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Synthesis, spectroscopic characterization and theoretical studies of (4-boronobenzoyl)serine

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ABSTRACT

(4-boronobenzoyl)serine (4BBS) was synthesized and investigated theoretically and experimentally by spectroscopic methods such as FT-IR, Raman and NMR. The molecular structure, spectroscopic parameters and geometric parameters were determined by computational methods. All theoretical calculations were carried out using B3LYP method and 6-311 + +G(d,p) basis set. Total energy distribution analysis of normal modes was performed to identify characteristic frequencies. To investigate structure of title molecule using NMR, ^{1}H, ^{13}C, ^{13}C APT, ^{1}H-^{17}O and ^{1}H-^{15}N HMQC, ^{1}H-^{13}C HMBC, ^{1}H-^{13}C HETCOR, ^{1}H-^{1}H NOESY and ^{1}H-^{1}H COSY NMR experiment were performed. These results should be useful for the experts in their studies based on functionalized phenylboronic acid derivatives.

1. Introduction

Serine (Ser) molecule is one of the most commonly found amino acid in proteins. Construction of building blocks for new cellular components required to to grow of cells. These components are proteins, lipids and nucleic acids. Amino acid such as serine, glycine, etc. and the carbon units satisfies many of these requirements. Therefore, amino acids are essential for all living creature [1–3].

On the other hand, boronic acid and its derivates have increasingly important due to their wide application potentials in the field such as material science, supramolecular chemistry, analytical chemistry, medicine, biology, catalysis and organic synthesis [4–6].

Phenylboronic acid and its derivatives and serine have been characterized by various spectroscopic and theoretical methods [7–14]. Much more effective and important molecules can reveal by bonding serine molecule with boronic acid derivative molecules.

The main objective of this work is to investigate the interactions and conformation states of title molecule having boronic acid and serine moieties together using various spectroscopic methods. The structure of title molecule was characterized by spectroscopic methods such as FT-IR, Raman and NMR. Moreover, geometric parameters, vibrational assignments and wavenumbers of title molecule were investigated using density functional theory (DFT) method. The results of these spectroscopic and theoretical studies are herein reported.

2. Materials and methods

2.1. Experimental

FT-IR spectrum of title molecule were recorded by KBr pellet technique in the region of 4000–400 cm^{-1} with Perkin Elmer Spectrum2 spectrometer at a resolution of 2 cm^{-1}. Raman spectrum was obtained by a Renishaw Invia spectrometer with 532 nm excitation having 2 cm^{-1} resolution in the spectral region of 4000–400 cm^{-1}. UV–VIS spectra of title molecule was recorded in the range of 200–400 nm with PerkinElmer Lambda 750S spectrophotometer.

NMR experiments of title molecule were recorded on JEOL ECZ 500R spectrometer at room temperature. The operating frequencies were 500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C, 67.78 MHz for ^{17}O and 50.66 MHz for ^{15}N. Deuterated dimethyl sulfoxide was used as solvent.

2.2. Synthesis

Step 1: Commercially available 4-carboxyphenylboronic acid 1, (1 eq.) was refluxed with $SOCl_2$ (excess) under nitrogen atmosphere for 1 h. Excess thionylchloride was evaporated under vacuum to obtain crude (4-(chlorocarbonyl)phenyl)boronic acid, 2 which was further used in next step without any purification.

Step 2: L-Ser-OH (1 eq.) was suspended in water. Upon addition of 1.0 N NaOH (2 eq.), L-Ser-OH was dissolved. Solution of product 2

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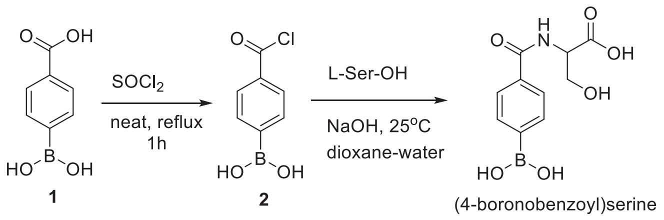


Fig. 1. Synthesis method for (4-boronobenzoyl)serine.

(1 eq.) in dioxane was added dropwise. Reaction mixture was allowed to stirr for 1 h. at room temperature. Dioxane was removed under vacuum and residue water solution was acidified to pH = 2–3 with 2.0 N HCl. Product was extracted with ethylacetate (3x 25 mL) dried over anhydrous sodium sulphate and filtrated. Collected organic layer was dried under vacuum to obtain (4-boronobenzoyl)serine in 82% yield as White microcrystals Fig. 1.

2.3. Computational details

All the calculations were performed using Gaussian 09 program package [15] and GaussView 5.0.8 [16] was used for determination geometric parameters, indication of the title molecule and simulation of the vibrational spectra. Based on orientations of boronic acid hydrogens against phenyl ring bonded to boron atom, the compound has four possible monomer isomers identified as cis-cis (cc), cis-trans (ct), trans-trans (tt) and trans-cis (tc) (Fig. 2). Moreover, title molecule has anhyride structure as is given in Fig. S1. For all the monomer computations, the tc isomers in C_1 symmetry were optimized using DFT method and B3LYP functionals in conjunction with the 6-311 + +G(d,p) basis set in the gas phase. Vibrational frequencies and geometric parameters were computed with 6-311 + +G(d,p) basis set in the gas phase. Vibrational frequencies were scaled with SQM program [17,18] to generate the corrected frequencies. The fundamental normal modes were assigned and the total energy distribution (TED) calculations were carried out by the SQM.

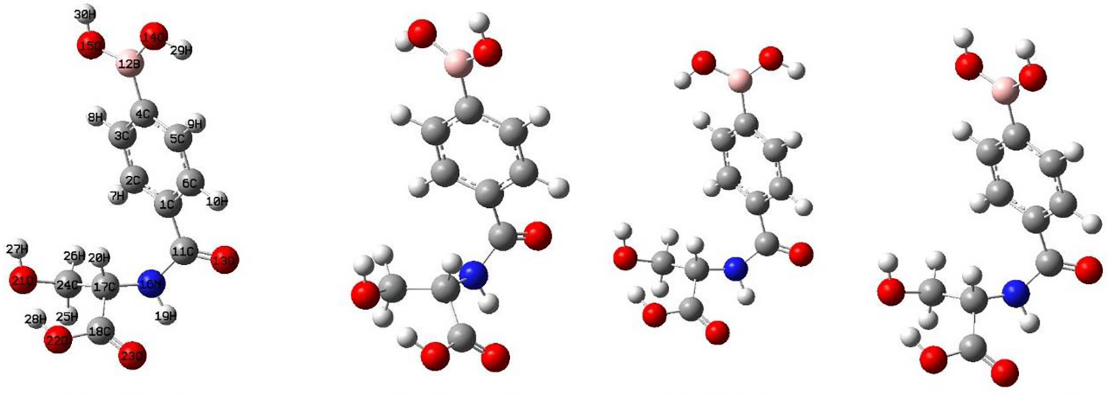
3. Results and discussion

3.1. Geometrical structure

Conformational analysis of title molecule was carried out with B3LYP method, 6-311 + +G(d,p) level of theory (Fig. 2). Energy values, imaginary frequencies and dipole moment of four conformational states of title molecule in the C1 point group were given in Table 1. Among the all conformation states, the most stable form was determined as tc conformer. Therefore, vibrational analysis and determination of geometrical parameters and HOMO-LUMO energy differences were carried out using tc isomer. Relative stability between tt, ct and cc conformers were calculated as 1.9306, 0.593 and 5.0046 kcal/mol, respectively. Therefore, all the experimental results including infrared, Raman wavenumbers were compared with trans-cis configuration. In addition to that, the calculated geometric parameters (bond lengths, bond and dihedral angles) were derived from transecis structure of the title molecule. Obtained geometric parameters were compared with previously reported studies [19,20] and there seems a remarkable agreement among the datas.

Bond lengths were calculated for C4-B, C11-O22, C1-C2 and B-O23 as 1.572, 1.219, 1.402 and 1.369 A°, respectively. Calculated bond angles of C13-C14-O15, H29-O24-B and C4-C5-C6 were 112.752, 111.974 and 121.514, respectively. Calculated dihedral angle of H29-O24-B-C4 and H29-O24-B-O23 are almost 180.00° and 0.578°, respectively. Moreover, optimized geometrical parameters such as bond lengths, bond angles and torsion angles are given in Table 2.

According to obtained torsion angles of H29-O14-B-O23 and H30-



Trans-Cis (tc) **Cis-Trans (ct)** **Cis-Cis (cc)** **Trans-Trans (tt)**

Fig. 2. Optimized structure of title molecule.

Table 1
Energy values of title molecule conformers.

Parameters	Cis-Trans	Cis-Cis	Trans-Cis	Trans-Trans
ΔG (Hartree)	−919.62946687	−919.622436462	−919.63041189	−919.62733527
ΔG (kcal/mol)	577067.4904	577063.0788	577068.0834	577066.1528
Relative stability (kcal/mol)	0.5930	5.0046	0	1.9306
Imaginary frequency	0	0	0	0
Mole fraction (%)	29.8	0.0	59.4	10.8
Dipole Moment (Debye)	7.1879	4.8106	6.0052	9.1210

O15-B-C4, it is determined that H30 atom is the same plane with O-B-O plane.

Table 2
Some geometrical parameters of title molecule.

Parameters	tc	ct	cc	tt	Exp.[a]
Bond lengths (Å)					
C1-C2	1.402	1.398	1.399	1.399	1.411
C1-C6	1.402	1.398	1.399	1.399	–
C4-B	1.572	1.570	1.579	1.565	1.566
C1-C11	1.499	1.506	1.505	1.504	–
C11-O22	1.219	1.215	1.215	1.216	–
C11-C12	1.518	1.504	1.505	1.504	–
C12-C13	1.571	1.545	1.546	1.546	–
C13-C14	1.522	1.548	1.549	1.548	–
C14-O17	1.204	1.200	1.199	1.998	–
C14-O15	1.351	1.340	1.341	1.341	–
O15-H16	0.969	0.979	0.978	0.978	–
C13-N	1.453	1.452	1.451	1.451	–
C13-H27	1.093	1.095	1.094	1.095	–
N-H19	1.015	1.016	1.016	1.015	–
B-O23	1.369	1.371	1.365	1.371	1.372
B-O24	1.363	1.363	1.363	1.369	1.367
O23-H28	0.960	0.963	0.960	0.961	0.960
O24-H29	0.963	0.960	0.963	0.961	0.963
C6-H10	1.083	1.084	1.091	1.083	–
Bond angles (°)					
H29-O24-B	111.974	112.012	113.057	115.942	112.5
H28-O23-B	114.568	114.280	113.294	115.705	115.6
C4-C5-C6	121.514	121.396	121.645	121.243	116.1
C4-C5-H9	120.357	118.932	119.715	119.129	119.3
C1-C11-O22	120.634	122.552	120.533	120.976	–
O22-C11-C12	119.552	111.062	122.532	122.713	–
H25-C12-H26	108.973	108.205	107.962	108.052	–
C11-C12-C13	109.660	111.012	111.126	110.897	–
O17-C14-O15	122.955	122.229	122.273	122.182	–
C14-O15-H16	106.772	108.617	109.804	109.724	–
H27-C13-N	108.654	109.476	109.328	109.305	–
C13-N-H20	109.829	110.526	109.787	110.007	–
C13-C14-O15	112.752	111.062	111.256	111.161	–
Torsion angles (°)					
H29-O24-B-C4	−179.212	−1.897	6.860	179.873	–
H29-O24-B-O23	0.578	−178.018	−173.221	0.697	–
B-C4-C3-H8	−0.643	−0.299	1.773	1.054	–
C11-C12-C13-C14	166.973	177.451	176.421	177.745	–
C11-C12-C13-N	−67.215	−54.058	−44.712	−46.004	–
O23-C18-C17-H20	−155.288	−111.689	−111.192	−111.917	–

[a] Refs. [21–26].

3.2. Vibrational studies

All the theoretical and experimental vibrational frequencies, vibrational assignments and intensity values of title molecule are given in Tables 3.

For title molecule, all the calculated frequencies presented in this manuscript were obtained within harmonic approximation. Therefore, vibrational motion can be described in terms of independent vibrational modes.

3.2.1. OH vibrations

The OH streching band was observed between 3600 and 3400 cm^{-1} as very broad band. It indicates intra and inter molecular hydrogen bonding, moreover it can be indicated to moisture residue [17–19].

In the IR spectrum, OH streching was observed at 3638, 3433 cm^{-1}, 3272 cm^{-1} and calculated as 3633, 3364 cm^{-1}, 2962 cm^{-1}, respectively. There are large differance between theoretical and experimental OH streching values. The difference between theoretical and experimental OH vibrational values is high level in B3LYP functional. Because, intermolecular hydrogen bonding formed between boronic acid groups of title molecule.

3.2.2. C═O vibrations

C═O streching bands of title molecule were observed at 1739, 1702 and 1190 cm^{-1} in IR spectrum. Moreover at 1725, 1700 and 1191 cm^{-1} in Raman spectrum. On the other hand, these bands were calculated as 1760, 1719 and 1191 cm^{-1}. They are almost a pure mode (85% and 82%, TED).

In plane COH bending vibrations were observed at 1351 cm^{-1} and 1373 cm^{-1} in the IR spectrum and Raman spectrum, respectively. This vibration was calculated at 1343 cm^{-1}. This streching mode contamined with B-C and B-O modes. Out of plane COH vibration was seen in infrared spectrum at 570 cm^{-1} and was not observed in Raman spectrum. That of calculated peak computed at 576 cm^{-1} and this band also was contamined by the other vibrations.

Table 3
The observed FTIR, FT-Raman and calculated wavenumbers of title molecule for tc monomer structure.

Modes	Assignments	Experimental		Monomer- 6-311 + + G(d,p)			
	TED(≥10%)	IR	Raman	Unscalled	Scaled	I_{IR}	I_R
υ_1	υ(N−H) (94)	3667	–	3882	3691	0.77	–
υ_2	υ(O−H) (100)	3638	–	3821	3633	0.97	–
υ_3	υ(O−H) (100)	3433	–	3541	3366	0.30	–
υ_4	υ(O−H) (100)	3272	–	3537	3363	42.19	–
υ_5	υ(C_{ar}−H) (95)	2926	3063	3115	2962	10.58	54.75
υ_6	υ(C_{ar}−H) (98)	2927	2958	3065	2914	12.39	80.18
υ_7	υ(C═O) (85)	1739	1725	1851	1759	2.07	8.84
υ_8	υ(C═O) (82)	1702	1700	1759	1718	8.38	45.11
υ_9	υ(C−C) (29) + υ(B−O) (13) + υ(C−O) (11) + β(CCC) (11)	1610	1615	1650	1612	1.60	147.26
υ_{10}	υ (C_{ar}−C_{ar})(46) + α(CCC) (10)	1542	1557	1592	1555	15.23	0.65
υ_{11}	υ (C_{ar}-C_{ar}) (23) + υ (B-O) (29)	1402	1463	1435	1401	21.09	2.90
υ_{12}	υ (C_{ar}−C_{ar}) (11) + υ (B-O) (45)	1365	1400	1400	1367	3.23	2.47
υ_{13}	υ (B−O) (17) + β(C−O−H) (18) + β(O═C−O)(16) + υ (B−C) (15)	1351	1373	1375	1343	9.08	25.82
υ_{14}	υ (C_{ar}−C_{ar}) (31) + β(H−C−C) (17)	1279	1308	1309	1278	4.98	5.99
υ_{15}	υ (C_{ar}−C_{ar}) (25) + β(H−C−C) (17)	1275	1256	1303	1273	34.76	13.09
υ_{16}	β(C−O) (47) + β(H−C−C) (12)	1190	1191	1219	1189	7.43	4.75
υ_{17}	υ (N−C) (31)	1161	1164	1185	1156	1.79	5.66
υ_{18}	υ(C−C) (33)	1096	1101	1112	1085	4.95	35.91
υ_{19}	β(CC) (49) + α(HCCN) (11)	1033	1025	1053	1028	3.49	2.97
υ_{20}	β (BOH) (47) + υ(BO)(12) + β(C−C−C) (16)	1015	–	1032	1008	32.12	–

(*continued on next page*)

Table 3 (*continued*)

Modes	Assignments	Experimental		Monomer- 6-311++G(d,p)			
	TED(≥10%)	IR	Raman	Unscalled	Scaled	I_{IR}	I_R
υ_{21}	γ(CH)(24) + υ(C−COOH)(44)	941	949	998	975	2.27	1.23
υ_{22}	υ (BO) (21) + β(B−O−H) (53)	915	915	992	969	42.39	1.52
υ_{23}	τ(CCCH) (49) + τ(CCCC) (25)	899	896	984	961	0.91	0.31
υ_{24}	τ(CCCH) (40) + τ(CCCC) (33)	877	864	876	854	4.37	0.79
υ_{25}	υ (CH) (45) + τ(HCCC) (33)	851	850	864	844	18.51	2.43
υ_{26}	τ(CCOH) (28) + τ(OCCN) (10)	820	832	832	812	14.97	2.55
υ_{27}	υ (CH) (47)	788	775	807	787	49.52	3.01
υ_{28}	τ(ONCC) (31)	764	–	796	777	13.96	–
υ_{29}	τ(HNCC) (14) + τ(CCCC) (25)	743	740	769	751	56.64	3.21
υ_{30}	β(OCN) (17) + β(CCC) (10)	689	–	720	703	35.58	–
υ_{31}	γ(CC) (24) + γ(BO) (10)	641	649	662	646	48.27	0.43
υ_{32}	α(CCC) (61)	625	629	648	633	4.43	5.14
υ_{33}	α(CCC) (13) + β(O=C-O)(37) + τ(HNCC) (13)	587	578	612	597	2.08	3.54
υ_{34}	γ(OH) (67) + γ(CC) (51) + φ(CCC) (23)	570	–	590	576	100	–
υ_{35}	β(BO) (17) + β(BC) (11)	556	–	575	561	83.58	–
υ_{36}	β(CCN) (24) + τ(HOBC) (25) + τ(HNCC) (25)	512	500	547	534	8.44	1.89
υ_{37}	β(BO) (81) + β(BC) (13)	481	–	486	475	6.45	–
υ_{38}	β(OBO) (18) + β(OCC) (11)	465	469	482	470	14.13	3.60
υ_{39}	β(BO) (25) + β(BC) (12)	439	–	445	435	98.5	–
υ_{40}	β(CCO) (22) + β(CCN) (11)	412	420	421	411	10.93	1.94

3.2.3. C−H and C−C vibrations

In present work, CH stretching modes of title molecule were observed at 3272, 2969, 2927 cm^{-1} in the Infrared spectrum, 3063, 2958 cm^{-1} in the Raman spectrum and were calculated as 3363, 2962, 2784 cm^{-1}. In plane and out of plane CH stretching modes were mentioned in Table 3. All results for CH strecthing of title molecule are in agreement with the literature [20,27].

Aromatic C−C strecthing modes are observed at 1610, 1542, 1402 cm^{-1} in the IR spectrum and 1615, 1557, 1463 cm^{-1} in the Raman spectrum in this study as seen in Table 3.

The experimental and theoretical infrared spectra are shown in Fig. 3 and theoretical and experimental Raman spectra of title molecule are shown in Fig. 4. These modes are agreement with experimental data after scalling using SQM. These modes were computed as 1612, 1555 and 1402 cm^{-1}.

CCC bending modes were observed between 1000 cm^{-1} and 600 cm^{-1}. CCC bending modes contaminated with other modes.

3.2.4. B−O and B−C vibrations

B−O strecthing band of title molecule was observed at 1365 cm^{-1} (IR), 1400 cm^{-1} (R) and calculated as 1368 cm^{-1} is a mixed type of B-O (TED, 45%), C−C (TED, 11%). Moreover, the C−B−O out-of-plane

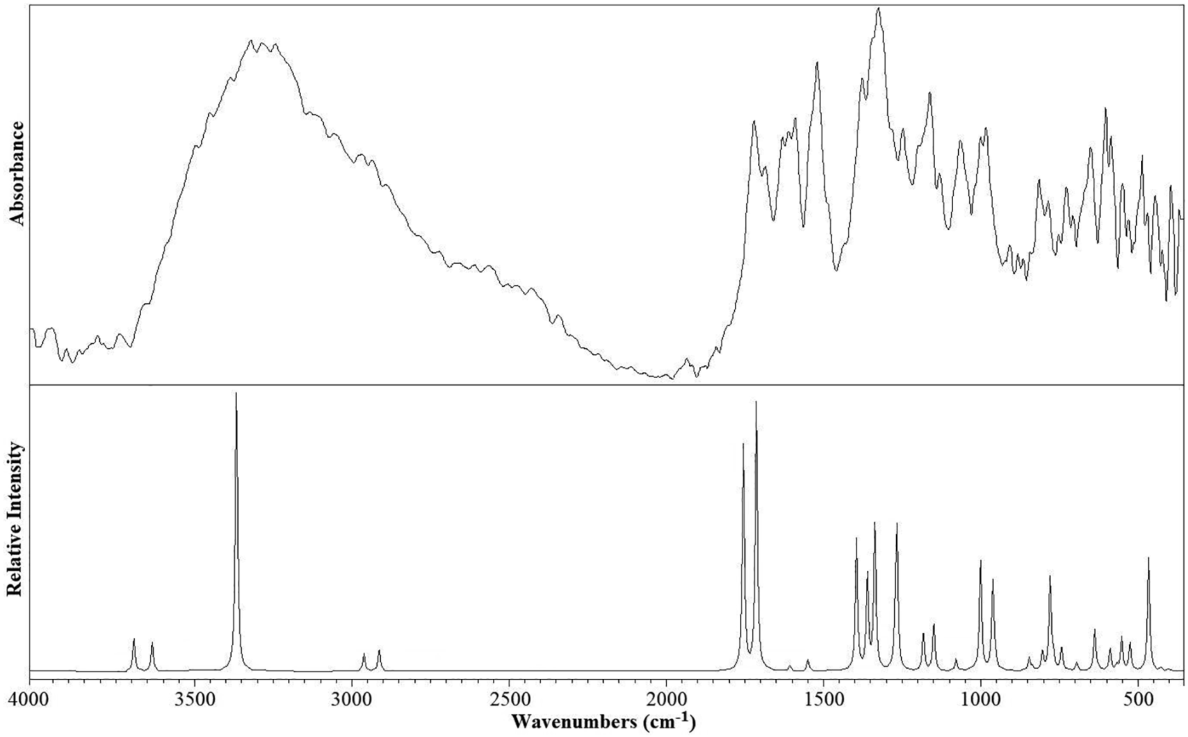


Fig. 3. Experimental (upper) and theoretical infrared spectra of title molecule.

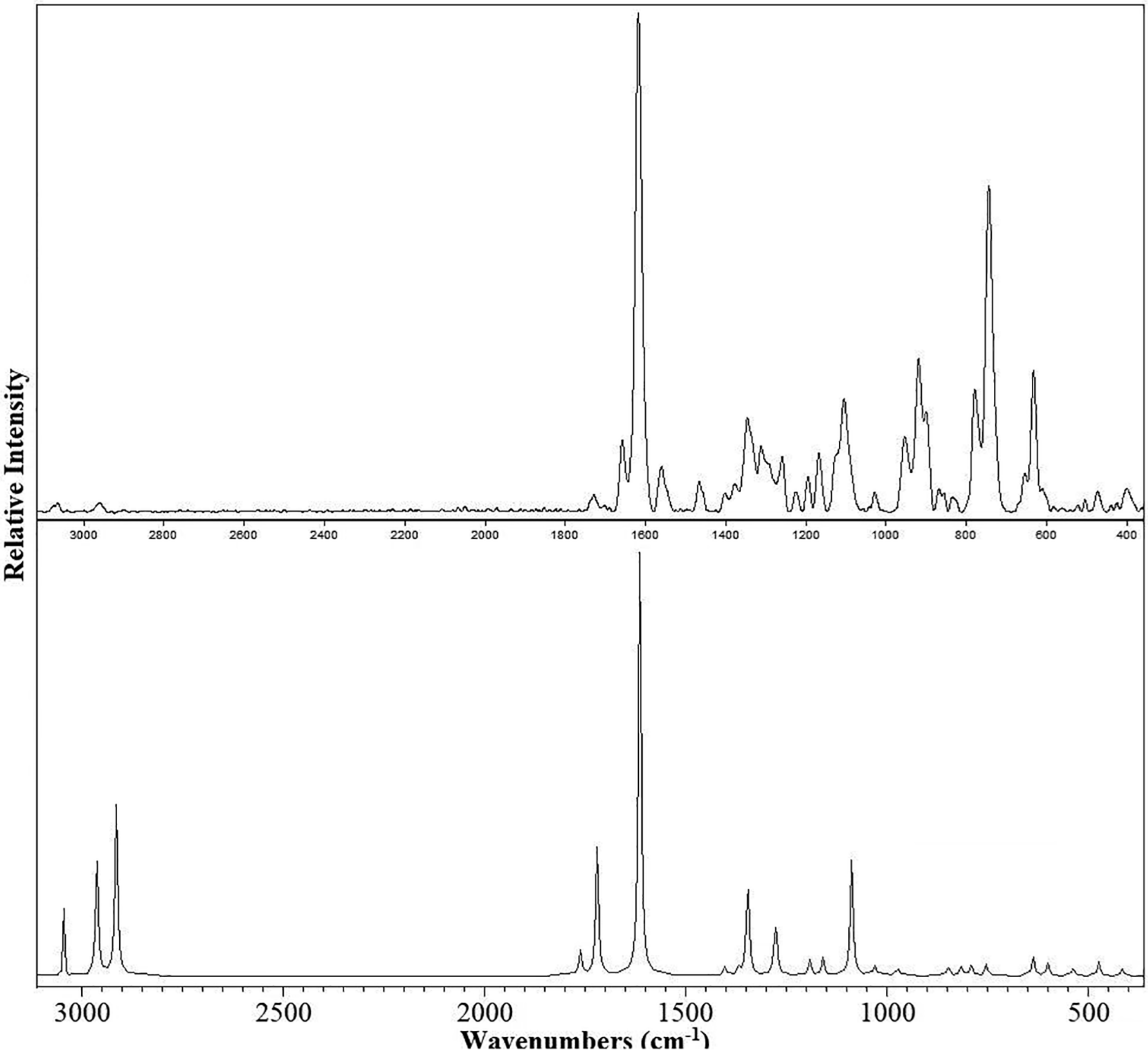


Fig. 4. Experimental (upper) and theoretical Raman spectra of title molecule.

bending vibrations were calculated for title molecule at 641 cm^{-1} in the IR, 689 cm^{-1} in the Raman spectrum and calculated as 634 cm^{-1} using B3LYP method. B—C strecthing mode as observed at 1351 cm^{-1} and 439 cm^{-1} in the IR, 1373 cm^{-1} in the Raman spectrum were calculated as 1343 cm^{-1} and 435 cm^{-1}. The C—B stretching vibrations also indicate combinations of several vibrations [21].

3.2.5. N—H vibrations

The N—H stretching vibration is observed at 3329 cm^{-1}. The N—H inplane bending modes are found at 1493 and 1450 cm in the infrared, and 1493 and 1444 cm^{-1} in Raman spectrum. The N—H out of plane bending vibrations are observed at 650 and 636 cm^{-1}.

In this study, N—H strecthing bands were observed at 3667 (TED, 94%) and 3638 cm^{-1} (TED, 86%) in the IR spectrum and calculated as 3691, 3633 cm^{-1}.

3.3. NMR studies

There are twenty hydrogen atoms attached in title molecule. In general, the chemical shift values of aromatic protons observed in the region between 8.00 and 7.00 ppm for organic molecules. However, these chemical shift values can change, depending on electronic environment of proton. If electron acceptor atoms directly attached or near by, they could reduce the shielding. Thus, the hydrogen atom attached to an electron-withdrawing atom or group could move towards to a higher frequency, whereas electron donating atoms raise the shielding and so, resonance of the attached hydrogens could move towards to a lower frequency [22,23].

The proton chemical shifts in the phenyl ring were observed range from 7.7 to 7.9 ppm. These peaks were appeared as doublet since spin splittings accur mutually. As seen in ^{1}H NMR spectrum (Fig. 5), H28 and H19 atoms belongs to OH groups were observed at 12.78 and 4.97 ppm as singlet, respectively, while H29 and H30 protons of $B(OH)_2$ group were observed at 8.23 ppm as doublet. Because of the fact that there are both cis form and trans form in the sample, this peak looks like a doublet. However, this is two seperate singlet peak which belongs to cis and trans forms of $B(OH)_2$ group of title molecule.

H28 atom of carboxy group was appeared in the lower magnetic field region because of 2 times oxygen atoms which are electronegative atoms. But, it is difficult to decide the peaks of the protons of OH groups and other groups. Therefore, proton exchanged experiment was carried out. For this experiment, after title molecule was dissolved in DMSO, only one drop of D_2O was added to the solution and immediately after, ^{1}H NMR experiment was performed. Thus, after exchange hydrogen atoms of carboxy (—COOH) and amide (—NHCO—) functions were disappeared (Fig. S2).

Moreover, solid sample and solved in DMSO sample were found to be mostly the anhydride form of title molecule. Due to esterify in D_2O,

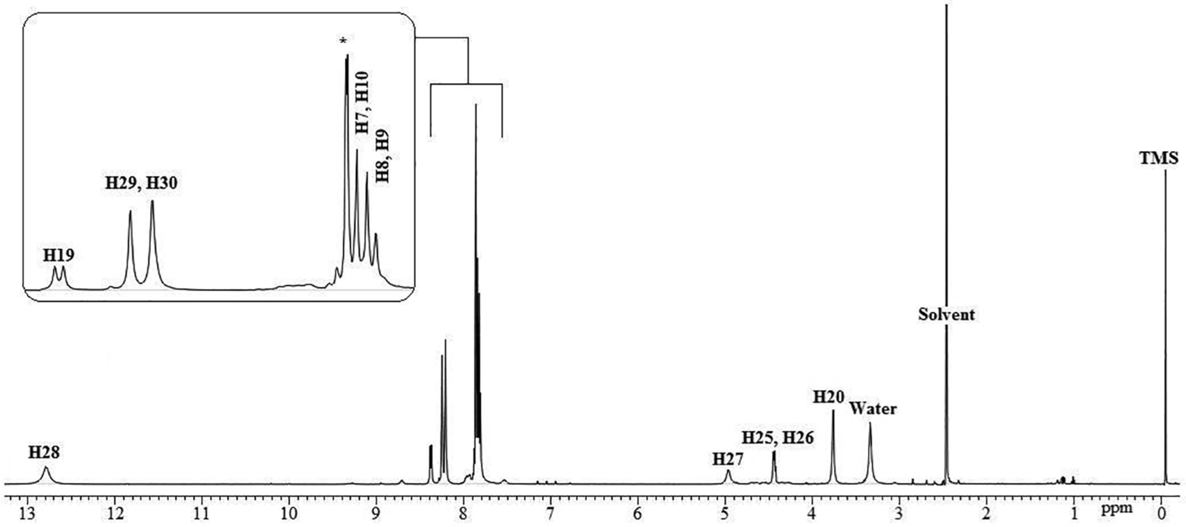


Fig. 5. ^{1}H NMR spectrum in DMSO of title molecule.

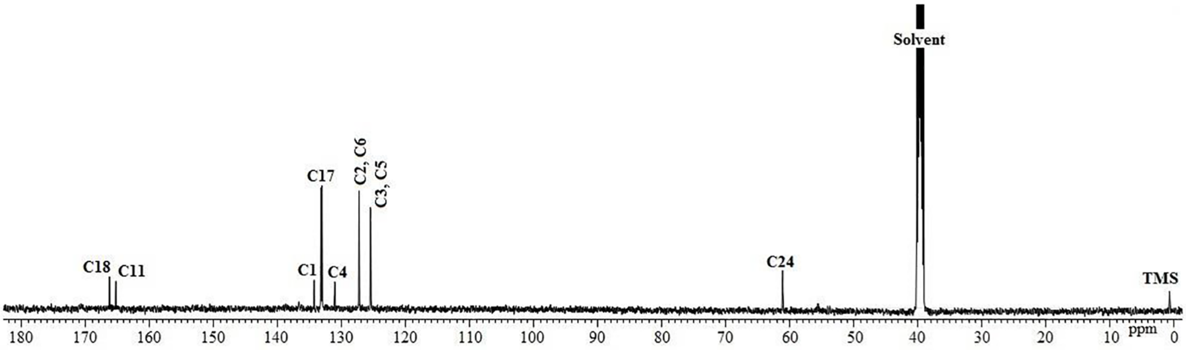


Fig. 6. ^{13}C NMR spectrum of title molecule.

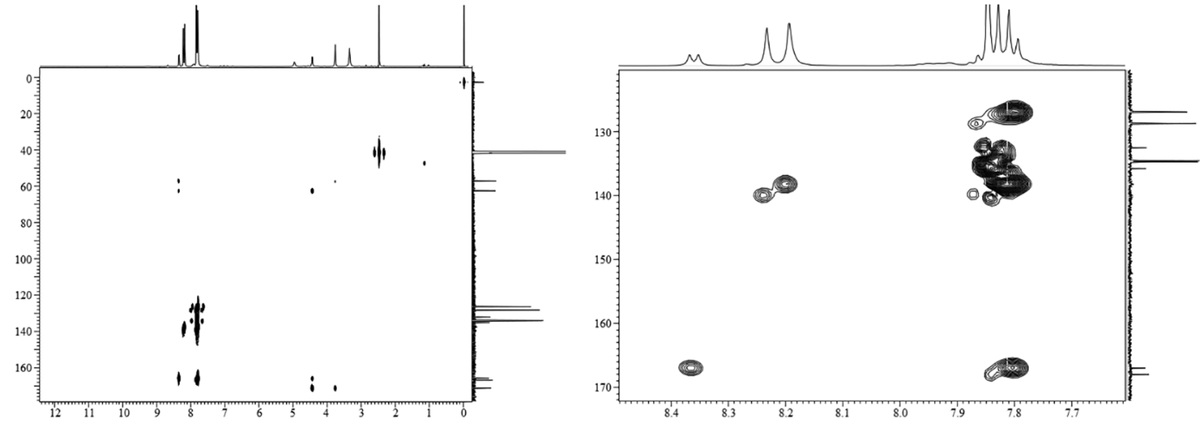


Fig. 7. ^{1}H-^{13}C HMBC NMR spectrum of title molecule.

especially in ^{1}H spectrum, peak of anhyride structure observed at 7.78 ppm are not observed according to ^{1}H spectrum of sample solved in DMSO.

In ^{13}C NMR spectrum of the title molecule (Fig. 6), C18 atom was appeared in the most low magnetic field area because of oxygen atoms of carboxy group. Since it is bonded to amide function, C1 atom was observed at 134.24 ppm because of the oxygen and nitrogen atoms.

In ^{13}C APT (Attached Proton Test) NMR spectrum (Fig. S3), C1, C4, C11 and C18 are quarterner carbon atoms, NMR signal of them are seen as negative whereas C17, C2&C6 and C3&C5 (CH) atoms appear as positive peaks.

Spin-spin coupling can be provide useful information to interpret the NMR spectra and so proton coupled ^{13}C NMR spectrum was obtained (Fig. S4). In Fig. S4, C2, C3, C5 and C6 atoms split into two lines

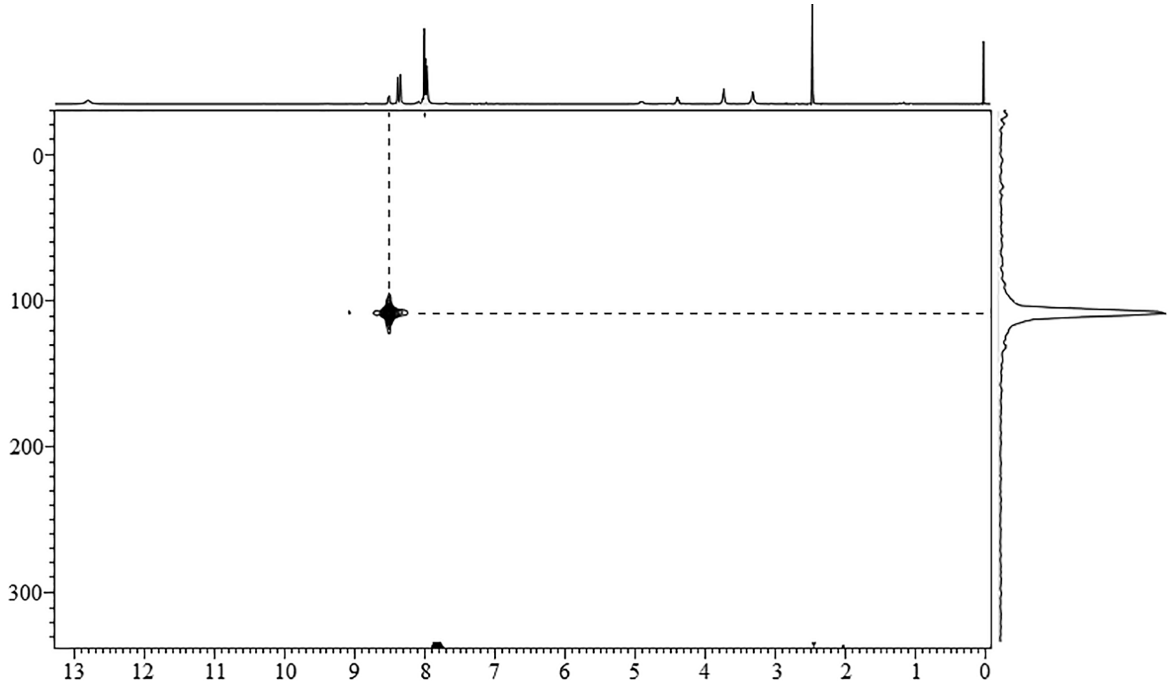


Fig. 8. ^{15}N-^{1}H HMQC NMR spectrum of title molecule.

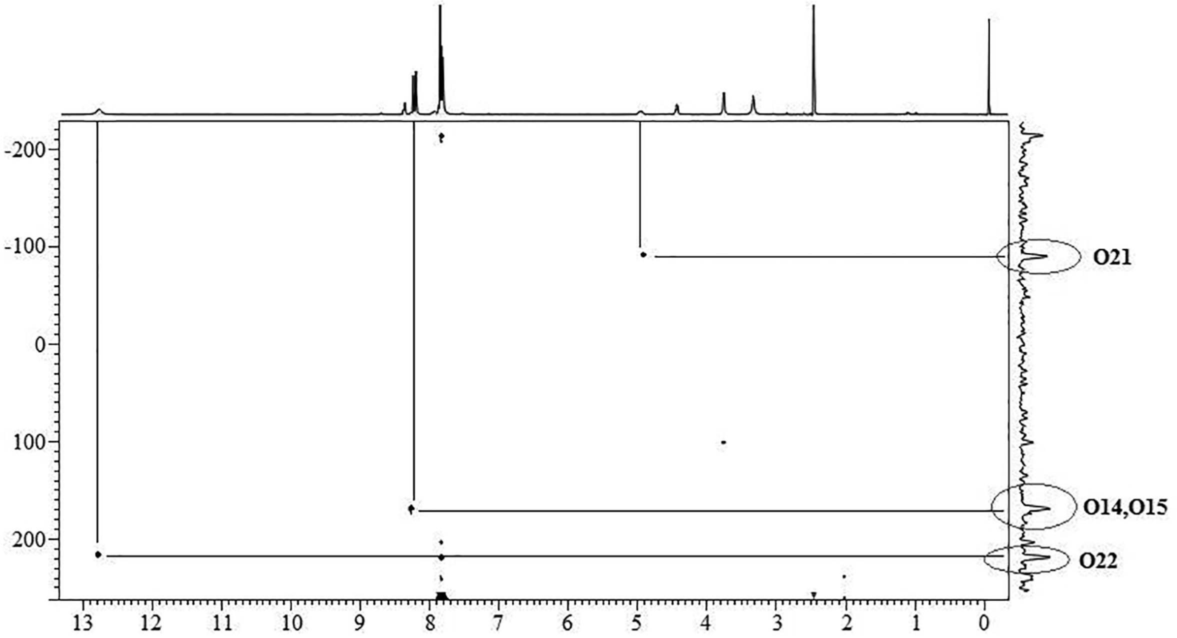


Fig. 9. ^{17}O-^{1}H HMQC NMR spectrum of title molecule.

by directly bonded hydrogen atoms with $^{1}J_{H7,\ C2} = 160$ Hz, $^{1}J_{H10,\ C6} = 160$ Hz, $^{1}J_{H9,\ C5} = 160$ Hz and $^{1}J_{H8,\ C3} = 160$ Hz. After splitting into two lines, the signals splint into two lines as well because of neighbour hydrogen atoms with $^{3}J_{H,\ C2} = 42.65$ Hz, $^{3}J_{H,\ C6} = 37.51$ Hz, $^{3}J_{H,\ C5} = 37.51$ Hz and $^{3}J_{H,\ C3} = 42.65$ Hz.

As seen in Fig. S5, COSY NMR spectrum showed that H25 and H26 atoms neighboured to both H2 and H19 atoms and H27 atom neighboured to H20 atom. Moreover, H8, H9 and H7, H10 atoms neighboured to each other.

There are interactions between H28, H29, H25/H26 and H25, H9, H20 of space, respectively.

There is a also a interaction between protons of water molecule and protons of $B(OH)_2$ group. The same situation was observed for H27 atom. On the other hand, because of the fact that there is no interaction between H20 and H19 atoms of space, there is no observed signal in the NOESY spectrum for these two atoms. According to this result, distance between these atoms are higher than 4 Angstrom and two atoms are almost the opposite direction to each other (Fig. S6).

In HETCOR NMR spectrum (Fig. S7), C24 → H25/H26, C17 → H29, C5/C3 → H9/H8 and C2/C6 → H7/H10 connections can clearly be seen.

In HMBC NMR spectrum (Fig. 7), C1 → H7/H18, C2, C6 → H7/H10,

Table 4
Calculation UV–VIS of title molecule in water and DMSO solvents by TD-DFT method at B3LYP/6-311+ +G(d,p) basis set.

Excited state	Solvents	E(eV)	Wavelength (nm)	F
65 → 67	Water	0.2145	266	0.0144
	DMSO	0.1943	241	0.0156
65 → 68	Water	0.2185	271	0.0153
	DMSO	0.1976	245	0.0170

C3/C5 → H8/H9, C4 → H9/H8, C18 → H25/H26 and C24 → H25/H26 connections can clearly be seen.

There is a only one nitrogen atom in the title molecule and this atom was observed at 110.85 ppm in the ^{15}N-^{1}H HMQC NMR spectrum. Moreover, as seen in Fig. 8, it was also determined that H19 atom neighboured to this nitrogen atom.

As seen in Fig. 9 as well, hydrogen atoms bonded to oxygen atom and chemical shift values of oxygen atoms were determined using ^{17}O-^{1}H HMQC NMR experiment. According to obtained spectrum, chemical shift values of O21, O22 and O14, O15 atoms bonded to H27, H28 and H29, H30 atoms, respectively.

3.4. Optical properties

In order to determine optical properties of title molecule, UV–VIS absorption spectrophotometer was used. UV–VIS absorption spectrum of title compound measured in water and DMSO solvents at room temperature. UV–VIS spectrum of title molecule was computed using method of TD-DFT/B3LYP with 6-311+ +G(d,p) basis set. All of the UV–VIS spectra are presented in Fig. S8. In water solvent, strong absorption bands were observed at 236 nm and 281 nm, these bands were observed at 238 nm and 284 nm in DMSO solvent. On the other hand, these bands were calculated as 241 nm and 266 nm in water, 245 nm and 271 nm in DMSO (Table 4). Energy values of these absorption bands are 0.1943 and 0.2145 nm in water, 0.1976 and 0.2185 nm in DMSO, respectively. The considered absorption peaks are accredited to the $\pi \rightarrow \pi^*$ transition in the organic cation. The results indicated that the most absorption peak was calculated for transfer from electron level of 65 → 67 with 241 nm, E = 0.1943 eV and F = 0.0156.

3.5. Electronic property

3.5.1. Frontier molecular orbital analysis

HOMO is highest occupied molecular orbital and LUMO is lowest unoccupied molecular orbital. HOMO is ability of electron giving of a molecule, whereas LUMO is ability of electron accepting. The nodes of HOMO orbital located on the ring and oxygen atoms. But, the nodes of LUMO located symmetrically all over the title molecule (Fig. 10). Red color and green color indicate positive charge and negative charge, respectively. Moreover, HOMO and LUMO show the π bonding character and π anti bonding character, respectively [28]. Energy gap determines charge transfer from HOMO to LUMO and charge transfer interactions in the molecule. HOMO and LUMO energies were calculated by B3LYP/6*311+ +G(d,p) method for gas phase. The energy gap indicates the eventual charge transfer interactions occurring in the molecule. The energy gap is that

$$\text{Energy}_{\text{HOMO}} = -7.0725\ \text{eV}$$
$$\text{Energy}_{\text{LUMO}} = -1.7764\ \text{eV}$$
$$\text{Energy Gap}_{\text{HOMO-LUMO}} = 5.2961\ \text{eV}$$

4. Conclusions

The structural and vibrational analyses of title molecule were performed using FT-IR, Raman, NMR spectroscopies and quantum chemical computations.

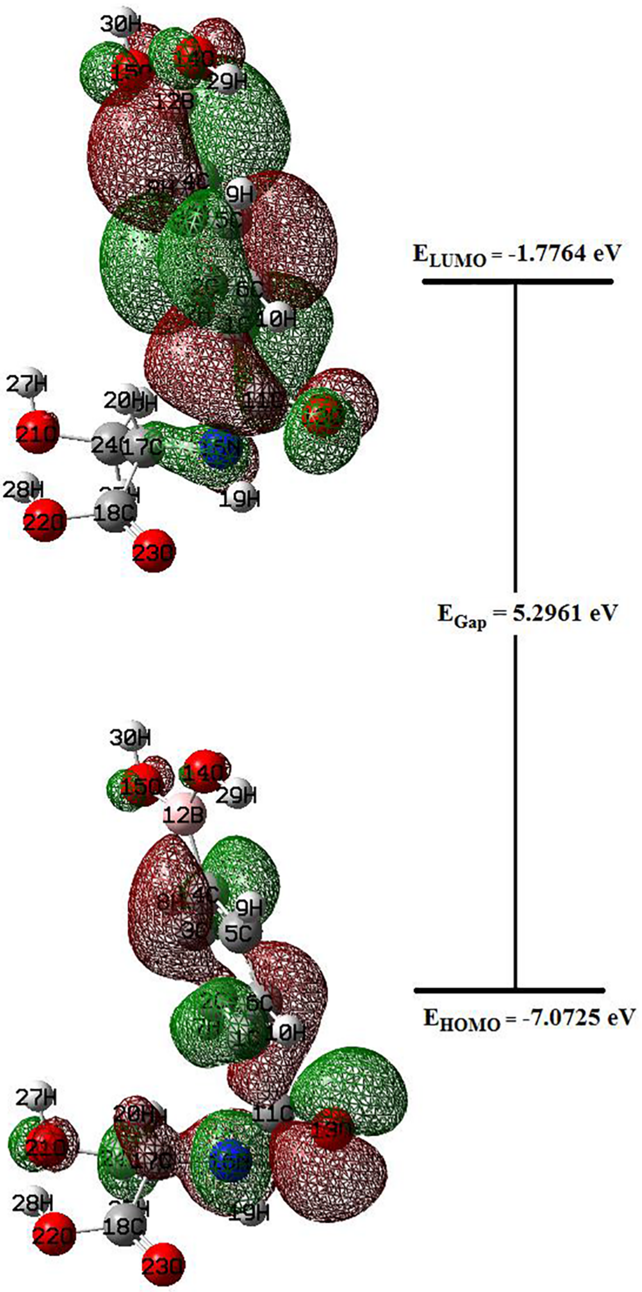


Fig. 10. Atomic orbital compositions of the frontier molecular orbital for title molecule.

To summarize, the following conclusions can be drawn:

(i) The B3LYP functional is reliable for characterizing title molecule.
(ii) tc tautomer form was found having the lowest optimized energy in the gas phase among the calculated conformers.
(iii) It was observed that there was a good agreement between experimental and theoretical vibration wavenumbers.
(iv) Synthesied molecule fully was characterized with NMR spectroscopy and it was observed that the molecule was synthesized successfully. However, it was esterified using D_2O solvent and title molecule transform monomer and trimer structures.
(v) It was found that B3LYP/6-31+ +G(d,p) level of theory indicates big frequency deviations for particularly OH stretchings of the title molecule. For the low wavenumber region experimental and calculated values were found more close to each other.

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Declaration of Competing Interest

There is no conflict of interest in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemphys.2019.110601.

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