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Macrocycles, adducts and monomeric boron compounds derived from 2,6-dimethanolpyridine and arylboronic acids

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Abstract

The reaction of 2,6-dimethanolpyridine with arylboronic acids at room temperature led to the formation of tetrameric compounds **1a**–**1e** in good yields. Since the tetrameric derivatives were insoluble in common organic solvents, their characterization was based on IR, mass spectrometry, as well as ^{13}C and ^{11}B NMR, in the solid state. Macrocyclic compounds **1a**–**1e** can be hydrolyzed upon heating in DMSO to give adducts **2a**–**2e**, which are only held by a coordination bond between the nitrogen and boron atoms, as demonstrated by ^{1}H, ^{13}C and ^{11}B NMR, in solution. Moreover, the presence of an additional carbon atom in the aliphatic chain of the ligand, as in the case of 2,6(β-diethanolamine)pyridine, leads exclusively to the formation of the monomeric specie **4**, as established by X-ray diffraction analysis.

Keywords: Boron; Macrocycles; Tridentate ligands; ^{11}B NMR solid state

1. Introduction

The chemistry of macrocycles has been extensively studied in the last years, due to possible applications of these systems in different fields such as chemistry, biology, physics and materials science [1]. Several synthetic strategies have been applied to the formation of macrocycles, in addition to the ones used in traditional organic synthesis [1c]. Thus, a number of organic and inorganic macrocycles have been prepared using template effects, or self-assembly processes via coordinative connections by reaction of bi-, tri- or oligo-dentate ligands with the appropriate metal [2].

The formation of macrocyclic structures using organic synthesis generally involves several steps, as a consequence, the products are obtained in low yields; this constitutes a major disadvantage over other preparative methods. Alternatively, coordinative connections are preferred for the formation of macrocyclic structures and these processes usually occur through self-assembly. These mechanisms are frequently kinetically favored; the main disadvantage is, however, that coordinative connections are normally thermodynamically weaker than covalent ones.

In this context, it is well known that boron atoms can form strong coordinative bonds with nitrogen atoms [3]. With this simple approach, it has been possible to grow several fragments to give macrocyclic structures via self-assembly processes using boron derivatives. The

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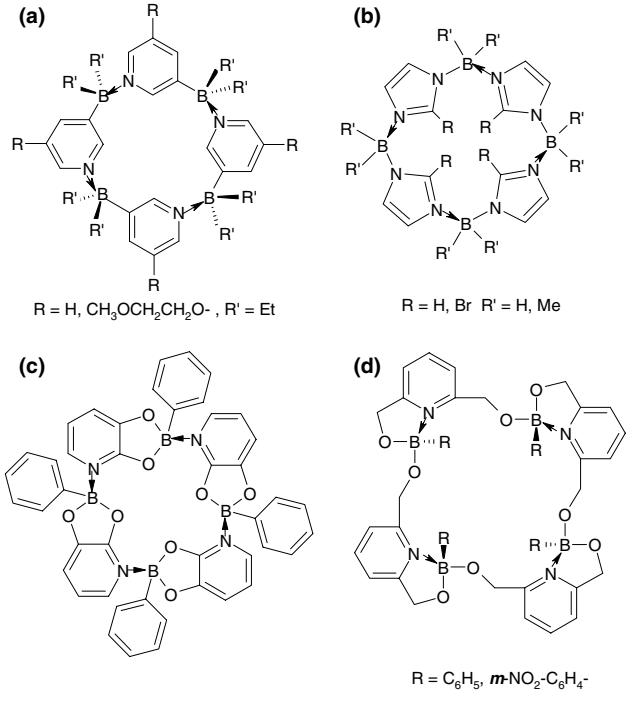
synthesis of boron macrocycles that contain coordinative bonds between the nitrogen and boron atoms has been achieved using the above method, and dimeric, trimeric, tetrameric and pentameric species have been reported [3].

On the other hand, 2,6-dimethanolpyridine (dmpy) acts as tridentate ligand with transition metals to form monomeric or dimeric complexes [4]. Nevertheless, in the case of the reaction of dmpy with arylboronic acids, two tetrameric species containing a 20-membered ring cavity have been obtained in good yields (>90%) [3b,3f] (Scheme 1(d)). These tetrameric compounds are stable to moisture, however, since they show poor solubility in common organic solvents, extensive spectral analysis was difficult. Fortunately, an X-ray diffraction analysis was possible and both structures were analyzed [3b,3f]. It is noteworthy that only a few tetrameric compounds have been described in the literature where the presence of N–B coordinative bonds favor self-assembly of the fragments (Scheme 1) [5].

In the present work, we describe the reaction of 2,6-dimethanolpyridine with five arylboronic acids. Different substituents have been introduced in the aromatic ring of the boronic acid fragment in order to study electronic effects along the N–B coordinative bond, and determine possible changes in the reaction pathway and solubility, with the aim to use them in host–guest chemistry. However, due to the fact that these derivatives were insoluble solids, it was necessary to carry out solid state NMR analyses in order to complete the characterization.



Scheme 1. Examples of tetrameric boron compounds obtained by self-assembly via the formation of N–B coordinative bonds.

It is important to remark that a wide variety of soluble boron compounds including boranes, carboranes, boron nitrides, metalloboranes and metallocarboranes have been extensively analyzed using ^{11}B NMR spectroscopy in the liquid state [6]. In contrast, ^{11}B NMR studies in the solid state are scarce and, to our knowledge, the only molecules analyzed so far are carboranes, borides, chalcogenides and carbides [7].

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were commercial products from Aldrich, Fluka and Merck and were used without further purification. The ^{13}C (CP-MAS) and ^{11}B (MAS) NMR spectra were determined on a Bruker ASX300 spectrometer. The ^{1}H, ^{13}C and ^{11}B NMR, as well as 2D spectra were determined on a Bruker Avance 300 spectrometer, using DMSO-d_6 as solvent and $(CH_3)_4Si$ and BF_3OEt_2 as internal references. Chemical shifts are reported in parts per million (ppm). Infrared spectra (IR) were obtained on a Perkin–Elmer 16F-PC coupled to FT-IR spectrometer. FAB mass spectra were determined with a Jeol JMS-700 spectrometer. Mass spectrum (EI) for **4** was determined on a Hewlett–Packard 5989A apparatus coupled to a gas-chromatograph series 5890 II. Melting points were determined with a Gallenkamp digital MFB-595 apparatus and have not been corrected. Elemental microanalysis for compound **4** was performed by Oneida Research Services, Whitesboro, NY 13492, and for Midwest Microlab, LLC. Indianapolis, IN 46250 [8].

The single-crystal X-ray diffraction study of **4** was determined on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation; $\lambda = 0.71073$ Å) with a graphite monochromator, $\omega = 2\theta$ in the interval $2 < \theta < 25$. Direct methods SHELXS-86 [9] were used for structure solution and the SHELXL-97 program [10], for refinement and final data. Crystallographic data for compound **4** have been deposited at the Cambridge Crystallographic Data Center No. 249146.

2.2. Syntheses of complexes

2.2.1. General method for the syntheses of tetrameric compounds (*1a–1e*)

Tetrameric compounds **1a**–**1e** were synthesized from 2,6-dimethanolpyridine and the corresponding arylboronic acid (1:1 ratio) in 20 ml of THF, the mixture was stirred for 30 min at room temperature yielding a white precipitate, which was recovered by filtration and washed twice with 5 ml of THF.

2.2.1.1. Tetrakis[[μ-(2,6-pyridinemethanolate-kN^1, kO^2, kO^6)](4-formylphenyl)boron]. Compound **1a** was prepared from 0.20 g (1.44 mmol) of 2,6-dimethanolpyridine and 0.21 g (1.44 mmol) of *p*-formylphenylboronic acid, a white solid was obtained, yield 83% (0.30 g, 0.30 mmol), $mp_{(decomp)}$ = 350 °C. FAB-MS (15 eV, *m*/*z*, %): 1011 [M^+, 37]; IR (KBr) *v*: 3420, 2918, 2848, 1694, 1622, 1478, 1212, 1188, 1130, 1112, 1090, 810, 790, 754 cm^{-1}.

2.2.1.2. Tetrakis[[μ-(2,6-pyridinemethanolate-kN^1, kO^2, kO^6)](3-methoxyphenyl)boron]. Compound **1b** was prepared from 0.20 g (1.44 mmol) of 2,6-dimethanolpyridine and 0.19 g (1.44 mmol) of *m*-methoxyphenylboronic acid, a white solid was obtained, yield 85% (0.29 g, 0.28 mmol), $mp_{(decomp)}$ = 316 °C. FAB-MS (10 eV, *m*/*z*, %): 1019 [M^+, 91]; IR (KBr) *v*: 3348, 2916, 2848, 1620, 1570, 1478, 1466, 1418, 1280, 1240, 1164, 1090, 1036, 750, 732 cm^{-1}.

2.2.1.3. Tetrakis[[μ-(2,6-pyridinemethanolate-kN^1, kO^2, kO^6)](3-tolyl)boron]. Compound **1c** was prepared from 0.20 g (1.44 mmol) of 2,6-dimethanolpyridine and 0.19 g (1.44 mmol) of *m*-tolylboronic acid, a white solid was obtained, yield 81% (0.28 g, 0.29 mmol), $mp_{(decomp)}$ = 272 °C. FAB-MS (10 eV, *m*/*z*, %): 955 [M^+, 66]; IR (KBr) *v*: 2916, 2848, 1620, 1570, 1478, 1466, 1418, 1280, 1240, 1164, 1090, 1036, 784, 750, 732 cm^{-1}.

2.2.1.4. Tetrakis[[μ-(2,6-pyridinedimethanolate-kN^1, kO^2, kO^6)](4-bromophenyl)boron]. Compound **1d** was prepared from 0.20 g (1.44 mmol) of 2,6-dimethanolpyridine and 0.22 g (1.44 mmol) of *p*-bromophenylboronic acid, a white solid was obtained, yield 85% (0.33 g, 0.30 mmol), $mp_{(decomp)}$ = 313 °C. FAB-MS (10 eV, *m*/*z*, %): 1219 [M^++2, 38], 1211 (36) [M^+]; IR (KBr) *v*: 3388, 2918, 2848, 1578, 1476, 1376, 1192, 1160, 1136, 1114, 1090, 1012, 930, 804, 790 cm^{-1}.

2.2.1.5. Tetrakis[[μ-(2,6-pyridinedimethanolate-kN^1, kO^2, kO^6)](3-thiophenyl)boron]. Compound **1e** was prepared from 0.20 g (1.44 mmol) of 2,6-dimethanolpyridine and 0.22 g (0.36 mmol) of 3-thiopheneboronic acid, a white solid was obtained, yield 81% (0.27 g, 0.29 mmol), $mp_{(decomp)}$ = 210 °C. FAB-MS (10 eV, *m*/*z*, %): 923 [M^+, 58]; IR (KBr) *v*: 3094, 2846, 1700, 1622, 1478, 1442, 1210, 1162, 1152, 1128, 1102, 1090, 1026, 702 cm^{-1}.

2.2.2. [2,6-Bis-(1,1-diphenyl-(1-ethoxy))]phenylboronate

Compound **4** was prepared from 0.50 g (1.06 mmol) of ligand **3** and 0.14 g (1.06 mmol) of phenylboronic acid in 50 ml of THF. The reaction mixture was stirred under reflux for 4 h and allowed to stand overnight; a white solid was obtained in 80% yield (0.47 g, 0.84 mmol). Suitable crystals for X-ray analysis were grown from mixture of the starting materials in CH_2Cl_2 at room temperature without stirring. $C_{39}H_{32}NBO_2$. mp = 191–193 °C. IR (KBr): 3056, 3022, 1482, 1442, 1368, 1352, 1310, 1024, 700 cm^{-1}. EI-MS (15 eV, *m*/*z*, %) 480 [($M^+ - C_6H_5$), 100], 436 (30), 271 (16), 183 (5), 105 (41), 77 (60). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.90–8.10 (28H, m, H_{arom}), 4.23 and 3.23 (4H, AB, *J* = 14.9 Hz, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 154.3, 151.0, 148.7, 134.9, 131.4, 130.8, 128.5, 128.3, 128.1, 127.7, 127.3, 126.8, 126.2, 125.1 (C_{arom}), 76.1 (C–O), 42.2 (CH_2). ^{11}B NMR (96 MHz, DMSO-d_6) δ: 4.3 ($h_{1/2}$ = 736 Hz) ppm. *Anal.* Calc. for $C_{39}H_{32}NBO_2$: C, 84.02; H, 5.75; N, 2.51. Found: C, 83.93; H, 5.78; N, 2.26%.

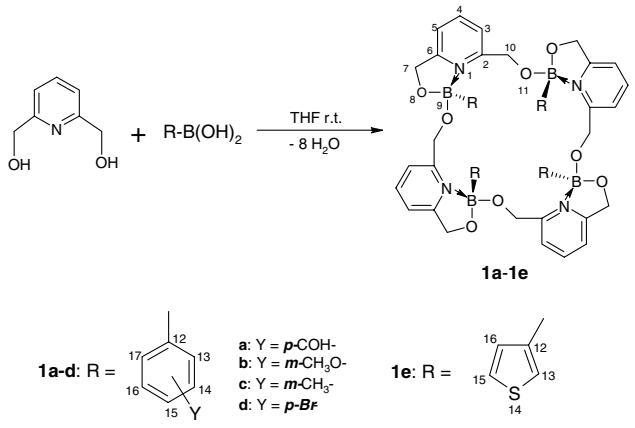
3. Results and discussion

Compounds **1a**–**1e** were synthesized by condensation of 2,6-dimethanolpyridine with 4-formylphenylboronic, 3-methoxyphenylboronic, 3-methylphenylboronic, 4-bromophenylboronic and 3-thiopheneboronic acids in THF at room temperature. After 30 min under stirring, a white precipitate was obtained in yields between 81% and 85% (Scheme 2).

The melting points for all five compounds were over 300 °C with decomposition and all of them were insoluble in common organic solvents. Nonetheless, compounds **1a**–**1e** were characterized using IR, FAB mass spectrometry, ^{13}C and ^{11}B NMR[1] in the solid state. The IR spectra for complexes **1a**–**1e** showed the disappearance of the bands corresponding to the OH groups, which are present in the starting material (dmpy). FAB mass spectrometry analysis showed, in all five cases, a molecular ion that corresponds to the tetrameric compounds. No peaks were observed at higher *m*/*z*, excluding in this way the formation of polymeric products.

Additional evidence for the formation of tetrameric compounds **1a**–**1e** is also based on the ^{13}C NMR CP-MAS experiments, which showed a single set of signals indicating the high symmetry of these molecules, in agreement with the X-ray diffraction data reported for related compounds (S_4) [3b,3f]. NMR spectral assignment for these compounds was carried out by comparison with analogous boron complexes described previously [3f,3g] and by using substituent chemical shift effects [11]. The ^{13}C NMR spectra showed the presence of two different signals for the methylene groups (Table 1), owing to the loss of symmetry of the dmpy moiety when the macrocycle containing a five-membered, as well as a 20-membered ring is formed. The signal in the range

[1] Electronic supplementary information (ESI) available: ^{13}C and ^{11}B NMR spectra for compound **1c**, also a view of the O–H···O interactions between complex **4** with one molecule of phenylboronic acid in the solid state.



Scheme 2. Synthesis of tetrameric boron derivatives (numbering scheme used for NMR assignment).

between $\delta = 56.2$ and $\delta = 58.8$ ppm was assigned to the CH_2 group which is part of the 20-membered heterocyclic ring (C-10). The signal from $\delta = 68.2$ to $\delta = 70.9$ ppm corresponds to the CH_2 group, which is part of the five-membered heterocyclic ring (C-7); The shift of C-7 to higher frequency is attributed to the shielding effect of the pyridyl group. For comparison, the starting material (dmpy) shows only a single signal for both methylene carbons C-7 and C-10. Also, for tetrameric compounds, carbon atoms 2 and 6, as well as 3 and 5, show different chemical shifts, indicating that the pyridine moiety is not symmetrical. The signal for the carbon attached to the boron atom (*C-12*) was observed between $\delta = 130.2$ and $\delta = 152.5$ ppm, the chemical shift for this carbon is not constant due to the different electronic effects of the substituent attached to the aromatic ring (Table 1).

The ^{11}B NMR spectra in the solid state showed signals between $\delta = 8.0$ and $\delta = 9.0$ ppm (Table 1), which are in agreement with the values reported in the literature [6,7] and are similar to the ^{11}B NMR shifts of samples determined in solution [3], evidencing that the boron atoms are tetracoordinate. It is important to remark that in accordance with the literature, chemical shifts for boron compounds are similar in the solid and liquid states [6,7].

In our efforts to dissolve the tetrameric compounds **1a**–**1e**, the samples were mixed with DMSO-d_6, placed in the NMR tubes and heated. After 1 h, the compounds were completely dissolved and the ^1H NMR spectra were determined showing that the signals were very similar to those of the starting materials (2,6-dimethanol pyridine and arylboronic acid). For example, the signals corresponding to the hydroxyl and methylene groups of the starting material were observed as triplet and doublet, respectively (see Table 2). In the ^{13}C NMR spectra, signals for only half of the pyridine moiety were observed, indicating that the 2, 2′, 3, 3′ and 5, 5′ carbons were equivalents by a C_2 symmetry axis (Table 3). The results above suggest that both oxygen–boron bonds were cleaved by hydrolysis, because of the presence of water in the solvent. Nevertheless, the ^{11}B NMR spectra showed signals with chemical shifts between 8.0 and 8.4 ppm, indicating that the boron atoms are in a tetrahedral environment and the N → B coordinative bond remains after hydrolysis of compounds **1a**–**1e**. Based on this evidence, we propose that the formation of adducts **2a**–**2e** must occur after heating the tetrameric compounds in hydrated DMSO (see Scheme 3). In anhydrous DMSO, the hydrolysis does not take place, nor are the compounds soluble. A possible coordination between DMSO and the boronic acids was excluded based on the fact that ^{11}B NMR analyses of the boronic acids in DMSO-d_6 gave signals with completely different chemical shifts, in the range between 25 and 30 ppm. These results provide additional evidence that N–B coordination remains even after hydrolysis, due to the high nucleophilicity of the nitrogen in the pyridine moiety.

To evaluate the effect of the chain length, a compound having an additional carbon atom between the hydroxyl group and the aromatic ring of the pyridine (**3**) was synthesized, according to the methodology described in the literature [12]. The reaction of ligand **3** with phenylboronic acid was carried out in THF. After 3 h under reflux, the mixture was slowly cooled to room temperature; a white solid was obtained and collected by filtration. In this case, the analysis showed that the reaction leads to the formation of a monomeric specie **4**

Table 1
^{13}C (75 MHz, CP-MAS) and ^{11}B (96 MHz, MAS) chemical shifts (ppm) for tetrameric compounds **1a**–**1e**

Compound	C2	C-3	C-4	C-5	C-6	C-7	C-10	C-12	C-13	C-14	C-15	C-16	C-17	^{11}B ($h_{1/2}$, Hz)
1a[a]	156.6	120.8	142.2	120.8	160.3	70.7	58.8	130.2	138.2	127.5	136.5	127.5	138.2	9.0 (321)
1b[b]	155.0	120.4	140.5	118.3	159.5	68.2	58.5	149.8	129.0	157.2	123.1	109.8	127.3	8.0 (344)
1c[c]	154.8	120.4	140.5	118.0	156.7	68.4	56.2	147.2	134.2	135.5	128.9	127.9	130.9	8.0 (358)
1d	156.9	122.1	142.5	120.4	158.3	70.4	58.1	148.2	136.7	132.3	122.1	132.3	136.7	9.0 (361)
1e[d]	157.2	121.2	144.3	121.2	159.2	70.9	58.6	152.5	128.6		132.6	128.6		9.0 (363)

[a] COH δ: 197.1 ppm, signals for C-3 and C-5 are overlapped.
[b] OMe δ: 56.3 ppm.
[c] Me δ: 22.4 ppm.
[d] Signals for C-3 and C-5 are overlapped.

Table 2
^{1}H NMR (300 MHz, DMSO-d$_6$) data for adducts **2a**–**2e**

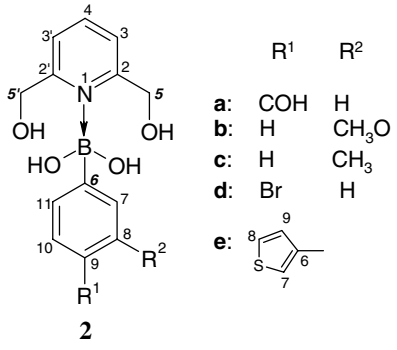
Compound	H-3	H-4	H-5	–OH	H-7	H-8	H-9
2a[a]	7.31 (d)	7.77 (t)	4.51 (d)	5.38 (t)	7.97 (d)	7.86 (d)	
	J = 7.3 Hz	J = 7.3 Hz	J = 5.9 Hz	J = 5.9 Hz	J = 8.1 Hz	J = 8.1 Hz	
2b[b]	7.31 (d)	7.78 (t)	4.52 (d)	5.50 (t)	7.32 (s)		6.94 (d)
	J = 7.7 Hz	J = 7.7 Hz	J = 5.8 Hz	J = 5.8 Hz			J = 6.8 Hz
2c[c]	7.31 (d)	7.78 (t)	4.52 (d)	5.38 (t)	7.59 (s)		7.20 (d)
	J = 7.7 Hz	J = 7.7 Hz	J = 5.9 Hz	J = 5.9 Hz			J = 8.1 Hz
2d	7.31 (d)	7.78 (t)	4.52 (d)	5.39 (t)	7.95 (d)	7.54 (d)	
	J = 7.8 Hz	J = 7.8 Hz	J = 5.7 Hz	J = 5.7 Hz	J = 8.3 Hz	J = 8.3 Hz	
2e	7.31 (d)	7.78 (t)	4.51 (d)	5.44 (t)	7.95 (dd)	7.40 (dd)	7.47 (dd)
	J = 7.7 Hz	J = 7.7 Hz	J = 5.8 Hz	J = 5.8 Hz	J = 7.9 Hz	J = 4.8, 0.8 Hz	J = 4.8, 2.3 Hz

[a] COH δ: 10.02 ppm.
[b] H-10 δ: 7.24 ppm (t, J = 6.8 Hz), H-11 δ: 7.34 ppm (d, J = 6.8 Hz), OMe δ: 3.64 ppm.
[c] H-10 δ: 7.21 ppm (t, J = 8.1 Hz), H-11 δ: 7.57 ppm (t, J = 8.1 Hz), Me δ: 2.29 ppm.

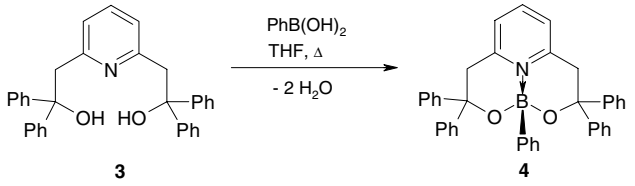
Table 3
^{13}C (75 MHz) and ^{11}B (96 MHz) NMR data in DMSO-d$_6$ for adducts **2a**–**2e**

Compound	C-2	C-3	C-4	C-5	C-7	C-8	C-9	^{11}B ($h_{1/2}$, Hz)
2,6-dmpy	160.4	118.2	136.8	64.4				
2a[a]	161.3	118.6	137.5	64.7	135.0	128.8	137.6	8.4 (237)
2b[b]	161.5	119.1	138.1	64.9	116.7	159.4	127.2	8.1 (321)
2c[c]	161.4	118.7	137.6	64.7	135.3	136.6	131.1	8.3 (167)
2d	161.7	118.9	137.9	65.0	137.1	131.2	125.0	8.2 (276)
2e	161.6	119.0	137.9	65.0	133.3	135.8	126.0	8.0 (485)

[a] COH δ: 193.9 ppm.
[b] C-10 δ: 129.5 ppm, C-11 δ: 119.7 ppm, OMe: 55.6 ppm.
[c] C-10 δ: 127.8 ppm, C-11 δ: 131.7 ppm, Me δ: 21.7 ppm. dmpy = 2,6-dimethanol pyridine. (In no case was C-6 observed.)



Scheme 3. Adducts obtained by hydrolysis of the tetrameric compounds (numbering scheme used for NMR assignment).



Scheme 4. Synthesis of a monomeric boron derivative.

(Scheme 4), rather than tetrameric species, as described for 2,6-dimethanol pyridine.

The EI mass spectrum showed a peak at m/z = 480 corresponding to the $(M - C_6H_5)^+$ ion, which is characteristic for this type of systems [3]. The selective formation of the [4.4.0] heterobicycle shows that six-membered ring heterocycles are favored over macrocyclic species, which is a result of the relief of annular tension in the six membered heterocycles. Also, the presence of phenyl groups adjacent to the hydroxyl group introduces important steric effects that restrict the formation of a macrocycle. A similar system containing an aromatic ring between the hydroxyl group and the pyridine ring has been reported in the literature [13]. In that case, the presence of the [4.4.0] heterobicycle and an intramolecular N–B coordinative bond has also been observed.

The ^{1}H NMR spectrum of compound **4** showed an AB system at δ = 4.23 and δ = 3.23 ppm, with a coupling constant of J = 14.9 Hz corresponding to the methylene group, that confirms the ring closure. ^{1}H NMR variable temperature experiments for compound **4** were carried out to evaluate the stability of the N–B coordinative bond, showing that, at least up to 150 °C, the N–B coordinative bond remains (as evidenced by the persistence of the AB system), consequently the

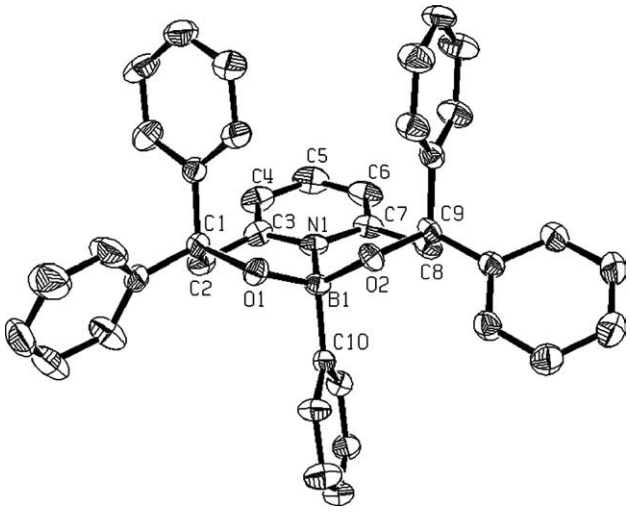


Fig. 1. Molecular structure for compound **4**.

activation energy of the coordination bond must be higher than 82.15 kJ/mol and for that reason compound **4** is highly stable. The ^{11}B NMR for this compound showed a signal at $\delta = 4.3$ ppm, indicative of a boron atom in a tetracoordinated geometry.

Crystallographic analysis[2] of compound **4** showed that there are two independent molecules in the asymmetric unit. The unit cell also contains two free molecules of phenylboronic acid and a molecule of dichloromethane. The O–H···O interactions between the OH groups of the boronic acid and the oxygen of compound **4** (distance, 2.54 Å) show that the additional molecule of phenylboronic acid stabilizes the system allowing its crystallization.

The molecular perspective (Fig. 1) showed a twist boat conformation for the two six-membered ring heterocycles, wherein the C(2), B(1) and C(8) atoms are in the upper corners of the boat. It can also be observed that two of the phenyl groups attached to the carbons are in pseudo-equatorial positions, while the other two occupy pseudo-axial positions of the six-membered ring; the phenyl group attached to the boron atom is also pseudo-axial. Table 4 summarizes the bond lengths and angles for compound **4**. It can be noticed that there are no significant differences between the angles and bond lengths of **4** compared with similar boronates described in the literature [3]. For example, the N–B bond length has a value of 1.608(6) Å (average), characteristic for species with a N–B coordinative bond [4a]; the angles around the boron atom are between 104.3(4)° and 114.1(4)° with a *Tetrahedral Character* value of 85%, showing in this way that the tetrahedral geometry for the boron atom is slightly distorted [3a].

Table 4
Selected bond lengths (Å) and bond angles (°) for compound **4**[a]

	Molecule 1	Molecule 2
Bond lengths (Å)		
B(1)–O(1)	1.479(6)	1.476(6)
B(1)–O(2)	1.459(6)	1.466(6)
B(1)–N(1)	1.602(6)	1.614(6)
B(1)–C(10)	1.627(7)	1.612(7)
O(1)–C(1)	1.435(6)	1.429(5)
O(2)–C(9)	1.428(5)	1.439(5)
C(1)–C(2)	1.531(7)	1.539(6)
C(2)–C(3)	1.493(8)	1.485(7)
C(3)–N(1)	1.345(7)	1.349(6)
N(1)–C(7)	1.367(6)	1.345(6)
C(7)–C(8)	1.487(8)	1.486(7)
C(8)–C(9)	1.542(7)	1.541(7)
Bond angles (°)		
O(2)–B(1)–O(1)	105.3(4)	104.3(4)
O(2)–B(1)–N(1)	108.2(4)	108.0(4)
O(1)–B(1)–N(1)	109.6(4)	107.6(4)
O(2)–B(1)–C(10)	114.1(4)	114.1(4)
O(1)–B(1)–C(10)	110.4(4)	113.1(4)
N(1)–B(1)–C(10)	109.0(4)	109.3(4)
C(1)–O(1)–B(1)	122.9(4)	125.9(3)
C(2)–C(1)–O(1)	108.5(4)	108.1(4)
C(9)–O(2)–B(1)	124.3(4)	123.4(3)
C(8)–C(9)–O(2)	108.9(4)	108.2(4)

[a] There are two independent molecules in the asymmetric unit.

4. Conclusions

Tetrameric species **1a**–**1e** were synthesized in good yields (>80%) using a one-pot procedure. The compounds are highly stable and it was observed that hydrolysis of the tetrameric compounds could be carried out only by heating, leading to the formation of adducts **2a**–**2e**. Derivatives **2a**–**2e** are held together only by a N–B coordinative bond, which is strong enough based on the ΔH value (>82 kJ/mol) obtained from the variable temperature NMR spectra for compound **4**. The fact that a monomeric [4.4.0] bicyclic structure is obtained from 2,6-(di-β-hydroxy) pyridine evidences that the structure of the ligand is also an important factor in macrocyclic formation. On the other hand, it has been shown that boron macrocycles which are insoluble in all common solvents can be studied using solid-state ^{13}C and ^{11}B NMR, this powerful technique constitutes an excellent tool that provides composition and structural information.

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[2] Crystal data for complex **4**: Triclinic, $a = 10.403(2)$ Å, $b = 12.451(2)$ Å, $c = 16.425(3)$ Å, $\alpha = 102.74(3)°$, $\beta = 95.43(3)°$, $\gamma = 110.12(3)°$, space group $P\bar{1}$, $V = 1914.4(6)$ Å^3, $T = 293$ K, $Z = 2$, μ(Mo Kα) = 0.145 mm^{-1}, 7120 reflections measured, 4163 unique, R_1 [$I > 2\sigma I$] = 0.0423, wR_2 (all data) = 0.1426.

Superior de la Investigación Científica in Spain for the award of a license for the use of the Cambridge Crystallographic Data Base.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica. 2005.03. 014.

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