



Use of 5-formylfuranboronic acid in the formation of bicyclic boronates with photophysical properties



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ABSTRACT

Treatment of 5-formyl-2-furanboronic acid with 2-aminophenol 4,5-(R)substituted (R = -Cl, -NO₂, -CH₃, -CO₂H, naphthyl) offers bicyclic boronates, in which a furan ring-opening reaction is involved. Even though the reaction proceeds in all cases, lower yields were obtained when aminophenol derivatives include electron withdrawing substituents. Evaluation of the photophysical properties for all compounds showed substantial solvatochromic and luminescent changes. The solvatochromic effect was clear noticed from changes in color solutions from solvents with different polarities/polarizabilities and hydrogen bonding capacities. Influence of the substituents is also appreciable at the absorption and emission spectra, in where the nitro derivatives showed poor absorbance and emission bands. In addition, computational NLO properties were calculated which showed β values from 29 to $139 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$, showing thus possible applications as optoelectronic materials.

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1. Introduction

Existence of rigid π conjugate systems in molecules permits high electronic mobility and, depending of the groups, charge-transfer states could be involved. This characteristic gives the possibility to the molecules to be functional for several applications as for instance, organic light emission diodes (OLEDs), sensors and imaging materials [1–6]. Between this fascinating and increasing number of molecules, organoboron compounds have been emerged as an important class of optoelectronic and luminescent materials [7–14]. In general, trisubstituted boron compounds are isoelectronic and isostructural with carbocations, in which the vacant *p* orbital of the boron atom gives an electron deficient character acting as a strong π -electron acceptor. In consequence, a significant electronic delocalization occurs when conjugated organic π -systems are present. Boronic acids derivatives [7–10], and arylboranes [11,12] are between the most explored trisubstituted boron compounds in the optoelectronic field, in where a common characteristic is the presence of a *p* π delocalized fragment. Four-coordinate boron compounds having π -electron donor ligands have also been investigated, in which their photoelectronic properties strongly depend of the ligands nature. In general, π -electrons chelate ligands are studied because their coordination with boron moieties forms cyclic rigid *p*-conjugated skeletons

allowing high fluorescence efficiency and high carrier mobility. Therefore, main chelate ligands used to form this class of four-coordinate boron compounds include hydroxyquinoline, pyridylphenolate, and N',N'-heterobicycles as BODIPYS derivatives [13,14]. Furthermore, four-coordinate boron compounds are proved to be with good chemical and thermal stability. Thus, several efforts have been made to address the molecular design of four-coordinate boron compounds with the aim to increase their potential photonic and optoelectronic applications [15–18].

Previously, we have described the preparation of bicyclic boron compounds with luminescent properties by reaction of 5-formyl-2-furanboronic acid with 2-aminophenol derivatives (Compounds **1**, **4** and **6**) [19]. Herein, we expanded these studies including 2-aminophenol derivatives with donor/acceptor electronic substituted groups in order to modify their photophysical properties. Our contribution would be fundamental insight into the design strategy of four-coordinate organoboron compounds for applications in OLEDs and related properties.

2. Results and discussion

2.1. Synthesis of boronate compounds

As an additional contribution of our studies about luminescent boron compounds, herein we have carried out the preparation of six heterocyclic derivatives in which a common characteristic is

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the presence of a high π -delocalization system. The compounds **2–3**, **5**, **7–9** were prepared from the reaction of two equivalents of the corresponding 2-aminophenol 4,5-(R)-substituted and one equivalent of 5-formyl-2-furanboronic acid, in accordance to the previously synthetic method used for compounds **1**, **4** and **6** [19].

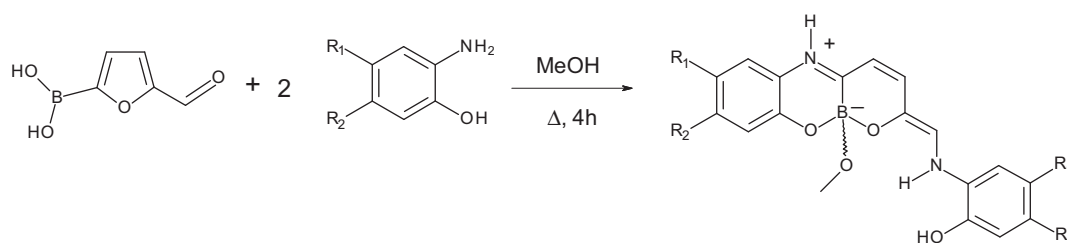
During the reaction process, one equivalent of the aminophenol reacts with the aldehyde group whereas a second equivalent reacts with the boronic acid group allowing the furan ring-opening reaction. In order to analyze the effectiveness of the reaction process, herein we have introduced donor and acceptor groups ($-H$ (**1**), $-Cl$ (**2,3**), $-NO_2$ (**4,5**), $-CH_3$ (**6,7**), and $-CO_2H$ (**8**)) in two specific positions (Scheme 1), both regarding to the *para* position respect of the two active groups (amine $-NH_2$, and hydroxyl $-OH$). Thus, variation of the substituent in those positions allowed to identify the influence on the reactivity in the heterobicycle formation. In addition, with the aim to increase the π -delocalized system, 3-amino-2-naphthol was used in the reaction with the boronic acid in order to improve the luminescent properties (**9**, Scheme 2). Reactions proceed with moderate yields which are around 70–75% for H, Cl, Me and naphthyl derivatives, nonetheless for the nitro derivatives; both products (**4** and **5**) were isolated in lower yields (23% and 17%, respectively). Thus, the presence of the electron-withdrawing NO_2 group, reduce the nucleophilic attack effectivity of the amine group, independently of the substituent position. Yield was also decreased using $-CO_2H$ but not drastically (64%). It is noteworthy to remark that, during the reaction processes significant solution color changes occurs, which start from paled yellow to finish in an intense purple or deep green colors. So, at the beginning, the yellow color present is consistent with the imine group formation as first step reaction, although we were unable to isolate this intermediate.

In another hand, the 5-formyl-2-furanboronic acid was allowed to react with 4-chloroaniline, the reaction was carried out in acetonitrile by 4 h under stirring at room temperature. Results indicate the formation of compound **10** (Scheme 2) as the only product, given evidence that in absence of the OH group the first step is the imine group formation before the furan ring-opening reaction. Suitable crystals for X-ray diffraction analysis were grown for compound **10** from slow evaporation of a concentrate methanol solution. Poor diffraction intensities gave place to low value of sine ($\theta_{max}/wavelength$), nonetheless the whole structure was observed (Fig. 1). During the formation of compound **10**, no color variation was observed as for previous reactions, only the characteristic yellow color was noticed indicating the imine formation. In addition, treatment of 5-formyl-2-furanboronic acid with 4-chloroaniline under same conditions as used for **1–9**, did not give the furan ring-opening reaction.

2.2. Structural characterization

FAB⁺ Mass Spectrometry analysis confirms the molecular structure for the boronate compounds **1–9**. Even if the whole molecular ion was only observed for methyl derivatives (**6** and **7**) at $m/z = 363$, in all cases, a common peak corresponding to the molecular weight with the loss of a methanol molecule ($[M-MeOH]^+$) was observed as the pattern ion. The last statement has been observed for related compounds in which it is very common the loss of the OR group attached to the boron atom [20–21]. For all compounds, the experimental CHN elemental analysis are related with the calculated values, except for carbon which showed values slightly different. It is known that boron compounds register incomplete combustion because of the boron carbides formation. Thus, sometimes it is not possible to get good values for carbon elemental analyses [22]. The IR analysis for compounds **1–9** showed the presence of a stretching band in the range 1624–1633 cm^{-1} assigned to the C=N group. Further evidence for the furan ring opening was obtained from the NMR analysis. For instance, in ¹H NMR the characteristic signals for the two hydrogens present in the five membered ring (furan) were not observed in its habitual chemical shift ($\delta = 7.60$ – 8.00 ppm), beside a new pair of doublets were observed to lower fields in the range of $\delta = 5.80$ – 6.80 ppm indicating thus the new heterocyclic six-membered ring formation. Furthermore, in ¹³C NMR spectra the signals for no substituted carbon atoms of the boronic acid furan ring, appears very close themselves at $\delta = 136.3$ and 137.6 ppm, whereas after formation of the products these signals have larger separation at $\delta \sim 107$ and ~ 144 ppm. In addition, the carbon signal base of the aldehyde group appears at $\delta = 147.3$ ppm before the opening ring reaction while it is observed in the range of $\delta = 135.8$ – 142.3 ppm in the new products. ¹¹B NMR spectra analysis reveals that all systems showed broad signals between $\delta = 1$ and 4 ppm, in accordance with chemical shifts observed for boron atoms in a tetrahedral environment as described for related compounds [19–21].

All compounds showed to be intense colored when solved in different solvents and the color change depends on the solvent polarity. In general, colors vary from deep blue when solved in low polarity solvents to deep pink using polar protic solvents. Fig. 2 shows a photograph color variation of compound **7** when solved in ten solvents of different polarities/polarizabilities and hydrogen bonding capacities. The color absence in hexane is because of the insolubility of the sample. For the other compounds, a similar color variation in solution was observed. In order to discard a possible color change due to decomposition process, a ¹H NMR spectrum for **1** after to stand 24 h in DMSO-*d*₆ solution was obtained without apparent changes.



Compound	1	2	3	4	5	6	7	8
R ₁	H	Cl	H	NO ₂	H	CH ₃	H	H
R ₂	H	H	Cl	H	NO ₂	H	CH ₃	COOH

Scheme 1. Synthesis of the boronate esters **1–8**.

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