



# Isolation and characterization of luminescent bicyclic boronates based on furan ring-opening reactions from 5-formyl-2-furanboronic acid



Victoria E. González<sup>a</sup>, Felipe Medrano<sup>a</sup>, Mario Rodríguez<sup>b</sup>, Pascal G. Lacroix<sup>c</sup>, Victor Barba<sup>a,\*</sup>

<sup>a</sup> Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca Morelos CP 62209, Mexico

<sup>b</sup> Centro de Investigaciones en Óptica, P. 1-948, León, Gto 37000, Mexico

<sup>c</sup> CNRS, LCC (Laboratoire de Chimie de Coordination), 205, Route de Narbonne, Toulouse F-31077, France

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## ABSTRACT

A new family of luminescent boronates was prepared from reaction of 5-formyl-2-furanboronic acid with 2-aminophenol derivatives. The furan ring-opening was favored by the presence of the boronic acid group. Evaluation of the photophysical characteristics for all compounds showed significant solvatochromic, fluorescent, and NLO properties.

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## Introduction

Chemosensors with high sensitivity and selectivity that offer easily detectable signals upon a chemical or physical change have received considerable attention.<sup>1</sup> In fact, photoluminescent and electroluminescent dyes have been under extensive research because of their applications in various research fields, especially when they are sensitive to the environment and solvent polarity.<sup>2</sup> Among all chemosensors reported, organoboron complexes have attracted interest because of their potential applications for the generation of functional materials including organic light-emitting devices (OLEDs),<sup>3</sup> optoelectronic materials,<sup>4</sup> fluorescent sensors,<sup>5</sup> and nonlinear optics.<sup>6</sup> There are a wide variety of organoboron polymers which exhibit strong fluorescence emission and *n*-type electronic conductivity due to the high electron affinity of boron atoms and are possible candidates to fabricate Organic Field-Effect Transistors (OFETs).<sup>7</sup>

Arylboranes have been widely used because of the remarkable color change or increased fluorescence properties when reacting with anions or neutral Lewis bases.<sup>8</sup> It is known that the aromatic substituents of triarylboranes are conjugated via the vacant boron *p*-orbital leading to the formation of a chromophore, for which the absorption and emission are red-shifted in comparison with the

individual aromatic substituents.<sup>4a</sup> Furthermore, the donor–acceptor interaction of boranes with Lewis bases leads to population of the boron *p*-orbital interrupting conjugation and, as a result, providing a turn-off/on response both in absorption and emission.<sup>9</sup>

In addition, arylboronic acids and esters have been used as molecular sensors for carbohydrates, metals, and anions.<sup>10</sup> Further, it is well known that the solvent polarity influences the solvatochromic properties of boronate esters.<sup>11</sup>

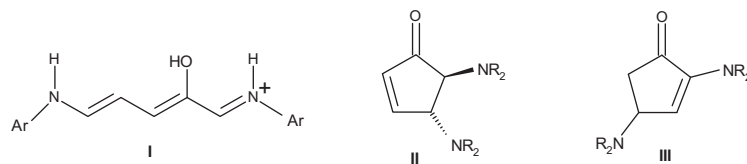
Herein, we carried out the reaction of primary aminophenols with 5-formyl-2-furanboronic acid, isolating novel bicyclic boronates-like compounds. The furan ring-opening is favored because of the presence of the boronic acid group which helps to activate the cleavage of the C–O bond. Furan ring-opening reactions using arylamines were first described by Stenhouse using furfural in an acidic medium. The resulting colored products are known as the Stenhouse salts (I) (Scheme 1).<sup>12</sup> Later, numerous aniline derivatives have been used for the reaction with furfural derivatives, which enabled the isolation of other products such as 2,4-diarylamino-cyclopent-2-enones (II) and the isomeric 4,5-diarylamino (III) derivatives.<sup>13</sup>

## Results and discussion

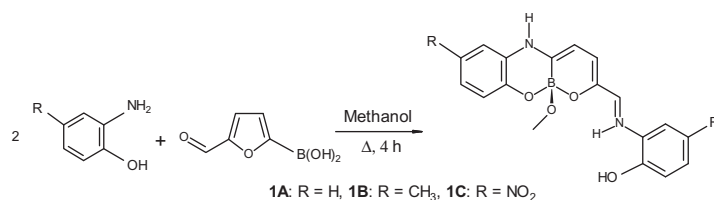
Our initial studies were focused upon the reaction of 5-formyl-2-furanboronic acid with aminophenol derivatives (2-aminophenol (1a), 4-methyl-2-aminophenol (1b), and 4-nitro-2-aminophenol

\* Corresponding author. Tel./fax: +52 777 329 7997.

E-mail address: [vbarba@uaem.mx](mailto:vbarba@uaem.mx) (V. Barba).



**Scheme 1.** Possible reaction products of furfural with aromatic amines.



**Scheme 2.** Reaction of 5-formyl-2-furanboronic acid with two equivalents of 2-aminophenol derivatives.

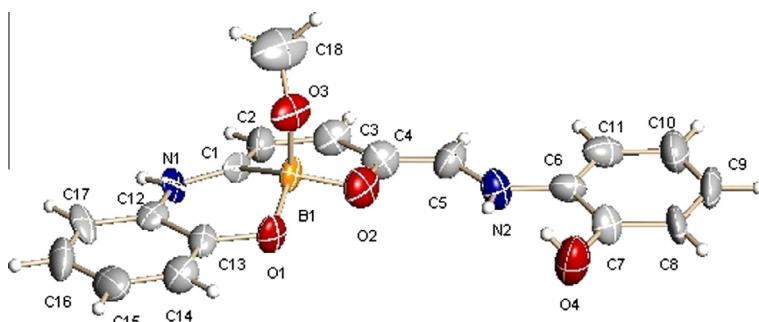
(**1c**), [Scheme 2](#)). The reactions were carried out in methanol under reflux for 4 h, giving solid products which were separated by filtration. During the reaction, the colored solutions showed remarkable changes from yellow to red and, at the end, the solids were isolated as intensive colored compounds (deep purple for **1a–1b** and deep green for **1c**) in moderate yields (91%, 52%, and 48% for **1a–c**, respectively).

The spectroscopic analyses revealed that the products correspond to boronate compounds as a result of the aperture of the furan ring forming bicyclic compounds having a delocalized  $\pi$ -system. In these, the boron atom acts as Lewis acid allowing the easy rupture of the C–O furan bond in accordance with the mechanisms proposed by Batey.<sup>13c</sup> To the best of our knowledge, this is the first furan ring-opening reaction involving the boronic acid group and trapping the opened Stenhouse product. Initially, evidence for the formation of compounds **1a–c** was obtained by mass spectrometry. For instance, the spectrum for compound **1b** showed the molecular ion at  $m/z = 363$ . A common fragmentation pattern in all three cases corresponds to the loss of a methanol molecule from the molecular ion.

1D (<sup>1</sup>H and <sup>13</sup>C) and 2D (COSY, HSQC, and NOESY) NMR experiments were carried out in order to complete the characterization of these structures. It is important to remark that for all compounds, small additional signals can be observed at the NMR spectra as a result of the partial decomposition in DMSO-*d*<sub>6</sub> solution. Nonetheless, purity of **1a–1c** was evaluated by CHN Elemental Analysis. The presence of the boron atom in the bicyclic products was corroborated in solution via the <sup>11</sup>B NMR spectra. For compounds **1a** and **1c**, a broad signal was observed at  $\delta = 3$  ppm confirming the tetra-substituted boron environment. For compound **1b** the signal was shifted to  $\delta = 4$  ppm.

The structure of **1a** was elucidated by single crystal X-ray diffraction analysis ([Fig. 1](#)).<sup>14</sup> It was noticed that the whole  $\pi$ -backbone skeleton has a planar conformation, from which only the boron atom deviates from the mean plane (O1–C13–C12–N1–C1) by 0.531 Å. This planarity is a result of the overall aromatic–aromatic delocalization, thus giving two possible zwitterion structures, **IV** and **V** ([Scheme 3](#)), in which the negative charge is located at the boron atom and the positive charge on either of the two nitrogen atoms. A theoretical approach<sup>15</sup> shows that the most stable molecular conformation corresponds to the resonance structure **V** wherein a minimum charge separation is present, in agreement with the observed experimental bond distances along the skeleton N1–C1–C2–C3–C4–C5–N2 with values of 1.310(9), 1.382(11), 1.388(10), 1.425(11), 1.377(11), and 1.294(9) Å, respectively.

Compounds **1a–1c** are slightly soluble in the most common organic solvents and the solubility increases with increasing solvent polarity, being enhanced for protic solvents. Interestingly, the colorimetric properties for compounds **1a–c** were noticed since they present a remarkable color change in solution as a result of the solvent polarity change ([Fig. 2](#), up). The observed solvatochromic effect can be attributed to the hydrogen bonding association with the solvent molecules as well as the  $\pi$ -delocalization throughout the whole structure. In addition, when a variety of solutions for **1a** were placed under an UV lamp (365 nm), fluorescence was observed for alcoholic solutions (methanol and ethanol) and its intensity was dependent on the concentration, whereas fluorescence was not observed in aprotic solvents ([Fig. 2](#), down). The possible methanol loss/interchange process explaining the distinct photophysical properties observed was considered but efforts to isolate the non-methanol containing compounds were unsuccessful.<sup>16</sup>



**Figure 1.** X-ray crystal structure of **1a**. Thermal ellipsoids were scaled to 50% probability level.

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