www.dergipark.gov.tr
ISSN:2148-3736
El-Cezerî Fen ve Mühendislik Dergisi
Cilt: 8, No: 1, 2021 (397-409)

El-Cezerî Journal of Science and Engineering
Vol: 8, No: 1, 2021 (397-409)
DOI:10.31202/ecjse.825888

ECJSE

Makale / Research Paper

2-Thienylboronic Acid: A DFT Study For The Spectral, Structural and Molecular Orbital Analysis

Ahmet KUNDURACIOĞLU

Bursa Uludağ University, Mustafakemalpaşa Vocational College, Bursa, TURKEY
akunduracioglu@uludag.edu.tr

Received/Geliş: 14.11.2020 **Accepted/Kabul:** 17.12.2020

Abstract: In this study, due to the increasing importance of boronic acids, 2-Thhenylboronic acid and its isomers were examined in terms of structural properties and molecular orbitals. HOMO-LUMO boundary surfaces and FT-IR, FT-RAMAN analyzes were carried out with an integrated understanding. The molecule was investigated in terms of structural properties such as bond lengths, bond angles and buckling angles. Isomers of the molecule are considered separately from each other. In quantum chemical calculations, the DFT method was used at the B3LYP level and with the 6.31G * base set. These calculations were carried out using SPARTAN-14 computational chemistry package program. The results calculated for the bond lengths were found to be very close to the experimental values in the literature, with an error margin of usually between 0.45 and 1.6%. This error in bond angles occurred between 0.49% and 5.52%. Considering that the molecule has moving parts, it can be said that results are very close to experimental values.

Keywords: Boronic acid derivatives, DFT, Spectral analysis, HOMO LUMO, Molecular structure

2-Tienilboronik Asid: Spektroskopik, Yapısal ve Molekül Orbital Analizi Üzerine Bir DFT Çalışması

Öz: Boronik asitlerin artan önemi nedeniyle bu çalışmada, 2-Tienilboronik asid ve izomerleri, Yapısal özellikler ve molekül orbitaller bakımından incelenmiştir. HOMO-LUMO sınır yüzeyleri ve FT-IR, FT-RAMAN analizleri tümleşik bir anlayışla gerçekleştirilmiştir.Molekül, bağ uzunlukları, bağ açıları ve burkulma açıları gibi yapısal özellikleri yönüyle araştırılmıştır. Molekülün izomerleri birbirinden ayrı olarak ele alınmıştır. Kuantum kimyasal hesaplamalarda, DFT yöntemi, B3LYP düzeyinde ve 6.31G* temel seti ile kullanılmıştır. Bu hesaplamalar, SPARTAN-14 hesapsal kimya paket programı kullanılarak gerçekleştirilmiştir. Bağ uzunluklarıyla ilgili hesaplanan sonuçların, genellikler % 0.45 ile 1.6 arasında hata payıyla, literatürdeki deneysel değerlere çok yakın oldukları görülmüştür. Bağ açılarında bu hata % 0.49 ile 5.52 arasında gerçekleşmiştir. Molekülün hareketli kısımları olduğu dikkate alınırsa, deneysel değerlere son derece yakın sonuçlar alındığı söylenebilir.

Anahtar Kelimeler: : Boronik asid türevleri, DFT, Spektroskopik analiz, HOMO LUMO, Molekül yapısı

1. Introduction

Like other boron compounds, boronic acid (BA) and its derivatives are gaining importance in today's innovative chemical studies. The importance of boron compounds especially "O" containing ones (Figure 1.) is on the rise due to oil shortage concerns in the future. Boron has a lack of e^- in its valence shell which makes boron compounds Lewis acids. Thanks to this property boron compounds can coordinate to lewis bases. Most BA derivatives exist as white crystalline solids, which can be kept and processed in the open air without further circumspection.

How to cite this article
Kunduracıoğlu, A., "*2-Thienylboronic Acid: A DFT Study For The Spectral, Structural and Molecular Orbital Analysis*" El-Cezerî Journal of Science and Engineering, 2021, 8(1); 397-409.

Bu makaleye atıf yapmak için
Kunduracıoğlu, A.,"*2-Tienilboronik Asid: Spektroskopik, Yapısal ve Molekül Orbital Analizi Üzerine Bir DFT Çalışması*" El-Cezerî Fen ve Mühendislik Dergisi 2021, 8(1); 397-409.
ORCID ID:0000-0002-6421-9912

BAs are chemically stable so that they have a shelf-life for long periods. However, derivatives with an alkyl substituted and some heteroaromatic ones have been shown to have limited stability under aerobic conditions. The reactivity and properties of BA derivatives depend upon the nature of their single variable substituent particularly the type of the –C–(BOH)$_2$ group which is directly bonded to boron atom. Some Oxygen-containing organoboron compounds have been depicted in Figure 1 [1-5]. Boron compounds are well known for their catalytic activities in organic and synthetic chemistry [6-12].

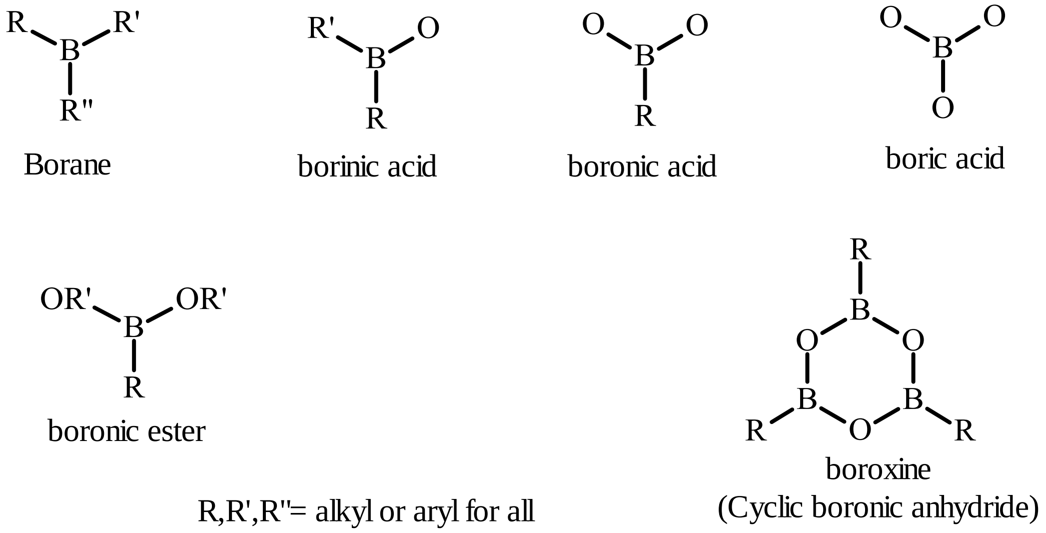
Borane
borinic acid
boronic acid
boric acid
boronic ester
boroxine
(Cyclic boronic anhydride)
R,R',R''= alkyl or aryl for all

Figure 1. Oxygen-containing organoboron compounds

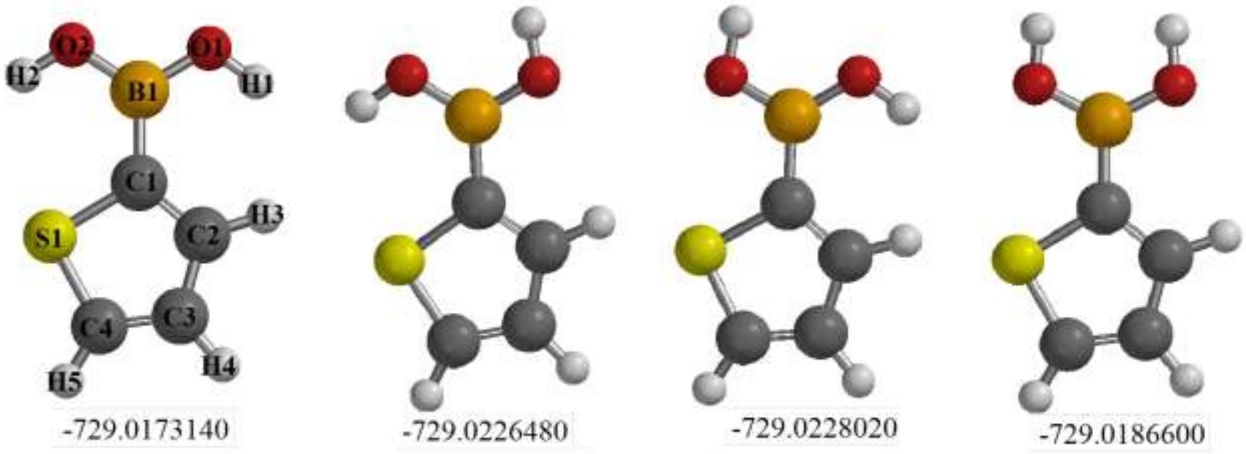

Figure 2. Isomeric forms of compound TBA (energies in Hartree)

2-Thienylboronic acid (TBA) isomers have been handled for its structural and spectral properties in this study (Figure 2). TBA is a crystalline white solid with a melting point of 138-140°C [1,3,12]. Some researchers had already performed comprehensive studies on its structural and spectral properties [14-16]. But in their study, the molecule had been handled as is. The calculations in the following study have been performed considering the isomeric structure of TBA.

2. Materials and Methods

2.1. Computational Details

For computational analysis of the compound TBA, 6-31G* basis set was used in the B3LYP level of DFT method [17-19] in the SPARTAN-14 quantum chemistry suite [20,21]. For calculations, TBA has four conformations; Cis-Cis, Cis-Trans, Trans-Cis and Trans-Trans (Figure 2).

Consequently, all calculations for the compound has been repeated for each of these conformations separately. The obtained results have been tabulated and discussed under corresponding divisions. MO surfaces and spectral graphics are depicted in corresponding figures in the following parts of this manuscript. For vibrational analysis, the results which software produced were used after they were corrected with a scaling factor of 0.96. There is a huge archive of spectral data for the compound TBA which had been studied by several researchers so far. 399ort his reason, in this study, the existing experimental spectroscopic and structural data have been used. Some data obtained from calculations have not been mentioned here, were added as supporting information files.

3. Results and Discussion

3.1. Structure of the Compound

As mentioned in the previous pages, the compound TBA has four geometrical isomers which will be called CC, CT, TC and TT (C for Cis- and T for Trans-) respectively in the following pages (Figure 2). As can be seen from Figure 2, the TC isomeric form which has -729.0228020 Hartree of energy was found as the least energetic form of the compound. In this study, the molecular structure of TBA and spectral data is going to be examined according to this fact [22].

3.1.1 Molecular Structure

Like any other compound, the molecular structure of TBA is determined by bond lengths, bond angles and dihedral (torsion) angles. In corresponding tables and figures, these properties have been depicted and argued comparatively.

TBA wasn't studied peculiarly for its molecular structure. But some very congener compounds were studied experimentally by Gosh et al. and Rettig et al. in their previous studies independently from each other [15,16]. In this study, the bond length and bond angles have been compared to the results of their studies (Figure 3. a, b).

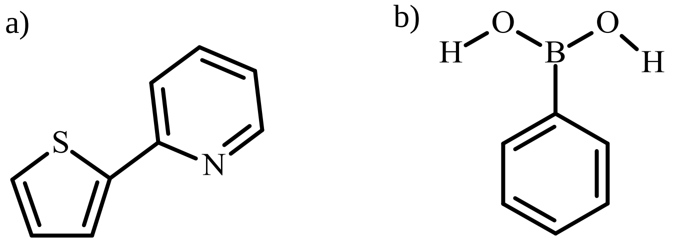

Figure 3. a) 2-(2'-thienyl)pyridine and b) phenylboronic acid

Calculated and experimental bond lengths are tabulated in Table 1 comparatively. As seen in Table 1, among the calculated values, the ones for TC are generally the closest results to experimental values as expected. However, it can not be said that the other results are very far from experimental measurements. The overall average is very close to the experimental results with a very small deviation which is between 0.454% and 1.611%. But the most prominent and disappointing deviation between calculated values and experimental ones is about almost 29% which corresponds to HnOn bonds. It is not surprising that excessive mobility in these groups causes such a deviation. Computationally found and experimentally measured bond angles of the compound TBA were tabulated comparatively in Table 2. It can be said at first glance that the results are more compatible, although there are many missing data in the experimental column. The values in the error% column lay between 0.195% and 5.5% which can be said to change within a reasonable range.

Table 1. Calculated and experimental bond lengths(Å) for the conformers of TBA

Bond	CC	CT	TC	TT	Ave.	Err.%	Exp*
H2,O2	0.966	0.967	0.969	0.967	0.967	28.967	0.750
H1,O1	0.965	0.969	0.966	0.967	0.967	28.900	0.750
O2,B1	1.368	1.375	1.367	1.375	1.371	0.679	1.362
O1,B1	1.369	1.368	1.375	1.375	1.372	-0.454	1.378
B1,C1	1.568	1.556	1.555	1.548	1.557	-0.717	1.568
C1,S1	1.752	1.753	1.748	1.750	1.751	1.611	1.723
S1,C4	1.728	1.729	1.727	1.728	1.728	0.935	1.712
C4,H5	1.082	1.082	1.082	1.082	1.082	nc	nd
C4,C3	1.370	1.370	1.371	1.371	1.371	0.772	1.360
C3,H4	1.085	1.085	1.085	1.085	1.085	nc	nd
C3,C2	1.424	1.424	1.423	1.423	1.424	1.173	1.407
C2,H3	1.087	1.085	1.088	1.085	1.086	nc	nd
C2,C1	1.379	1.378	1.380	1.379	1.379	0.730	1.369

From ref: 14,15 and 16 nc= not calculated, nd: No data in lit.

Again isomer TC is noticed to show relatively most realistic values and error% would be smaller if only TC were noticed.

Table 2. Calculated and experimental bond angles (°) for the conformers of TBA

Angle	CC	CT	TC	TT	Ave.	Err.%	Exp*
H2,O2,B1	113.990	114.160	110.920	114.990	113.515	2.266	111.00
H1,O1,B1	112.970	110.480	113.210	114.540	112.800	1.622	111.00
O2,B1,O1	114.950	117.830	118.080	124.480	118.835	2.180	116.30
O1,B1,C1	121.790	117.650	123.360	117.480	120.070	-3.944	125.00
O2,B1,C1	123.270	124.520	118.550	118.040	121.095	1.846	118.90
B1,C1,S1	121.910	122.920	121.020	122.010	121.965	nc	nd
B1,C1,C2	129.260	127.770	129.600	128.320	128.738	5.523	122.00
C1,S1,C4	92.810	92.510	92.390	92.210	92.480	0.195	92.30
C2,C1,S1	108.840	109.320	109.380	109.670	109.303	-1.084	110.50
S1,C4,H5	120.390	120.300	120.420	120.360	120.368	nc	nd
S1,C4,C3	111.330	111.360	111.760	111.750	111.550	0.495	111.00
C4,C3,H4	123.500	123.310	123.740	123.570	123.530	nc	nd
C4,C3,C2	112.360	112.550	112.070	112.250	112.308	-0.876	113.30
C3,C2,H3	122.320	123.910	122.520	123.880	123.158	nc	nd
C3,C2,C1	114.670	114.270	114.400	114.120	114.365	1.298	112.90
H3,C2,C1	123.010	121.820	123.080	122.000	122.478	nc	nd
C2,C3,H4	124.140	124.140	124.190	124.180	124.163	nc	nd
C3,C4,H5	128.280	128.340	127.820	127.900	128.085	nc	nd

*= borrowed from ref (14,15 and 16, nc= not calculated, nd: No data in lit.

As a presupposition, any small compound with an aromatic ring can be expected to be perfectly planar. The compound TBA is not an exception. According to the calculated values, the dihedral angles of the compound are 180° and 0.00°. Unfortunately, there is not an experimental data-set to compare those results for verifying. According to data in Table 3. TBA can be supposed to have a perfectly planar structure without bending. But it doesn't mean the molecule is a rigid planar sheet, it bends, twists and wriggles in a limited space continually.

Table 3. Calculated Dihedral angles (°) for the conformers of TBA

Bond	CC	CT	TC	TT
H2,O2,B1,O1	180.00	180.00	0.00	0.00
H1,O1,B1,O2	180.00	0.00	180.00	0.00
H2,O2,B1,C1	0.00	0.00	180.00	180.00
H1,O1,B1,C1	0.00	180.00	0.00	180.00
O2,B1,C1,S1	0.00	0.00	0.00	0.00
O1,B1,C1,C2	0.00	0.00	0.00	0.00
O2,B1,C1,C2	180.00	180.00	180.00	180.00
O1,B1,C1,S1	180.00	180.00	180.00	180.00
B1,C1,S1,C4	180.00	180.00	180.00	180.00
B1,C1,C2,C3	180.00	180.00	180.00	180.00
C1,C2,C3,C4	0.00	0.00	0.00	0.00
S1,C4,C3,C2	0.00	0.00	0.00	0.00
C1,S1,C4,C3	0.00	0.00	0.00	0.00
B1,C1,C2,H3	0.00	0.00	0.00	0.00

3.1.2. HOMO-LUMO Analysis and Electronic Transitions

As the TC isomeric form has the minimum energy according to calculations, it has been accepted as the most stable form and other values have been compared according to this value. This conformer is 3.44, 0.09 and 2.60 kcalmol^{-1} more stable than CC, CT and TT isomeric forms respectively. In Table 5 calculated energies and energy differences have been presented comparatively.

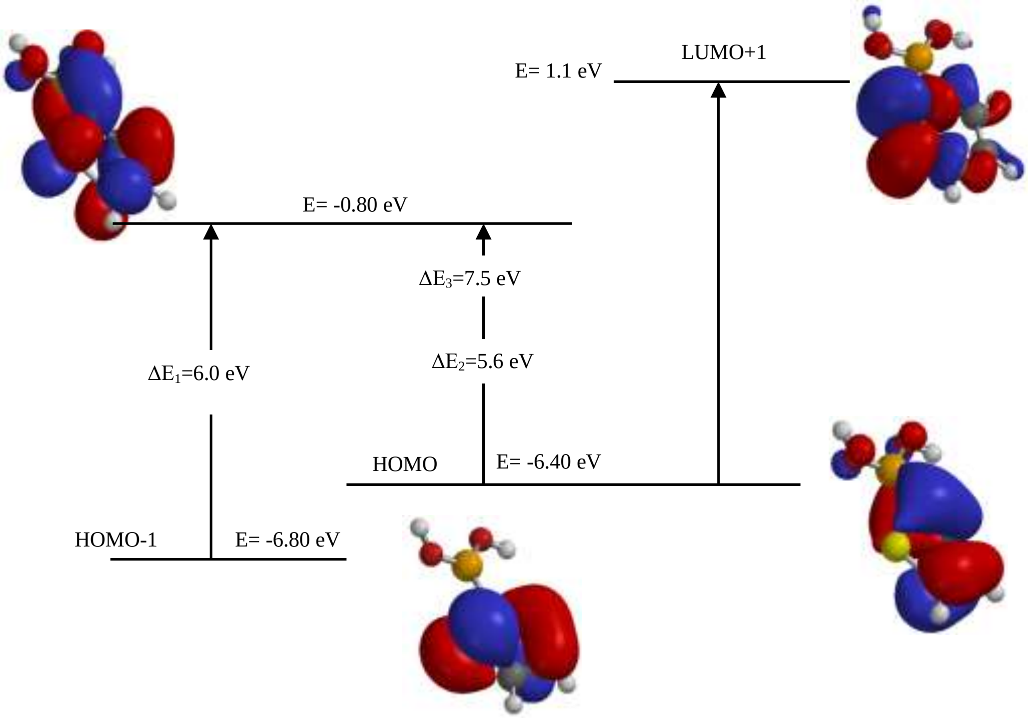

Figure 4. Electron transitions and energy differences between MO's.

Energy differences were calculated according to Equation (1) below [23, 24].

$$\Delta E = E(_{C}{}^{0}) - E(_{TC}) \tag{1}$$

Due to these differences between the calculated energies, TC conformer has been handled as a symbol for representing the electronic transitions and visualization of e^- transfer between MO's in Figure 4. The calculated UV-Vis spectra plots were depicted in Figure 5. Besides brief tables of transitions and HOMO LUMO surfaces for the compound have been added in the following lines. Table 4 summarizes the energy values for HOMO&LUMO boundary surfaces and in Table 5 the differences have been tabulated in different energy units.

Table 4. Calculated Energies (eV) of the MO surfaces.

M.O.	CC	CT	TC	TT	Ave
LUMO{+1}	0.40	0.50	1.10	1.00	0.750
LUMO	-1.10	-0.90	-0.80	-0.60	-0.850
HOMO	-6.70	-6.40	-6.40	-6.20	-6.425
HOMO{-1}	-7.10	-6.90	-6.80	-6.50	-6.825
HOMO{-2}	-8.50	-8.60	-8.60	-8.80	-8.625
HOMO{-3}	-8.80	-9.10	-9.00	-8.90	-8.950
HOMO{-4}	-9.60	-9.40	-9.40	-9.40	-9.450
HOMO{-5}	-10.00	-9.90	-9.90	-9.60	-9.850
HOMO{-6}	-10.00	-10.00	-10.00	-9.80	-9.950
HOMO{-7}	-10.80	-10.40	-10.50	-10.20	-10.475
HOMO{-8}	-10.90	-10.70	-10.70	-10.60	-10.725
HOMO{-9}	-11.20	-10.90	-10.80	-10.70	-10.900

Table 5. The energy equivalencies for the transitions between the conformers for the compound

Conformers	Energy (Hartree)	Energy Differences			Eq. Freq. (cm^{-1})	Dip. Momnt (Debye)
		(Hartree)	($kcalmol^{-1}$)	(eV)		
CC	-729.017314	0.0054880	3.443769392	0.149337261	1204.45136	2.85
CT	-729.022648	0.0001540	0.096636386	0.004190586	33.79837999	4.60
TC	-729.022802	0.0000000	0.0000	0.0000	0.0000	2.53
TT	-729.018660	0.0041420	2.599142278	0.112710447	909.04474	5.39
Av.	-729.020356	0.0024460	1.534887014	0.066559574	536.82362	3.84

3.1.3. Mulliken Charge Distribution

Generally, the electronic distribution on a molecule is not homogenous because of the electronegativity differences between the atoms. This heterogeneity causes the localization 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 and electronically poor sites are more suitable for nucleophilic 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 and depicted in figure 6. As can be seen in the graphic, all of the H atoms have a considerable positive charge but especially H1 and H2 which are next to O1 and O2 atoms have dramatically huge positive charges. C atoms have negative charges as expected due to S and B atoms which are not much electronegative. C2 and C3 have relatively smaller charges but C1 and C4 have obtrusive negative charges due to their neighbors. Even so, the most striking negative charges localized on the O1 and O2 atoms which are the most electronegative parts of the molecule.

Table 6. Molecular orbital energies and differences forthe conformers of TBA (* From Ref. [14])

Conformer	**HOMO-1**	**HOMO**	**LUMO**	**LUMO+1**	**ΔE (eV)**			**λmax**			
					ΔE_1	**ΔE_2**	**ΔE_3**	**Calculated (Vac)**			**Exp.* (Methanol)**
CC	-7.1	-6.7	-1.1	0.4	6	5.6	7.1	206.64	221.4	174.62	236.5
CT	-6.9	-6.4	-0.9	0.5	6	5.5	6.9	206.64	225.42	179.68	
TC	-6.8	-6.4	-0.8	1.1	6	5.6	7.5	206.64	221.4	165.31	
TT	-6.5	-6.2	-0.6	1	5.9	5.6	7.2	210.14	221.4	172.2	

*Borrowed from Ref. (14)

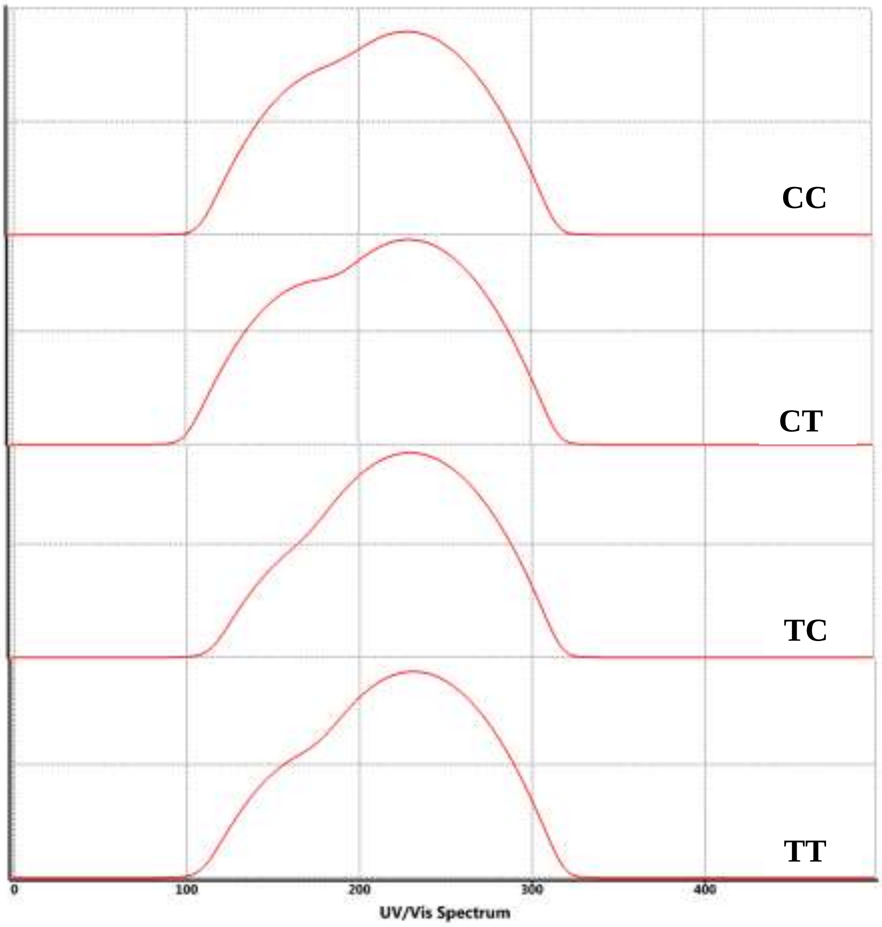

Figure 5. Calculated UV-Vis spectra for the isomers of TBA

These details can also be tracked from the models' ESP Maps depicted in Figure 6 according to color. Also, all charge values including natural and electrostatic charges can be found in the supplementary material.

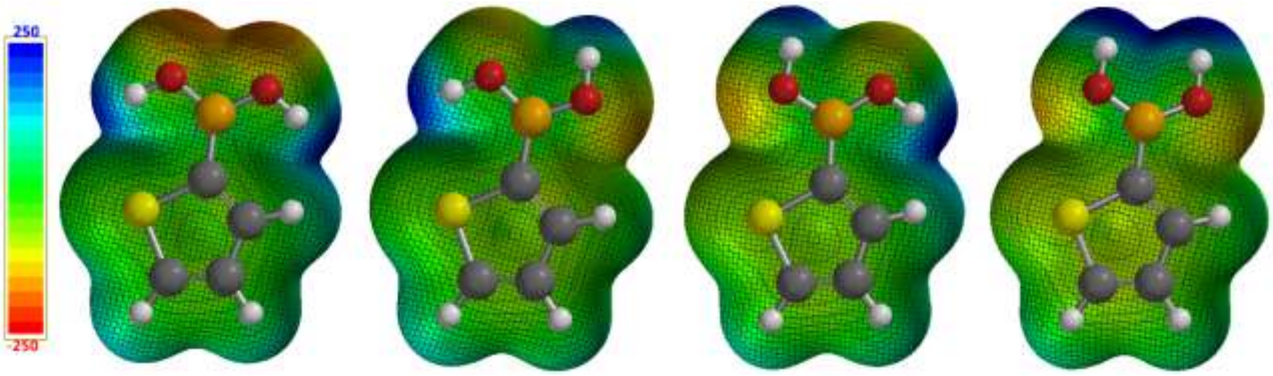

Figure 6. Electrostatic potential map (ESP Map) for the isomers of TBA

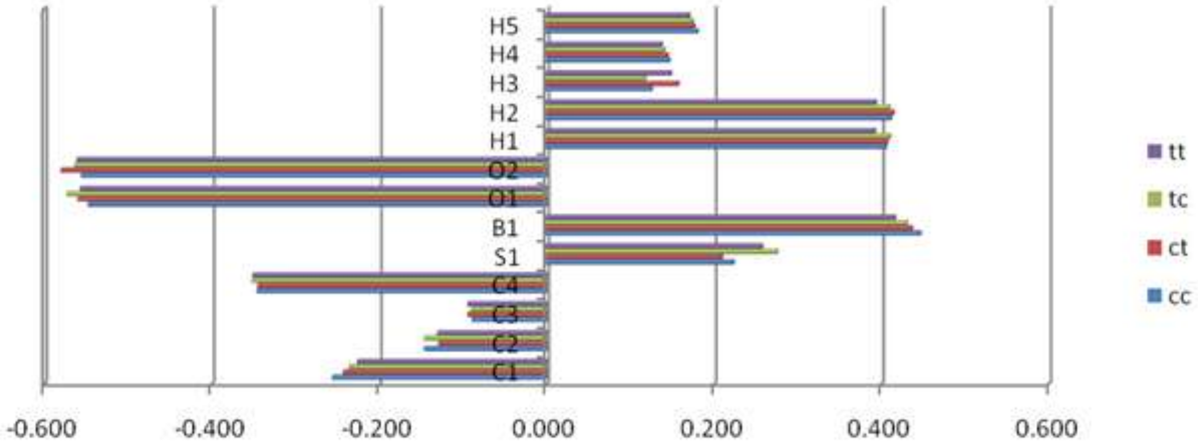

Figure 8. Calculated Mulliken charge distribution of the isomers of TBA

3.1.4. Vibrational Spectroscopy (FT-IR and FT-RAMAN)

The molecule has 13 atoms and that means 33 vibrational modes in two main parts. $–B(OH)_2$ and ring groups. The most mechanically active part of the molecule is the $–B(OH)_2$ group which gives motion to the molecule. It exhibits swinging, rocking and every kind of mechanical motions which adds isomeric transformations to the molecule.

As a brief analysis, the frequencies and their corresponding bonds have been tabulated in Table 7 and Figure 7. In the table, the isomers of the molecule were involved comparatively. These results also can be found in supplementary material as well. Most experimental values are in an agreement with the results taken for methyl and phenylboronic acids [23,24]. Even so, some dramatic points should be underlined [17].

1. From a rapid view, it can be said the differences between the experimental and calculated values are dramatically rising after the 3000s.
2. In the experimental spectrum, the broad peak in 3219cm^{-1} refers to $–C(BOH)_2$ group which is generally seen in the 3300-3200cm^{-1} band due to its bonded –O-H stretch [9].

Table 7. Comparison of theoretical and experimental FT-IR and FT-RAMAN spectra for the conformers of TBA

No	A	DFT / B3LYP 6.31G								Experimental[1]		Total energy Distribution[2,1]
		CC	i_{CC}	CT	i_{CT}	TC	i_{TC}	TT	i_{TT}	FT-IR	Raman	
1*	A"i	53	*0.14*	22	*5.82*	42	*2.65*	59	*0.13*			τ(C-B) (64), τ(B-O) (24)
2*	A"	148	*1.02*	139	*1.84*	141	*2.01*	136	*4.21*			β(C-B) (64), β(CBO) (33)
3*	A'	154	*3*	145	*0.58*	149	*1.91*	149	*10.65*			γ(BCCτ) (76), γ(CBOO) (12)
4*	A'	332	*2.95*	324	*5.74*	325	*9.54*	328	*6.46*			β(CBO) (45), υ(C-B) (19), υ(C-τ) (11), Δ1(R) (10)
5*	A'	393	*12.79*	393	*7.22*	392	*3.66*	356	*0.37*		**393 s**	β(CBO) (48), β(C-B) (16), υ(C-τ) (15)
6*	A"	406	*3.91*	434	*27.05*	446	*17.51*	395	*2.42*			τ2 R (70), τ(B-O) (10), γ(B-C) (10)
7*	A"	447	*22.16*	460	*153*	471	*158.4*	439	*64.2*	**457 w**	**498 vs**	τ(B-O) (80)
8*	A"	524	*161.5*	547	*4.3*	547	*32.42*	518	*141.3*			τ(B-O) (39), τ1R (34), τ2R (14)
9*	A'	564	*0.31*	547	*41.84*	553	*14.85*	563	*43.05*	**547 m**	**536 s**	β(OBO) (41), Δ1(R) (26), υ(C-B) (13)
10*	A"	575	*0.85*	591	*21.54*	592	*9.58*	584	*25.67*			τ1R(67), τ(B9-O10) (15)
11	A"	651	*40.84*	652	*10.41*	662	*1.2*	658	*40.78*	**647 s**		υ(C-τ) (48), Δ1(R) (23)
12	A'	658	*0.43*	659	*58.38*	663	*59.61*	661	*6.02*		**667 s**	γ(CBOO)(68), γ(BCCτ) (16)
13	A"	727	*80.84*	727	*66.07*	732	*75.67*	731	*63.34*	**713 s**		γ(C-H) (99)
14	A'	750	*1.75*	751	*1.92*	752	*2.56*	752	*1.78*			Δ2(R) (66), υ(C-τ) (32)
15	A"	848	*4*	862	*15.07*	847	*2.95*	863	*3.91*	**799 s**		γ(C-H) (88)

Table 7. Comparison of theoretical and experimental FT-IR and FT-RAMAN spectra for the conformers of TBA (Cont.)

No	A	DFT / B3LYP 6.31G								Experimental[1]		Total energy Distribution[2,1]
		CC	i_{CC}	CT	i_{CT}	TC	i_{TC}	TT	i_{TT}	FT-IR	Raman	
16	A’	863	*12.48*	865	*4.29*	866	*14.13*	865	*21.51*	**857 m**		υ(C-τ) (67), Δ1(R) (19)
17	A”	920	*0.3*	932	*0.76*	917	*0.5*	929	*1.11*	**884 m**	**880 vs**	γ(C-H) (85), τ1R (14)
18	A'	978	*13.17*	982	*69.03*	979	*22.38*	949	*193.5*	**944 w**	**956 m**	υ(B-O) (39), β(O-H) (35), υ(C-τ) (13)
19	A'	1017	*249.5*	1030	*122.9*	1034	*157.7*	983	*78.14*			β(O-H) (78), υ(B-O) (19)
20	A'	1057	*101*	1047	*97.39*	1054	*165.2*	1052	*101.8*			β(O-H) (34), υ(C-τ) (21), υ(C-B) (12)
21	A'	1092	*27.93*	1089	*27.4*	1093	*3.77*	1094	*7.17*	**1054 m**		υ(C-C) (56), β(C-H) (29)
22	A'	1121	*9.83*	1122	*1.17*	1121	*21.46*	1123	*9.49*	**1087 m**	**1076 m**	β(C-H) (66), υ(C-C) (23)
23	A'	1258	*4.42*	1246	*20.09*	1259	*0.32*	1249	*8.74*	**1196 s**	**1161 m**	β(C-H) (51), υ(C-C) (29)
24	A'	1345	*420.3*	1354	*215.2*	1361	*172.3*	1359	*109.2*		**1327 m**	υ(C-C) (34), υ(B-O) (14), β(C-H) (21)
25	A'	1389	*176.6*	1402	*222.8*	1400	*220.8*	1405	*167.2*			υ(B-O) (51), υ(C-C) (11)
26	A'	1456	*184.3*	1438	*249.4*	1443	*237.3*	1420	*265.6*	**1365 vs**		υ(B-O) (45), υ(C-C) (16), β(C-H) (13)
27	A'	1482	*76.94*	1485	*113.7*	1484	*134*	1486	*114.5*	**1425 vs**	**1423 m**	υ(C-C) (69), β(C-H) (10)
28	A'	1586	*41.45*	1586	*57.66*	1589	*70.69*	1588	*68.05*	**1518 vs**		υ(C-C) (48), Δ(R) (34)
29	A'	3198	*16.15*	3222	*4.73*	3191	*19.25*	3219	*5.34*		**3008 w**	υ(C-H) (98)
30	A'	3231	*6.96*	3237	*4.86*	3229	*9.02*	3233	*8.31*		**3086 m**	υ(C-H) (99)
31	A'	3272	*0.98*	3271	*1.13*	3266	*1.71*	3265	*2.15*		**3163 m**	υ(C-H) (98)
32	A'	3818	*36.78*	3771	*59.58*	3773	*61.68*	3787	*8.77*	**3219 vs**		υ(O-H) (100)
33	A'	3824	*25.44*	3802	*30.55*	3809	*28.08*	3792	*50.87*			υ(O-H) (100)

[1]Received from Ref. 14, 23, 24 [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

1. 3008, 3086 and 3163 cm^{-1} peaks assign the C-H stretching motions which belong to the thienyl ring part.
2. There are two kinds of CC bonds in the ring; -C-C- and –C=C- of which stretchings are seen as 1518 and 1423cm^{-1} peaks.
3. As a resulting word, the calculations and experiments can be supposed to be an agreement in 500 to 1600 cm^{-1} but the deviations between results rise in peaks of 3000+ cm^{-1}.

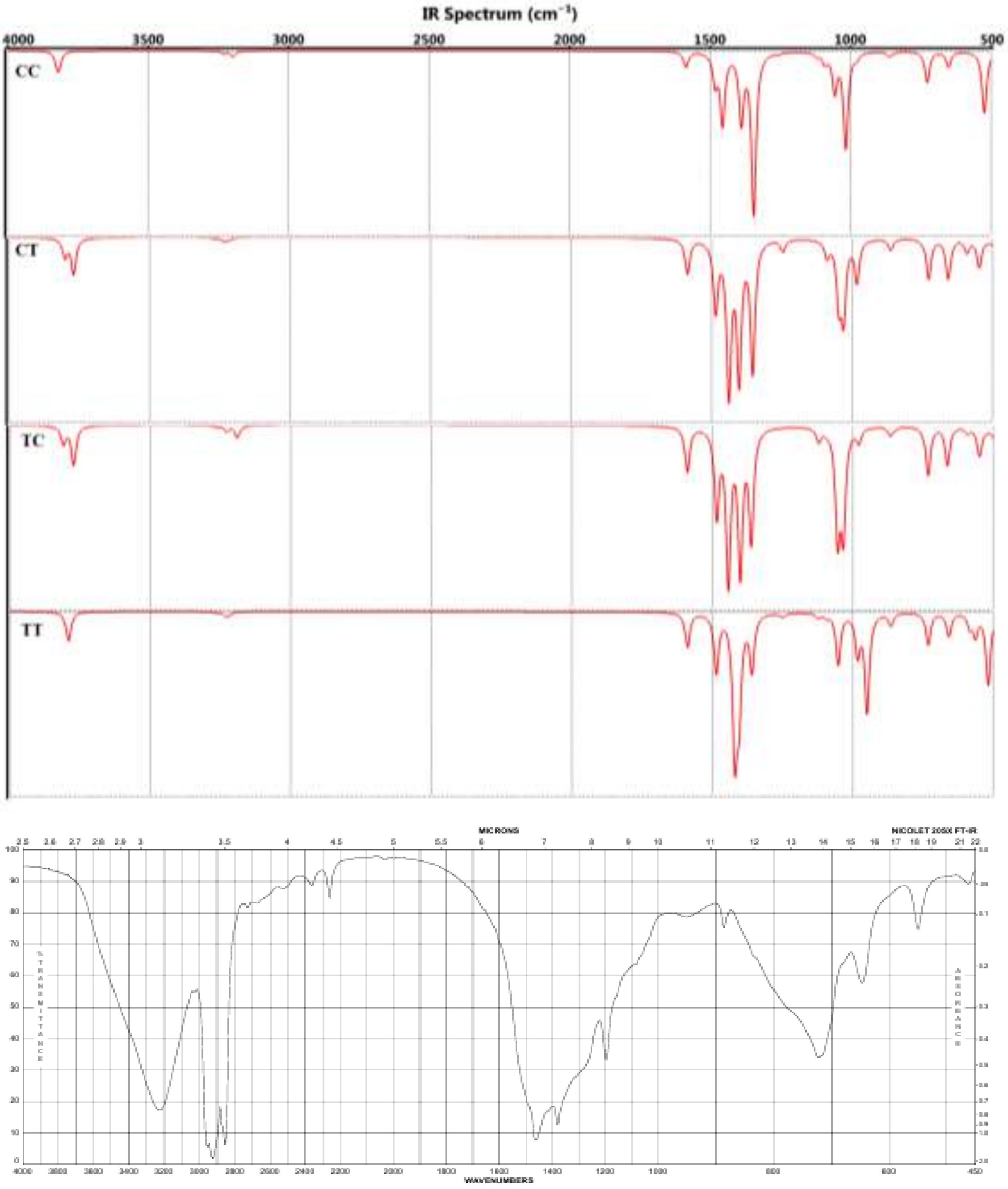

Figure 7. Calculated and experimental* FT-IR spectra of the compound TBA (*=from ref. 12)

4. 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 from a new point of view, isomeric transformations were examined for the first time as well.

The experimental values taken from the literature were compared to calculated ones and found to be very close with small deviations. It was seen that the calculations related to vibrational analysis moved away from the experimental results after 3000 cm^{-1}, but the values were very close in the range of 500-1600 cm^{-1}. Due to the lack of experimental crystallographic data in the literature, the calculated geometric values were compared with 2 different molecules structurally similar to TBA. As a result of all studies, the calculated and experimental values were found to be very close and in agreement.

Acknowledgment

The software SPARTAN-14 used in this study was bought with the financial support of Pamukkale University Scientific Research Support Unit (Project no: HZL-2014/5). Besides, the experimental FT-IR spectrum of the compound TBA was received from the Sigma Aldrich product page and was used with gratitude for their kindness.

The supplementary data file contains some additional data such as NMR spectra FT-RAMAN spectra and some extra tables about the title molecule TBA. Available from the authors upon reasonable request,

References

[1]. Hall, D.G., Boronic acids: preparation and applications in organic synthesis and medicine, DOI:10.1002/3527606548, Wiley-VCH Verlag GmbH & Co. KGaA, 2006.

[2]. Kar, A., Pharmacognosy and Pharmacobiotechnology 2nd Ed., New Age International (P) Ltd. Publishers, New Delhi, 2007.

[3]. Tjarks, W., Anisuzzaman A.K., Liu L., Soloway S.H., Barth R.F., Perkins D.J., Adams D.M., Synthesis and in vitro evaluation of boronated uridine and glucose derivatives for boron neutron capture therapy. J. Med. Chem., 1992, 35, 1628-1633.

[4]. Zepeda-Velazquez, L.C., Synthesis and characterızation of novel stimuli-responsive silicone-boronic acid materials, Ph.D. thesis, McMaster University, Hamilton, Ontario, 2015.

[5]. Christophersen, C., Begtrup, M., Ebdrup, S., Petersen, H., Vedsø, P., Synthesis of 2,3-Substituted Thienylboronic Acids and Esters. The Journal of organic chemistry, 2003, 68(24), 9513-9516.

[6]. Wang, Y., Liao, J., Wang, B., Chen, H., Zhao, H., Peng, M., Fan, S., Synthesis and Properties of Novel Borondipyrromethene (BODIPY)-Tethered Triphenylamine Conjugates, Aust. J. Chem., 2015, 68(10), 1485-1491.

[7]. Fang, Y., Zhang, X., Targeting NEK2 as a Promising Therapeutic Approach for Cancer Treatment, Cell Cycle, 2016, 15(7), 895-907.

[8]. Fa-Bao, L., Xun, Y., Tong-Xin, L., Guan-Wu, W., Fullerenyl Boronic Esters: Ferric Perchlorate-Mediated Synthesis and Functionalization, Organic Letters, 2012, 14(7), 1800-1803.

[9]. Lu, G.P., Voigtritter, K. R., Cai, C., Lipshutz, B., H., Ligand effects on the stereochemical outcome of Suzuki-Miyaura couplings. The Journal of organic chemistry, 2012, 77(8), 3700-3703.

[10]. Karabacak, M., Kose, E., Sas, E.B., Kurt, M., Asiri, A.M., Atac, A., DFT calculations and experimental FT-IR, FT-Raman, NMR, UV–Vis spectral studies of 3-fluorophenylboronic acid, Spectrochim. Acta, Part A, 2015, 136, 306-320.

[11]. Zheng, H., Ghanbari, S., Nakamura, S., Hall, D.G., Boronic Acid Catalysis as a Mild and Versatile Strategy for Direct Carbo- And Heterocyclizations of Free Allylic Alcohols, Angewandte Chemie Int. Ed., 2012, 51(25), 6187-6190.

[12]. https://www.sigmaaldrich.com/catalog/product/aldrich/436836?lang=en&region=TR 04/23/2020.

[13]. Zheng, H., Lejkowski, M., Hall, D.G., Mild and selective boronic acid-catalyzed 1,3-transposition of allylic alcohols and Meyer–Schuster rearrangement of propargylic alcohols, Chem. Sci., 2011, 2(7), 1305-1310.

[14]. Sachan, A. K., Pathak, S. K., Sinha, L., Prasad O., Karabacak, M., Asiri, A. M., A combined experimental and theoretical investigation of 2-Thienylboronic acid: Conformational search, molecular structure, NBO, NLO and FT-IR, FT-Raman, NMR and UV spectral analysis, Jour. of Molec. Struct., 2014, 1076, 639-650.

[15]. Ghosh, R., Simonsen, S.H., Structure of 2-(2'-thienyl)pyridine at 193 K, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 49(5), 1993, 1031-1032.

[16]. Rettig, S.J., Trotter, J., Crystal and molecular structure of phenylboronic acid (C6H5B(OH)2 Can. J. Chem. 1977, 55, 3071-3075.

[17]. Silverstein, R. M., Webster, F. X., Kiemle, D.J. Spectrometric Identification of Organic Compounds, 7th Ed., John Wiley Sons INC., 2005.

[18]. Ramachandran, K. I., Deepa, G., Namboori, K., Computational Chemistry and Molecular Modeling: Principles and Applications, Springer-Verlag Heidelberg, Berlin, 2008.

[19]. Jensen, F., Introduction to Computational Chemistry, Wiley, 2016.

[20]. SPARTAN’14, Wavefunction Inc. Irvine CA, USA, 2014.

[21]. Hehre, W. J., SPARTAN’14 Tutorial and User's Guide, Wavefunction Inc., 2014.

[22]. Peter, K., Vollhardt, C., Schore, N. E., Organic chemistry: structure and function, 6th ed. Freeman&Comp., NY-US, 2011.

[23]. Rani, U., Karabacak, M., Tanrıverdi, O., Kurt, M., Sundaraganesan, N., The spectroscopic (FTIR, FT-Raman, NMR and UV), first-order hyperpolarizability and HOMO-LUMO analysis of methyl boronic acid, Spectrochim. Acta, Part A, 2012, 92, 67-77.

[24]. Karabacak, M., Kose, E., Atac, A., M. Cipiloglu, A., Kurt M., Molecular structure investigation and spectroscopic studies on 2,3-difluorophenylboronic acid: A combined experimental and theoretical analysis, Spectrochim. Acta, Part A, 2012, 97, 892-908.