### Tetrahedron 68 (2012) 3761-3767

Contents lists available at SciVerse ScienceDirect

# Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Imino- and aminomethylphenylboronic acids: stabilizing effect of hydrogen bonds

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## ARTICLE INFO

Article history: Received 2 December 2011 Received in revised form 10 February 2012 Accepted 27 February 2012 Available online 9 March 2012

Keywords: Boronic acids Hydrogen bond B–N bond Schiff bases Mannich bases MP2/6-31+G\*\* SESE

# ABSTRACT

ortho-Iminomethylphenylboronic acids were synthesized from the reaction of 2-formyl-phenylboronic acid with primary aromatic amines. Reduction of these compounds yielded the corresponding aminomethylphenylboronic acids. For both types of the compounds, the crystal structure was determined by single crystal X-ray diffraction method. Hydrogen-bonded dimers with an additional intramolecular B-O-H...N hydrogen bond have been observed. Calculations at  $MP2/6-31+G^{**}$  level proved that the most stable form is that with the above-mentioned intramolecular hydrogen bond while the form with dative  $N \rightarrow B$  bond is less favoured. Since the calculated energy difference is small, the competition between possible forms was analyzed in terms of substituent effect stabilization energy (SESE). In the case of *p*-iminomethylphenylboronic acid, both hydroxyl groups are engaged in intermolecular O-H...O interactions resulting in a supramolecular ribbon motif.

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# 1. Introduction

Arylboronic acids are systems that attract increasing scientific interest due to their new applications in organic synthesis, catalysis, supramolecular chemistry, biology, medicine and material engineering.<sup>1</sup> Hydrogen bond plays the key role in the supramolecular assemblies formed by boronic acids.<sup>2</sup> In addition to strong intermolecular hydrogen bonds in typical dimeric units and lateral hydrogen bonds connecting them,<sup>3</sup> there are many examples of inter- and intramolecular bond formation, which together with the intermolecular interactions tune the crystal architecture.<sup>4</sup> The special case is the presence of the *ortho* substituent able to form a hydrogen bond with the B–O–H group. Intramolecular hydrogen bonds are formed in this way with alkoxy,<sup>5</sup> polyoxaalkyl,<sup>6</sup> fluorine,<sup>7</sup> or formyl<sup>8</sup> groups. However, an intramolecular hydrogen bond is not formed in case of the compounds with acetyl<sup>9</sup> or methoxycarbonyl<sup>10</sup> group at the *ortho* position.

The compounds with aminomethyl substituent at the *ortho* position of phenylboronic acids play a special role due to their wide applications. Compounds with tertiary aminomethyl groups are applied in a variety of sugars' receptor systems.<sup>11</sup> Iminomethyl compounds (Schiff bases), which can be obtained in the reaction of

formylphenylboronic acids with primary amines, can be further functionalized due to the presence of the C=N bond. For instance, boronic acids with the aminophosphonate group have been synthesized from the reaction of Schiff bases with tris(trimethylsilyl) phosphite.<sup>12</sup>

There are several examples of crystal structures, in which an intramolecular B-O-H...N hydrogen bond is formed.<sup>8,13-20</sup> In the case of phenylboronic acid possessing both fluorine and aminomethyl groups at *ortho* positions, an intramolecular hydrogen bond is formed with the nitrogen atom but not with the fluorine one.<sup>14</sup>

Esterification of the boronic group precludes the formation of hydrogen bonds. Instead, formation of intramolecular  $N \rightarrow B$  bond is observed for many systems. The majority of open and cyclic boronic esters with secondary and tertiary aminomethyl group form crystals, in which such a bond is formed.<sup>18,21–31</sup> Another example of an intramolecular  $N \rightarrow B$  bond is the pinacol ester of naphthylboronic acid with an amino substituent.<sup>32</sup> A similar structure was also observed for the ester of 1,8-bis(dimethyl-amino)-9-boronoanthracene.<sup>33,34</sup> The exceptions are the compounds with bulky substituents at nitrogen,<sup>35–39</sup> where intramolecular  $N \rightarrow B$  bond is not formed due to steric hindrance. The  $N \rightarrow B$  interaction is also not present in compounds with -CH=N-NH- groups, in which E configuration of the double bond and an *anti* arrangement of boron and imine nitrogen atoms is observed.<sup>40–42</sup>





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<sup>0040-4020/\$ –</sup> see front matter @ 2012 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2012.02.072

The presence of an oxygen atom in the system makes the formation of the structures with intramolecular B-O-H...O bond possible. For instance, in phenylboronic acids with amido groups at the *ortho* position, the  $O \rightarrow B$  bond is observed instead of the  $N \rightarrow B$ one.<sup>13,29</sup> Zwitterionic structures with methanol molecules, in which the B $^--O(Me)...H-N^+$  intramolecular hydrogen bond was formed, were obtained for several esters of boronic acids.<sup>18,19,43</sup>

In boroxins, similarly to the boronic esters, there are no hydroxyl groups at boron able to form hydrogen bonds. Hence, the aminomethyl substituents can interact with the boron centre with the formation of the N $\rightarrow$ B bond. There are examples of crystals with one,<sup>44</sup> two,<sup>18,28,45,46</sup> or three<sup>32</sup> intramolecular N $\rightarrow$ B bonds depending on the substituents on the nitrogen atoms. Structures of unsymmetrical boroxins with one aminomethyl phenyl group were also described.<sup>47</sup>

The results of a computational investigation of the nitrogenboron interaction in o-(N,N-dialkylaminomethyl)arylboronate systems have been recently reported.<sup>48</sup>

Contrary to the numerous examples of phenylboronic acids with  $CH_2-NR_2$  groups at the *ortho* position, there are only a few examples of structures with  $CH_2-NHR$  groups (Mannich bases)<sup>16</sup> and one with the CH=NR group (Schiff base).<sup>8</sup> For such Mannich bases, there is a possibility of three types of intramolecular interaction:  $N \rightarrow B, B-O-H...N$  or B-O...H-N. The aim of the present work was to determine crystal and molecular structures of this type of compounds and to compare the energy of possible structures with various intramolecular interactions to determine the most stable form.

## 2. Results and discussion

#### 2.1. Synthesis

In the reaction of aldehydes possessing a boronic group with amines, several products can be formed (Scheme 1).



**Scheme 1.** Possible products of the reaction of *o*-formylphenylboronic acid with amines.

In addition to the desired product I, ester II can be formed, when the reaction is conducted in alcohol. Dehydration leads to the formation of the boroxin III. Moreover, benzoxaboroles IV can also be formed, especially for secondary amines.<sup>49,50</sup>

For the typical reaction conditions applied in the synthesis of Schiff bases (reflux in ethanol), the product contains various amounts of ester II (path b). Moreover, elevated temperature and azeotropic distillation of water promotes the formation of the boroxin III (path c). It is possible to hydrolyze both products to the desired boronic acid during the crystallization from water, but the product may be contaminated by the products of hydrolysis of the Schiff base fragment. Comparison of the results of the reactions conducted in various solvents (ethanol, dichloromethane) and temperatures allowed us to find the optimal conditions, described for the synthesis of the compound **1a**. The Mannich base **2b** was obtained by the reduction of the corresponding Schiff base with sodium borohydride.<sup>51</sup> For comparison, *para*-substituted Schiff base **3** was synthesized. The reaction scheme and the structures of the synthesized compounds are shown in Scheme 2.

#### 2.2. Structures

The molecular structures of Schiff and Mannich bases, **1a** and **2b**, respectively, are shown in Fig. 1.

The molecules of **1a** and **2b** both crystallize in the monoclinic system with one molecule in the asymmetric unit (Table S1, Supplementary data). In both **1a** and **2b** molecules the boronic moiety, B(OH)<sub>2</sub>, shows similar geometry with syn and anti conformation of OH groups (Fig. 1). The CH<sub>2</sub>N group of the ortho substituents is situated in such a way that the B...N distances are 3.196(2) and 3.287(2) Å in 1a and 2b, respectively. These distances are almost twice as long as those observed for the  $N \rightarrow B$  dative bonds.<sup>18,21–31</sup> Moreover, in both cases the boronic group is planar with the boron atom being out of the plane defined by O1O2C1 atoms by only 0.018(1) and 0.015(1) Å for **1a** and **2b**, respectively. Hence, the  $N \rightarrow B$  dative bonds are not observed. Instead, in both cases the nitrogen atoms interact with the syn hydroxyl group through intramolecular O-H...N hydrogen bond forming a sevenmembered ring (Fig. 1). The formation of the H-bonded ring causes the boronic group to be tilted in such a way that the B1C1C2 angle increases to  $129.2(6)^{\circ}$  and  $126.6(2)^{\circ}$  in **1a** and **2b**, respectively. In 1a, the dihedral angle between the boronic group's plane and the phenyl ring is only 6.56(6)°. Both the C7 and N1 atoms show the geometry in accordance with a  $sp^2$  hybridization and hence the H-bonded seven-membered ring is almost flat with the highest deviation from planarity being less than 0.043(1) Å. In case of **2b** the twist of the boronic group towards the phenyl ring is significantly higher and amounts to 26.61(9)°. This, and the sp<sup>3</sup> geometry of both C7 and N1 atoms, causes the H-bonded sevenmembered ring to be undulated and its geometry can be best described as an envelope with O1, H1 and N1 atoms lying at the same side of the plane formed by B1C1C2C7 atoms (see torsion angles in Table S2, Supplementary data).

Further, the second hydroxyl group (anti) is a donor in an intermolecular O-H...O hydrogen bond while the acceptor is the syn oriented hydroxyl group's oxygen atom in the molecule related by the inversion centre. Hence, compounds 1a and 2b exist in the crystalline state as hydrogen-bonded centrosymmetric dimers (Fig. 1). The O-H...O bridges are relatively strong, with O...O distances 2.761(1) and 2.772(1) Å for **1a** and **2b**, respectively (Table 1). It should be noted that in **1a** the dimers are generally flat and the only deviation from planarity is caused by the twist of the phenyl groups of the iminomethyl substituents (the dihedral angle is 29.34(3)°). In **2b** the whole aminomethyl group is almost perpendicularly oriented towards the boronic acid dimeric [B(OH)<sub>2</sub>]<sub>2</sub> unit (the dihedral angle equals to 83.02(3)°). These differences influence the secondary supramolecular structure in 1a and 2b (Fig. 2), although in both cases the most significant C-H...O hydrogen bonds are formed between the same pair of atoms (C5-H5 group is a donor while O2 atom is an acceptor). In the case of 1a these



Scheme 2. Synthesis of the compounds described in this work.

secondary H-bonds leads to 2-D layer structure on (100) plane, while in **2b** they form a ribbon propagating along [010] direction (Fig. 2).

These ribbons are further joined by weak C–H... $\pi$  interactions, while planes in **1a** are joined by weaker C-H...O interactions. The interesting feature of Mannich base derivative 2b is the fact that NH group is not engaged in any intermolecular interactions as a hydrogen bond donor. It is worth to compare the above described structures with the crystal structure of the phenylboronic acid with para-substituted Schiff base (3). The molecules of 3 crystallize in triclinic system with two crystallographically independent



Fig. 1. Basic centrosymmetric dimers in crystals of 1a and 2b with the atom numbering scheme. Thermal ellipsoids are drawn with 50% probability level. The intramolecular O-H...N hydrogen bonds are denoted with dots while intermolecular O-H···O bonds with dashes.

molecules (denoted as A and B in Fig. 3) in the asymmetric unit. The geometry of molecules A and B is comparable and the slight difference is only in the twist of the iminomethyl substituent (see torsion angles in Table S2). The boronic group orientation shows syn-anti conformation and the geometry of the phenylboronic moiety is very close to that observed in the ortho derivative (Table S2). The BC1C2 and B1C2C6 angles in **3** are close to 120° showing symmetrical orientation of the boronic group, which is one of the consequences of the lack of an ortho substituent. The most important difference connected with the absence of the nitrogen atom at the ortho position is the inability of the formation of the  $N \rightarrow B$ dative bond as well as O-H...N intramolecular interaction. As mentioned above, the molecules of **1a** are almost planar with only a slight twist of the boronic unit towards phenyl ring. In case of 3 the B(OH)<sub>2</sub> moiety is twisted by approx. 30°. Thus the geometry resembles more the Mannich base derivative 2b than 1a.

Table 1

The geometry of intra- and intermolecular interactions in crystals of 1a, 2b and 3 (Å, °)

	НА	DA	D–H…A
1a			
01-H1N1	1.67(2)	2.616(2)	166(2)
02–H2…01 <sup>b</sup>	1.85(2)	2.761(1)	177(2)
C5–H5O2 <sup>c</sup>	2.48(2)	3.449(2)	166(1)
C4–H4…Cg2 <sup>d</sup>	2.87(2)	3.774(2)	154(1)
2b			
01-H1N1	1.84(2)	2.744(2)	162(2)
02–H201 <sup>e</sup>	1.85(2)	2.772(1)	172(2)
C5–H5…O2 <sup>f</sup>	2.60(1)	3.512(2)	153(1)
C4 – H4Cg2 <sup>g</sup>	2.83(2)	3.689(2)	146(1)
C14–H14B…Cg1 <sup>h</sup>	2.77(2)	3.565(2)	137(1)
3			
02A-H20A01A <sup>i</sup>	1.87(2)	2.754(2)	175(2)
O2B-H20BO1B <sup>j</sup>	1.83(2)	2.738(2)	175(2)
01A–H1A…02B <sup>k</sup>	2.00(2)	2.759(2)	152(2)
01B-H1B02A	1.95(2)	2.764(2)	153(2)

<sup>a</sup> Cg(1) and Cg(2) denote the centroids of the phenyl ring of the phenylboronic moiety and the imino/aminomethyl substituent, respectively.

- Symmetry codes: 1/2-*x*, 5/2-*y*, 1-*z*.
- Symmetry codes: 1/2-x, -1/2+y, 1/2-z.
- <sup>d</sup> Symmetry codes: x, 1-y, -1/2+z.
- Symmetry codes: -x, 2-y, -z.
- Symmetry codes: -x, 1-y, -z,
- <sup>g</sup> Symmetry codes: x, -1+y, z. Symmetry codes: 1-x, 1/2+y, 1/2-z.
- <sup>i</sup> Symmetry codes: 2–x, 1–y, 1–z.
- Symmetry codes: 2-x, 2-y, 1-z
- <sup>k</sup> Symmetry codes: x, 1+y, z.



**Fig. 2.** Secondary supramolecular structure formed by C–H...O hydrogen bonds: (a) 2-D layer on (100) plane in crystals of 1a; (b) 1-D ribbon motif along [100] direction in crystals of 2b. In both cases the hydrogen atoms not involved in H-bonds are omitted for clarity.

alternately joined by O1–H1 donors and O2 acceptors forming second type of eight-membered H-bonded rings. It is noteworthy that all O...O separations in **3** are shorter than those observed for O–H...O bonds in **1a** and **2b** (Table S2). The ribbons are further connected through weak CH...O interactions into layers enclosed with the iminomethyl substituents. Therefore the 3-D structure is achieved by weak CH... $\pi$  interactions. The nitrogen atom in **3** is not engaged in any significant intermolecular interactions as an acceptor.

### 2.3. Calculations

Starting from experimental geometries, a conformational analysis has been performed (in the case of **2b** the methyl group has been omitted for simplicity). Two forms of 1 were found: (a) stabilized by H-bond (1A) or (b) stabilized by  $N \rightarrow B$  donor-acceptor interaction (1B) (Fig. 4). Although the lowest energy molecule is the system existing in the crystal lattice, the difference in energy between both forms is very small (ca. 3.3 kcal/mol), so the  $N \rightarrow B$ donor-acceptor interaction may efficiently compete with an intramolecular H-bond in solution or gas phase. Therefore, the possibility of formation of the polymorph stabilized by the dative bond cannot be excluded. In the case of **2**, a system with  $N \rightarrow B$ donor-acceptor interaction and two forms of H-bond stabilized structures where OH or NH groups may play a role of hydrogen bond donors, were analyzed. Both systems stabilized by intramolecular hydrogen bond differ in energy by 6.5 kcal/mol, whereas a system with a dative bond is placed in the middle. Similarly to the



**Fig. 3.** (a) Molecular structure of molecules A and B in crystals of **3** with the atom numbering scheme. Thermal ellipsoids are drawn with 50% probability level; (b) Basic supramolecular ribbon motif along [010] direction. The intermolecular O–H...O hydrogen bonds are denoted with dashes.

Another consequence of the absence of the intramolecular hydrogen bond is a completely different basic supramolecular motif observed in crystals of **3** (Fig. 3b). In this case it is a ribbon motif formed by O-H...O hydrogen bonds, oriented along [010] direction. In the ribbon, molecules A are bonded through two O-H...O bridges with molecules A related by an inversion centre forming eight-membered dimers (Table S2). The B molecules form the analogous motif (Table S2). The A and B dimers are further

Schiff base (1), it is less stable by 3.3 kcal/mol as compared with the most stable conformer (**2C**). Interestingly, due to much higher flexibility of the aminomethyl group, the distance between boron and nitrogen atoms is much smaller in the Mannich base (1.798 Å, **2A**), compared to the Schiff base (2.458 Å, **1A**). However, the OH...N distance is the reverse: it is longer in the Mannich base (H...N distance equal to 1.808 Å, **2C**) and shorter in the Schiff base (H...N distance equal to 1.683 Å, **1B**). The latter observation is in line with



Fig. 4. Possible conformations of 1 and 2. The relative energies in respect to the lower energy conformer given in kcal/mol. The data in brackets refer to the molecules with hydrogen atom replacing the phenyl ring bonded to nitrogen atom.

the experimentally determined geometries. Replacing the phenyl ring at nitrogen by a hydrogen atom essentially does not change the relative stability of the systems, they agree within 1 kcal/mol. Notably, the B...N distance is shorter in the Mannich base (1.723 Å), approaching a covalent single bond,<sup>53</sup> whereas in the Schiff base it is even longer as compared with the methylene derivative (2.579 Å).

Although the stabilities of the above forms are comparable, introduction of a substituent at the phenyl ring and/or at the nitrogen may influence the relative energies and favour one of the structures. This point may be analyzed in terms of substituent effect stabilization energy (SESE),<sup>54–56</sup> which is the measure of the increase/decrease in the stability of a system due to interactions between the substituents at the *ortho* position. The SESE may be accounted for by the following homodesmotic reaction (Scheme 3).



Scheme 3. Homodesmotic reaction.

The resulting energies lead both to information about the extent of each interaction and the influence of substituents at the *meta*- or *para*-position. The boronic group is a weakly electron accepting group ( $\sigma_m$ =-0.01,  $\sigma_p$ =0.12).<sup>57</sup> Similarly to the CH=NPh group ( $\sigma_m$ =0.35,  $\sigma_p$ =0.42)<sup>57</sup> or CH=NH, it should be stabilized by electron donating substituents both in *para* or *meta* position in the phenyl ring, whereas the CH<sub>2</sub>-NH<sub>2</sub> ( $\sigma_m$ =-0.03,  $\sigma_p$ =-0.11)<sup>57</sup> or -CH<sub>2</sub>-NH-Ph fragment should be stabilized in the reverse way. Strong electron donating (NH<sub>2</sub>,  $\sigma_m$ =-0.16,  $\sigma_p$ =-06)<sup>57</sup> or electron accepting (NO<sub>2</sub>,  $\sigma_m$ =0.71,  $\sigma_p$ =0.78)<sup>57</sup> groups have been chosen to analyze the subtle interplay between substituents with and through the phenyl ring to find whether they can support dative bond or hydrogen bond formation. The results are given in Table 2.

As expected, the highest stabilization of both systems is always due to hydrogen bond formation between the boronic group, where hydroxyl group plays a role of hydrogen donor, and the nitrogen at  $\beta$  position in *ortho* substituent is an acceptor. The dative bond is only a little less favourable, but the differences are small enough to be easily formed. The most striking observation is, however, that the substituents in the ring practically do not influence the preference of hydrogen bond or dative bond formation. They modify the strength of the interaction between B(OH)<sub>2</sub> and CH<sub>2</sub>–NH<sub>2</sub> or CH=NH only in a very subtle way. The most important factor that results in dative N  $\rightarrow$  B bond formation seems to be the esterification of the hydroxy groups. In the absence of hydrogen atoms at oxygen atoms, the boronic group turns by ca. 90° to form a donor–acceptor interaction, which is very significant and stabilizes the system. Since obviously the environment of this process is

# Table 2

The SESE values for Schiff and Mannich bases. *para* and *meta* position is given in respect to the boronic group. The values given in kcal/mol

System/substituent	Н	m-NH <sub>2</sub>	p-NH <sub>2</sub>	$m-NO_2$	p-NO <sub>2</sub>
	3.0	3.3	3.0	3.1	3.2
HO B OH NH	4.7	4.6	4.7	5.1	4.5
HO, B, OH, NH	-0.3	-1.0	-0.5	a	-0.5
HO, J B V	7.4	7.5	7.2	7.7	7.9
HO B OH NH2	7.9	8.0	7.6	8.0	8.0

<sup>a</sup> one of the component of the reaction did not converge.

crucial,  $^{58}$  the influence of intramolecular factors that stimulate esterification is more important than the intramolecular effects due to substitution.  $^{59,60}$ 

#### 3. Conclusion

Both aminomethyl- and iminomethylphenylboronic acids are stabilized by intramolecular hydrogen bonds involving hydroxyl fragment at boronic group and nitrogen atom in  $\beta$  position of the substituent at *ortho* position. Due to small difference in energy between possible forms, the structures with dative bond N  $\rightarrow$  B may exist in solution, gas phase, and although we were not able to detect other polymorphs, they possibly may also exist in the solid state. Notably, the substituents at the phenyl ring practically do not influence the preference of hydrogen bond or dative bond formation.

# 4. Experimental

# 4.1. Synthesis

4.1.1. 2-(*Phenyliminomethyl*)*phenylboronic* acid (**1a**). Aniline (0.84 g, 9.00 mmol) was added to a solution of *o*-formylphenylboronic acid (0.90 g, 6.00 mmol) in dichloromethane (18 mL). The clear yellow solution was stirred at room temperature for 0.5 h and refluxed for 9 h in the flask fitted with a Dean–Stark water separator. The reaction mixture was stored at -4 °C overnight. Crystalline precipitate was filtered and vacuumdried to give **1a** (1.14 g, 84.4%), yellowish crystals, mp 234–238 °C; Anal. Calcd for C<sub>13</sub>H<sub>12</sub>BNO<sub>2</sub>: C 69.38%, H 5.37%, N 6.22%; Found: C 69.30%, H 5.37%, N 6.25%. <sup>11</sup>B NMR (128.3 MHz, acetone-*d*<sub>6</sub>):  $\delta$ : 27.6 ppm.

4.1.2. 2-(o-Tolyliminomethyl)phenylboronic acid (**1b**). This compound was synthesized in the same way from o-toluidine and o-formylphenylboronic acid. Yield: 86.0%, yellowish crystals, mp 220–224 °C; Anal. Calcd for C<sub>14</sub>H<sub>14</sub>BNO<sub>2</sub>: C 70.33%, H 5.90%, N 5.86%, Found: C 70.44%, H 5.93%, N 5.95%. <sup>11</sup>B NMR (128.3 MHz, acetone- $d_6$ ):  $\delta$ : 27.5 ppm.

4.1.3. 4-(*p*-Tolyliminomethyl)phenylboronic acid (**3**). This compound was synthesized in the same way from *p*-toluidine and *p*-formylphenylboronic acid. Yield: 80.9%, yellowish crystals, mp 204–230 (dec); Anal. Calcd for C<sub>14</sub>H<sub>14</sub>BNO<sub>2</sub>: C 70.33%, H 5.90%, N 5.86%; Found: C 69.19%, H 5.83%, N 5.89%. <sup>11</sup>B NMR (128.3 MHz, acetone-*d*<sub>6</sub>):  $\delta$ : 27.7 ppm.

4.1.4. 2-(o-Tolylaminomethyl)phenylboronic acid (**2b**). Sodium borohydride (0.52 g, 13.8 mmol) was added slowly to 0.66 g, (2.76 mmol) of 2-(o-tolyliminomethyl)phenylboronic acid (1b) in anhydrous methanol (33 mL). The reaction was stirred at room temperature for 2 h and then poured into ice–water (15 mL). Hydrochloric acid (1 M, 7 ml) was added slowly and the mixture stirred for 30 min. Crystalline precipitate was filtered and dried in air to give **2b** (0.54 g, 80.6%), yellowish crystals, mp 138–146 °C; Anal. Calcd for C<sub>14</sub>H<sub>16</sub>BNO<sub>2</sub>: C 69.75%, H 6.69%, N 5.81%; Found: C 69.38%, H 6.49%, N 5.18%. <sup>11</sup>B NMR (128.3 MHz, acetone-*d*<sub>6</sub>):  $\delta$ : 29.4 ppm.

## 4.2. X-ray diffraction

Crystal data and details of structure refinement for compounds 1a, 2b and 3 are specified in Table 1. X-ray diffraction data were collected on a KUMA CCD k-axis diffractometer with graphitemonochromated Mo-Ka radiation (0.71073 Å). The crystals were positioned at 62.3 mm from the KM4CCD camera. Data collection and reduction were performed with CrysAlis CCD and CrysAlis RED programs, respectively.<sup>61</sup> The data were corrected for Lorentz and polarization effects but no absorption correction was applied. The structures were solved by direct methods and refined with the fullmatrix least-squares technique using the SHELXS97 and SHELXL97 programs, respectively.<sup>62</sup> The positions of H atoms were refined freely. The presented figures were generated using ORTEP-3 for Windows v.1.08 program<sup>63</sup> and DIAMOND,<sup>64</sup> while the geometric calculations were done by PLATON package.<sup>65</sup> Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 854576 (1a), 854577 (2b) and 854578 (3). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk). Crystal data for the compounds **1a**, **2b** and **3** are collected in Table S2 (Supplementary data).

### 4.3. Calculations

All systems were fully optimised at MP2/6-31+G\*\* level of theory. The systems with hydrogen atoms replacing the phenyl ring at nitrogen (see Fig. 4) corresponded to real minima at the potential energy surface as checked by frequency calculations at the same level of theory  $(MP2/6-31+G^*)$ . Their energies were corrected for Zero Point Energy correction (ZPE). The molecules used for estimation of aromatic stabilization energies were calculated in their most stable conformations, except the case where dative bonds were considered. Here phenylboronic acid, aminophenylboronic acid or nitrophenylboronic acid had boronic group perpendicular to the phenyl ring, to avoid the correction due to effect of rotation of the group. These compounds had negative frequencies due to rotation of the group. The differences between planar and nonplanar phenylboronic acid, *p*-aminophenylboronic acid *m*-aminophenylboronic acid, p-nitrophenylboronic acid or m-nitrophenylboronic acid were 2.7 kcal/mol, 3.5 kcal/mol, 3.5 kcal/mol, 2.5 kcal/mol or 1.9 kcal/mol, respectively. The calculations were carried out using Gaussian03 program.<sup>66</sup>

#### Acknowledgements

This work was supported by the Ministry of Science and Higher Education (grant N204 01932/0614). B.T.F. acknowledges the 120000-501/68-BW-1681/17/05 grant for financial support of the X-ray study and Interdisciplinary Centre for Mathematical and Computational Modeling (Warsaw) for computational facilities. A.A.-W., I.D.M. and A.S. acknowledge the financial support from Warsaw University of Technology.

#### Supplementary data

Crystal data and selected geometrical parameters for the compounds **1a**, **2b**, and **3**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/ j.tet.2012.02.072. These data include MOL files and InChiKeys of the most important compounds described in this article.

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