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## Synthesis, characterization, X-ray studies and DFT calculations of fused five-six and seven-six membered ring of new heterobicyclic system of boron compounds

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#### HIGHLIGHTS

- Reaction of tridentate ligands with phenylboronic acid gave [4.3.0] and [4.5.0] heterobicyclic systems.
- Reaction conditions must be full controlled to obtain just one product.
- DFT calculations, PBE/6-31G(d,p), were performed in order to evaluate steric effects in the structures.
- Seven membered ring shows a chair conformation but the difference in energy with boat is minimal.
- Suzuki reaction can be achieved because a tricoordinated boron atom is found in some of the structures.

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#### G R A P H I C A L A B S T R A C T

Reaction of tridentate ligand 2-[(2-Hydroxy-ethylimino)-phenyl-methyl]-phenol **5b** with one and two equivalents of phenyl and naphthyl boronic acid in toluene during 24 h and 1 h. give place to the synthesis of the monomeric boronates with fused five-six membered rings [4.3.0] and fused six-seven membered rings [4.5.0] respectively.

#### ABSTRACT

Two tridentate ligands derivated from ethanolamines and 2-hydroxyacetophenone and 2-hydroxybenzophenone were reacted with phenylboronic acid and naphthylboronic acid in different proportions to obtain compounds **7a**, **8b** and **9a** which are [4.3.0] and [4.5.0] heterobicyclic systems. Compounds **7a**, **8b** and **9a** were fully characterized and the structures of **7a** and **8b** have been analyzed by X-ray diffraction, where a series of parameters such as bond distances, bond angles, torsion angles, tetrahedral character at the boron atom, steric effects and deviation of the boron atom from the mean plane have been evaluated and comparated. DFT calculations, PBE/6-31G(d,p), were performed in order to evaluate steric effects and the stability of [4.3.0] and [4.5.0] heterobicyclic system.

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#### 1. Introduction

In the last years there has been a great interest in the study of organoboron compounds, due to a great variety of applications found, for example in medicinal chemistry, as anticancer agents in the technique known as boron neutron capture therapy used

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for the treatment of certain brain tumors [1–3]; in supramolecular chemistry [4,5]; macrocyclic chemistry [6,7]; organometallics [8]; dendrimers [9,10]; they also display applications in organic synthesis [11]; in the Suzuki reaction [12–15]; and as materials with fluorescence [16]. Some groups have reported several studies in  $N \rightarrow B$  coordination bond [17–20] and recently the synthesis and characterization of boron complexes obtained from the condensation of 3-amino-phenylboronic acid and 1,3-diketones [21]. In this context the synthesis and characterization of boron complexes with fused five-six membered rings, [4.3.0] heterobicyclic systems [22] and the synthesis, characterization of fused six-seven membered rings, [4.5.0] heterobicyclic systems derived from optically active tridentate ligands [23] have been reported. Those studies indicate that fused five-six membered ring compounds are obtained under strong reaction conditions such as reflux of toluene for 36 h. and fused six-seven-membered rings compounds are obtained using two equivalents of phenylboronic acid and one equivalent of the tridentate ligand in reflux of toluene for approximately 1 h. (Scheme 1) [23]. The results from X-ray diffraction and computational analyses indicated that reaction of tridentate ligand 5a with two eq. of phenylboronic acid or two eq. of naphthylboronic acid to obtain [4.5.0] heterobicyclic systems cannot occur due to the steric effect caused in the two methyl groups located in the aliphatic carbons (Schemes 2 and 3). The synthesis of polyolefins, styrene and substituted biphenyls compounds by the Suzuki reaction can occur because of the presence of a trisubstituted boron atom in structure **8b** [12–15]. In this work, we report the synthesis of three new heterobicyclic compounds, 7a, 8b and 9a. We determined the geometry of compounds 6a-b, 7a-b, 8b and 9b in gas phase, describing the most stable conformations and evaluating the influence of steric factors in the formation of reaction products between the tridentate ligands **5a** and **5b** and the corresponding phenyl- or naphthyl-boronic acid.

#### 2. Computational details

The geometry of each closed shell structure was fully optimized by using the GAUSSIAN 09 software package [24] and their vibrational frequencies were calculated using the density functional theory (PBE) [25,26] in combination with the 6-31G(d,p) [27,28] basis set. For the calculations of <sup>11</sup>B NMR shielding constants the GIAO-DFT (gauge-independent atomic orbital) with the 6-31G(d,p) basis set approach was used. Results were analyzed with the Chemcraft program v1.6 [29].

#### 3. Experimental

#### 3.1. Instrumentation

NMR spectra were recorded in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> solutions on Bruker Avance 300 spectrometer. Chemical shifts (ppm) are relative to  $(CH_3)_4$ Si for <sup>1</sup>H (300.13 MHz) and <sup>13</sup>C (75.47 MHz) and BF<sub>3-</sub> •OEt<sub>2</sub> for <sup>11</sup>B (96.29 MHz). Coupling constants are reported in Hz. Infrared spectra were recorded on a Perkin-Elmer 16F-PC FT-IR spectrometer. Mass spectra were recorded on a Hewlett-Packard model 5989A MS engine, coupled to a GC 5890 series II. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Elemental analyses were carried out on a FLASH (EA) 1112 series, thermo Finnigan apparatus. The X-ray diffraction study was determined on an Enraf-Nonius-Fr590 Kappa-CCD  $(λ_{MoK\alpha} = 0.71073 \text{ Å}, \text{ graphite monochromator}, T = 293 \text{ K}, \text{ CCD rotat-}$ ing images scan mode) and the crystals were mounted on a LINDE-MANN tube. Absorption correction was not necessary. All reflections data set were corrected for Lorentz and Polarizations effects. Structure solution and refinement were performed using the SHELX-S-97 program and then SHELX-L-97 program was applied



Scheme 1. Monomeric and dimeric boronates obtained using different reactions conditions [23].



Scheme 2. Synthesis of monomeric boronates 6*a* [22] and 7*a* with fused five-six membered rings. Structures of monomeric oligodiboronates 6*b* and 7*b* with fused six-seven membered rings were modeled by PBE/6-31G(d,p).



Scheme 3. Synthesis of monomeric boronates 8a [22], 8b and 9a with fused five-six and six-seven membered rings. Monomeric oligodiboronate 9b with fused six-seven membered rings was not obtained but modeled by PBE/6-31C(d,p).

for refinement and output data [30,31]. All software manipulations were done under the WINGX environment program set [32]. Single crystal structure validation was done with PLATON [33]. Molecular perspectives were drawn under ORTEP-3 [34].

### 3.2. Reagents

All reactants and solvents were purchased from Aldrich Chemical Co. and solvents were dried previous to use [35]. Single crystals were grown using spectroscopic grade solvents.

#### 3.3. Synthesis

# 3.3.1. General method for the preparation of tridentate ligands **5a** and **5b**

In order to prepare the tridentate ligands **5a** and **5b**, equimolecular quantities of the corresponding aminoalcohol and 2-hydroxyacetophenone and 2-hydroxybenzophenone, were refluxed in ethanol for 1 h. The solvent and water formed during the reaction were eliminated with a Dean–Stark trap to yield yellow solids that were washed with methylene chloride and used without further purification. Tridentate ligands **5a** and **5b** have already been published [36–43].

3.3.2. General method for the preparation of compounds 7a, 8b and 9a 3.3.2.1. (2S,4R,5S)-2-(Naphthyl)benzo[j]-4-phenyl-5,7-dimethyl-6aza-1,3-dioxa-2-borciclononen-6-ene. 7a. Compound 7a was synthesized from 0.30 g. (1.11 mmol) of 5a and 0.19 g. (1.11 mmol) of naphthylboronic acid. The reaction was carried out in toluene under reflux, using a Dean-Stark trap during 24 h. The product was obtained as a yellow solid 0.33 g. (0.81 mmol), yield, 73.3%,  $[\alpha]_{D}^{25} = +127.5$  (c 0.102 CHCl<sub>3</sub>), mp: 214–218 °C. IR  $\upsilon_{max}$  (KBr): 3060, 2925, 2860, 1634 (C=N), 1551, 1463, 1438, 1312, 1259, 1169, 1072, 1039, 858, 751, 696, 647, 578, 521, 470 cm<sup>-1</sup>, <sup>1</sup>H NMR (300.13 MHz, DMSO-d<sub>6</sub>) [δ, ppm]: 0.99 (d, 3H, J 1/4 6 Hz, CH<sub>3</sub>), 2.63 (s,3H, CH<sub>3</sub>), 4.36 (m, 1H, H-8), 5.50 (d, 1H, J 1/4 5 Hz, H-9), 6.85 (t, 1H, J 1/4 8.1 Hz, H-5), 7.06 (d, 1H, J 1/4 8.2 Hz, H-3), 7.15-7.29 (m, 4H, H-22, H-24, H-17, H-18), 7.30 (t, 1H, I<sup>1</sup>/<sub>4</sub> 8.1 Hz, H-4), 7.35-7.39 (m, 3H, H-12, H-16, H-19), 7.40-7.43 (m, 2H, H-21, H-25), 7.48-7.54 (m, 4H, H-6, H-11, H-15, H-23). <sup>13</sup>C NMR (75.47 MHz, DMSO-d<sub>6</sub>) [δ, ppm]: 14.7 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>), 62.9 (C-8), 80.2 (C-9), 119.0 (C-5), 120.6 (C-1), 121.2 (C-3), 124.8 (C12), 124.9 (C-14), 126.2 (C-19), 126.5 (C-22, C-24), 127.4 (C-16), 127.5 (C-15), 128.1 (C-6), 128.2 (C-23), 128.3 (C-21, C-25), 129.8 (C-11), 130.3 (C-17), 133.0 (C-13), 133.2 (C-18), 136.7 (C-4), 139.6 (C-10), 139.8 (C-20), 160.6 (C-2), 166.9 (C-7) <sup>11</sup>B NMR (96.29 MHz, CDCl<sub>3</sub>), [δ, ppm]: 6.1. ( $h_{1/2}$  = 294 Hz.). MS (m/z,%): 405 (M<sup>+</sup>, 0.2), 298 (6), 278 (100), 262 (1), 162 (30), 117 (1). Anal. Calc. for C<sub>27</sub>H<sub>24</sub>BNO<sub>2</sub>: C, 80.01; H, 5.97; N, 3.46. Found C, 79.96; H, 5.92; N, 3.41%.

3.3.2.2. 9-Phenyl-2,4-diphenylbenzo[j]-8-aza-1,3,5,2,4-trioxadiboracycloundec-8-ene. 8b. Compound 8b was synthesized from 0.50 g. (2.07 mmol) of 5b and two equivalents 0.51 g. (4.14 mmol) of phenylboronic acid. The reaction was carried out under reflux of toluene for 1 h, using a Dean-Stark trap. The product was obtained as a yellow solid 0.68 g. (1.58 mmol), yield, 76.2%, mp: 208-212 °C. IR v<sub>max</sub> (KBr): 3010, 2944, 1956, 1608 (C=N), 1549, 1468, 1432, 1273, 1149, 1068, 1027, 993, 949, 835, 744, 700, 639, 560, 504, 435 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, DMSO-d<sub>6</sub>) [δ, ppm]: 3.63 (dd, 1H, / = 7.3 Hz, / = 6.5 Hz, H-8a), 3.73 (dd, 1H, / = 8.1 Hz, / = 5.8 Hz, H-8b), 3.89 (dd, 1H, / = 6.9 Hz, 5.5 Hz, 9a), 4.18 (dd, 1H, / = 5.9 Hz, 7.7 Hz, 9b), 6.70 (t, 1H, / = 8.0 Hz, H-5), 7.11 (d, 1H, / = 8.4 Hz, H-3), 7.21-7.33 (m, 4H, H-6, H-12, H-14, H-26), 7.35-7.58 (m, 8H, H-4, H-11, H-13, H-15, H-18, H-20, H-24, H-27), 7.59-7.68 (m, 3H, H-19, H-23, H-25), 8.08 (dd, 2H, J = 1.1 Hz, J = 7.7 Hz, H-17, H-21). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) [δ, ppm]: 53.3 (C-8), 64.4 (C-9), 118.5 (C-5), 120.2 (C-3), 120.4 (C-1), 126.8 (C-22), 127.3 (C-6), 127.4 (C-26), 127.5 (C-18, C-20), 127.9 (C-12, C-14), 128.2 (C-19), 129.6 (C-24), 130.4 (C-13), 130.6 (C-25), 131.1 (C-11, C-15), 132.3 (C-27), 135.1 (C-17, C-21), 135.8 (C-23), 137.7 (C-4), 159.9 (C-2), 169.8 (C-7). <sup>11</sup>B NMR (96.29 MHz, CDCl<sub>3</sub>), [δ, ppm]: 3.8, 27.0.  $(h_{1/2} = 282, 692 \text{ Hz.})$ . MS (m/z,%): 431  $(M^+, 0.1), 354 (41),$ 250 (100), 174 (32), 167 (0.2). Anal. Calc. for C<sub>27</sub>H<sub>23</sub>B<sub>2</sub>NO<sub>3</sub>: C, 75.22; H, 5.38; N, 3.25. Found C, 75.15; H, 5.40; N, 3.27%.

3.3.2.3. (*Rac*)-2-(*Naphthyl*)*benzo*[*j*]-7-*phenyl*-6-*aza*-1,3-*dioxa*-2-*borciclononen*-6-*ene*. **9a**. Compound **9a** was synthesized from 0.30 g (1.24 mmol) of **5b** and 0.21 g (1.24 mmol) of naphthylboronic acid. The reaction was carried out in toluene under reflux, using a Dean-Stark tramp during 24 h. The product was obtained as a yellow so-lid 0.31 g (0.85 mmol), yield, 69%, mp: 199–203 °C, IR  $\upsilon_{max}$  (KBr): 3059, 2930, 2863, 1629 (C=N), 1549, 1473, 1453, 1316, 1257, 1169, 1074, 1036, 863, 750, 698, 648, 576, 523, 469 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, DMSO-d<sub>6</sub>) [ $\delta$ , ppm]: 3.09 (dd, 1H, J <sup>1</sup>/<sub>4</sub> 3.4 Hz, J <sup>1</sup>/<sub>4</sub> 8.8 Hz, H-8b), 3.36 (dd, 1H, J <sup>1</sup>/<sub>4</sub> 3.2 Hz, J <sup>1</sup>/<sub>4</sub> 4.9 Hz, H-8a), 3.81 (m, 1H, H-9a), 4.22 (m, 1H, H-9b), 6.83 (t, 1H, J <sup>1</sup>/<sub>4</sub> 7.0 Hz, H-5),

6.99 (d, 1H, J <sup>1</sup>/<sub>4</sub> 8.1 Hz, H-3), 7.02 (d, 1H, J <sup>1</sup>/<sub>4</sub> 6.0 Hz, H-6), 7.21–7.33 (m, 3H, H-11, H-17, H-18), 7.39–7.43 (m, 3H, H-22, H-23, H-24), 7.42–7.47 (m, 2H, H-21, H-25), 7.49–7.53 (m, 3H, H-12, H-16, H-19). <sup>13</sup>C NMR (75.47 MHz, DMSO-d<sub>6</sub>) [δ, ppm]: 53.2 (C-8), 60.5 (C-9), 119.2 (C-5), 120.5 (C-1), 121.4 (C-3), 124.6 (C-12), 124.7 (C-14), 126.1 (C-19), 126.6 (C-22, C-24), 127.0 (C-16), 127.1 (C-15), 127.9 (C-6), 129.3 (C-21, C-25), 129.7 (C-11), 130.1 (C-17), 131.7 (C-23), 133.2 (C-13), 133.4 (C-18), 136.9 (C-4), 139.1 (C-10), 139.3 (C-20), 160.6 (C2), 168.9 (C7). <sup>11</sup>B NMR (96.29 MHz, CDCl<sub>3</sub>), [δ, ppm]: 4.1. ( $h_{1/2}$  = 270 Hz.). MS (m/z,%): 377 (M<sup>+</sup>, 0.2), 250 (100), 234 (1), 209 (31), 181(1), 104.10 (0.2). Anal. Calc. for C<sub>25</sub>H<sub>20</sub>BNO<sub>2</sub>: C, 79.52; H, 5.30; N, 3.71. Found C, 79.22; H, 5.41; N, 3.78%.

#### 4. Results and discussion

It is well known that tridentate ligands obtained from aldehydes or ketones with different ethanolamines react in mild conditions with electron acceptor molecules to give heterocyclic systems. In this work tridentate ligands **5a** and **5b** were allowed to react with one and two equivalents of phenylboronic acid and naphthylboronic acid as described [22,23] to obtain compounds **7a**, **8b** and **9a** in yields between 69.0% and 76.2%. Due to the formation of a new chiral center at the boron atom it is possible to induce its stereochemistry. Compound **7a** is derived from chiral (1S,2R)-(+)-Norephedrine which induces the attack of the phenyl and naphthylboronic acid in the less hindered face of the molecule (Scheme 4). In contrast compound **8b** is obtained as a racemic mixture from the achiral ethanolamine, the attack of the phenyl and naphthylboronic acid can occur in both sides of the tridentate ligand **5b** at the same time.

<sup>1</sup>H and <sup>13</sup>C chemical shifts were unequivocally assigned by 2D experiments HETCOR and COSY of the boron compounds 7a, 8b and **9a** and comparing with the spectra of the ligands **5a** and **5b** in the same solvent. <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds**7***a*, **8b** and **9a** in DMSO-*d*<sub>6</sub>, at room temperature, show no significant changes in the chemical shift and coupling constants, as compared with those of the ligands. The proton NMR analysis showed that the signals corresponding to the aliphatic atoms C8 and C9 in 7a, 8b and 9a are in the range from 3.09 to 4.22 ppm and the fact that a new chiral center is been created at the boron atom, compounds **8b** and **9a** were obtained as a racemic mixture. Because compound 7a was obtained from a chiral ethanolamine just one product is observed by NMR. The aromatic protons are in the range from 6.85 to 7.54, 6.70-8.08 and 6.99-7.53 for **7a**, **8b** and **9a** respectively (Table 1). The existence of the  $N \rightarrow B$  bond in compounds **7a**, **8b** and **9a** was established by <sup>11</sup>B NMR which shows the signals between 3.8 and 6.1 ppm, characteristic for the tetracoordinated boron





Frontside Attack hindered

**Scheme 4.** Attack of the phenyl and naphthylboronic acid occur from the less hindered backside of the molecule.

**Table 1** Selected  $\delta$  (ppm, DMSO- $d_6$  at 25 °C) <sup>1</sup>H and <sup>13</sup>C NMR for **7***a*, **8***b* and **9***a*. Proton signals are displayed in italics.

	7	8	9
( <b>7</b> a)	166.9	62.9	80.2
		4.36 ( <i>m</i> )	5.50 (d)
( <b>8b</b> )	169.8	53.3	64.4
		3.63(dd), 3.73(dd)	3.89 (dd), 4.18 (dd)
( <b>9</b> a)	168.9	53.2	60.5
		3.09( <i>dd</i> ), 3.36 ( <i>dd</i> )	3.81 ( <i>m</i> ), 4.22 ( <i>m</i> )

atom and a signal in 27 ppm for the tricoordinated boron atom in compound **8a**, [36–40]. <sup>11</sup>B NMR chemical shifts for **7a**, **8b** and **9a** were calculated using NMR by the method GIAO with isotropic protection and they are relative to BF<sub>3</sub>·OEt<sub>2</sub>, the results are very close to the experimentally observed, as shown in Fig. 1. The characteristic signal in the <sup>13</sup>C NMR spectra for the imine group appears in 166.9, 169.8 and 168.9 ppm, and it was confirmed by the band for (C=N) in the infrared experimental spectra in 1634, 1608 and 1629 cm<sup>-1</sup> for **7a**, **8b** and **9a** respectively, while C=N stretching vibrations calculated by PBE/6-31G(d,p) appeared in 1619, 1618 and 1616 cm<sup>-1</sup> for **7a**, **8b** and **9a** respectively. The mass spectra give the molecular ions in low abundance, and the base peak corresponds to the [M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>] ion in agreement with previous results, [22,23].

Compounds **7a** and **8b** provided crystals suitable for X-ray analyses. The X-ray structures are shown in Fig. 2. The crystallographic data are summarized in Table 2. The structure of compound **7a** corresponds to the fused five-six membered rings, [4.3.0] where the naphthyl group attached to the boron atom prefers the position in the same face of the other substituents. The phenyl group bonded to the aliphatic carbon C9 is big enough to induce the configuration at the boron atom. The structure of compound **8b** corresponds to the fused six-seven membered rings, [4.5.0]. The N  $\rightarrow$  B coordination bond distances for **7a** and **8b** are 1.589(3) and 1.603(3) Å and they are similar to those observed in boron

Table 2

Crystallographic data for compounds 7a and 8b.

Compound	7a	8b
Chemical formula	C <sub>27</sub> H <sub>24</sub> BNO <sub>2</sub>	$C_{27}H_{23}B_2NO_3$
Formula weight	405.29	431.08
Space group	$P2_{1}2_{1}2_{1}$	Рсаb
Crystal system	Orthorhombic	Orthorhombic
Crystal size (mm <sup>3</sup> )	$0.2\times0.2\times0.1$	$0.2\times0.1\times0.1$
Unit cell dimensions		
a (Å)	9.6762(2)	13.0321(2)
b (Å)	13.9307(4)	15.9638(3)
<i>c</i> (Å)	16.2949(5)	21.7660(5)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Formula units per cell	4	8
$\delta_{\text{calc.}} (\text{g cm}^{-3})$	0.545	1.265
F(000)	384	1808
Т (К)	293(2)	293(2)
θ (°)	3.58-27.48	3.46-27.88
Reflections collected	4858	10,151
Independent reflections	4858	10,719
Observed reflections, $(F_o)^2 > 4\sigma(F_o)^2$	3337	5385
$R = \Sigma  F_{\rm o}  -  F_{\rm c}   / \Sigma  F_{\rm o} $	0.0446	0.0499
$R_{w} = \left[\sum w( F_{o}  -  F_{c} )^{2} / \sum wF_{o}^{2}\right]^{1/2}, w = 1/\sigma^{2}$ (all data)	0.0825	0.1581
Goodness-of-fit (GOF)	1.039	0.909
No. of parameters	377	391
Maximun $\Delta/\sigma$	-0.105	-0.029
$\Delta \rho_{\rm min} ({\rm e}{\rm \AA}^{-3})$	-0.091	-0.128
$\Delta \rho_{\rm max} ({\rm e}{\rm \AA}^{-3})$	0.102	0.155

complexes [36–40]. The bond angles around the tetracoordinated boron atom B1 for compounds **7***a* and **8***b* are in the range between 100.92° and 115.19° (Table 3). The average value for the bond angles in the five and seven membered rings are 104.63° and 120.27° for **7***a* and **8***b* respectively.

The values for the tetrahedral character (THC) [44] for boron atoms B1 are 69.0% and 89.3% for **7a** and **8b** respectively, these



**Fig. 1.** <sup>11</sup>B chemical shifts (ppm) obtained by NMR experimental analyses (red), with its NMR calculated values obtained by the method GIAO (black) with isotropic protection. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. ORTEP representation of compounds 7a and 8b, hydrogens are omitted for clarity and ellipsoids containing 50% probability level.

#### Table 3

Selected bond distances (Å), bond angles (°) and dihedral angles (°) for compounds **7***a* and **8***b*.

Compound	7a	8b
Bond distances (Å)		
N(1)-C(8)	1.478(2)	1.474(3)
N(1)-C(7)	1.294(2)	1.300(2)
O(1) - C(2)	1.347(2)	1.330(2)
O(3) - C(9)	-	1.428(3)
O(2) - C(9)	1.423(2)	-
C(8) - C(9)	1.553(3)	1.486(4)
C(1) - C(7)	1.452(3)	1.449(3)
C(7)–C(22)	1.498(3)	1.491(3)
B(1)—O(1)	1.498(2)	1.474(3)
B(1)—O(2)	1.443(2)	1.432(3)
B(1)—N(1)	1.589(3)	1.603(3)
B(1)-C(10)	1.614(3)	1.612(3)
B(2)—O(2)	-	1.340(3)
B(2)—O(3)	-	1.358(3)
B(2)-C(16)	-	1.565(3)
Bond angles (°)		
N(1)-B(1)-O(1)	103.66(14)	108.8(15)
N(1)-B(1)-O(2)	100.92(14)	109.6(17)
N(1)-B(1)-C(10)	114.07(15)	107.9(15)
O(1)-B(1)-C(10)	109.50(15)	109.9(17)
O(2)-B(1)-C(10)	115.19(16)	113.7(17)
O(1)-B(1)-O(2)	112.75(15)	106.8(16)
N(1)-C(7)-C(1)	116.52(16)	119.6(17)
C(7)-C(1)-C(2)	117.7(17)	119.9(17)
C(1)-C(2)-O(1)	121.75(16)	121.92(17)
C(9)-C(8)-N(1)	98.20(14)	113.8(2)
C(8) - N(1) - B(1)	109.48(15)	114.3(16)
B(1) - O(1) - C(2)	113.85(14)	124.5(15)
C(7) - N(1) - B(1)	121.90(15)	124.1(16)
C(8) - N(1) - C(7)	126.71(16)	121.7(17)
B(1) - O(2) - C(9)	109.59(14)	-
O(2) - C(9) - C(8)	104.94(15)	-
B(1) - O(2) - B(2)		138.3(17)
O(2)-B(2)-O(3)	-	124.4(2)
B(2) - O(3) - C(9)	-	125.4(19)
O(3) - C(9) - C(8)	-	116.2(2)
Dihedral angles (°)		
O(1)-B(1)-C(10)-C(15)	17.7(2)	-61.4(2)
O(2)-B(1)-C(10)-C(11)	72.4(2)	-4.7(3)
N(1)-B(1)-C(10)-C(15)	133.29(17)	57.1(2)
N(1)-B(1)-C(10)-C(11)	-43.7(3)	-126.6(19)
Deviation from mean plane (Å)		
Plane: $C(2) - C(1) - C(7) - N(1) - B(1) - O(1)$	B(1)-0.327	O(1)0.068

values show that the boron atom is more distorted in compound 7a with fused five-six membered ring. The deviations from the membered mean plane of the six ring C(2)-C(1)-C(7)-N(1)-B(1)-O(1) in **7a** and **8b** are -0.327 (B1) and 0.068 (01) Å respectively, showing that the largest deviation from the mean plane corresponds to (B1) in compound 7a which presents the less THC. The dihedral angles for the O1-B1-C10-C15 fragment in compounds 7a and 8b are 17.63° and -61.47° which are indicative of the two conformations preferred around C-B bond, eclipsed and gauche. The conformation in the five member ring in compound **7***a* is envelope where C9 is out the plane formed by C8, N1, B1 and O2; the conformation in the seven member ring in compound **8b** is chair, N1 is above the plane formed by B1, O2, B2 and C8, C9, O3 Fig. 3. Structure 7a shows intermolecular hydrogen bond interactions between O1···H21 and O2···H12, with distances of 2.65 Å and 2.69 Å, in both cases the distances are less than the sum of the van der Walls radii (2.72 Å) [45] Fig. 4.

The geometries of **6a–b**, **7a–b**, **8b** and **9b** were optimized in gas phase using the density functional theory (PBE) in combination with the 6-31G(d,p) basis set. All structures were characterized by



Fig. 3. Envelope and chair conformations in compounds 7*a* and 8*b* by X-ray diffraction.



Fig. 4. Intermolecular interactions in compound 7a.



**Fig. 5.** Superimposition of the fused rings in compounds **7a** and **8b** obtained by X-ray diffraction analyses (gray), with its modeled structure (black).

calculating their vibrational modes. The calculated structures were compared with the IR and NMR spectroscopic data of the herein synthesized compounds, which were in good agreement. The theoretical results are validated when superimposed structures obtained by gas phase calculations (black) and X-ray diffraction in the solid state (gray) of the compounds 7a (fused five-six membered ring) and 8b (fused six-seven membered ring), Fig. 5. The structures 6a and 7a correspond to heterobicyclic systems [4.3.0], whereas the rest of the molecules modeled correspond to heterobicyclic systems [4.5.0]. In all structures, there is a coordination bond N1–B1 with a bond distance between 1.59 and 1.63 Å characteristics for this type of compounds [17–23]. The bond distances B1–O1 (~1.48 Å) are slightly longer than the corresponding B1–O2 (~1.45 Å) in the seven-membered rings. The angles around tetracoordinated boron atom are in the range of 106–114° and tricoordinated boron atom in the range of 116–123°. The boat conformation reduces the steric effect between the two methyl groups in **6b** and **7b** in accordance with the torsion angles of the fragments H<sub>3</sub>C--C7=N1--C8 (7.11°,6.90°) and C7=N1-C8-CH<sub>3</sub> (98.64°,98.33°). It is also noted that naphthyl groups bonded to the boron atoms in 7b and 9b are perpendicular avoiding steric repulsion.



Fig. 6. Boat conformation calculated for structures 6b and 7b by PBE/6-31G(d,p), the hydrogen are omitted for clarity.



Fig. 7. Boat and chair conformations calculated for structures 8b and 9b by PBE/6-31G(d,p), hydrogens are omitted for clarity.

The synthesis, characterization and crystal structure of compound **6a** was previously reported by our research group [22], while the crystal structure of **7a** is discussed in this paper, however it was not possible to obtain experimentally compounds **6b** and **7b**, (Scheme 2), but we could determine the minimum energy structures for compounds **6b** and **7b**, showing a significant steric repulsion between the two methyl groups bonded to carbons C7 and C8, which avoid the formation of the systems [4.5.0] in compounds *6b* and *7b*. The modeled structures adopt a boat conformation as the most stable for the seven-membered heterobicyclic boronates, Fig. 6. The distances N1–B1, B1–O2, O2–B2, B2–O3 are 1.63, 1.45, 1.35, 1.39 Å for *6b* and 1.63, 1.45, 1.34, 1.38 Å for *7b*.

The seven membered ring in **8b** shows a chair conformation, which was proved by X-ray diffraction; calculations were made

to model the boat conformation showing a minimal difference in energy of 1.46 kcal/mol. In the structures calculated the energy difference is negligible, so that experimentally both conformations are possible, Fig. 7. Although **9b** could not be isolated the computational analyses indicate that it is possible to obtain it. The distance N1—B1 in the structures calculated for boat conformation is 1.61 and 1.60 Å while the chair conformation is 1.60 and 1.59 Å for **8b** and **9b** respectively, which indicates a better coordination N  $\rightarrow$  B in the chair conformation. Heating fused six-seven membered oligoboronates conduce to obtain fused five-six membered boronates compounds.

#### 5. Conclusions

Three new heterobicyclic systems of monomeric boronates with fused rings, one of which is seven-membered while the other two are five-membered, were prepared in good yields. PBE/6-31G(d,p) analysis indicates that structures 6b and 7b cannot be obtained because a high steric factor is observed; even using solvents with high boiling points no results could be achieved. DFT calculations of <sup>11</sup>B NMR and IR spectra are in accordance with the experimental values. The X-ray analysis of 7a and 8b confirm that addition of one and two equivalents of the boronic acid implies the formation of different compounds. When two equivalents of the boronic acid are reacted with the tridentate ligands, structures with two boron atoms can be obtained, one boron atom been tetrahedral and the second boron atom with a trigonal planar geometry. Finally, the results analyzed by X-ray diffraction and PBE/6-31G(d,p) calculations indicates that the most stable compounds are those with fused five-six membered rings and can be obtained from compounds with fused six-seven membered rings by heating. Compound 8b can be applied in the Susuki reaction that involves the formation of new C-C bonds because a tricoordinated boron atom is present in the structure.

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#### **Appendix A. Supplementary material**

Tables of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles, as well as a list of structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 270364 and 270361 for **7a** and **8b**, respectively). Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data\_request/cif). MOL structural files can be downloaded from the online version of the article in ScienceDirect to view the details of the chemical structures calculated. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.08.039. These data include MOL files and InChiKeys of the most important compounds described in this article.

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