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2–Amino–5–Bromobenzoic Acid: A Dft Study for Structural and Molecular Orbital Analysis of Tautomeric Forms

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Abstract - 2–Amino–5–bromobenzoic acid (ABBA) and its tautomeric forms have been investigated for structural properties and molecular orbitals. HOMO–LUMO surfaces and FT–IR, FT–RAMAN analysis were carried out in an integrated approach. The molecule was handled as a sum of three tautomeric forms one of which has four isomers. The molecule was examined as a whole and partially according to tautomeric forms and geometrical isomers. For quantum chemical calculations, DFT was used in the B3LYP level and 6.31G* basis set. Computations were carried out via SPARTAN 14 software.

Keywords: benzoic acid derivatives, DFT, Spectral analysis, HOMO LUMO, tautomery

2–Amino–5–Brom Benzoik Asidin Tautomerik Formlari:Yapisal Ve Moleküler Orbital Analizi İçin Bir Dft Çalişmasi

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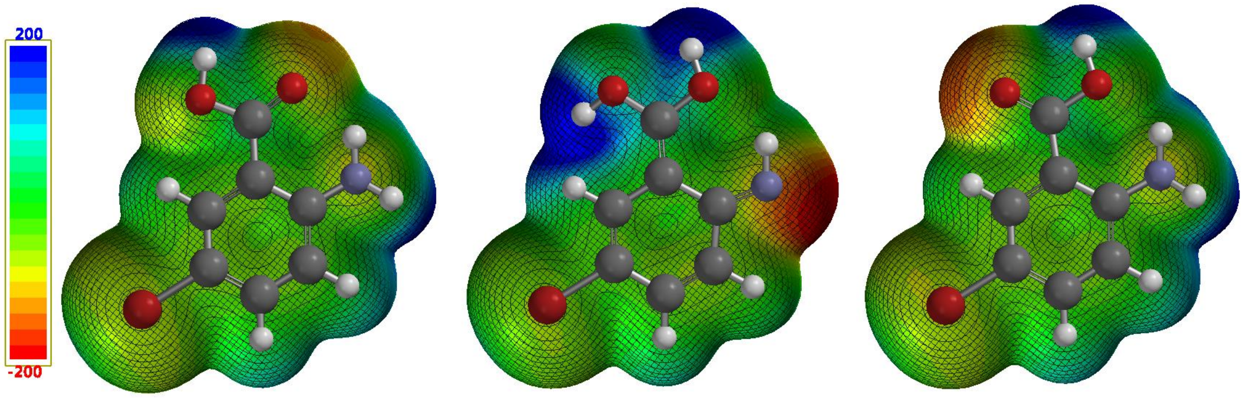
Öz - 2–Amino–5–brom–benzoik asit (ABBA) ve tautomerik formlarını yapısal özellikleri, molekül orbitalleri bakımından incelenmiştir. HOMO–LUMO yüzeyleri ve FT–IR, FT–RAMAN analizleri tümleşik bir yaklaşımla gerçekleştirilmiştir. Molekül, içlerinden biri dört geometrik izomere sahip olan üç tautomerik formun bir toplamı olarak ele alınmıştır. Molekül bir bütün olarak ve kısmen de geometrik izomerlere göre araştırılmıştır. Kuantum kimyasal hesaplamalarda B3LYP düzeyinde ve 6.31G* temel setinden yararlanarak DFT (YFK) kullanılmıştır. Tüm hesaplama işlemleri SPARTAN 14 yazılımıyla gerçekleştirilmiştir.

Anahtar kelimeler: Benzoik asit türevleri, DFT, Spektroskopik analiz, HOMO LUMO, Tautomerlik

GRAPHICAL ABSTRACT: Tautomeric Forms of 2–Amino–5–Bromobenzoic Acid: A DFT Study for Structural and Molecular Orbital Analysis



1. Introduction

Benzoic acid (BA) is an organic compound that is widely found in animal and plant tissues and is used in a wide area of applications. Benzoic acid and derivatives are mostly used for their miticidal activities and pharmacological activities. Also, they are used as co–anesthetics [1].

BA is particularly found in plants, free and in the form of compounds. Gum benzoin from where BA was obtained for the first time contains 20% benzoic acid. BA is found in most of the fruits (approximately 0.05%) in the urine of the herbivorous mammals as the form of benzoyl glycine (hippuric acid) derivative. BA is easily soluble in hot water, alcohol and ether. BA is slightly soluble in cold water as well. Its solubility in water increases in the presence of alkali substances such as borax and trisodium phosphate. It also dissolves in substances such as chloroform, acetone, carbon tetrachloride, benzene, carbon sulfide, turpentine, essential oils [2–4]. The aqueous solution is acidic and slightly stronger than acetic acid. It has irritant effects on the skin, eyes and mucous membranes, causes coughs when breathed. It is commercially manufactured by the chemical reaction of toluene with oxygen at temperatures around 200°C using cobalt and manganese salts as catalysts. Pure benzoic acid melts at 122°C. BA derivatives and BA esters are used for the protection of foods, oils, juices, alkaloid solutions, etc., producing benzoates, benzoyl compounds and colorants, as mordants in fabric printing, tobacco processing. Also, it is used as a standard in volumetric and calorimetric analyzes in analytical chemistry. Some prominent derivatives of benzoic acid are sodium benzoate, used as a food preservative, benzyl benzoate, used as a miticide, and benzoyl peroxide, used in initiating chemical reactions for producing plastics materials and in bleaching flour [5, 6].

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. Experimental and theoretical chemists carried out a large number of studies on BA 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 AXBA[7]. The crystal structure of m–bromobenzoic acid [8], 3,5–dibromo–4–aminobenzoic acid [9] and 4–amino–3–bromobenzoic acid were published by Tanaka et al., Pant and Arshad et al respectively [10]. Ferguson and Sim analyzed the molecular structure of 2–bromobenzoic acid in detail [11]. Swaminathan et al. carried out a spectroscopic and theoretical study on the vibrational spectra of 2–bromobenzoic acid

[12]. Sundaraganesan et al. [13–15] have experimentally studied the FT–IR and FT–Raman spectra of 5–amino–2–chlorobenzoic acid, methyl benzoate and 2–amino–4,5–difluorobenzoic acid. The antibacterial activity and effect on bacterial DNA synthesis of 4–aminobenzoic acid were examined by Richards and Xing [16]. 4–aminobenzoic acid and 2–aminobenzoic acid were investigated for their toxicity on cell suspension cultures of Solanum mammosum by Syahrani et al. [17].

Swislocka et al recorded the vibrational and NMR spectra of 4–aminobenzoic acid and its alkali metal salts [18]. 2,3,4–chlorobenzoic acids' IR and Raman spectra were investigated for the effect of the position of chloride in the aromatic ring [19]. Both spectroscopic properties and biological activities of the compounds similar to 2–amino–5–bromobenzoic acid (ABBA) were investigated by Xavier and Joe with F, Cl and Br [8]. The vibrational behaviors of ABBA were examined by Sundaraganesan et al. [20].

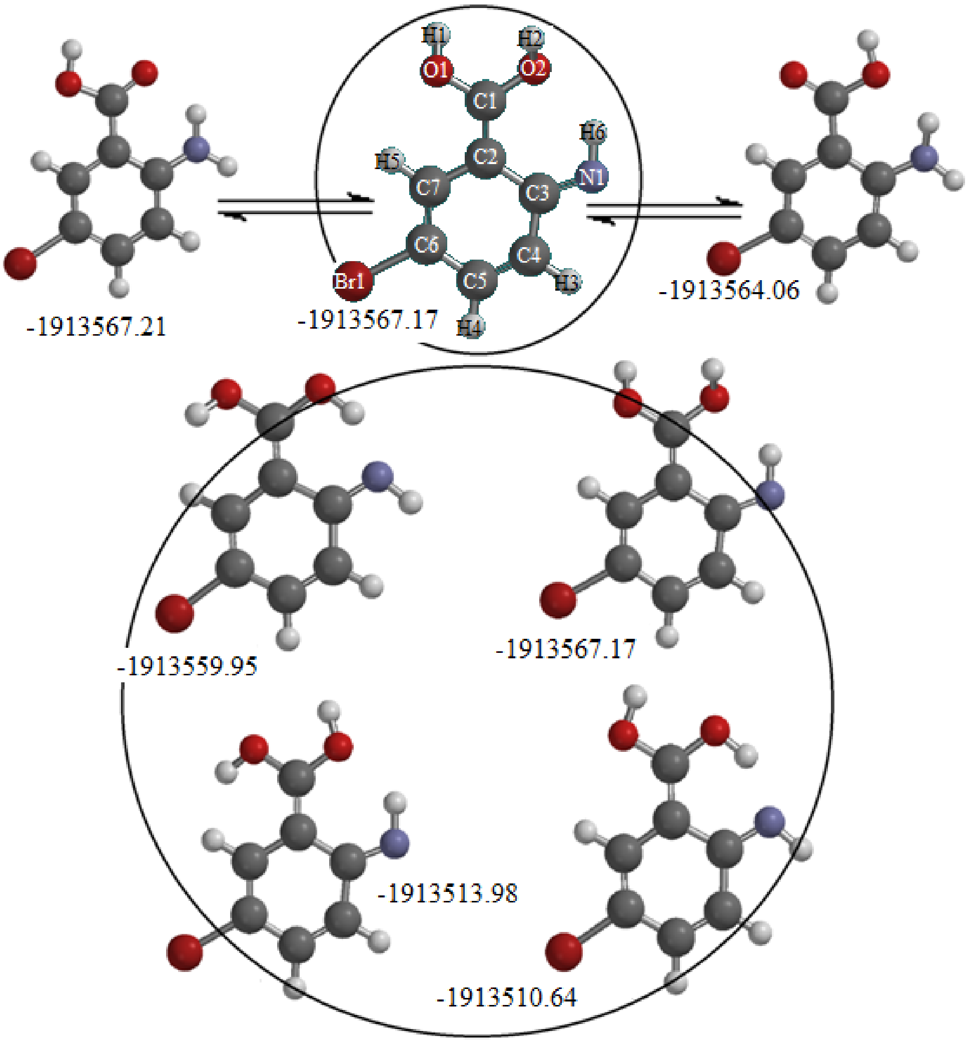


Figure 1. Tautomeric forms of compound ABBA and isomers of the hypotethical tautomer 2 (energies in kcalmol^{-1})

2. Experimental Part

2.1. Computational details

For computational analysis of the compound ABBA, the SPARTAN–14 quantum chemistry suite was used [21,22]. For the theoretical calculations, 6–31G* basis set was used in the B3LYP level of DFT method [23–25]. There are two reasons for choosing the method and basis set; first, the former studies handled the same molecule so that an opportunity for comparison was obtained. Later, this system is widely used for reducing the time needed [26]. ABBA has three tautomeric forms one of which has four conformations; Cis–Cis, Cis–Trans, Trans–Cis and Trans–Trans (Figure.1). For this reason, all calculations for the second tautomer has been repeated for each of these conformations separately. Although it is claimed in the literature that this tautomeric form does not exist, this fact does not prevent us from examining this isomer, at least hypothetically. The obtained results have been tabulated under corresponding divisions. MO surfaces and spectral graphics are depicted in corresponding figures in the following parts of this manuscript. The results which software produced were used as they were obtained without any scaling factors or any further refined corrections. To keep the study simple and to focus on some certain details some detailed studies were left out for further studies such as more complicated computational studies or medical applications etc.

There is a huge archive of spectral data for the compound ABBA which had been studied by several researchers so far. For this reason, in this study, the existing experimental spectroscopic data have been used.

2.2. Structure of the compound

As mentioned before the title compound has three tautomeric forms (T1, T2 and T3) and one of these tautomeric forms has four geometrical isomers which will be called CC, CT, TC and TT (C for Cis– and T for Trans–) respectively in the following lines (Figure 1). As can be seen from Figure 1, the least energetic tautomer of the compound was found to be the first form which has a carboxylic and a primary amine moieties together. In this study, the molecular structure of the title compound and spectral data is going to be examined according to this fact [28]. Although the second tautomer is only a hypothetical form it is worth to be examined for understanding the reason for its absence in real conditions.

Molecular Structure: Like any other compound, the molecular structure of ABBA 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 structure [9, 10] and after some adaptations, these values were used.

Calculated and experimental bond lengths are tabulated in Table 1 comparatively. As seen in Table 1, among the calculated values, T1 is the closest to the experimental results comparing with the others. It is an expected reflection of the fact that T2 is an intermediate step with different conformers. In table 1 some relatively abnormal values that are made evident by being underlined and italicized reflect migrations of H atoms between tautomeric forms. Another notable point in Table 1 is that the T1 and T2/TC values are comparatively close to each other among the other ones.

Table 1. Calculated and experimental bond lengths(Ǻ) for the compound ABBA.

BOND	T1	T2					T3	Exp*
		CC	CT	TC	TT	Total		
O1,C1	1.356	1.358	1.352	1.357	1.360	1.352	1.215	1.234
O2,C1	1.227	1.218	1.340	1.227	1.358	1.340	1.371	1.312
C1,C2	1.470	1.487	1.373	1.469	1.364	1.373	1.479	1.462
C2,C7	1.409	1.408	1.452	1.409	1.455	1.452	1.409	1.376
C7,C6	1.381	1.384	1.353	1.381	1.350	1.353	1.380	1.382
C6,Br1	1.920	1.917	1.919	1.921	1.920	1.920	1.920	1.888
C6,C5	1.402	1.400	1.443	1.402	1.446	1.443	1.401	1.407
C5,C4	1.383	1.384	1.352	1.382	1.351	1.352	1.383	1.377
C4,C3	1.415	1.415	1.467	1.416	1.467	1.467	1.415	1.365
C3,N1	1.363	1.365	1.294	1.358	1.293	1.294	1.372	1.376
C3,C2	1.426	1.427	1.495	1.427	1.499	1.495	1.424	1.402
H1,O1	*2.240*	0.970	0.971	0.975	0.974	0.971	0.975	0.820
H2,O2	*5.230*	0.986	0.974	*1.928*	0.974	0.974	*5.246*	**
H6,N1	1.013	1.009	1.020	1.007	1.021	1.020	1.009	0.920
H5,C7	1.082	1.086	1.087	1.083	1.083	1.087	1.083	0.930
H4,C5	1.085	1.085	1.085	1.085	1.085	1.085	1.085	0.930
H3,C4	1.087	1.087	1.085	1.087	1.085	1.085	1.087	0.930

*= borrowed from ref (5 and 10)   **= not exist for this conformer/isomer

Computationally found and experimentally measured bond angles of the compound ABBA have been tabulated comparatively in Table 2. In this table again some comparatively abnormal values that are underlined and italicized, reflect migrations of H atoms between tautomeric forms. These values are not stable between conformers. Except for these unstable values which reflect the immigrant H's the general results are in a close agreement with experimental ones. However, the most plausible results were seen surprisingly at T3 excluding H1O1C1 and H2O2C1 angles.

As a presupposition, any small compound with a benzene ring can be expected to be perfectly planar. But the compound ABBA has slightly deviated from this rule. When Table 3 was revised in a sketchy way, the first point to be noticed is; T2/TC column is filled with 180 and 0.00 degrees which shows the molecule is perfectly planar. But in other columns, there are different degrees even less or more. The experimental values are very near to 180° (and/or 0.00°) with about 7.1 (172.9)° as the biggest torsion degree.

HOMO–LUMO analysis and Electronic Transitions: As the T1 Tautomeric form has the minimum energy according to calculations, it has been accepted as the reference point and other values have been compared according to this value. In Table 5 calculated energies and energy differences have been presented comparatively. In the table, the data are presented in two parts. In the first part, the energy values and the differences in the T1 form are shown. In the second part, the values of the T2/TT isomeric form are presented. The energy differences can be calculated using Eq.1.

$$\Delta E = E(C0) - E(T1) \qquad \text{or}$$

$$\Delta E = E(C0) - E(TC) \qquad \text{Eq. 1}$$

Table 2. Calculated and experimental bond angles (°) for the compound ABBA

BOND ANGLE	T1	T2						Exp*
		CC	CT	TC	TT	Total	T3	
H1,O1,C1	110.14	108.61	110.12	102.63	109.12	110.14	*6.49*	109.5
H2,O2,C1	108.28	107.33	108.27	106.40	109.01	108.28	*56.57*	109.5(!)
O1,C1,O2	110.68	114.01	110.68	114.35	114.72	110.68	120.38	121.8
O2,C1,C2	123.15	123.09	123.16	124.15	123.30	123.15	125.80	123.4
O1,C1,C2	126.17	122.90	126.15	121.50	121.97	126.17	113.81	114.7
C2,C7,C6	120.96	121.90	120.96	121.71	120.44	120.96	120.61	120.2
C7,C6,Br1	120.26	121.68	120.28	121.79	120.25	120.26	120.00	119.5
Br1,C6,C5	118.17	117.46	118.16	117.53	117.70	118.17	119.66	119.0
C7,C6,C5	121.56	120.86	121.55	120.68	122.04	121.56	120.35	121.5
C6,C5,C4	119.62	122.47	119.63	122.59	119.74	119.62	119.79	117.1
C5,C4,C3	123.74	120.70	123.73	120.62	123.38	123.74	121.64	121.8
C3,C2,C7	119.09	117.55	119.10	118.21	119.23	119.09	119.81	118.5
H6,N1,C3	111.60	110.78	111.58	110.40	111.09	111.60	117.67	116.0
N1,C3,C2	128.93	122.27	128.92	122.04	128.49	128.93	122.22	121.6
N1,C3,C4	116.32	121.31	116.34	121.77	116.48	116.32	119.96	121.3
C3,C2,C1	122.57	118.85	122.57	119.24	119.23	122.57	120.22	120.7
C1,C2,C7	118.30	123.59	118.29	122.54	117.56	118.30	119.96	120.7
H3,C4,C5	121.35	121.16	121.35	121.20	121.52	121.35	119.61	119.1
H4,C5,C6	119.18	118.17	119.17	118.02	119.10	119.18	120.25	119.6
H5,C7,C2	120.18	118.76	120.18	117.62	118.32	120.18	118.82	119.9
*= borrowed from ref (5 and 10)								

TORSION ANGLE	T1	T2					T3	Exp*
		CC	CT	TC	TT	Total		
H1,O1,C1,O2	–169.90	–167.70	164.20	0.00	42.72	164.20	–152.79	x
H2,O2,C1,O1	0.00	164.11	–9.14	0.00	36.38	–9.04	–0.10	x
H1,O1,C1,C2	9.78	12.40	–16.15	180.00	–138.00	–16.15	26.68	x
H2,O2,C1,C2	–179.64	–16.00	171.19	180.00	–142.89	171.31	–179.63	x
O2,C1,C2,C3	–0.92	17.08	–8.55	0.00	8.58	–8.55	–2.21	–5.3
O2,C1,C2,C7	178.08	–161.01	173.77	180.00	–173.43	173.77	177.22	178.0
O1,C1,C2,C7	–1.58	18.89	–5.84	0.00	7.36	–5.84	–2.28	–3.7
O1,C1,C2,C3	179.41	–163.02	171.83	180.00	–170.64	171.85	178.29	172.9
C1,C2,C3,N1	–3.21	1.68	7.58	0.00	–6.26	7.56	–3.61	175.6
C1,C2,C7,C6	–178.63	–179.92	173.16	180.00	–175.32	173.12	–178.95	176.3
C2,C7,C6,Br1	–179.94	179.97	179.31	180.00	179.75	179.13	179.77	179.5
C2,C7,C6,C5	0.18	–0.23	0.26	0.00	–0.02	0.27	0.01	–0.9
C2,C3,C4,C5	0.58	1.53	–4.16	0.00	3.25	–4.13	0.43	–3.2
H4,C5,C4,H3	0.33	–0.19	–0.37	0.00	0.35	–0.38	0.53	x
H6,N1,C3,C4	–171.89	15.23	–178.63	0.00	178.31	–178.65	–167.53	x
C1,C2,C3,C4	178.26	179.31	–171.39	180.00	173.78	–171.38	178.69	–176.8
C1,C2,C7,H5	1.07	2.97	–10.25	0.00	4.01	–10.32	0.73	x
C2,C3,N1,H6	9.60	–167.19	150.08	180.00	–1.65	2.43	14.79	x
C2,C3,C4,H3	–179.88	–178.69	176.98	180.00	–178.01	177.00	179.90	x
N1,C3,C4,H3	1.55	–1.62	–2.13	0.00	2.03	–2.08	2.07	x
H4,C5,C6,Br1	–0.14	–1.58	2.28	0.00	–0.58	2.47	0.01	x
Br1,C6,C7,H5	0.37	–1.43	2.67–	0.00	0.44	2.53	0.10	x
H2,O2,O1,H1	**	48.79	146.04	180.00	74.57	146.14	**	**
*= borrowed from ref (5 and 10) **= not exist in this conformer/isomer x=not found in literature								

Table 3. Calculated and experimental Dihedral angles (°) for the compound ABBA.

Table 4. Calculated Energies of the MO surfaces.

EMO (Ev)	**T1**	**T2**						**T3**
		CC	**CT**	**TC**	**TT**	**Ave**	**Total**	
LUMO{+1}	–0.0	–0.4	–0.2	0.0	0.0	**–0.15**	–0.2	–0.1
LUMO	–1.4	–1.6	–1.9	–1.4	–2.0	**–1.725**	–1.9	–1.4
HOMO	–5.7	–5.9	–5.3	–5.7	–5.4	**5.575**	–5.3	–5.8
HOMO{–1}	–7.4	–7.5	–6.7	–7.3	–6.8	**–7.15**	–6.7	–7.3
HOMO{–2}	–7.7	–7.8	–7.4	–7.7	–7.4	**–7.575**	–7.4	–7.7
HOMO{–3}	–7.8	–8.0	–7.7	–7.8	–7.7	**–7.8**	–7.7	–7.8
HOMO{–4}	–7.9	–8.1	–8.0	–7.9	–7.8	**–7.95**	–8.0	–7.8
HOMO{–5}	–8.8	–8.8	–9.1	–8.8	–9.0	**–9.025**	–9.1	–8.9
HOMO{–6}	–9.5	–9.7	–9.9	–9.5	–9.8	**–9.775**	–9.9	–9.5
HOMO{–7}	–10.0	–10.2	–10.1	–9.9	–9.9	**–10.025**	–10.1	–9.9
HOMO{–8}	–10.3	–10.5	–10.3	–10.3	–10.1	**–10.3**	–10.3	–10.1
HOMO{–9}	–10.8	–10.9	–10.6	–10.8	–10.4	**–10.675**	–10.6	–10.9

According to these results, T1 was found to be 56.57 and 3.15 kcalmol^{-1} more stable than T2 and T3, while TT isomeric conformer of T2 was found to be 7.22, 53.19 and 56.53 kcalmol^{-1} more stable than the conformers CC, CT and TC respectively.

Due to these relations between energy values T1 form has been chosen as a symbol for representing the electronic transitions and visualization of e^{-} transfer between MO's in Figure 2.

Table 5 The energy equivalencies for the transitions between other conformers and T1 and T2/TT

Conformers	Energy (Hartree)	Energy Diff.			Eq. Freq. (cm^{-1})	Dip. Moment (Debye)
		(Hartree)	($kcalmol^{-1}$)	(eV)		
T1	–3049.46281	0.0	0.00	0.00	0.00	2.41
T2	–3049.37266	0.09015	56.569991	2.4531076	19785.638	4.60
T3	–3049.45779	0.00502	3.1500982	0.13660122	1101.7626	4.87
CC	–3049.45124	0.01151	7.2226356	0.3132032	2526.153	2.85
CT	–3049.37798	0.08477	53.193989	2.3067103	18604.864	4.60
TC	–3049.37266	0.09009	56.532341	2.4514749	19772.469	2.53
TT	–3049.46275	0.0000	0.0000	0.0000	0	5.39

Table 6 Molecular orbital energies and differences for conformers of the compound ABBA (* From Ref[1])

		HOMO–1	HOMO	LUMO	LUMO+1	ΔE (eV)			λ_{max}					
						ΔE_1	ΔE_2	ΔE_3	Calc.			Exper* (Eth/water/Gas)		
Isomers & Conformers	T1	–7.4	–5.7	–1.4	0.0	6.0	4.3	5.7	206.64	288.34	217.52	346 / 324 / 337.5	257 / 250 / 269.2	**217** / **210** / **249.2**
	T2	–6.7	–5.3	–1.9	–0.1	4.8	3.4	5.2	258.30	364.66	238.43			
	T3	–7.3	–5.8	–1.4	–0.2	5.9	4.4	5.6	210.14	281.78	221.40			
	CC	–7.5	–5.9	–1.6	–0.4	5.9	4.3	5.5	210.14	288.34	225.43			
	CT	–6.7	–5.3	–1.9	–0.2	4.8	3.4	5.1	258.30	364.66	243.11			
	TC	–7.3	–5.7	–1.4	0.0	5.9	4.3	5.7	210.14	288.34	217.52			
	TT	–7.4	–5.4	–2.0	0.0	5.4	3.4	5.4	229.60	364.66	229.60			

*Borrowed from Ref. (5)

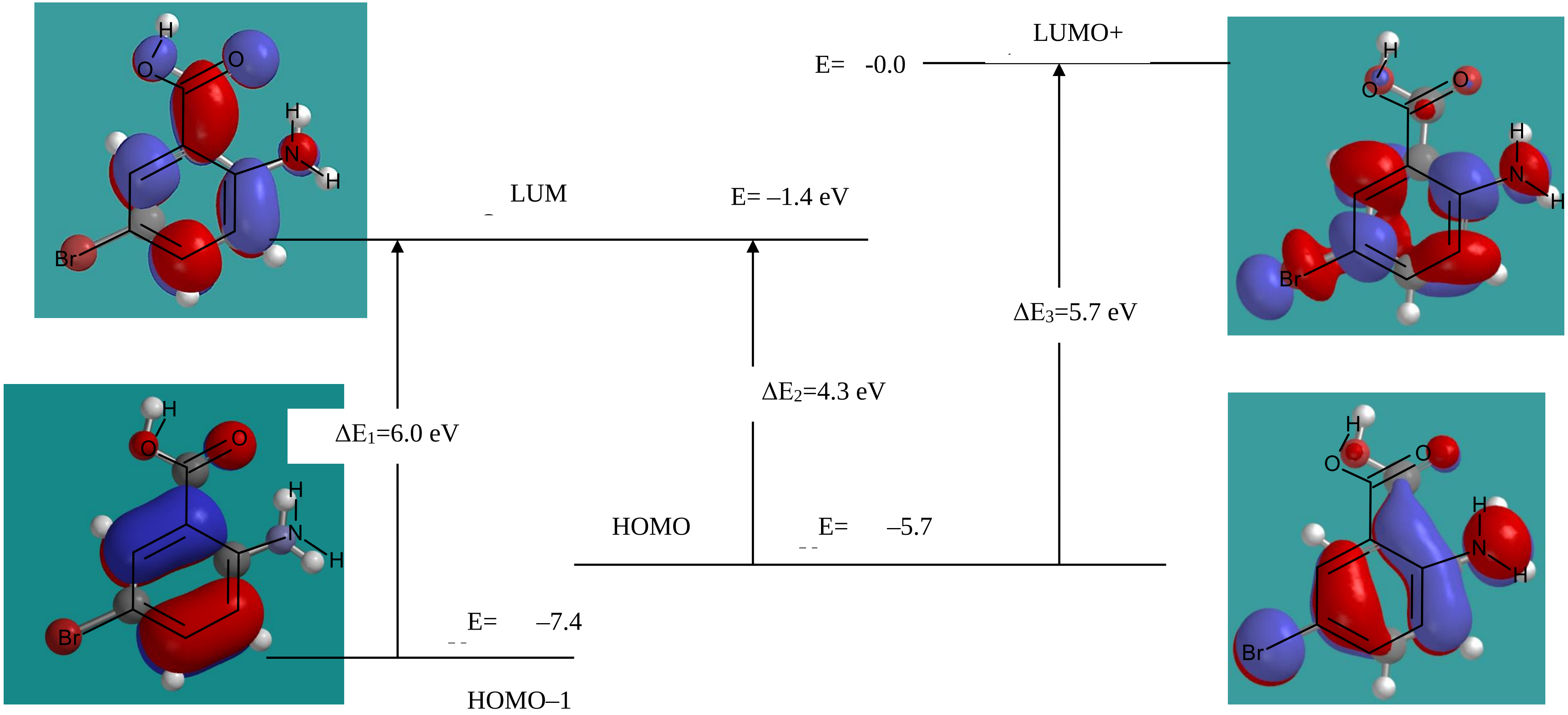


Figure 2. Electron transitions and energy differences between MO’s.

Mulliken charge distribution: On a molecule, the electronic distribution causes heterogeneity of charges so that some parts of the molecule gains a negative or positive charge depending on the electronic density. The electron-rich parts of the molecule form a preferred site for electrophilic attacks.

Mulliken charge distribution was calculated according to the DFT / B3LYP method and 6.31G* basis set. The calculated values were transferred into Graph 1. As shown in the graphic, all of the H atoms have a considerable positive charge. C atoms have divided into mainly two species according to atomic charges; C6 slightly negative due to Br1 while C1,2,3 which are neighbors to O1, O2 and N1 atoms prominently have positive charges. But C4, C5 and C7 have negative charges due to the H atoms which are electropositive. The most dramatic negative charges have been observed on the O1, O2 and N1 atoms. The calculated Mulliken charge distribution graphics were depicted in Figure. 3 and Graph. 1 respectively. Also, all charge values including natural and electrostatic charges can be found in the supplementary material.

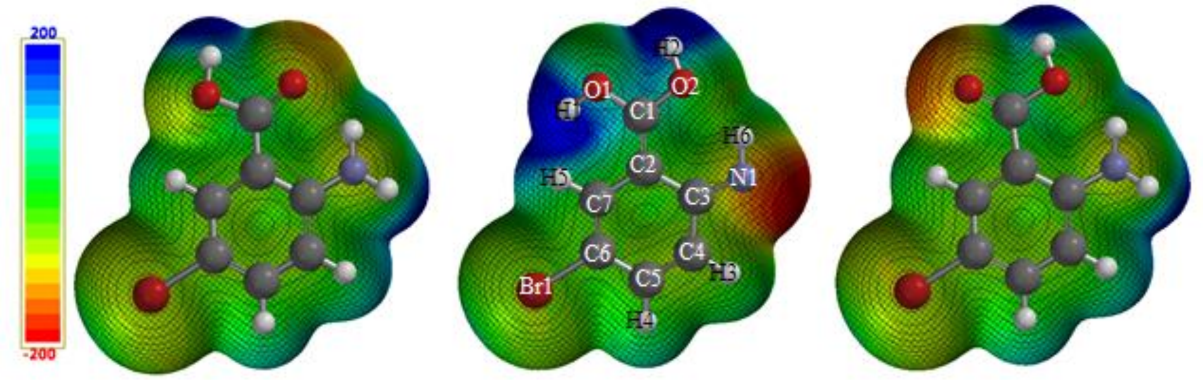
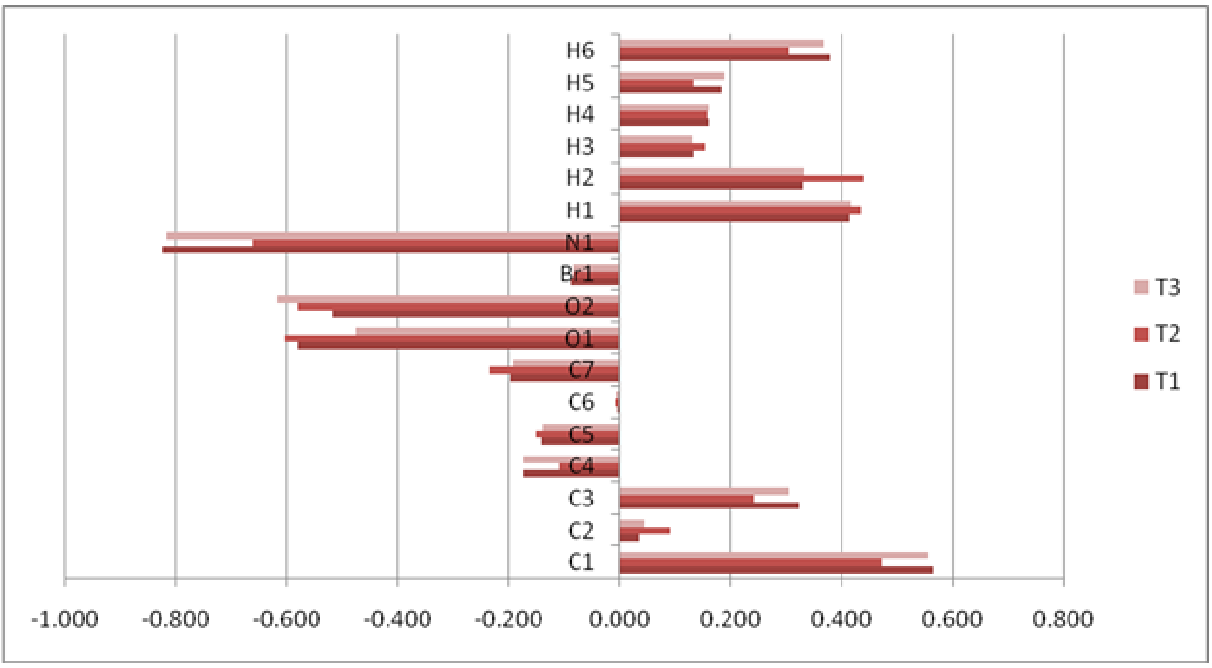


Figure 3. Electrostatic potential map (ESP Map) for the forms of the compound ABBA



Graph. 1. Calculated Mulliken charge distribution of compound ABBA

2.3. Vibrational spectroscopy (FT–IR and FT_RAMAN)

The molecule has 17 atoms and that means 45 vibrational modes in three main parts. Carboxyl group, amine group and benzene. The most mechanically active parts of the molecule are the carboxyl group and the amine group. They exhibit rocking, swinging and every kind of mechanical motions beside H immigrations between each other. For this reason, the molecule is not a simple carboxylic acid and nor a primary amine.

In the literature that ignored the tautomeric forms, F, Cl and Br analogs of ABBA were described as planar but in this study, the calculations clearly showed that some forms of the molecule have a considerable torsion.

As a brief analysis, the frequencies and their corresponding bonds have been tabulated in Table 7. In the table, the isomers of T2 were not involved. These results can be found in the supplementary material. Even so, some dramatic points should be underlined.

In T1 carbonyl C=O (C1O1) bond length is 1.227Ǻ while the same distance 1.234Ǻ which is 7Ǻ longer than the former for T3. The frequency values are in agreement with this difference 1776cm^{-1} and 1810cm^{-1} respectively.

C3–N1 bond distance is 1.363 and 1.372 between T1 and T3 respectively. The frequency values which are 883cm^{-1} and 873cm^{-1} are in good agreement with them.

Table 7. The calculated and experimental vibrational spectra for ABBA

No	DFT / B3LYP6.31G			Experimental[1]			Total energy Distribution[2,3]
	T1	T2	T3	FT–IR[a]	FT–IR[b]	FT–RAMAN	
1*	75	66	62			68	τCOOH (79)
2*	117	94	110			103	γCNH2 (33) +γC–Br (21)
3*	140	129	144			130	γ(2A5BrBA) (83)
4*	146	150	147			186	δC–Br (53) +r(C–COOH) (29)
5*	285	268	286				ωNH2 (90)
6*	291	278	301			282	υC–Br (53)
7*	310	287	312				r(C–COOH) (63) +γC–Br (22)
8*	314	365	378			315	γ(2A5BrBA) (88)
9*	380	397	384			382	r(C–NH2)(21)+υ(C–COOH) (18)+δCCC(16)+δ(C–COOH) (16)
10*	423	414	404				δ(C–C=O) (39) + r(C–NH2)(34)
11*	429	423	434	441		435	γCCC (77)
12*	524	449	494				r(C–COOH) (37)+r(CNH2)(19)
13*	530	507	532	518			γCCC (63)
14*	596	539	550	555			γOH (81)
15*	614	612	601				τNH2 (94)
16	647	636	648	629	616	628	Ring def. (47) + υC–Br (18)
17	669.	638	650				δC=O (51)
18	707	726	706	688	676		γCCC (61) +γC–C–OH (24)
19	778	740	768	789	778	784	υCC (33) +υC–COOH (13)
20	787	825	783	816	815		δC–C–OH (72)
21	824	838	822	870	874	869	γCH (73) + δCCC (11)
22	883	877	879	888	890		δCCC (42) +υC–NH2 (10)
23	921	894	939	912	1046		γCH (87)
24	959	999	960	1089	1084	1090	γCH (82)
25	1078	1058	1076				rNH2 (40) +υCC (28)
26	1100	1068	1116				υC–OH (33) + υCC (20)
27	1135	1114	1120	1127	1124		υCC(41)+ υC–OH (12)

28	1197	1203	1194	1158	1159		δCH (40) + υCC (22) + δOH (17) + υC–COOH (10)
29	1209	1208	1207	1168	1160	1167	δCH (34) + δOH (26)
30	1313	1270	1294	1238	1230	1239	δCH(39) +υCC (26) +υC–NH2(10)
31	1351	1282	1331	1292	1256		δCH (42) + υCC (16) + δNH of NH2 (12) +υC–NH2 (11)
32	1371	1353	1357	1311	1290		υCC (31) +υC–NH2 (18)
33	1414	1411	1390	1342	1354	1339	υCC (29) +υC–COOH(16) + γOH (15) +υC–OH (14)
34	1458	1446	1469	1422	1424	1405	υCC (49)
35	1527	1461	1530	1481	1484	1484	δCH (48) +υCC (23)
36	1599	1594	1607	1547	1560	1551	υCC (52) + γNH of NH2 (18)
37	1642	1612	1658	1583	1586		ρNH2 (43) +υCC (35)
38	1678	1670	1691	1609	1618	1613	υCC (39)+ρNH2 (29) + υC–NH2 (10)
39	1776	1706	1810	1667	1692	1633	υC=O (71)
40	3186	3182	3182	2988	2521 2570 2623 2705 2834 2875 2972		1292+1583 cmb. 1167×2 o.t. CH ipb 1158+1547 cmb. (1311×2) o.t. CC str. 1481+1089 cmb. 1609+912 cmb. υCH (100)
41	3221	3212	3222				υCH (100)
42	3255	3229	3246			2722	υCH (100)
43	3542	3509	3590			2786	υ(NH2)sym. (100)
44	3692	3711	3689			2864	υ(NH2)asym. (100)
45	3700	3755	3705			2952	υOH (100)

[1]Received from Ref. 5 [2]values less then 10% omitted. [3]υ= stretching; δ= in–plane bending; γ=out of plane bending; ρ= scissoring; ω= wagging; τ= torsion; t, twisting; r, rocking. [Frequency (cm−1), a=in solid–phase b= as dissolved in 1,4–dioxane

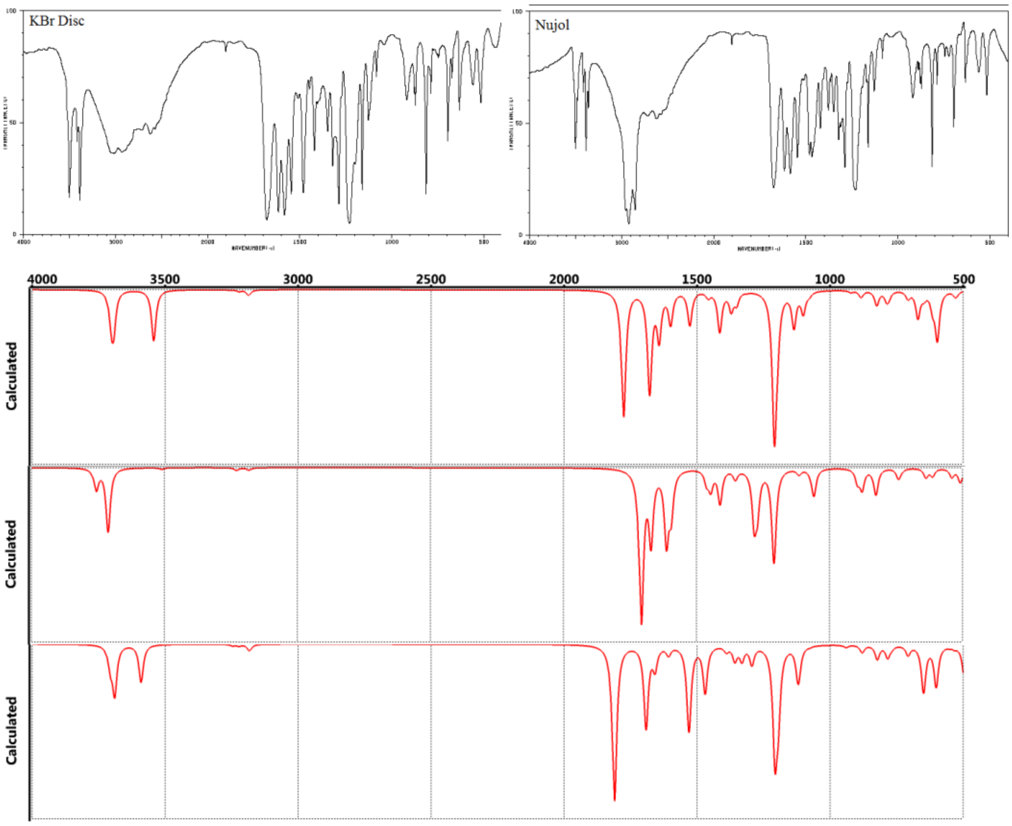


Figure 4. Calculated and experimental FT–IR spectra of compound ABBA

3. Conclusions

The molecular structure and HOMO–LUMO analysis have been carried out by using the SPARTAN 14 suite via DFT theory in the B3LYP level and 6.31 G* basis set. Also, FT–IR and FT–RAMAN spectra were calculated and compared to experimental results as well.

The compound had been studied by different research groups from different aspects but in this study, the calculations were handled in a new point of view, tautomeric transformations were examined for the first time as well.

As a result of all studies, the calculated and experimental values were found to be very close and in agreement.

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References

1. Hiji Y., Miyoshi M., Ichikawa O., Kasagi T., Imoto T., *Effects of butyric acid and analogues on amylase release from pancreatic segments of sheep and goats,* Arch. Int. Physiol. Biochem. 95 (1987) p. 113–120.
2. Ana del Olmo, Javier Calzada, and Manuel Nun~ez " Benzoic acid and its derivatives as naturally occurring compounds in foods and asadditives: Uses, exposure, and controversy" Critical Reviews In Food Science And Nutrition (2017) 57,(14), 3084–3103
3. Lewandowski W., Fuks L., Kalinowska M., Koczon P., *The influence of selected metals on the electronic system of biologically important ligands,* Spectrochim. Acta Part A 59 (2003) p. 3411–3420.
4. Dr Wibbertmann A., Dr Kielhorn J., Dr Koennecker G., Dr Mangelsdorf I., and Dr Melber C.,"*Benzoic Acid And Sodium Benzoate Cicad*" Fraunhofer Institute for Toxicology and Aerosol Research, Hanover, Germany
5. Karabacak M., Cinar M., *FT–IR, FT–Raman, UV spectra and DFT calculations on monomeric and dimeric structure of 2–amino–5–bromobenzoic acid,* Spectrochimica Acta Part A 86 (2012) p. 590 –599
6. Saxena A., Agrawal M., Gupta A., *Vibrational study, molecular properties and first-order molecular hyperpolarizability of Methyl 2–amino 5–bromobenzoate using DFT method,* Optical Materials 46, 2015, p. 154–167
7. Xavier T.S., Hubert.J., *FT–IR, Raman and DFT study of 2–amino–5–fluorobenzoic acid and its biological activity with other halogen (Cl, Br) substitution*, Spectrochimica Acta Part A, 79 (2011) p. 332–337.
8. Tanaka N., Ashida T., Sasada Y., Kakudo M., *Structural Determination, spectroscopic and nonlinear optical features of 2–acetamido–5–bromobenzoic acid by experimental techniques and quantum chemical calculations*, Bull. Chem. Soc. Jpn. 40 (1967) p. 2717–2723.

9. Pant A.K., *The crystal structure of 3,5–dibromo–p–aminobenzoic acid at room temperature (25°C approx.) and at –l50°C,* Acta Crystallogr. 19 (1965) p. 440–448.
10. Arshad M.N., Tahir M.N., Khan I.U., Shafiq M., Waheeda A., *4–Amino–3–bromobenzoic acid,* Acta Crystallogr. E 65 (2009) p. o640
11. Ferguson G., Sim G.A., *Crystal structure of 2–bromo-benzoic acid at 120 K: a redetermination* Acta Crystallogr. 15 (1962) p. 346–350.
12. Swaminathan J., Ramalingam M., Saleem H., Sethuraman V., M.T.N. *FT–IR and FT–Raman vibrational assignment of 2–bromobenzoic acid with the help of ab initio and DFT calculations* Spectrochim, Acta Part A 74 (2009) p. 1247–1253.
13. Sundaraganesan N., Joshua B.D., Settu K., *Vibrational spectra and assignments of 5–amino–2–chlorobenzoic acid by ab initio Hartree–Fock and density functional methods* Spectrochim. Acta Part A 66 (2007) p. 381–388.
14. Sundaraganesan N., Joshua B.D., *Vibrational spectra and fundamental structural assignments from HF and DFT calculations of methyl benzoate,* Spectrochim. Acta Part A 68 (2007) p. 771–777.
15. Sundaraganesan N., Ilakiamani S., Joshua B.D., *FT–Raman and FT–IR spectra, ab initio and density functional studies of 2–amino–4,5–difluorobenzoic acid,* Spectrochim. Acta Part A 67 (2007) p. 287–297.
16. Richards R.M.E., Xing D.K.L., *The effect of p–aminobenzoic acid on the uptake of thymidine and uracil by Escherichia coli* Int. J. Pharm. 116 (1995) p. 217–221.
17. Syahrani A., Ratnasari E., Indrayanto G., Wilkins A.L., *Biotransformation of o– and p–aminobenzoic acids and N–acetyl p–aminobenzoic acid by cell suspension cultures of Solanum mammosum,* Phytochemistry, 51 (1999) p. 615–620.
18. Swislocka R., Samsonowicz M., Regulska E., Lewandowski W., *Molecular structure of 4–aminobenzoic acid salts with alkali metals,* J. Mol. Struct. 792–793 (2006) p. 227–238.
19. Koczon P., Baranska H., Lewandowski W., *Vibrational and NMR studies on o–, m–and p–chlorobenzoic acids,* Asian J. Phys. 3 (1994) p. 71–79.
20. Sundaraganesan N., Saleem H., Mohan S., *FTIR and laser Raman spectra of 2–amino–5–bromobenzoic acid,* Indian J. Phys. 78 (6) (2004) p. 489–494.
21. SPARTAN’14 Wavefunction Inc. Irvine CA, USA, (2014)
22. Hehre W.,J., “*SPARTAN’14 Tutorial and User's Guide*”, 2014 Wavefunction, Inc
23. Silverstein R., M., Webster F., X. Kiemle D., J. “*Spectrometric Identification of Organic Compounds*” 7th Ed. John Wiley Sons INC. 2005
24. Ramachandran K. Deepa I., G., Namboori K., “*Computational Chemistry and Molecular Modeling: Principles and Applications*”, Springer–Verlag 2008 Heidelberg Berlin.
25. Jensen F., “*Introduction to Computational Chemistry*” Wiley 2016
26. Karakaş-Sarıkaya, E., “*Investigation molecular and radical structures of three-carboxyfuran by DFT and EPR on gas-phase*”, Journal of Spectroscopy and Molecular Sciences 2(2) (2020),

p. 44–50

27. Peter K., Vollhardt C., Schore N., E.. “*Organic chemistry: structure and function*” 6th ed. Freeman&Comp. 2011 NY–US pp. 682,731,742,870–90