring + νCC (12)
ν34	A″	426 vw		422	415	9.1	0.3	432, 431	425, 424	τCCCC (68) + τCCCO (13)
ν35	A′		377 vw	370	364	10.1	1.6	392, 380	385, 373	δCCO (27) + δCCC (24) ring + νCC (23)
ν36	A″		312 vw	318	313	0.0	0.8	320, 320	315, 315	τCCCBr (32) + τCCCH (28) + τCCCO (22)
ν37	A′		283 s	290	285	1.2	1.5	321, 320	316, 315	νCBr (50) + δCCC (34) + δCCO (29)
ν38	A′			279	275	0.3	6.4	281, 280	276, 275	νCBr (52) + δCCBr (19)
ν39	A′		188 s	145	142	0.5	1.9	192, 167	189, 164	δCCBr (52) + νC—COOH (33)
ν40	A″			141	139	0.7	1.3	155, 146	152, 143	τCCCC (58) + τCCCO (29)
ν41	A″			127	125	0.1	0.2	122, 120	120, 118	τCCCO (45) + τCCCBr (34)
ν42	A″		76 vs	77	76	0.6	0.8	81, 68	80, 67	τCCCO (80) + τCCCBr (12)

[a] Wave numbers in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983, respectively [25].
[b] TED; total energy distribution; ν, stretching; δ, in plane bending; γ, out-of-plane bending; τ, torsion; vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

plane bends is assigned to the FT-IR and FT-Raman bands at 1312, 1222 and 1318, 1226, 1152 cm^{-1}, respectively. The calculated values of the CH in plane bends are 1305, 1226, and 1144 cm^{-1} which shows well agreement with the experimental values. The CH out-of-plane bends are assigned to the FT-IR bands in the range from 957 to 826 cm^{-1} are not observed in the Raman spectrum. The calculated values are excellent agreement with assigned in experimental values (For example, one of them is 957 cm^{-1} calculated and assigned value). The change in the frequencies of these deformations from the values in benzene is almost determined exclusively by the relative position of the substituents and is almost independent of their nature [47,48]. Both the in plane and out-of-plane bending vibrations are described as mixed modes. The TED contribution of the in plane and out-of-plane modes indicates that out-of-plane modes are also highly pure modes like the in plane bending fundamentals. Akkaya and Akyüz [22], assigned the CH in plane (1369, 1228, 1108 cm^{-1}) and CH out-of-plane (from 819 to 970 cm^{-1}) for 4-amino-salicylic acid. For 3-amino-salicylic acid, these bands are observed at 1229, 1150, 1068 cm^{-1} and 962, 781 cm^{-1} in plane and out-of-plane, respectively. The above conclusions are in very good agreement with literature values [25,43,46,49–51].

The most characteristic feature of carboxylic group is a single band observed usually in the 1700–1800 cm^{-1} region. This band is due to the C=O stretching vibration. In the solid state most of carboxylic acids form a dimeric structure that is due to the result of hydrogen bonding between two neighbouring —COOH groups. In such a case two v(C=O) are expected: one that is Raman active (in phase, symmetric stretching vibration) and the other one, out-of-phase (antisymmetric stretching vibration), is IR active only. The asymmetric stretch is usually at higher wavenumber than the symmetric stretch. Therefore, the C=O stretching mode ($v6$, asymmetric stretching vibration) is observed at 1660 cm^{-1} in FT-IR spectrum and observed at 1629 cm^{-1} (symmetric stretching vibration) in FT-Raman spectrum The theoretically computed value of the C=O band shows very good agreement with experimental results, which is predicted at 1660 and 1724 cm^{-1} for C1 and C2 conformers, respectively. This mode is predicted at ca. 1750 cm^{-1} for other conformers. The hydrogen bonding effect through the carboxyl groups, therefore C1 dimer conformation the C=O stretching mode calculated at 1663 and 1642 cm^{-1}. The TED values in Table 3 reveal that this mode is coupled with COH bending vibration. But this may be almost pure mode is evidenced from 68% of TED. By the bromo substitution in place of hydrogen atom, the bromo position versus carboxylic anion influence the C=O mode form remarkably. For salicylic acid, the C=O stretching mode is observed to 1662 cm^{-1} in FT-IR spectra. The C=O stretching mode is assigned at 1538, 1592, and 1584 cm^{-1} for 3-, 4-, 5-amino-salicylic acid [3]. In 4-amino-salicylic acid, the C=O stretching mode is observed at 1659 cm^{-1} with the strongest absorption in the IR spectrum which is predicted at 1642 cm^{-1} C1 conformer by Akkaya and Akyüz [22]. Nogueira [23] observed this band 1649 and 1652 cm^{-1} IR and Raman spectra for 3-amino-salicylic acid, respectively.

Empirical assignments of vibrational modes for peaks in the fingerprint region are difficult. In the wavenumber region of 600–1660 cm^{-1}, the spectrum observed in the experiments closely resembles the calculated spectrum, except for differences in details. These wavenumbers in the same range are in reasonable agreement with experimental results (see Table 3). The ring stretching vibrations are very much important in the spectrum of benzene and its derivatives are highly characteristic of the aromatic ring itself. The ring carbon–carbon stretching vibrations occur in the region 1400–1650 cm^{-1} in benzene derivates. In general, the bands are of variable intensity and are observed at 1625–1590, 1590–1575, 1540–1470, 1465–1430 and 1380–1280 cm^{-1} from the frequency

ranges are given by Varsanyi [46] for the five bands in this region. For 3-amino-salicylic acid, the CC stretching modes are observed in the range from 1460 to 1567 cm^{-1} IR and from 1456 to 1572 cm^{-1} Raman spectra [23]. Akkaya and Akyüz [22] assigned 1642 cm^{-1} IR spectra title band for 4-amino-salicylic acid. In the present work, five CC stretching modes are expected and the highest one is observed at 1606 cm^{-1} ($v7$) in the FT-IR spectrum. As revealed by TED, the ring-breathing mode which can be described as the 'trigonal ring breathing' vibration or the 'star of David' vibration [52] of the aromatic ring at ($v18$) 1084 cm^{-1} for two conformers (C1 and C2), which is observed at 1096 and 1079 cm^{-1} in the FT-IR and FT-Raman spectrum, respectively. For 4-amino-salicylic acid, the ring breathing mode is predicted at 960–969 cm^{-1} for stable conformers which is observed at 955 cm^{-1} in the IR and at 962 cm^{-1} in the Raman spectrum [22]. The theoretically calculated C—C—C in plane and out-of-plane bending modes have been obtained to be consistent with the recorded spectral values. The ring assignments proposed in this study is also in agreement with literature values [22,35,43,46,49–51].

The assignments of the C—Br stretching and deformation vibrations have been made on the basis of the calculated TED. Some vibrational modes were shown to be Br-sensitive modes whereas others were calculated in a narrow frequency range. Involving the ring-halogen modes are related partially to C—Br stretching and bending modes. The theoretical wavenumbers of C—Br stretching vibration coupled with other group vibrations. According to the calculated TED, our calculations show that there is no pure C—Br band vibration. The C—Br stretching mode appears at longer wavelength region (200–480 cm^{-1}) as reported by Varsanyi [46]. In FT-Raman spectrum of 5-BrSA, the band at 283 cm^{-1} is assigned to C—Br stretching vibration coupled with ring deformation (mode $v37$). The theoretical wavenumber of this band 285 cm^{-1} coincides well with the experimental, and the calculated TED (in 50%), confirms this assignment. Moreover, modes $v29$ and $v38$, calculated at 625 and 275 cm^{-1}, involve some contribution from the C—Br stretching vibration. The C—Br out-of-plane bending vibration is assigned to 312 cm^{-1} FT-Raman, which shows excellent agreement with calculated value (313 cm^{-1}). This is in agreement with the literature data [46,51,53,54]. The C—Br in plane bending vibration is calculated 142 cm^{-1} which is assigned to 188 cm^{-1} FT-Raman. The remainder of the observed and calculated frequencies accounted in Table 3.

The infrared intensity for this molecule from experimental fundamentals ($v6$) at 1660 cm^{-1} is very strong, theoretical intensity (all conformation) of these fundamentals is in the same order. The most calculated intensity is 467.2 Km mol^{-1} which corresponds to CO stretching mode ($v6$) for C1 conformer. The most Raman scattering activity (154.4 Å^{-4}amu^{-1}) peak is calculated corresponds to the CH stretching mode ($v4$).

The calculated wavenumbers for dimer 5-BrSA shown in Fig. 1 are tabulated in Table 3. As seen in Table 3, the hydrogen bonding effect through the carboxyl groups is clearly observed (For example in $v1$, $v6$, $v10$, $v16$, and $v30$ modes). This is in agreement with literature [3,22,40].

5. Conclusions

In this study, we have performed the experimental and theoretical vibrational analysis of 5-BrSA, for the first time. A comparison of the result of experimental and theoretical study gave us a full description of the geometry and vibrational properties of this molecule. Based on calculated energy differences, the C1 conformer is found to be most the stable conformer and the other conformers are predicted the unstable conformer. Intermolecular and intramolecular hydrogen bonding between H and O is expected in C1 conformer. Dimeric molecules held together by hydrogen bridges

between carboxyl groups. The calculated geometric parameters and vibrational frequencies obtained with density functional theory calculations (B3LYP/6-311++G(d,p)) method are in good agreement with the experimental values obtained for the investigated molecule.

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