Research article

The DFT study on the electronic structure of boronic acid derivatives and its esters with fructose

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Abstract: *Theoretical investigations are carried out to examine the geometrical structure and parameters of electron transitions to the lowest excited states of two boronic acid derivatives: 3-aminophenylboronic acid and 3-(acetamidomethyl)phenyl boronic acid and its cycling esters with fructose, using the DFT based 6-31 G(d,p) method. The most stable ester isomer of each acid has been selected. Predicted excitation wavelength are shorter (less than 0.5 eV) than experimental ones, what is in a good agreement considering limitations of the DFT method. In case of almost every calculated molecule the analysis of electronic transitions shows that transition $S_0 \rightarrow S_1$ involves electron transfer mainly from the HOMO to LUMO orbital.*

Keywords: *boronic acid derivatives, TD-DFT method, boronic esters with fructose.*

Introduction

3-aminophenylboronic acid (3APBA) and 3-(acetamidomethyl)phenyl boronic acid (3AAPBA) are the phenylboronic derivatives with one boron atom. Both acids are fluorophores, similarly to other boronic derivatives containing phenyl ring in the molecule. 3APBA has amino group in meta-position, while 3AAPBA has acetamidomethyl group in the same position. As it is well known, boronic acid derivatives, at neutral pH has two hydroxyl groups linked to the boron atom. In this case boron atom is trigonal (sp^2) hybridized. At alkaline solution, third hydroxyl group is attached to the boron atom, and as a consequence hybridization of boron atom changes to tetrahedral (sp^3). It means that at pH under pK_a of each boronic acid, molecules with trigonal hybridized boron atom represent the majority population of all boronic acid molecules, while at pH above pK_a, molecules with tetrahedral hybridized boron atom are in majority.

The characteristic feature of boronic acid derivatives is that they bind sugar molecules which lead to formation of cycling covalent bond. Boronic acids bind sugar molecules by two hydroxyl groups, connected with boron atom. For the majority of boronic acids this reaction causes quenching of their fluorescence

[1-3]. Sugar quenching effect on 3APBA fluorescence was also examined by our group previously [4]. Sensitivity of boronic acid derivatives fluorescence on mono- and di-saccharides makes it possible to use them as optical saccharide sensor component. Since the longtime researches have been investigated the use of boronic acid derivatives as an optical sensor component responsible for sugars detection in solution [5, 6]. Particular attention has been paid to the detection of glucose in human body fluids, with the aim to create a glucose sensor working in vivo for people with diabetes [7-9]. However, studies on boronic acids – saccharides optical interactions demand sophisticated apparatus (spectrophotometer, spectrofluorometer and time-resolved fluorometer) and are very time consuming. It is well known that monoboronic acid derivatives are most sensible for fructose [10, 11]. From this reason there are many scientific reports which aim at searching for boronic acid derivative of greater sensitivity and selectivity for other saccharides [10, 12-14] particularly for glucose. Such screening researches require synthesis of more and more complex and sophisticated structures of mono- and multi-boronic acid derivatives [6, 15, 16]. In such a synthesis problems with solubility and stability of investigated compounds may occur. Theoretical studies offer possibility for rational screening of the collection of molecules with the aim to select the most promising and easy to synthetize components of sugar sensor. In this way theoretical studies may reduce time and experimental efforts. Determination of geometrical and electronic properties of boronic acids derivatives and its esters with fructose is the first important step in the rational design of promising sugar sensor component.

In this report we have applied theoretical DFT(B3LYP) method for the calculation of the geometrical structures and electronic transitions of 3APBA and 3AAPBA and its esters with fructose. The theoretically predicted parameters of electronic transitions to the lowest excited state ($S_0 \rightarrow S_1$) were compared with experimental data to get more insight into the nature of the electronic transitions.

Materials and Methods

Geometry optimization and the subsequent vibrational frequencies calculations of: 3APBA, 3AAPBA and its esters with β-D-fructofuranose, have been performed using Gaussian 09 and GaussView 5 suite of programs [17, 18].

The calculations have been carried out at the density functional theory (DFT) level with the use of B3LYP functional and 6-31G(d,p) basis set in vacuum. Analyzing the calculated vibrational frequencies, no imaginary frequencies have been found, which indicated that the optimized structures corresponded to the local minima on the potential energy hypersurface.

TD DFT/6-31G(d,p) calculations of the electronic transitions to the lowest excited singlet states have been carried out using the DFT(B3LYP) optimized geometries. Solvent effects have been included within the PCM model.

Absorbance spectra of the studies compound in water (Millipore H_2O) were collected using a Nicolet Evolution 300 spectrophotometer (Thermo Scientific, USA) with 10-mm path-length quartz cells. The measurements were performed at room temperature.

Results and Discussion

The optimized structure of 3APBA and 3AAPBA

At first we have calculated geometrical structures of both acids with trigonal and tetrahedral hybridized boron atom. We used DFT(B3LYP)/6-31G(d,p) method because of its reasonable computational cost. This method has been applied successfully in the previous reported studies of phenylboronic acid [19], methylphenyl boronic acid [20] and 3-hydroxyphenylboronic acid [21].
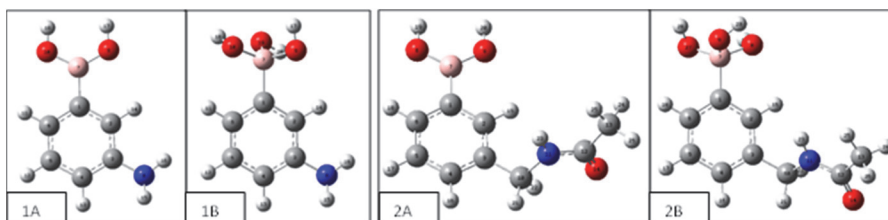
Figure 1. Optimized geometry of 1A – sp^2 hybridized 3APBA, 1B – sp^3 hybridized 3APBA, 2A – sp^2 hybridized 3AAPBA and 2b – sp^3 hybridized 3AAPBA. The different colors (pink, blue, red) represent atoms of: boron, nitrogen, oxygen

Table 1. The DFT(B3LYP)/6-31G(d,p) calculated key geometrical parameters of the optimized geometries for 3APBA and 3AAPBA

	3APBA		3AAPBA	
	sp^2	sp^3	sp^2	sp^3
d_{C1-B7}	1.563	1.654	1.564	1.651
d_{B7-O9}	1.376	1.476	1.374	1.484
d_{B7-O10}	1.375	1.478	1.374	1.493
$d_{B7-O19(27)}$	-	1.500	-	1.483
d_{C3-N8}	1.401	1.426	-	-
$\angle O_9B_7O_{10}$	123.48	111.28	123.92	107.42
$d_{N11-C12}$	-	-	1.368	1.353
$d_{C12-O14}$	-	-	1.225	1.231
$\angle N_{11}C_{12}O_{14}$	-	-	122.91	123.34
$\angle C_2C_3C_{10}N_{11}$	-	-	51.06	63.34

Optimized geometries are displayed graphically in Fig. 1. The key geometrical parameters of the optimized geometries for each structure are gathered Table 1 and the calculated electronic properties are presented in Table 2. In the both acids molecules with sp^2 hybridized boron atom, m-phenyl ring, boronic group (boron atom linked with hydroxyls groups) and nitrogen atom in case of 3APBA, carbon C10 in case of 3AAPBA, are situated on the same plane. After the attachment of third hydroxyl group to boron, hybridization of boronic group becomes spatial, but the rest of the molecule skeleton is still planar.

From Table 2 it can be seen that for both acids, the calculated dipole moment value is higher for molecules with tetrahedral hybridized boron atom. This is

a consequence of different charge distribution and may influence the reactivity of the molecules.

Table 2. Total energy (E), electric dipole moment (μD), HOMO energy (EHOMO), LUMO energy (ELUMO) and HOMO/LUMO energy gap (E_g) for 3APBA and 3AAPBA molecules

		E [a.u.]	μ_D [D]	E_{HOMO} [eV]	E_{LUMO} [eV]	E_g [eV]
3APBA	sp^2	-463.65	2.79	5.52	0.54	4.97
	sp^3	-539.59	7.35	5.11	0.69	5.81
3AAPBA	sp^2	-655.63	5.43	6.48	0.69	5.79
	sp^3	-731.57	7.09	5.63	0.33	5.96

Comparing the geometrical parameters of 3APBA molecule with sp^2 and sp^3 hybridized boron atom it can be seen that bonds in molecule are slightly shorter when molecule is in planar distribution. Bonds are elongate by 0.1 Å (in case of B-O bond) when the conformation of boron atom turns to tetrahedral.

In 3APBA molecule, amino group is directly connected to aromatic ring, while in 3AAPBA amide group is separated from aromatic ring by one carbon. There are no significant differences between the corresponding bonds lengths in both acids. In 3AAPBA slight elongation of the bonds is also observed in molecule with sp^3 hybridized boron atom as compared to molecule with sp^2 hybridized boron atom. There are also no significant differences in the bond angles. This indicates that changes in boronic acid derivatives structure caused by replacing amino group in meta position with the acetamidomethyl group have no influence on boronic group geometry.

The calculated geometrical parameters concerning acetamidomethyl substituent are similar in molecules with both sp^2 and sp^3 hybridization of boron atom.

The optimized structures of both acids were used for subsequent TD/DFT(B3LYP)/6-31G (d,p)/PCM calculation of electron transition parameters to the lowest electron state $S_0 \rightarrow S_1$. The obtained results were compared with experimentally derived absorbance spectra of both acids in water. The obtained results are gathered in Table 3.

From Table 3 it may be seen that the TD DFT(B3LYP) predicted excitation wavelengths are shorter than those determined experimentally. This discrepancy between theoretical and experimental data may be related with systematic overestimation of the TD(DFT)/B3LYP of electronic transitions energies especially for molecules with internal charge transfer and for molecules exhibiting extended π-systems [22]. Our calculated data are within the typical error of TDDFT (0.1-0.5 eV) [22]. Moreover, the applied theoretical method well reproduce quality trend that excitation wavelength of boronic acid derivatives with sp^3 hybridized boron atom is shift to the shorter wavelength compared to excitation wavelength of molecules with sp^2 hybridized boron atom.

Table 3. The theoretically predicted TD/DFT(B3LYP)/6-31G(d,p)/PCM(water) absorption wavelengths (λ) of the lowest $S_0 \rightarrow S_1$ electronic transition corresponding to the lowest (in energy) absorption band in the experimental absorbance spectra (Exp. λ) of 3APBA and 3AAPBA

			λ (nm)	f	Exp. λ (nm)
3APBA	sp^2	H$\rightarrow$L	283.57	0.0617	295
	sp^3	H$\rightarrow$L	248.11	0.0356	261
	sp^2	H$\rightarrow$L	247.50	0.0029	277
3AAPBA		H$\rightarrow$L (S_0-S_1)	246.92	0.00001	270
	sp^3	H$\rightarrow$L+1 (S_0-S_2)	235.66	0.0073	261

The analysis of electronic transitions shows that transition $S_0 \rightarrow S_1$ involves electron transfer mainly from HOMO to LUMO for 3APBA (sp^2 and sp^3) molecules and for 3AAPBA molecules with sp^2 hybridized boron atom.

In case of 3AAPBA molecule with sp^3 hybridized boron atom transition $S_0 \rightarrow S_1$ is very low intensity (has little oscillator force). It can be obscured by intense (f = 0.0073) $S_0 \rightarrow S_2$ transition (which may mainly be described as HOMO to LUMO+1 transition).

The graphical representation of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) predicted by the TD DFT(B3LYP) method is shown in Fig. 2.
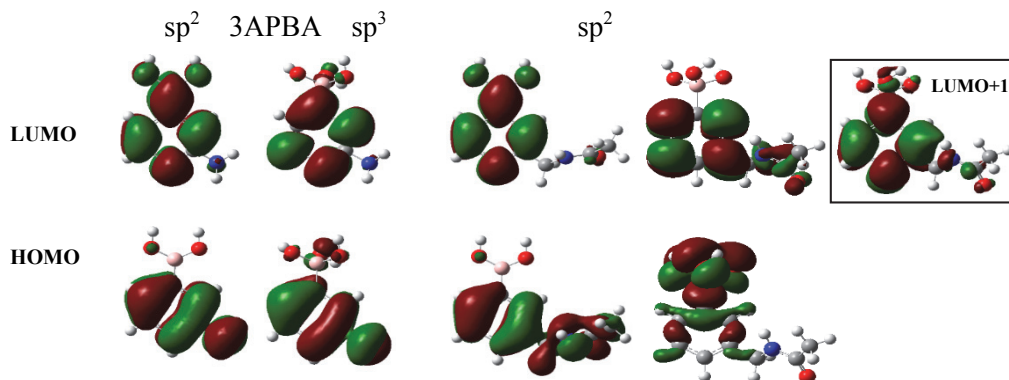
Figure 2. Graphical representation of the orbitals participating in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 3APBA and 3AAPBA

It may be seen that the HOMO orbitals of both molecules with sp^2 hybridized boron atom are localized on phenyl ring and amino/acetamide group, while the LUMO orbital are mainly localized on phenyl ring and on boronic group (Fig. 2). This may suggest that $S_0 \rightarrow S_1$ excitation may involve charge transfer from amino/acetamide to the boronic group (nitrogen atom is a donor of electron and boron atom is a charge acceptor).

When in 3APBA boron atom is tetrahedral hybridized, the HOMO orbital is localized similarly as for molecule with trigonal hybridized boron atom. LUMO orbital is mainly localized only on phenyl ring with small coefficient on boronic group. In this case $S_0 \rightarrow S_1$ excitation may be considered as charge transfer from amino group (nitrogen is a donor of electron) to phenyl ring.

For 3AAPBA with tetrahedral hybridized boron atom, localization of the HOMO and LUMO orbitals is quite different. In this case HOMO orbital is localized mainly on boronic group and on phenyl ring to a small extent. The LUMO orbital is localized mainly on phenyl ring with small coefficient on acetamide group. Bearing in mind that LUMO orbital has small oscillator force the LUMO +1 orbital is also presented. The LUMO + 1 orbital is localized on phenyl ring, with small coefficient on boronic and acetamide group. In this case it seems that $S_0 \rightarrow S_1$ excitation is accompanied by the charge transfer from boronic group (the donor of electron) to phenyl ring (acceptor of electron). These observations indicated that addition of the third hydroxyl group to boron atom caused changes in HOMO and LUMO orbitals distribution as well as in charge transfer processes accompanying the $S_0 \rightarrow S_1$ transition.

The optimized electronic structures of 3APBA and 3AAPBA esters with fructose

Our previous experimental results indicated that among the tested six sugars (glucose, fructose, galactose, maltose, lactose and saccharose) fructose interacts with both acids the most strongly [4]. It has been shown that fructose quenched fluorescence intensity of both acids with the highest efficiency. From this reason we have optimized the structures of the studied esters with fructose.

The structures of esters were generated using the D-furanose molecule with syn-periplanar configuration of pairs of hydroxyl groups, since it has been previously proved [23, 24] that only syn-periplanar pairs of hydroxyl groups in D-furanose form of monosaccharides are available for boronic acids binding. This means that binding with acid concern only hydroxyl groups attached to second, third and sixth carbon of fructose. In the first ester (2,6 ester) boronic acid is linked with second and sixth hydroxyl group, in the second one (3,6 ester) the third and sixth hydroxyl groups are bonded with acid and in the third ester, denoted as 2,3 ester second and third hydroxyl groups are involved in binding with acid.

The optimized geometries of esters are presented in Table 4 and Table 5. The calculated electronic parameters (values of the optimized total electronic energy, dipole moments) are gathered in Table 3.

Table 4. The DFT(B3LYP)/6-31G(d,p) calculated key geometrical parameters of the optimized geometries for three isomers of 3APBA esters with fructose

	3APBA-fru sp^2			3APBA-fru sp^3		
	2,6 ester	3,6 ester	2,3 ester	2,6 ester	3,6 ester	2,3 ester
d_{C1-B7}	1.556	1.567	1.548	1.630	1.634	1.628
d_{B7-O9}	1.369	1.372	1.389	1.489	1.469	1.473
d_{B7-O10}	1.400	1.376	1.373	1.525	1.488	1.504
d_{B7-O19}	-	-	-	1.476	1.519	1.495
d_{C5-N8}	1.400	1.403	1.397	1.420	1.419	1.419
$\angle O_9B_7O_{10}$	122.81	126.25	112.59	110.46	113.27	104.49

Table 5. The DFT(B3LYP)/6-31G(d,p) calculated key geometrical parameters of the optimized geometries for three isomers of 3AAPBA esters with fructose

	3AAPBA-fru sp^2			3AAPBA-fru sp^3		
	2,6 ester	3,6 ester	2,3 ester	2,6 ester	3,6 ester	2,3 ester
d_{C1-B7}	1.571	1.564	1.549	1.634	1.640	1.634
d_{B7-O9}	1.375	1.378	1.380	1.543	1.532	1.511
d_{B7-O10}	1.366	1.369	1.375	1.489	1.493	1.514
d_{B7-O19}	-	-	-	1.455	1.450	1.448
$\angle O_9B_7O_{10}$	125.88	124.69	112.84	109.66	110.52	102.25
$d_{N11-C12}$	1.372	1.368	1.368	1.369	1.354	1.354
$d_{C12-O14}$	1.234	1.226	1.227	1.229	1.231	1.231
$\angle N_{11}C_{12}O_{14}$	120.36	122.90	122.76	120.36	123.35	123.27
$\angle C_1C_2C_{10}N_{11}$	-10.56	71.45	109.98	-144.43	66.12	64.28

Table 6. Total energy (E) and electric dipol moment (μD) of 3APBA and 3AAPBA esters with fructose molecules

		E [a.u.]	μ_D (Debey)
3APBA-fru sp^2	2,6 ester	-997.969	3.305
	3,6 ester	-997.973	5.516
	2,3 ester	**-997.987**	1.526
3APBA-fru sp^3	2,6 ester	-1073.942	3.537
	3,6 ester	-1073.940	5.094
	2,3 ester	**-1073.952**	1.859
3AAPBA-fru sp^2	2,6 ester	-1189.959	6.944
	3,6 ester	-1189.961	3.423
	2,3 ester	**-1189.968**	4.467
3AAPBA-fru sp^3	2,6 ester	-1265.908	2.647
	3,6 ester	-1265.907	9.605
	2,3 ester	**-1265.934**	4.145

Comparing the geometrical structures of 3APBA and 3AAPBA 2,3 esters with that of parent acids molecules no significant differences were found in bond lengths. Similarly to the parent (unbounded to fructose) acid molecules, a slight elongation of bond lengths in ester molecules with tetrahedral hybridization of boron atom has been noticed.

Comparing the calculated total energy values it may be indicated that 2,3 ester is the most stable isomer and this ester isomer will be considered in subsequent calculations.

The optimized geometries of 2,3 esters were used for subsequent TD DFT calculation of the electronic parameters for $S_0{\rightarrow}S_1$ transition. The obtained results were compared with the recorded absorbance spectra of the aqueous esters solutions (Table 7).

Table 7. The theoretically predicted (TD/DFT(B3LYP)/6-31G) absorption wavelength (λ) [nm], oscillator strength (f) of the lowest $S_0{\rightarrow}S_1$ electronic transition corresponding to the lowest (in energy) absorption band in the experimental absorbance spectra (Exp. λ) of 3APBA and 3AAPBA 2,3 ester with fructose

2,3 ester			λ (nm)	f	Exp. λ (nm)
3APBA/fructose	sp^2	H$\rightarrow$L	292.47	0.0711	294
	sp^3	H$\rightarrow$L	251.04	0.0470	260
3AAPBA/fructose	sp^2	H$\rightarrow$L	248.53	0.0209	270
	sp^3	H$\rightarrow$L	239.91	0.0119	260

Excitation energies of esters are almost identical as those corresponding to the parent free acids. The calculated excitation wavelengths are shorter as compared to the experimental values, which may be related with the previously [22] reported tendency of the TD DFT(B3LYP) method to overestimate the excitation energies of molecules with charge transfer character.

Analyzing the calculated electronic transitions in 2,3 esters of both acids with sp^2 and sp^3 hybridized boron atom it may be indicated that $S_0{\rightarrow}S_1$ transition involves predominantly electron charge transfer from the HOMO to LUMO orbital.

The graphical representation of the HOMO and LUMO orbitals of most stable ester isomer of 3AAPBA is shown in Figure 3.

2,3ester 3AAPBA/fructose sp^2 2,3ester
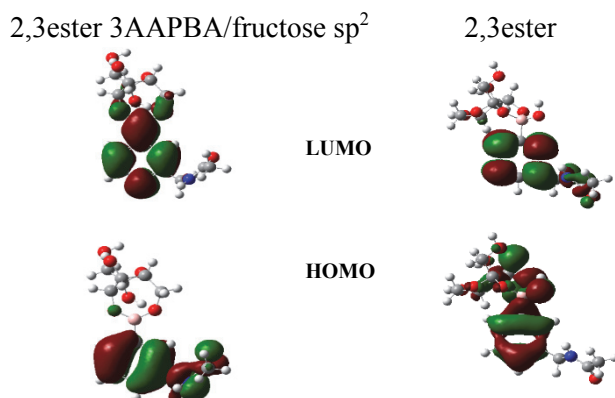
LUMO

HOMO

Figure 3. Graphical representation of the orbitals participating in the lowest electronic transitions of 2,3 ester of 3AAPBA (with sp^2 and sp^3 hybridized boron atom)

The distribution of the HOMO and LUMO orbitals in 3APBA esters is similar to those for the parent acid molecules. The HOMO-LUMO transition is accompanied by the electronic charge transfer from nitrogen to boron atom (data not shown). For 3AAPBA esters with two oxygens attached with boron, the HOMO orbital is localized on phenyl ring and on acetamidomethyl group. The LUMO orbital is localized symmetrically on phenyl ring and boronic group. Such a HOMO and LUMO charge distribution may indicate that the charge transfer occurs from acetamidomethyl group (electron donor) to boronic group (electron acceptor).

When boron is in tetrahedral hybridization, the electron density plots of the HOMO and LUMO are different from those for molecule with trigonal hybridize boron atom. It means that the HOMO orbital is mainly localized on phenyl ring and, to the lesser extent, also on boronic group and fructose part of ester. The LUMO orbital is localized on phenyl ring and acetamidomethyl group.

Analyzing the obtained theoretical results it may be concluded that sugar part of the 2,3 ester has negligible influence on the charge transfer process accompanying the $S_0 \rightarrow S_1$ electronic transition.

Conclusions

In this study the DFT(B3LYP) and TD DFT(B3LYP) methods have been applied to determine geometrical structures and electronic parameters of $S_0 \rightarrow S_1$ transition for 3-aminophenylboronic acid, 3-(acetamidomethyl)phenyl boronic acid and its 2,3 esters with fructose. Our calculations have shown that 2,3 esters of 3APBA and 3AAPBA are the most stable isomers of the studied esters of boronic acid derivatives with fructose.

The theoretically predicted electronic parameters of $S_0 \rightarrow S_1$ transition of boronic acids and its esters are in quite good agreement with experimental absorption spectra.

The obtained theoretical results have indicated that the $S_0 \rightarrow S_1$ transition is mainly the HOMO-LUMO transition and has the charge transfer character.

From the comparison of the electronic structures of the boronic acid esters with those for parent acid molecules it has been concluded that sugar part of the 2,3 ester has negligible influence on the charge transfer process accompanying the $S_0 \rightarrow S_1$ electronic transition.

The results obtained in this theoretical study may be useful for rational design of other boronic acid derivatives for sugar sensing applications.

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