



Boronate esters: Synthesis, characterization and molecular base receptor analysis



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HIGHLIGHTS

- Boronate esters formation in moderate yields.
- Donor–acceptor interactions.
- Modulation of boron acidity by changing the substituents of the aryl moiety substituents.
- Modulation on the donor capacity by changing the base nature.

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ABSTRACT

The synthesis of three boronate esters obtained by reacting 4-fluorophenylboronic (1), 4-iodophenylboronic (2) and 3,4-chlorophenylboronic (3) acids with 2,4,5-trihydroxybenzaldehyde is reported. The structural characterization was determined by spectroscopic and spectrometric techniques. The boron atom was evaluated to acts as Lewis acid center in the reaction with pyridine (Py), triethylamine (TEA) and fluoride anion (F^-). The titration method was followed by UV–Vis and ^{11}B NMR spectroscopy; results indicate the good interaction with the fluoride ion but poor coordination towards pyridine in solution.

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Introduction

The electronic structure of the boronic acid group ($RB(OH)_2$) allows to have a Lewis or Brønsted acid behavior, this feature has shown to be useful for properties as recognition, sensing and assembly processes [1,2]. In addition, reacting boronic acids with alcohols leads to boronate esters formation, in where the Lewis acidity character has been exploited for molecular recognition using donor–acceptor interactions [3]. In fact, it is well known the behavior of trivalent boron derivatives to react with anionic or neutral Lewis bases to generate tetra-substituted boron species.

By the way, the aryl–boron derivatives are widely used in the molecular recognition because of the associate properties involved as color and/or fluorescence changes when reacting with anions or neutral Lewis bases [4,5]. Beside the wide diversity of Lewis bases available to react with the boron centers, mainly the small anion F^- is between the most explored because of the strong covalent character of the B–F formed bonds [6–8]. It is well known that strong

bases as fluorine leads to population of the boron *p*-orbital interrupting conjugation and, as a result, provide a turn-off/on response both in absorption and emission spectra of boranes [9]. The ability of boronate esters to interact with the great diversity of donors permits the construction of molecular sensors with interesting properties as modeling fluorescent [10], dye displacement assays [11] and even as fluorophore quencher [12].

Furthermore, the high stability of the B–O covalent bond presents in the boronate esters allows to build reversible molecular assemblies, such stability may be increased by the formation of N–B dative bonds when a nitrogen containing ligand is present. There are many full papers and reviews involving the study on N–B coordination bond, which is useful for the formation of macrocycles, cages and polymeric structures using the self-assembly process [13–17].

Recently, we have described the acceptor behavior of macrocyclic boronate esters towards Py, TEA and F^- , in where a 1:1 ratio was observed even at the presence of several boron acid centers at the molecular structure [18]. In this work, a series of three boronic esters derived from the condensation reaction of arylboronic acids [(4-fluorophenylboronic (1), 4-iodophenylboronic (2) and

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3,4-dichlorophenylboronic (3) acid] with 2,4,5-trihydroxybenzaldehyde were prepared. Their Lewis base receptor behavior was evaluated towards pyridine, triethylamine and the fluoride anion and monitored by UV–Vis and ^{11}B NMR spectroscopy.

Results and discussion

The preparation of the boron esters was carried out by the condensation reactions of 2,4,5-trihydroxybenzaldehyde with the corresponding arylboronic acid (4-fluorophenylboronic (1), 4-iodophenylboronic (2), 3,4-dichlorophenylboronic (3)) in a 1:1 M ratio (Scheme 1). The reaction proceeds as follow, the boronic acid was solved in benzene and then the aldehyde was added, the reaction mixture was stirred for 4 h under reflux, then part of the solvent and water formed through the condensation reaction was removed using a Dean–Stark trap. The final products were recovered by filtration and purified by washing twice with 5 mL of benzene; light green powders were obtained in moderate yields which were soluble mainly in polar solvents.

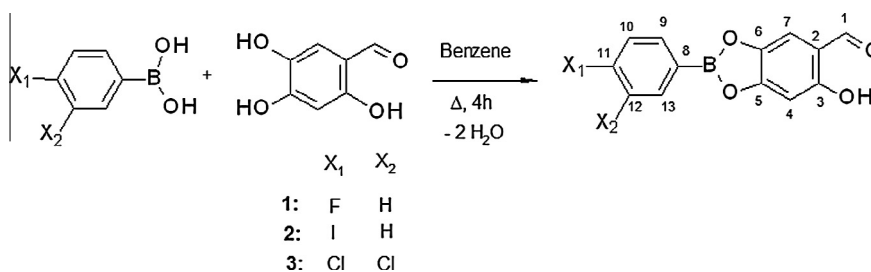
The first information about the presence of these five-membered chelate rings was proved by EI^+ mass spectrometry, wherein in all three cases the corresponding peak for the molecular ion was observed. Thus, the spectra showed peaks at $m/z = 258$, 366 and 308 for compounds 1, 2 and 3 respectively. In case of compound 3, the isotopic pattern observed is consistent with the two chloride atoms present at the molecular formula. It is important to remark that in all three cases the pattern peak corresponds also to the base peak indicating the high stability for the complexes. The ^1H NMR analysis was done in order to complete the characterization of the systems. The spectra showed the characteristic signals for the OH and aldehyde groups at ca. $\delta = 10.35$ and 9.87 ppm respectively, the aromatic protons are in the region of $\delta = 6.34$ to 9.74 ppm (see experimental part). In addition, for the Fluor derivative, the corresponding coupling of the aromatic protons with the Fluor atom ($^3J_{\text{H-F}} = 8.8$, 6.6 Hz) was observed. In addition, the ^{11}B NMR spectra indicated the trivalent character for the boron atom showing chemical shifts at $\delta = 33$, 33 and 32 ppm for 1–3 respectively. Lately, the UV–Vis spectra were obtained in which three intense absorption bands were observed clearly for these compounds at ca. 244, 286 and 354 nm (see experimental part). All of these absorption bands correspond to the $\pi-\pi^*$ transitions which include the overlap of the p free orbital of the boron atom.

As mention above, the donor–acceptor interaction analysis of the three boronate esters was evaluated using the bases: triethylamine, pyridine and fluoride anion. The ^{11}B NMR spectroscopy allows to follow the coordination change of the boron atom over the addition of Lewis base from tricoordinated to tetracoordinated geometry. As described above, the chemical shift for the boronate esters 1–3 was around $\delta = 32$ –33 ppm, nonetheless after the TEA addition the chemical shift change being observed at $\delta = 18$, 13 and 13 ppm, for 1–3 respectively (Fig. 1), showing the sp^3 hybridization change for the boron atom in each case. However, using

pyridine as base no changes at the ^{11}B NMR spectra were observed – even with addition of an excess of the base (10 equiv) – indicating there are not donor–acceptor interaction (N–B bond formation). The results are in accordance with the reports of macrocyclic or polymeric structures wherein the N–B coordinative bond (from pyridine ligands) is a fundamental part for the complex stability in solid state, but in many cases the N–B dative bond is broken in solution [19–21]. In fact, a recent study of association constants for the binding of pyridine derivatives to boronate esters determined by ^1H NMR, was found to be in the range of 10^1 – 10^4 M^{-1} [22] indicating weak to moderate interactions. In another hand, the titration with the fluoride anion shows also to the tetra-coordinate environment of the boron atom via the donor–acceptor interaction (B–F). Adding the fluoride ion, the ^{11}B chemical shift was observed at $\delta = 13$, 13 and 12 ppm for 1–3 respectively, which corresponds to tetracoordinated boron environment and being similar for related species [23]. From that, it could be corroborate that the donor acceptor interaction is favored in solution but using only strong bases. Unfortunately, efforts to get suitable crystals for X-ray analysis were unsuccessful and attempts to carry out ^1H NMR titrations experiments were frustrated by significant broadening of the relevant signals.

In addition, the titration of compounds 1–3 with the bases (TEA, Py, and F^-) was followed also by UV–Vis spectroscopy showing interesting changes. In all three cases, the titration with TEA showed a bathochromic effect at the three observed bands with an increasing of intensity for the band located around 350 nm and decreasing intensity for the other two bands. The data were adjusted to an equation considering a 1:1 stoichiometry. By the way, the association constants calculated are in the order of 6.7×10^5 , 6.8×10^5 and $8.3 \times 10^5 \text{ M}^{-1}$ for compounds 1–3 respectively (Fig. 2). In can be noticed that the slightly higher association constant obtained corresponds to the compound including two chlorine atoms at the Ar–B fragment perhaps because of the two electron-withdrawing effect over the phenyl ring which increase the acidity of the boron atom. By the way, using pyridine as base, the titration plots showed the intensity decreasing in all three cases (Fig. 3), however a large dispersion was observed and the experimental data could not be fitted. Respect to the fluoride ion titration (Fig. 4), the graphics showed also the bathochromic shifted as observed during TEA titration and the three absorption bands decrease in the same magnitude order. The corresponding adjustment showed that the corresponding association constants using fluoride ion (4.9×10^2 , 1.9×10^3 , $1.7 \times 10^3 \text{ M}^{-1}$ for 1 to 3, respectively) are two or three magnitude order lower than for TEA, nonetheless are in agreement with the values for related boron compounds [24–25]. The fact that compound 1 gave the lowest constant value is attributed mainly to the low acidity of the boron atom because of the resonance electronic donor effect of the fluorine atom present at the *para* position of the derivative.

The presence of a hydroxyl group at the structure of compounds 1–3, could suggest the possibility of a Brönsted acid interaction



Scheme 1. Synthesis of the boronate esters 1–3. Labeling for the ^1H and ^{13}C NMR assignments.

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