

DFT Calculations, FT Raman, FTIR Spectra and Vibrational Assignment of 2-amino 5-bromobenzoic Acid

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ABSTRACT

The experimental FT-IR and FT-Raman spectra of the molecule 2-amino-5-bromobenzoic acid has been recorded and analyzed in the region 4000–400 cm^{-1} and 3500–50 cm^{-1} , respectively. 2-amino-5-bromobenzoic acid, a single crystal, belongs to the amino acid group. The observed bands were interpreted with the aid of normal coordinate analysis and force field calculations. Molecular structure, vibrational wavenumbers and complete vibrational analysis of 2-amino-5-bromobenzoic acid is performed by combining the experimental and theoretical information based on density functional theory (DFT) using B3LYP functional theory (DFT) using B3LYP functional with 6-311+G and 6-3++G basis sets. The complete assignments were performed on the basis of the potential energy distribution (PED) of the vibrational modes, calculated with scaled quantum mechanical (SQM) method. The molecular structure and vibrational frequencies, infrared intensities and Raman scattering actives have been calculated frequency showed the best agreement with experimental results. The molecule has been studied for optical properties. The quantitative analysis on the molecule had been carried out using Fourier transform infrared (FTIR) and Fourier transforms Raman (FT-Raman) spectral measurements. FT-IR and FT-Raman analysis were carried out in an integral approach. The normalized frequencies were observed with scaled values and were compared with experimental FT-IR and FT-Raman spectra. Most of the modes have wavenumbers in the expected range and the error obtained was very rare in general. The optimized geometric parameters (bond lengths and bond angles) were given and are in agreement with the corresponding experimental values. The biological activity of 2-amino-5-bromo benzoic acid has been predicted based on these values. The Fourier-transform Raman and infrared spectra of 2-amino-5-bromo benzoic acid has been recorded and analyzed².

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KEYWORDS: 2-Amino-5-bromobenzoic acid, DFTTD-DFT calculations, FT-IR, FT-Raman and UV spectra

1. INTRODUCTION

Benzoic acid is a compound comprising a benzene ring core carrying a carboxylic acid substituent. It has a role as an antimicrobial food preservative, an EC 3.1.1.3 (triacylglycerol lipase) inhibitor, an EC 1.13.11.33 (arachidonate 15-lipoxygenase) inhibitor, a plant metabolite, a human xenobiotic metabolite, an algal metabolite and a drug allergen. Due to the prevalence and widespread use of benzoic acid, many

studies have been conducted both structural and to find new uses by researchers from every corner of the world.

Benzoic acid and its derivatives are widely distributed in nature. Benzoic Acid is particularly found in plants, free and in the form of compounds. Gum benzoic from where Benzoic Acid was obtained for the first time contains 20% benzoic acid. Benzoic

Acid is found in most of the fruits (approximately 0.05%). Hippuric acid, found in the urine of herbivores mammals as the form of benzoyl glycine (hippuric acid) derivative. Other natural products containing benzoic acid are the bark, foliage, fruits, and seeds of various plants, including cherries and prunes benzoic acid is easily soluble in hot water, alcohol and ether. Benzoic Acid is slightly soluble in cold water as well. Its solubility in water increases in the presence of alkali substances such as borax and tri sodium phosphate. It also dissolves in substances such as chloroform, acetone, carbon tetrachloride, benzene, carbon sulfide, turpentine, essential oils³⁶⁻³⁸. Like any other compound, the molecular structure of 2-amino-5-bromobenzoic acid is determined by bond lengths, bond angles and dihedral (torsion) angles. In corresponding tables and figures, these properties have been depicted comparatively. Benzoic acid was among the first organic crystals structures to be examined by X rays (Bragg 1921-22) but the detail study of the atomic arrangement does not appear to have been made.

Experimental and theoretical chemists carried out a large number of studies on benzoic acid and its substituted derivatives. A computational and experimental study on 2-amino-5-halogeno-Benzoic acid (X= F, Cl and Br) was carried on by Xavier and Joe, they also investigated biological activities of the AXBA³². The crystal structure of m-bromobenzoic acid. It is a conjugate acid of a benzoate. Benzoic acid is cheap and readily available, so the laboratory synthesis of benzoic acid is mainly practiced for its pedagogical value. It is a common undergraduate preparation. A fungistatic compound that is widely used as a food preservative. It is conjugated to GLYCINE in the liver and excreted as hippuric acid. As the sodium salt form, sodium benzoate is used as a treatment for urea cycle disorders due to its ability to bind amino acids. This leads to excretion of these amino acids and a decrease in ammonia levels. The name benzoic acid originates from gum benzoin, a balsamic resin obtained from a South Asian plant called styrax. The extraction of benzoic acid was carried out by SCHEELE in 1775. Its structure was determined by LIEBIG and WOËHLER in 1832. The initial production methods were developed in the late 1800s. They were based on the hydrolysis of benzotrichloride or the decarboxylation of phthalic anhydride. Today, benzoic acid is produced by oxidation of toluene with air, which has displaced dichromate and nitric acid oxidation processes.

Benzoic acid occurs widely in plants and animal tissues along with vitamin B-complex and is used in miticides, contrast media in urology,

cholecystographic examinations, and in the manufacture of pharmaceuticals. Derivatives of benzoic acid are also the subject of investigation for many reasons. For instance, they are known to enhance the action of local anesthetics, as evaluated by measuring the pain sensibility of human skin in vivo and the action potentials from the crayfish giant axon and the rat cervical vagus in vitro⁴.

The hydrogen bonding present in the crystal have been studied by Deuterium isotope effect (Robertsen and Ubbelohde 1939)²¹. Recent research shows that sodium benzoate may be beneficial as an add-on therapy (1 gram/day) in schizophrenia. Total Positive and Negative Syndrome Scale scores dropped by 21% compared to placebo. 2-Amino-5-bromo benzoic acid is used for the counter selection of TRP1, a commonly used genetic marker in the yeast *Saccharomyces cerevisiae* (Toyn *et al.*, 2000). The ability to counter select, as well as to select for, a genetic marker has numerous applications in microbial genetics²⁰.

The system by which research and development lead to new products is fundamentally different than it was in the twentieth century. An understanding of living organisms is leading toward cures of diseases once thought untreatable¹. 2-amino-5-bromo benzoic acid is an amino benzoic acid that is anthracitic acid in which the hydrogen at position 5 on the phenyl ring is replaced by Bromine. It has a role as an ant metabolite. It is an amino benzoic acid and an organ fluorine compound. It derives from anthracitic. A complete vibrational analysis is performed by combining the experimental and theoretical information using Pulay's density functional theory (DFT) based on a scaled quantum mechanical approach. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes. A detailed structural analysis of 2-amino-5-bromo benzoic acid was carried out by Ferguson and Sim⁵. Swaminathan *et al.* reported a detailed theoretical and experimental investigation of the vibrational spectra of 2-amino-5-bromo benzoic acid⁶. A detailed structural analysis of the FT-IR and FT-Raman spectra of 5-amino-2-chlorobenzoic acid, methyl benzoate and 2-amino-4,5-difluorobenzoic acid have been recorded by Sundaraganesan *et al.*⁷⁻⁹. Richards and Xing¹⁰ investigated the antibacterial activity of 4-aminobenzoic acid and its effect on bacterial DNA synthesis. Chlorinated organic compounds have been known for their fascinating properties as Bromine can impart significant effects on their properties such as increased chemical/metabolic stability, lipophilicity,

solubility, dipole-dipole, and hydrogen bonding interactions. As a result, they have a number of applications: (i) about 30–35% of drugs in pharmaceuticals contain at least one Halogenated atom in their molecules. (ii) Amides are prevalent in medicinally important compounds not only because they are particularly stable, but also because they are polar (they contain regions of high positive and negative electrical charge density), which allows amide-containing drugs to interact with biological receptors and enzymes. More recently, the use of Chlorinated compounds in ‘self disproportionation of enantiomers’ of increased magnitude has been reported and it is believed that Chlorinated containing substances may hold great potential in facilitating the study and further practical applications in the self disproportionation of enantiomers.

2. Experimental

The pure sample of 2-amino-5-bromo benzoic acid (solid) was obtained from M/s Sigma Chemical Co, (St Louis, MO, USA) and used as such without any further purification. The mid-infrared spectrum of the compound in the region 400–4000 cm^{-1} was recorded with a Bruker RFS 100/S Fourier transform spectrometer equipped with a Globar source, Ge/KBr beam splitter, and a TGS detector. For the spectrum acquisition, 50 interferograms were collected at 5 cm^{-1} resolution. The UV absorption spectra of the compound were examined in the range 200–400 nm using Shimadzu UV-1800 PC, UV–VIS recording Spectrophotometer in ethanol and water solutions. FT-Raman spectrum of the sample was recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 50–4000 cm^{-1} on a Bruker RFS 100/S FT-Raman. The laser power was set at 250 mW and the spectrum was recorded over 500 scans at a fixed temperature. The sample was mounted in the sample illuminator using an optical mount and no sample pretreatment of any kind was undertaken. The detector is liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 5 cm^{-1} resolution using a laser power of 100 mW. The molecular structure of 2-amino-5-bromobenzoic acid is determined by bond lengths, bond angles and dihedral (torsion) angles. In corresponding tables and figures, these properties have been depicted comparatively.

There is no experimental data for the molecular structure of the compound as of today. But in literature, some very similar molecules were elucidated in terms of molecular structures. From literature, the compound 4-amino-5-bromo benzoic acid was chosen due to its similarities in structure³⁹⁻⁴⁰ and after some adaptations, these values were used.

Compared with the existing synthetic method, the present invention has the advantages of low price and easy acquirement of the raw materials, mild reaction condition, simple and safe operation process, etc., and is a preparation method with easy industrialization. In all this, the other interesting aspect is that how the molecules are self-assembled in the solid-state leading to minimum energy (or at least low energy) ensembles in the shallow regions of lattice energy surfaces. Earlier view about organic Bromine is that it hardly involves in hydrogen bonding and does not contribute to the crystal packing.

3. Computational Methods

The entire calculations conducted in the present work were performed at Hartree-Fock (HF), and B3LYP levels included in the Gaussian 03W package program together with the 6-31G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization. The first task for the computational work was to determine the optimized geometry of the compound. Since the experimental geometry of free 2-amino-5-bromobenzoic acids is not available, the spatial coordinate positions of 4-amino-3-bromobenzoic acid, as obtained from an X-ray structural analysis¹¹. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of 2-amino-5-bromobenzoic acid was used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. These procedures are implemented in the Gaussian 03 program package. The optimum geometry was determined with the keyword OPT, by minimizing the energy concerning all geometric parameters without imposing molecular symmetry constraints.

It is well known in the quantum chemical literature that the hybrid HF/6-311+G method based on DFT yields a good description of harmonic vibrational wavenumbers for small and medium-sized molecules. Experimental and computed results show a good agreement after scaling with a scaling factor. Analytic frequency calculations at the optimized geometry were done to confirm the optimized structures to be an energy minimum and to obtain the theoretical vibrational spectra. The electronic properties, such as HOMO–LUMO energies, dipole moment, absorption wavelengths, and oscillator strengths were calculated using HF/6-311+G method of the time-dependent DFT (TD-DFT).

4. Results and Discussion

Molecular geometry

Optimized geometrical parameters of 2-amino-5-bromo benzoic acid calculated by HF and DFT-B3LYP levels with the 6-31G(d,p) basis sets are listed in the Table 1 in accordance with the atom numbering scheme given in Fig.3. Table1 compares the calculated bond lengths and angles for 2-amino-5-bromo benzoic acid with those experimentally available from Literature data

From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values, due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. Comparing bond angles and lengths of HF with those of B3LYP, as a whole the formers are on higher side than the latter and the B3LYP calculated values correlates well compared with the experimental results. In spite of the differences, calculated geometric parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational modes and thermodynamic properties.

Fig. 3 shows the structures of uracil and 2-amino-5-bromo benzoic acid molecules with classical numbering of the atoms. No structural studies are available for 2-amino-5-bromo benzoic acid molecule in the literature. Owing to its structure, the molecule belongs to the C_s symmetry point group with the normal modes distribution as: $31A_g + 14A_u$. The frequencies observed in the IR and Raman spectra along with their assignments are collected in Table 2. Comparison of the vibrational modes calculated at HF and B3LYP with the experimental reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the wavenumber values smaller in comparison with the HF wavenumber data.

Experimental data of the isolated molecule in the gaseous phase has not been reported. Since bond lengths in the crystal data are usually smaller than in the gas phase, the HF calculations may describe the bond lengths of 2-amino-5-bromobenzoic acid in the gaseous phase correctly. In general, the values obtained in bond lengths and angles are very similar in accordance with the microwave data⁷, and NMR results reported in the case of benzoic acid (BA) molecule. The differences are in accordance with the average errors reported for these methods. However, some particular differences may be seen.

By minimizing the energy with respect to all the geometrical parameters, the structural parameters of

the stable conformer of the molecule were optimized. 2-amino-5-bromobenzoic acid is substituted benzene ring with three different functional groups; Br atom, NH_2 and $COOH$ group. Molecular structure of 2-amino-5-bromobenzoic acid with rotational angles is shown in Fig. S1 (supporting information). The potential energy scans of the internal rotations about the $O13-C11-C1-C2$ and the $H15-O14-C11-C1$ single bonds were obtained by allowing the ring- $COOH$ ($\&$) or the $C-OH$ dihedral angles to vary every 10° from 0° to 360° . The optimized position of amino group is also defined as planer with internal rotations about the $H17-N10-C2-C3$ (μ), as shown in Fig. S1 (supporting information). The conformational energy profile shows two maxima near 90° and 270° for $\&$ and $\$, 120^\circ$ and 300° for μ angle. It is clear from Fig. S1, there are three local minima observed at 0° , 180° and 360° for all rotational dihedral angles. Therefore, the most stable conformers are obtained 180° , 0° (or 360°) and 0° (or 180°) for $\&$, $\$$ and μ torsion angles, respectively. The energy value of these conformers is 0.108731 a.u. using AM1 method for all torsion angles.

The optimized bond lengths and bond angles of 2-amino-5-bromo benzoic acid using HF/6-311+G* are given in Table 1. The labeling of the atoms is shown in Fig. 5. Experimental data of the isolated molecule in the gaseous phase has not been reported. Since bond lengths in the crystal data are usually smaller than in the gas phase, the HF calculations may describe the bond lengths of 2-amino-5-bromo benzoic acid in the gaseous phase correctly. The structural parameters of the stable conformer of the molecule were optimized by minimizing the energy concerning all the geometrical parameters. 2-amino-5-bromo benzoic acid is a substituted benzene ring with three different functional groups; Br atom, NH_2 and $COOH$ group. The molecular structure of 2-amino-5-bromo benzoic acid with rotational angles is shown in Fig. S1 (supporting information). The optimized structural parameters of the molecule computed by B3LYP are presented in Table 1. In addition, the computed parameters were compared with the corresponding values obtained from the experimental data for 4-amino-3-bromobenzoic acid¹⁹.

It is noted that the benzene rings appear a little distorted with larger $C1-C2$, $C5-C6$ and $C1-C6$ bond lengths and shorter $C2-C3$, $C3-C4$ and $C4-C5$ and angles slightly out of the regular hexagonal structure.

Table 1 — Optimized geometrical parameters of 2-amino-5-bromo benzoic acid

| Bond lengths (Å) | HF/6-311+G* | Expt7 | Bond angles (°) | HF/6-311+G* | Expt7 |
|---|-------------|-------|------------------------------|-------------|--------|
| C(1)–C(6) | 1.376 | 1.409 | C(6)–C(5)–Br(12) | 118.5 | 120.2 |
| C(1)–C(2) | 1.402 | 1.424 | C(4)–C(5)–Br(12) | 119.0 | 119.6 |
| C(1)–C(11) | 1.462 | 1.469 | C(3)–C(4)–C(5) | 118.1 | 119.9 |
| C(5)–C(6) | 1.389 | 1.378 | C(2)–C(3)–C(4) | 121.2 | 121.7 |
| C(4)–C(5) | 1.412 | 1.400 | C(1)–C(2)–C(3) | 118.8 | 117.7 |
| C(5)–Br(12) | 1.789 | 1.918 | C(1)–C(2)–N(10) | 122.6 | 122.5 |
| C(3)–C(4) | 1.354 | 1.380 | C(3)–C(2)–N(10) | 120.3 | 119.8 |
| C(2)–C(3) | 1.316 | 1.414 | C(1)–C(11)–O(13) | 124.4 | 125.6 |
| C(2)–N(10) | 1.328 | 1.361 | C(1)–C(11)–O(14) | 113.7 | 113.9 |
| C(11)–O(13) | 1.125 | 1.221 | O(13)–C(11)–O(14) | 120.8 | 120.5 |
| C(11)–O(14) | 1.309 | 1.356 | C(11)–O(14)–H(15) | 108.5 | 106.5 |
| O(14)–H(15) | 0.790 | 0.968 | C(2)–N(10)–H(17) | 117.0 | 118.9 |
| N(10)–H(16) | 0.892 | 1.010 | C(2)–N(10)–H(16) | 119.0 | 119.7 |
| N(10)–H(17) | 0.829 | 1.005 | H(16)–N(10)–H(17) | 117.9 | 120.0 |
| Bond angles (°) Intra- and intermolecular O–H, O–N bonds and angles | | | | | |
| C(6)–C(1)–C(2) | 117.4 | 119.5 | O(13)···H(17) H(15)···O(14r) | 1.949– | 1.949 |
| C(6)–C(1)–C(11) | 121.5 | 119.6 | | | 1.679 |
| C(2)–C(1)–C(11) | 121.5 | 120.2 | O(13)···H(17)–N(10) | 2.586 | 2.675 |
| C(1)–C(6)–C(5) | 121.2 | 120.6 | O(14)–H(15)···O(14r) | – | 2.656 |
| C(4)–C(5)–C(6) | 120.5 | 120.3 | O(13)···H(17)–N(10) | 128.4° | 127.0° |

Wavenumbers

The observed IR and Raman bands with their relative intensities, calculated wavenumbers and assignments are presented in Table 2.

C=O vibrations — The C=O bond is strongly polarized towards oxygen. Oxygen compounds featuring double or cumulated double bonds, provide a unique spectrum, typically with a single ^{34,35} normally intense absorption in the range 2290-2300 cm⁻¹. Electron withdrawing groups, such as -Cl, -F, -Br, -NO₂, -OH or CF₃, decrease the IR band intensity and increase the wavenumber value to the higher limit of the characteristic spectral region²⁴, whereas electron- donating groups, such as the amino group, increase the IR intensity and decrease the wavenumber.

Experimentally in mono-substituted benzoic acid, this vibration appears in the range 2240-2260 cm⁻¹, whereas in disubstituted benzoic acid at 2270 cm⁻¹ in accordance with scaled values of 2259 cm⁻¹ in 4-amino-5-bromo benzoic acid with an IR intensity that varies from medium-weak to strong depending on the substituent. In the present case, the stretching mode $\nu(\text{C}=\text{O})$ is observed at 1655 in IR and at 1652 cm⁻¹ in Raman corresponding to theoretically observed band at 1672 and 1641 cm⁻¹ (Table 2). As in benzoic acid molecule and its derivatives, this stretching mode appears with the strongest Raman intensity. The intensity is enhanced by the conjugation of the phenyl ring.

In organic chemistry, a carbonyl group is a functional group composed of a carbon atom double-bonded to an oxygen atom: C=O. The term carbonyl can also refer to carbon monoxide as a ligand in an inorganic or organo metallic complex (a metal carbonyl, e.g. nickel carbonyl. The C=O group is affected insignificantly by a new substituent on the phenyl ring. Hence, the vibrational wavenumber of the carbonyl group remains almost unchanged from the benzoic acid molecule. Intermolecular hydrogen bonds can be responsible for the geometry and the stability of a predominant conformation; the intermolecular formation of hydrogen bonding between a hydroxyl group O COH cause the present structure of compound to be the most stable. Electron withdrawing groups, such as -Cl, -F, -Br, -NO₂, -OH or CF₃, decrease the IR band intensity and increase the wavenumber value to the higher limit of the characteristic spectral region²⁸, whereas electron- donating groups, such as the amino group, increase the IR intensity and decrease the wavenumber. In the present case, the stretching mode $\nu(\text{C}=\text{O})$ is observed at 1655 cm⁻¹ in IR and at 1652 cm⁻¹ in Raman corresponding to theoretically observed band at 1672 cm⁻¹ and 1641 cm⁻¹ (Table 2). As in benzoic acid molecule and its derivatives, this stretching mode appears with the strongest Raman intensity.

C- Br vibration — The vibrations belonging to the bond between the ring and the halogen atom are worth to discuss since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence

of heavy atoms on the periphery of the molecule. The assignments of C-Br group vibrations have been made by comparison with the halogen- substituent benzene derivatives. Mooney^{32,33} assigned vibrations of C-X group (X = Cl, Br, I) in the frequency range 1129-480 cm⁻¹. The C-Br stretching vibrations give generally strong bands in the region 710-505 cm⁻¹. However, vibrational coupling with other groups may result in a shift in the absorption band as high as 840 cm⁻¹. For simple bromine containing organic compounds C-Br absorptions are in the region 750-700 cm⁻¹. In the present study, the band observed at 635 cm⁻¹ in the Raman spectrum and 631 cm⁻¹ in IR spectrum has been identified as C-Br stretching corresponding to theoretically calculated value 617 cm⁻¹ (HF/6-31G*) and 607 cm⁻¹ (HF/6-311G*). This mode is not pure but contains significant contributions from other modes.

C-H vibrations — The C-H stretching vibrations occur above 3000 cm⁻¹ and are typically exhibited as weak to moderate bands^{34,35}. In the present study, the bands observed at 3121 cm⁻¹ in the Raman spectra are identified as the C-H stretching modes of the phenyl ring, which correspond to theoretically calculated values 3065 cm⁻¹. The band is absent in IR spectra which corresponds to theoretical value of 3065 cm⁻¹.

The out-of-plane and in-plane C-H bending vibrations of the phenyl ring are expected to appear in the range 700-1000 cm⁻¹ and 1000-1300 cm⁻¹, respectively. Generally, the C-H out-of-plane deformations with the higher wavenumbers have weaker intensity than those absorbing at lower wavenumbers. In the present study, the out-of-plane C-H vibrations are identified at 875 cm⁻¹ in the Raman spectrum and at 845 cm⁻¹ in the IR spectrum which correspond to theoretically calculated values 817 cm⁻¹ in Raman and IR spectrum.

C-C vibrations—There are six equivalent C-C bonds in benzene and consequently, there will be six C-C stretching vibrations. In addition, there are several in-plane and out-of-plane bending vibrations of the ring carbons. The bands observed at 1623, 1561, 1410, 1360, 790 cm⁻¹ in IR spectrum and 1651, 1525, 1417, 1333, 756 cm⁻¹ in Raman spectrum are identified as ring stretching modes. The corresponding calculated values for these modes appear at 1629, 1551, 1420, 1431, 778, 321 in Raman spectra and 1630, 1554, 1419, 1432, 789, 312 in IR spectra (HF).

Table 2 — Calculated vibrational wavenumbers (scaled), measured infrared and Raman bands positions and assignments in 2-amino-5-bromo benzoic acid

| No. | $\nu[(\text{HF}/6-311+ \text{G}^*) (\text{cm}^{-1})]$ | $\nu(\text{HF}/6-31\text{G}^*) (\text{cm}^{-1})$ | Experimental | | IR Intensity | Raman activity | Assignments |
|-----|---|--|-----------------------------------|--------------------------------------|--------------|----------------|---|
| | | | $\nu(\text{IR}) (\text{cm}^{-1})$ | $\nu(\text{Raman}) (\text{cm}^{-1})$ | | | |
| 1 | 3022 | 3045 | 3461 | | 112 | 148 | νOH (100) |
| 2 | 3547 | 3547 | 3401 | | | 90 | $\nu(\text{NH}_2)\text{asym.}$ (100) |
| 3 | 3414 | 3414 | 3398 | 3391 | 111 | 160 | $\nu(\text{NH}_2)\text{sym.}$ (100) |
| 4 | 3065 | 3065 | | 3121 | 1 | 45 | νCH (100) |
| 5 | 3054 | 3054 | | | 0 | 121 | νCH (100) |
| 6 | 3029 | 3033 | 2915 | | 12 | 112 | νCH (100) |
| | | | 2853 | | 425 | 95 | (1287 + 1566) combination |
| | | | 2798 | | 201 | 26 | (1399 × 2) overtone CH in plane bending |
| | | | 2712 | | 198 | 6 | (1135 + 1577) combination |
| | | | 2682 | | 85 | 29 | (1341 × 2) overtone CC stretching |
| | | | 2545 | | 80 | 31 | (1465 + 1080) combination |
| | | | 2490 | | 21 | 18 | (1416 + 1074) combination |
| 7 | 1672 | 1641 | 1655 | 1652 | 99 | 10 | $\nu\text{C}=\text{O}$ (71) |
| 8 | 1630 | 1629 | 1651 | 1623 | 45 | 14 | νCC (39) + $p\text{NH}_2$ (29) + $\nu\text{C}-\text{NH}_2$ (10) |
| 9 | 1578 | 1583 | 1601 | | 42 | 10 | $p\text{NH}_2$ (43) + νCC (35) |
| 10 | 1554 | 1551 | 1525 | 1561 | 3 | 5 | νCC (52) + $i\text{NH}$ of NH_2 (18) |
| 11 | 1455 | 1479 | 1490 | 1485 | 182 | 9 | $i\text{CH}$ (43) + νCC (25) |
| 12 | 1419 | 1420 | 1417 | 1410 | 229 | 25 | νCC (47) |
| 13 | 1432 | 1431 | 1333 | 1360 | 90 | 19 | νCC (25) + $\nu\text{C}-\text{COOH}$ (18) + $i\text{OH}$ (16) + $\nu\text{C}-\text{OH}$ (14) |
| 14 | 1345 | 1345 | 1305 | | 131 | 8 | νCC (31) + $\nu\text{C}-\text{NH}_2$ (18) |

| | | | | | | | |
|----|------|------|------|------|-----|----|---|
| 15 | 1331 | 1327 | 1285 | | 5 | 7 | ν CH (42) + ν CC (16) + ν NH of NH ₂ (12) + ν C–NH ₂ (12) |
| 16 | 1294 | 1294 | 1247 | 1265 | 1 | 2 | ν CH (39) + ν CC (26) + ν C–NH ₂ (10) |
| 17 | 1241 | 1240 | 1171 | 1155 | 0 | 5 | ν CH (34) + ν OH (26) |
| 18 | 1160 | 1160 | 1165 | | 15 | 15 | ν CH (40) + ν CC (22) + ν OH (17) + ν C–COOH (10) |
| 19 | 1117 | 1114 | 1117 | | 41 | 1 | ν CC (41) + ν C–OH (12) |
| 20 | 1085 | 1086 | | | 15 | 2 | ν C–OH (33) + ν CC (20) |
| 21 | 1023 | 1023 | | 1189 | 16 | 29 | ν NH ₂ (40) + ν CC (28) |
| 22 | 965 | 965 | 1055 | | 15 | 5 | μ CH (82) |
| 23 | 912 | 911 | 899 | | 68 | 6 | μ CH (87) |
| 24 | 868 | 865 | 882 | | 25 | 8 | ν CCC (42) + ν C–NH ₂ (11) |
| 25 | 817 | 817 | 845 | 875 | 21 | 2 | μ CH (73) + ν CCC (12) |
| 26 | 675 | 678 | 821 | | 131 | 4 | ν C–C–OH (65) |
| 27 | 789 | 778 | 756 | 790 | 6 | 0 | ν CC (36) + ν C–COOH (14) |
| 28 | 788 | 787 | 666 | | 0 | 0 | μ CCC (65) + μ C–C–OH (27) |
| 29 | 688 | 686 | | | 4 | 2 | ν C=O (52) |
| 30 | 607 | 617 | 631 | 635 | 8 | 6 | Ring def. (48) + ν C–Br (20) |
| 31 | 585 | 585 | | | 10 | 4 | ν NH ₂ (96) |
| 32 | 941 | 857 | 552 | | 2 | 3 | μ OH (79) |
| 33 | 435 | 431 | 521 | | 8 | 4 | μ CCC (58) |
| 34 | 544 | 528 | | | 1 | 8 | ν (C–COOH) (36) + ν (C–NH ₂) (20) |
| 35 | 312 | 321 | 445 | 439 | 185 | 2 | μ CCC (77) |
| 36 | 435 | 432 | | | | 2 | ν (C–C=O) (40) + ν (C–NH ₂) (36) |
| 37 | 381 | 376 | | 390 | 19 | 0 | ν (C–NH ₂) (22) + ν (C–COOH) (19) + ν CCC (18) + ν (C–COOH) (16) |
| 38 | 529 | 520 | | 325 | 14 | 1 | μ (2A5BrBA) (88) |
| 39 | 328 | 328 | | | | | ν (C–COOH) (83) + ν C–Br (23) |
| 40 | 274 | 274 | | 295 | | | ν C–Br (43) |
| 41 | 222 | 220 | | | | | ω NH ₂ (92) |
| 42 | 188 | 181 | | 189 | | | ν C–Br (54) + ν (C–COOH) (30) |
| 43 | 147 | 139 | | 131 | | | μ (2A5BrBA) (85) |
| 44 | 112 | 110 | | 110 | | | μ CNH ₂ (34) + μ C–Br (22) |

ν , stretching; ι , in plane bending; μ , out of plane bending; p , scissoring; ω , wagging; τ , torsion; t , twisting; r , rocking. [Frequency (cm⁻¹), IR intensities, I_{IR} (K mmol⁻¹), Raman scattering activities, S_{Raman} (Å amu⁻¹)].

Table 3 Calculated energies values, chemical hardness and dipole moments of 2-amino-5-bromo benzoic acid in Ethanol and Water.

| DFT/B3LYP/6-311++G(d,p) | Ethanol | Water | Gas |
|-------------------------------|----------------|----------------|----------------|
| E_{total} (hartree) | -3048.75896426 | -3048.75215879 | -3048.74589620 |
| E_{HOMO} (eV) | -6.10251 | -6.6523 | -6.12564 |
| E_{LUMO} (eV) | -1.48752 | -1.79523 | -1.89452 |
| $O_{EHOMO-LUMO}$ gap (eV) | 4.28361 | 4.25642 | 4.21546 |
| E_{HOMO-1} (eV) | -6.915656 | -7.65231 | -7.72102 |
| E_{LUMO+1} (eV) | -0.6825 | -0.65214 | -0.25469 |
| $O_{EHOMO-1-LUMO+1}$ gap (eV) | 7.23553 | 7.23587 | 6.12546 |
| Chemical hardness (ι) | 3.14231 | 2.12569 | 2.23568 |
| Dipole moment (Debye) | 3.1365 | 2.85610 | 2.21503 |

5. Vibrational analyses

The 2-amino-5-bromo benzoic acid molecule consists of 17 atoms, and so it has 45 normal vibrational modes. On the assumption of C_s symmetry point group, the number of vibrational modes of the 45 fundamental vibrations is divided into $31A_r + 14A_{rr}$. The vibrations of the A_r species are in plane modes and those of the A_{rr} species are out-of-plane modes. Therefore, the structure was not a minimum energy structure. However, if the molecule has C_1 symmetry there would not be any relevant distribution and molecule has minimum energy structure. The experimental (in solid state) and theoretical (in vacuum) Infrared and Raman spectra of in 2-amino-5-bromo benzoic acid are shown in Fig. 3, where the calculated intensity is plotted against the wavenumbers. The experimental (in solid state) and theoretical (in vacuum) Infrared and Raman spectra of in 2-amino-5-bromo benzoic acid are shown in Fig. 3, where the calculated intensity is plotted against the wavenumbers.

The high frequency region above 3000 cm^{-1} is the characteristic region for the ready identification of C–H and O–H stretching vibrations⁴³. The O–H stretching is characterized by a very broad band appearing near about $3400\text{--}3600\text{ cm}^{-1}$. The carboxylic acid O–H stretching bands are weak in the Raman spectrum, so IR data are generally used. On the other hand, the hydrogen-bonded carboxylic acid possesses a form that has a center of symmetry and hence the two monomers can vibrate in-phase and out-of-phase with respect to each other. The in-phase (symmetric) vibration is only Raman active, whereas the out-of-phase (antisymmetric) vibration is only IR active. The band observed in FT-IR at 3461 cm^{-1} is assigned to out-of-phase O–H stretching. While the in-plane O–H bending modes were observed at 1158 and 1165 cm^{-1} in FT-Raman.

The three adjacent hydrogen atoms around the ring give rise three C–H stretching modes. As expected, all stretching vibrations are very pure modes. The C–H in-plane bending frequencies appear in the range of $1000\text{--}1300\text{ cm}^{-1}$ and C–H out-of-plane bending vibration in the range of $750\text{--}1000\text{ cm}^{-1}$. Both in plane and out of plane C–H bending vibrations were assigned in the expected region (see Table 2). According to the calculated TED, the out-of-plane vibrations are described as pure. The change in the frequencies of these deformations from the values in benzene is almost determined exclusively by the relative position of the substituent and is almost independent of their nature.

The band observed in the $1700\text{--}1800\text{ cm}^{-1}$ region due to the C=O stretching vibration is one of the characteristic features of the carboxylic group. Carboxylic acids with two vibrations, symmetric and antisymmetric, are expected like O–H stretching. The antisymmetric stretch is usually seen at a higher wavenumber than the symmetric stretch⁴⁵. On this basis, the vibrational wavenumber described by mode 7 is assigned to the C=O stretching mode. The antisymmetric C=O stretch is observed in FT-IR as very strong band at 1655 cm^{-1} (symmetric stretching vibration at 1652 cm^{-1} in Raman) and is predicted at 1669 cm^{-1} . Due to the hydrogen bonding effect through the carboxyl groups, and therefore C=O stretching mode in dimer conformation, this vibration was calculated at 1672 and 1641 cm^{-1} . The symmetric and antisymmetric stretches due to the amino group appear in the spectral region as O–H stretching bands. The antisymmetric stretching for the CH_2 , NH_2 and has magnitude higher than the symmetric stretching⁴⁴. The amino group bands were obtained at 3401 for FT-IR, antisymmetric stretching and 3398 , 3391 for FT-IR and FT Raman, symmetric stretching respectively.

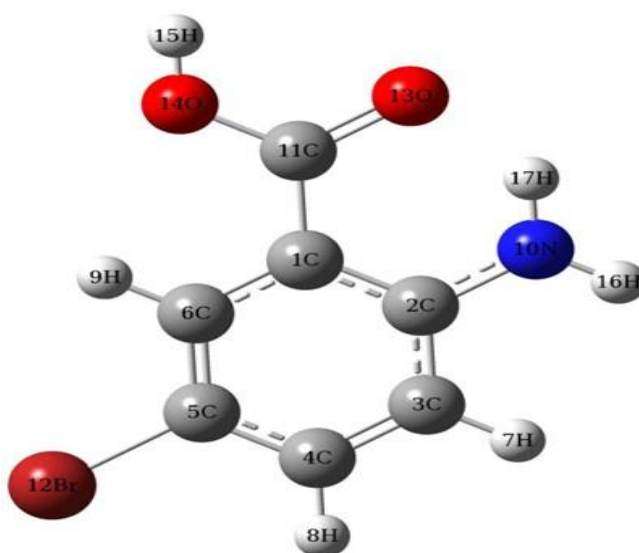


Fig. 3: The theoretical optimized structure and atom 2-amino-5-bromo benzoic acid

In order to investigate the performance of vibrational wavenumbers of the title compound, root mean square (RMS) values between calculated and observed wavenumbers were calculated using the following expression⁶³.

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

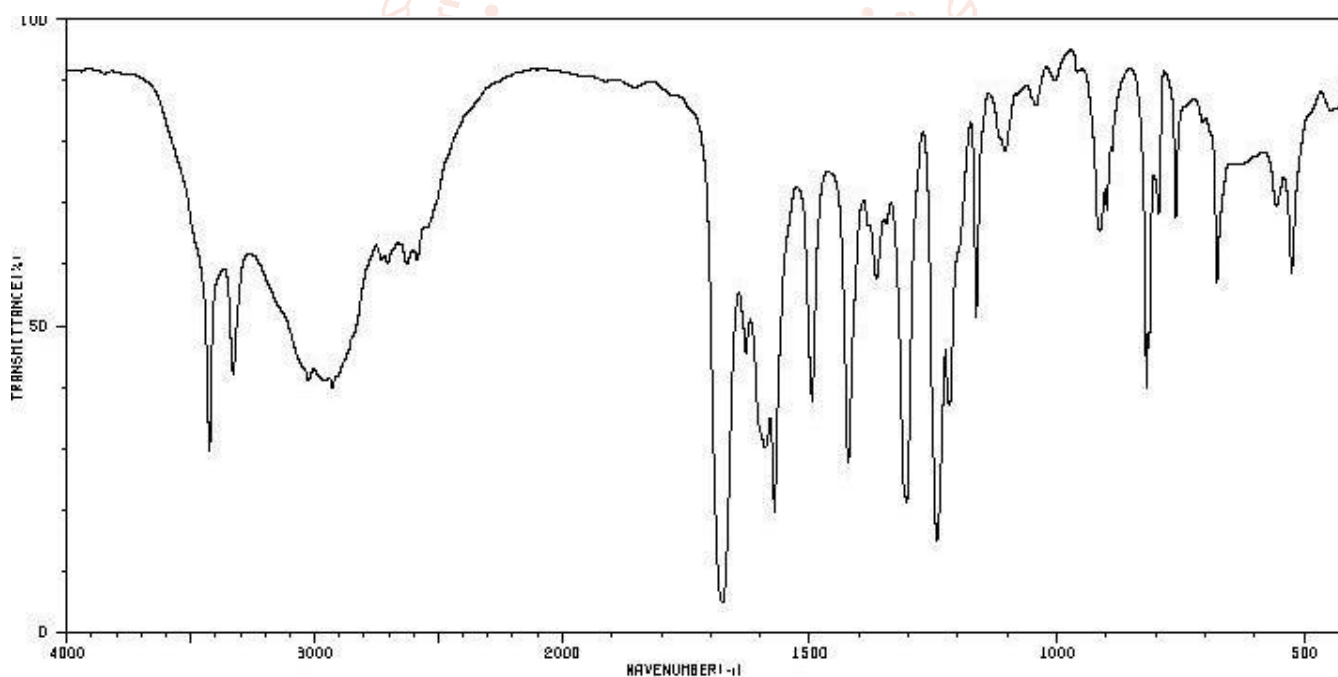
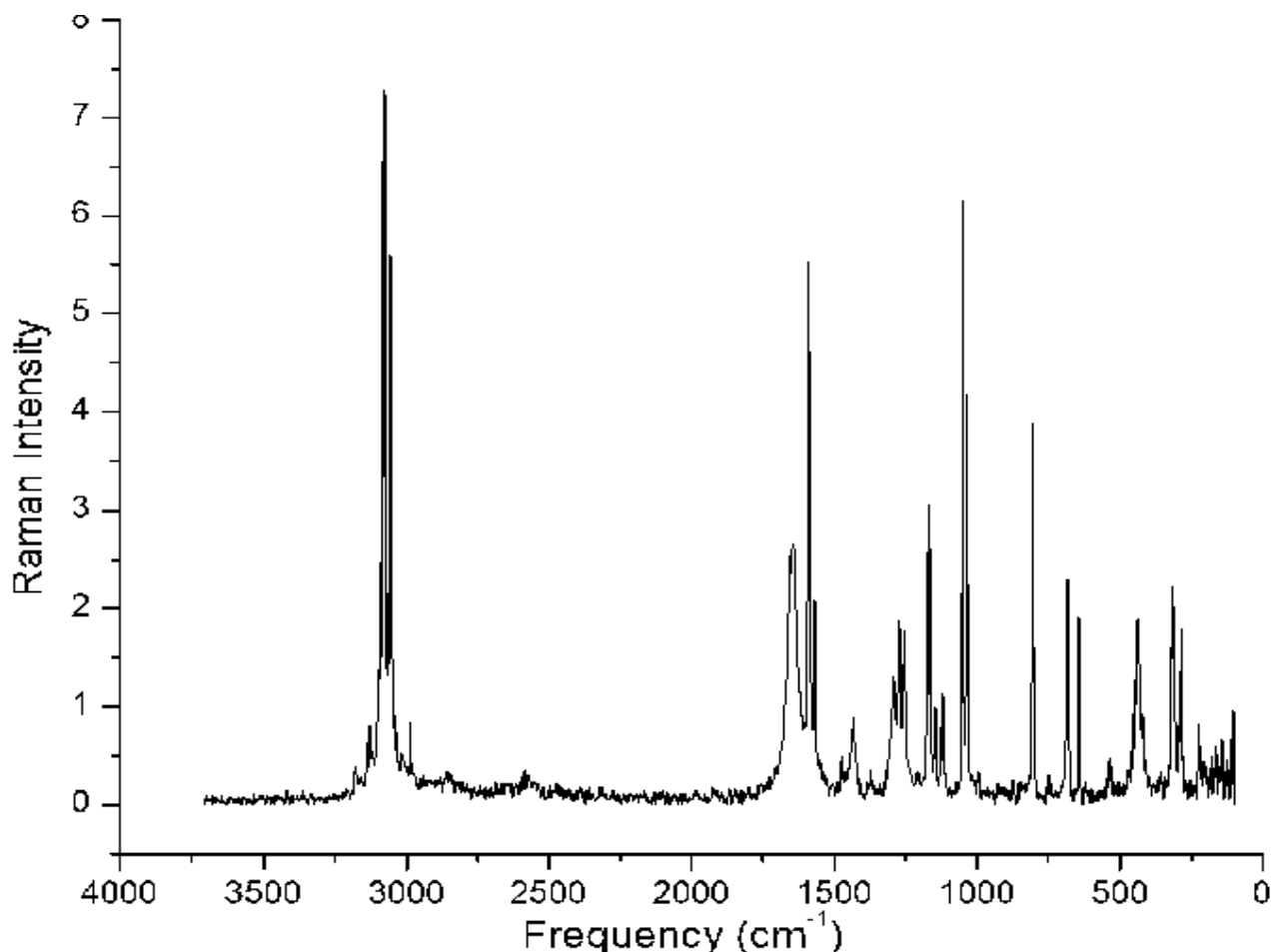
The RMS error of the observed IR and Raman bands were found to be 38.76 (HF/6-31G*), 23.74 (HF/6-311+G*) and 36.32 (HF/6-31G*), 23.69 (HF/6-311+G*), respectively. The small difference between experimental and calculated vibrational modes is observed. It must be due to the fact that hydrogen bond vibrations present in the crystal lead to strong perturbation of the IR wavenumbers and intensities of many other modes. Also, we state that experimental results belong to the solid phase and theoretical calculations belong to the gaseous phase.

First hyperpolarizability—In present study, the electronic dipole moment, molecular polarizability, anisotropy of polarizability and molecular first hyperpolarizability of present compound were investigated. It is known that the significance of the polarizability and the first hyperpolarizability of molecular systems is dependent on the efficiency of electronic communication between acceptor and the donor groups. Analysis of organic molecules having conjugated π -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has been evolved as a subject of research⁴⁷. The potential applications of the substituted benzonitriles demand the investigation of their structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectra. In the present study, the ring stretching bands at 1655, 1651, 1525, 1417, 1333, 756 cm^{-1} observed in IR have their counterparts in Raman at 1652, 1623, 1561, 1410, 1360, 790 cm^{-1} , respectively and their relative intensities in IR and Raman spectra are comparable. The first hyperpolarizability (β_0) of this molecular system can be calculated using HF/6-311+G* basis set, 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. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry⁴⁶. The components of β 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:

6. Conclusions

The equilibrium geometries and the harmonic frequencies of 2-amino-5-bromobenzoic acid were determined and analyzed. The small distortions of the benzene ring are explained in terms of the change in hybridization affected by the substituent at the carbon site to which it is appended. An accurate assignment of the vibrational bands was carried out with the help of HF method. The difference between the observed and calculated wavenumber values of most of the fundamentals is very small and therefore, the assignment seems to be correct. The most stable monomer conformer of compound was determined, and according to the results the dimer conformation was analyzed with B3LYP/6-311++G level of theory. Based on calculated energy differences, the C1 conformer is found to be most the stable conformer. The hydrogen bonding between a hydroxyl group O=COH was determined as dimer structure. Besides the recorded vibrational spectra, SQM have also been used to calculate total energy distributions in order to make conspicuous vibrational assignments. The overtone and combination bands were described in region 2500–2900 cm^{-1} in FT-IR spectrum.

Attempts have been made in the present work for the proper vibrational band assignments for the compound 6-aminouracil from the FTIR and FT Raman spectra. The equilibrium geometries and harmonic frequencies of 6-aminouracil were determined and analyzed both at HF and DFT levels of theories utilizing 6-31G(d,p) basis set, giving allowance for the lone pairs through diffuse functions. It is apparent that good reproductivity of the experimental wavenumber is obtained at the B3LYP level, and the percentage error is very small. Any discrepancy noted between the experimental and the calculated vibrational bands assignments may be due to the fact that the calculations have been actually done on a single molecule, whereas the experimental values are recorded in the presence of inter molecular interaction. Therefore, the assignments made at higher levels of theory with only reasonable deviations from the experimental values seem to be correct.



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