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Note

# Boron complexes derived from the condensation reaction of 3-aminophenylboronic acid and 1,3-diketones

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ABSTRACT

The structural analogy of 1,3-dicarbonyl compounds with 2-hydroxybenzencarbonyl compounds allowed to do an analysis towards the reactivity with 3-aminophenylboronic acid, in order to evaluate the synthesis of macrocyclic boron compounds having calixarene like structures. The results indicate that the chelate form is preferred over the reaction of the amino group with carbonyl groups. Thus the reaction of 1,3-diketones (1,3-diphenyl-1,3-propanedione, 1-phenyl-1,3-butanedione and 2,4-pentanedione) with 3-aminophenylboronic acid using methanol or propanol as solvent medium, afforded the six-membered boron chelates as the only product.



## 1. Introduction

In the last decade, boronic acids have been employed for the construction of macrocyclic boron compounds by means of self-assembly reactions [1]. It is well known that, using electron donor–acceptor interactions the synthesis of macrocycles containing a large cavity has been possible [2]. In this context, it has been described that molecules containing nitrogen atoms as Lewis bases reacts with compounds having boron atoms as Lewis acids forming strong N–B coordination bonds [1–3]. In fact, N–B coordination bonds have been used to build a large number of macrocycles like dimeric [4], trimeric [5], tetrameric [6] or pentameric [7] compounds. Furthermore, the OH moiety of boronic acids is able to react with alcohols to give boron esters through the formation of covalent B–O bonds [8]. The high thermodynamic stability of the boron esters promotes the formation of cyclo-oligomeric and polymeric boron compounds [9].

Recently, the formation of calixarenes [10] and hemicarcerands [11] boron compounds by reaction of 3-aminophenylboronic acid with salicylaldehyde derivatives was described (Scheme 1). In this type of compounds, the first step is the reaction between carbonyl and amine groups to give an imine moiety. In the second step, the phenolic OH group reacts with the OH attached to the boron atom to give a B–O covalent bond and finally, the nitrogen atom is coordinated to the nitrogen atom. The synthesis of these complexes involves the formation of both, N–B coordination and B–O covalent bonds that enhance the macrocyclic stability. The simple formation of these compounds using one-pot reactions increases the versatility for possible host–guest chemistry applications. In fact, calix-like compounds have shown to be useful for the inclusion of small organic molecules such as benzene and THF [10a], as well as amines and ammonium salts [10b]. In this work, 1,3-dicarbonyl compounds were allowed to react with 3-aminophenylboronic acid in order to analyze the reactivity towards the formation of boron macrocycles.

## 2. Results and discussion

It is well known that 1,3-diketones are under keto-enol equilibrium, this characteristic has been used to analyze their reactivity towards primary amines, wherein one of the carbonyl groups reacts to give an imine while the other one remains in the enol form [12]. In this work, 1,3-diketone derivatives were used as synthetic equivalent of 2-hydroxybenzencarbonylic compounds (Scheme 2) in order to compare their reactivity towards 3-aminophenylboronic acid. Thus, 2,4-pentanedione, 1,3-diphenyl-1,3-propanedione and 1-phenyl-1,3-butanedione were allowed to react with 3-aminophenylboronic acid. The reaction conditions used were similar to those reported previously for the synthesis of trimeric compounds [5,10]. The reactions were carried out under reflux of methanol for compounds **1a**–**1c** and propanol for compound **1d**. In all four cases

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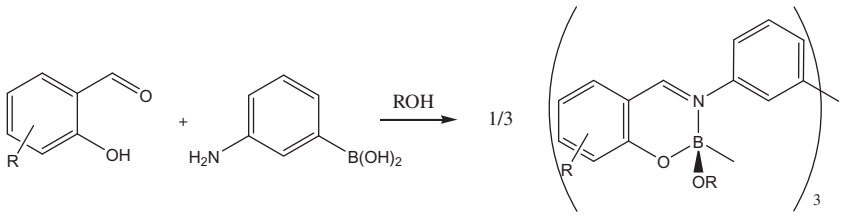
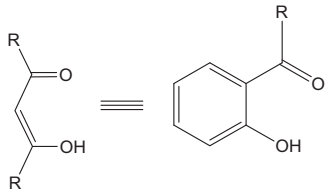
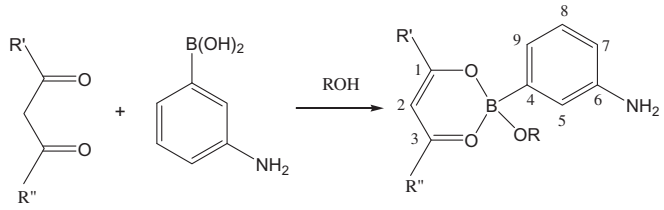



**Scheme 1.** Calix-like compounds formed by reaction of salicylaldehyde with 3-aminophenylboronic acid.




**Scheme 2.** Structural comparison between the enol form of 1,3-diketones and 2-hydroxybenzencarbonyl compounds.




| | R | R' | R'' |
|---|---|---|---|
| **1a** | Me | Ph | Ph |
| **1b** | Me | Ph | Me |
| **1c** | Me | Me | Me |
| **1d** | Pr | Ph | Ph |

**Scheme 3.** Boron chelate compounds formation from 1,3-dicarbonyl compounds and 3-aminophenylboronic acid.

colored solid products (yellow-red) were obtained in moderate yields (Scheme 3). The spectroscopic analysis evidenced that the formation of boron chelate complexes is preferred over the macrocyclic compounds. Herein, both oxygen atoms of the diketone moiety are attached to the boron atom while the amino group remains unreacted. This behavior has been observed before for 1,3-dicarbonyl compounds reacting with arylboronic acids wherein six-membered rings are obtained [13].

The mass spectra showed the molecular ion corresponding to the OCCCOB chelate for the complexes **1a**–**1d**, in all four cases, the corresponding ion indicating the loss of one RO-group was also observed. These types of fragments, wherein the ligand remains coordinated to the metal center through both oxygen atoms, are in accordance with previous studies even with representative [13] or transition metals [14].

The $^{1}$H NMR analysis showed that the signal corresponding to the hydrogen located between the carbonyl groups (H-2) is shifted to lower fields when phenyl groups are present ($\delta$ = 7.35 and 7.34 ppm, for **1a** and **1d**, respectively). Nonetheless, in the presence of methyl groups, the signal is shifted to higher fields at 6.07 and 5.23 ppm in **1b** and **1c**, respectively. The electronic delocalization present in the six-membered rings is suggested by the $^{13}$C NMR spectra. For instance, the compounds derived from symmetric diketones, showed only one carbonyl base signal ($\delta$ = 185.8, 160.8 and 184.8 for **1a**, **1c** and **1d**, respectively), the more shifted signals correspond to compounds having phenyl moieties (**1a** and **1d**). The signal corresponding to the carbon atom adjacent to both carbonyl groups (C-2) remains without significant changes for **1a**, **1b** and **1d** compounds, it appears around 93 ppm. Nonetheless, the signal for the same carbon in **1c** is shifted to lower field (98.2 ppm). The $^{11}$B NMR analysis evidenced the tetrahedral character of the boron atoms, in all four cases the chemical shift was observed in the range from 3 to 4 ppm, in accordance with previous reports [10–12].

Suitable crystals for X-ray diffraction analysis for **1a**, **1b** and **1d** were grown by slow diffusion of dichloromethane into a methanol solution. The three structures are shown in Fig. 1 and the crystallographic data are depicted in Table 1. Selected bond lengths and bond angles are listed in Table 2. From the data, only small differences in the bond distances around the six-membered heterocycles were observed, giving evidence of the delocalization present in this fragment, as noticed previously for analogous compounds [13]. For example, the C–O bond distances are the same in the three compounds *ca.* 1.29 Å, while the B–O distances are quite different

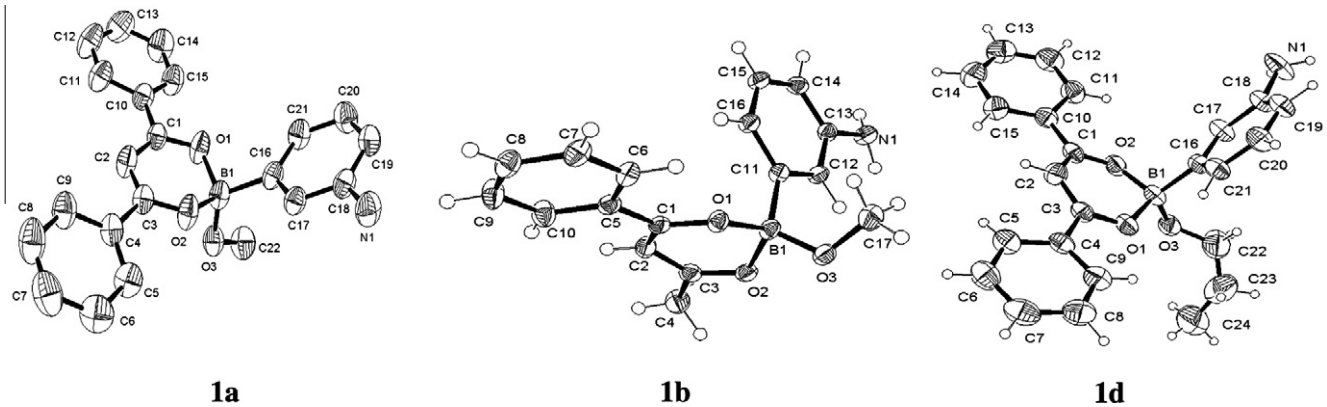



**Fig. 1.** Molecular structure for compounds **1a**, **1b** and **1d**.

**Table 1**
Crystallographic data for compounds **1a**, **1b** and **1d**.

| Identification code | 1a | 1b | 1d |
|---|---|---|---|
| Empirical formula | $C_{22}H_{20}B_1N_1O_3$ | $C_{17}H_{18}B_1N_1O_3$ | $C_{24}H_{24}B_1N_1O_3$ |
| Formula weight | 357.20 | 295.13 | 385.25 |
| Crystal size ($mm^3$) | 0.42 × 0.32 × 0.18 | 0.26 × 0.18 × 0.14 | 0.48 × 0.26 × 0.22 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| *Unit cell dimensions* | | | |
| *a* (Å) | 8.447(2) | 8.2247(12) | 8.499(2) |
| *b* (Å) | 11.049(2) | 9.6337(14) | 11.175(3) |
| *c* (Å) | 11.301(2) | 10.7003 (15) | 11.667(3) |
| α (Å) | 94.27(3) | 115.999(2) | 78.623(4) |
| β (°) | 110.43(3) | 92.452(3) | 75.851(5) |
| γ (Å) | 106.93(3) | 96.986(2) | 76.390(5) |
| Volume ($Å^3$) | 927.1(3) | 752.21 (19) | 1032.8(5) |
| *Z* | 2 | 2 | 2 |
| $\rho_{calc}$ ($g\,cm^{-3}$) | 1.280 | 1.303 | 1.239 |
| μ ($mm^{-1}$) | 0.084 | 0.088 | 0.080 |
| Collected reflections | 3426 | 3660 | 6070 |
| Independent reflections ($R_{int}$) | 3241(0.0141) | 2447(0.0146) | 3583 (0.0299) |
| Parameters | 245 | 271 | 331 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0493 | 0.0465 | 0.0784 |
| $wR_2$ (all data) | 0.1636 | 0.1192 | 0.1952 |
| Goodness of fit (GOF) | 1.082 | 1.028 | 1.061 |

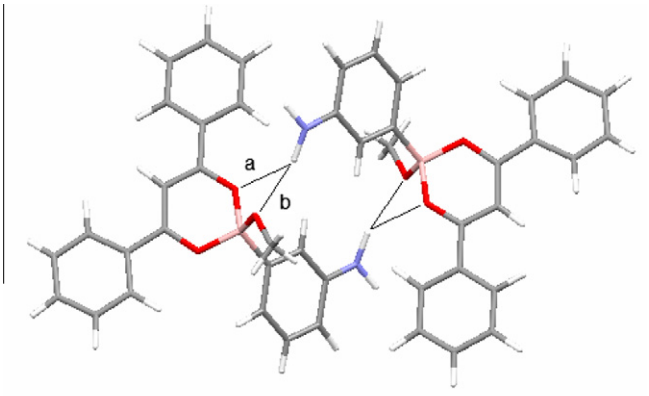
(Δ*d* = 0.017, 0.014 and 0.034 for **1a**, **1b** and **1d**, respectively). A comparison of the C1–C2 and C2–C3 bond distances reveals that only compound **1a** shows a clear difference (Δ*d* = 0.072 Å) indicating less delocalization in this fragment. The bond angles around the boron atom remain close to the tetrahedral values. Nevertheless, in compound **1a** there are two values that are slightly different from $sp^3$ hybridization, the O3–B1–C16 angle has the largest value (120.1°), at the same time, the O2–B1–O3 angle decreases (97.6°). Interestingly, the O–B–O angle inside the heterocycle is similar (*ca.* 106.3°) in all three compounds; nonetheless it is the shorter angle of the heterocycle. The other angles into the six-membered heterocycle have values closer to $sp^2$ hybridization being in the range from 118.8° to 126.6°.

At the unit cell, hydrogen bonding interactions owing to the existence of $NH_2$ groups together with the presence of several oxygen atoms in the molecules give rise to dimeric and polymeric arrangements. The formation of dimeric molecules results from intermolecular interactions from a bifurcate hydrogen bond (N1–H···O1 and N1–H···O3). As depicted in Fig. 2, in all three cases one N(1)H moiety interacts with two oxygen atoms of the neighboring molecule with distances of 2.894 (O3) to 2.171 (O1) Å. Previous reports have shown the dimeric arrangement involving N–H···O motives in boron complexes [15]. Also in all three cases, the oxygen atom of the alkyl group (O3) participate in two hydrogen bonds, the first one was described previously forming the dimeric structure while the second one forms an interaction with the other NH moiety of a third molecule giving rise to the formation of 1D polymeric chains (Fig. 3). The polymeric intermolecular N1–H···O3 hydrogen bond distances are 2.243, 2.048 and 2.472 Å for **1a**, **1b** and **1c**, respectively. It is important to remark that, the molecular arrangement at the unit cell was not affected by the presence of the different substituents present in the 1,3-diketones.

**Table 2**
Selected bond distances (Å) and angles (°) for compounds **1a**, **1b** and **1d**.

| | 1a | 1b[a] | 1d[b] |
|---|---|---|---|
| O1–B1 | 1.490(3) | 1.5352(19) | 1.508(5) |
| O1–C1 | 1.294(2) | 1.2956(19) | 1.293(4) |
| B1–O2 | 1.473(3) | 1.521(2) | 1.540(4) |
| B1–O3 | 1.512(3) | 1.426(2) | 1.417(5) |
| B1–C16 | 1.648(3) | 1.593(3) | 1.602(5) |
| C1–C2 | 1.379(3) | 1.394(2) | 1.385(5) |
| C2–C3 | 1.307(3) | 1.383(2) | 1.364(5) |
| C3–O2 | 1.289(2) | 1.2971(19) | 1.292(4) |
| O1–B1–O2 | 106.4(2) | 106.30(12) | 106.9(3) |
| O1–B1–O3 | 115.5(2) | 108.85(13) | 104.7(3) |
| O1–B1–C16 | 101.0(2) | 109.77(13) | 109.3(3) |
| O2–B1–O3 | 97.6(2) | 104.61(13) | 107.8(3) |
| O2–B1–C16 | 116.3(2) | 109.57(14) | 109.3(3) |
| O3–B1–C16 | 120.1(2) | 117.13(14) | 118.2(3) |
| B1–O1–C1 | 120.1(2) | 119.90(12) | 123.5(3) |
| O1–C1–C2 | 124.0(2) | 120.91(15) | 119.9(3) |
| C1–C2–C3 | 118.8(2) | 119.00(15) | 121.5(3) |
| C2–C3–O2 | 119.7(2) | 121.65(15) | 120.5(3) |
| C3–O2–B1 | 126.6(2) | 119.26(12) | 122.7(3) |

[a] For compound **1b** the C16 = C11.
[b] For compound **1d** O1 = O2 and O2 = O1.




*NH···O interactions (Å)*

| | *a* | *b* |
|---|---|---|
| *Comp. **1a*** | 2.978 | 2.171 |
| *Comp. **1b*** | 2.372 | 2.764 |
| *Comp. **1d*** | 2.894 | 2.274 |

**Fig. 2.** Dimeric molecular structure formed by N–H···O interactions (compound **1a** is showed).

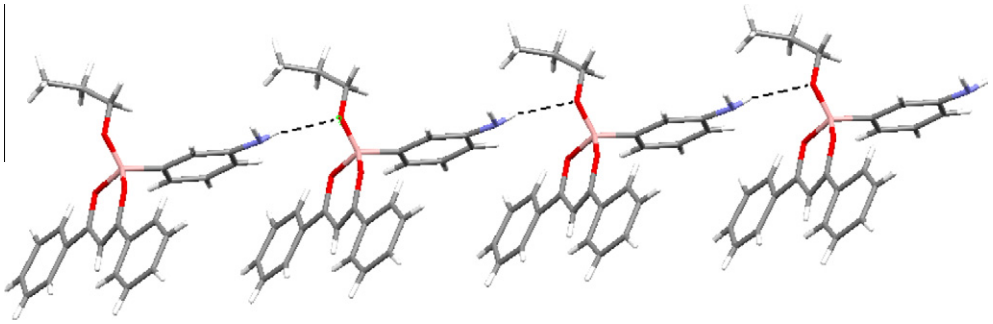


**Fig. 3.** Polymeric structure formed by N–H···O interactions (compound **1d** is showed). N–H···O interaction distances (Å): 2.243 (**1a**), 2.048 (**1b**) and 2.472 (**1d**).

## 3. Experimental

### 3.1. Materials

All reagents and solvents used were obtained from commercial suppliers and used without further purification.

### 3.2. Instrumentation

The $^{1}H$, $^{13}C$ and $^{11}B$ NMR spectra were recorded at room temperature using a Varian VXR 400 spectrophotometer. As standard references were used TMS (internal, $^{1}H$, $\delta = 0.00$ ppm, $^{13}C$, $\delta = 0.0$ ppm) and $BF_3{\cdot}OEt_2$ (external, $^{11}B$, $\delta = 0.0$ ppm). The 2D COSY and HECTOR experiments have been carried out for the unambiguous assignment of the $^{1}H$ and $^{13}C$ NMR spectra. Infrared spectra have been recorded on a Bruker Vector 22 FT-IR spectrophotometer. Mass spectra were obtained with a MStation Jeol JMS 700 equipment. Melting points were determined with a Büchi B-540 digital apparatus.

### 3.3. X-ray crystallography

X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector, Mo Kα-radiation, $\lambda = 0.71073$ Å, graphite monochromator. Frames were collected at $T = 293$ K by $\omega$-rotation ($\Delta/\omega = 0.3°$) at 10 s per frame. The measured intensities were reduced to $F^2$. Structure solution, refinement and data output were carried out with the SHELXTL program package [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model.

### 3.4. General method for the preparation of boron complexes *1a–1d*

Compounds **1a–1d** were synthesized by reacting equimolecular quantities of 3-aminophenylboronic acid monohydrated and the corresponding 1,3-dicarbonyl compound using 20 ml of MeOH as solvent, in the case of **1d** acetonitrile was used as solvent adding 2 ml of *n*-propanol. The reaction mixtures were refluxed 1 h under stirring. After that, the solvent was completely removed using a vacuum pump. The products were purified by recrystallization in solvent mixtures $MeOH/CH_2Cl_2$ (1:3 ratio).

Compound **1a** was prepared from 0.30 g (1.93 mmol) of 3-aminophenylboronic acid monohydrated and 0.43 g (1.93 mmol) of 1,3-diphenyl-1,3-propanedione. The product was obtained as an orange powder. Yield: 0.52 g (75%); mp = 187–191 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.17 (4H, d, $J = 7.3$ Hz, H-o), 7.81 (1H, s, H-5), 7.60–7.80 (10H, m, H-m, p), 7.55 (1H, t, $J = 7.7$ Hz, H-8), 7.35 (1H, s, H-2), 7.01 (1H, d, $J = 7.7$ Hz, H-9), 6.97 (1H, d, $J = 7.7$ Hz, H-7), 3.58 (3H, s, H-Me). $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 185.8 (C-1,3), 147.9 (C-6), 133.6 (C-*o*), 129.6 (C-*p*), 129.1 (C-*i*), 128.3 (C-8), 127.9 (C-*m*), 121.8 (9), 120.6 (C-5), 116.4 (C-7), 93.8 (C-2), 49.9 (Me). $^{11}B$ NMR (64 MHz, $CDCl_3$) $\delta$: 4.2 ppm ($h_{1/2} = 1420$ Hz). IR (KBr) $\overline{\nu}$ ($cm^{-1}$) = 3346, 2918, 2850, 1618, 1598, 1576, 1560, 1540, 1508, 1488, 1456, 1448, 1362, 1302, 1268, 1230, 756, 716, 708, 682, 668. EI-MS *m*/*z* (%): 357 ($M^+$, 12), 224 (75), 223 (90), 207 (5), 178 (5), 165 (5), 147 (44), 105 (100), 93 (7), 77 (86), 51 (30). Elem. *Anal.* Calc. for $C_{22}H_{20}B_1N_1O_3$: C, 73.97; H, 5.64; N, 3.92. Found: C, 73.66; H, 5.56; N, 3.91%.

Compound **1b** was prepared from 0.30 g (1.93 mmol) of 3-aminophenylboronic acid and 0.31 g (1.93 mmol) of 1-phenyl-1,3-butanedione. The product was obtained as an orange powder. Yield: 0.30 g (53%); mp = 210–213 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.2 (2H, S, $NH_2$), 7.92 (2H, dd, $J = 7.7, 2.2$, H-*o*), 7.77 (1H, s, H5), 7.63 (1H, t, $J = 7.7$, H-*p*), 7.45 (1H, t, $J = 6.4$, H8), 7.35 (1H, t, $J = 7.7$, H-*m*), 6.95 (2H, d, $J = 6.4$, H7, H9), 6.07 (1H, s, H2), 2.5 (3H, s, OMe), 2.19 (3H, s, $CH_3$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 186.5 (C-1), 162.2 (C-3), 147.2 (C-6), 135.0 (C-4), 131.0 (C-*p*), 129.1 (C-*i*), 128.1 (C-*m*), 127.5 (C-8), 126.5 (C-*o*), 121.6 (C-9), 119.7 (C-5), 115.5 (C-7), 93.3 (C-2), 39.0 (OMe), 20.1 (Me) ppm. $^{11}B$ NMR (64 MHz, $CDCl_3$) $\delta$: 3.1 ppm ($h_{1/2} = 3848$ Hz). IR (KBr) $\overline{\nu}$ ($cm^{-1}$) = 3391, 2373, 1601, 1576, 1522, 1488, 1440, 1373, 1325, 1286, 1068, 1027, 752, 707, 555. EI-MS *m*/*z* (%): 295 ($M^+$, 40), 280 ($[M-CH_3]^+$, 20), 236 (100), 218 (40), 130 (15), 93 (100), 84 (40). Elem. *Anal.* Calc. for $C_{17}H_{18}B_1N_1O_3$: C, 69.18; H, 6.14; N, 4.74. Found: C, 68.67; H, 5.92; N, 4.61%.

Compound **1c** was prepared from 0.30 g (1.93 mmol) of 3-aminophenylboronic acid and 0.19 g (1.93 mmol) of 2,4-pentanedione. The product was obtained as a yellow powder. Yield: 0.18 g (41%); mp = 140–143 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.17 (2H, s, $NH_2$), 7.61 (1H, d, $J = 7.6$, H9), 7.55 (1H, s, H5), 7.35 (1H, t, $J = 7.6$, H8), 7.25 (1H, d, $J = 7.6$, H7), 5.23 (1H, s, H2), 3.37 (3H, s, OMe), 2.01 (3H, s, $CH_3$–C1), 1.99 (3H, s, $CH_3$–C3) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 160.8 (C-1,3), 138.5 (C-6), 131.8 (C-8), 130.4 (C-9), 129.2 (C-5), 126.9 (C-7), 98.2 (C-2), 39.7 (OMe), 20.3 ($CH_3$–C1,3) ppm. $^{11}B$ NMR (64 MHz, $CDCl_3$) $\delta$: 3.2 ppm ($h_{1/2} = 4104$ Hz). IR (KBr) $\overline{\nu}$ ($cm^{-1}$) = 3379, 1617, 1590, 1551, 1433, 1344, 1313, 1157, 750, 711. EI-MS *m*/*z* (%): 218 ($[M-CH_3]^+$, 10), 204 (5), 175 (25), 160 (70), 132 (30), 117 (15), 101 (100). Elem. *Anal.* Calc. for $C_{12}H_{16}B_1N_1O_3$: C, 61.83; H, 6.91; N, 6.00. Found: C, 61.45; H, 6.73; N, 5.91%.

Compound **1d** was prepared from 0.30 g (1.93 mmol) of 3-aminophenylboronic acid and 0.43 g (1.93 mmol) of 1,3-diphenyl-1,3-propanodione. The product was obtained as a red powder. Yield: 0.53 g (72%); mp = 187–190 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$: 8.16 (4H, d, $J = 7.3$, H-*o*), 7.70 (1H, s, H5), 7.70–7.40 (7H, m, H-*m*, *p*, 8), 7.34 (1H, s, H2), 6.95 (1H, dt, $J = 8.70, 2.90$, H9), 6.58 (1H, dt, $J = 6.3, 2.9$, H7), 4.39 (2H, t, $J = 5$, H10), 1.43 (2H, sex, $J = 7.2$, H11), 0.83 (3H, t, $J = 7.2$, H12) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$: 184.8 (C-1,3), 147.2 (C-6), 134.0 (C-4), 132.8 (C-*p*), 128.6 (C-*m*), 128.0 (C-*i*), 127.5 (C-8), 127.1 (C-*o*), 121.6 (C-9), 119.7 (5), 115.5

(7), 93.1 (C-2), 62.4 (C-10), 25.7 (C-11), 10.5 (C-12) ppm. $^{11}$B NMR (64 MHz, $CDCl_3$) $\delta$: 3.1 ppm ($h_{1/2}$ = 4372 Hz). IR (KBr) $\overline{\nu}$ ($cm^{-1}$) = 3007, 2969, 1717, 1630, 1436, 1365, 1224, 1093, 902, 530. EI-MS *m*/*z* (%): 385 ($M^+$, 5), 350 (50), 294 (40), 224 (100), 146 (70), 104 (95), 77 (55). Elem. *Anal.* Calc. for $C_{24}H_{24}B_1N_1O_3$: C, 74.82; H, 6.27; N, 3.63. Found: C, 74.77; H, 6.02; N, 3.54%.

## 4. Conclusions

In all four cases, reacting 1,3-diketones with 3-aminophenylboronic acid leads to the six-membered boron compounds. So, the chelate form is preferred over the reaction of the amino group with carbonyl groups to get the iminic moieties. A complete delocalization in these chelates was not observed as confirmed from the measure of the C–C internal distances of the heterocycle which are slightly different. Although discrete molecules are obtained, in the solid state dimeric and polymeric structures are observed as a result of hydrogen bonding interactions.

## Acknowledgements

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## Appendix A. Supplementary material

CCDC 752003, 752004 and 752005 contain the supplementary crystallographic data for **1a**, **1b** and **1d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.05.008.

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