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# Synthesis of tris(4-amino-2,6-dimethylphenyl)borane and facile extension of its $\pi$ -conjugated system by utilizing the reactivity of the amino groups

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# ABSTRACT

Tris(4-amino-2,6-dimethylphenyl)borane (**1**), a triarylborane bearing an unsubstituted amino group on all of its aryl substituents, and related triarylboranes were synthesized via Ullmann condensation. The facile dehydration reactions of **1** with benzaldehyde and nitrosobenzene gave tris[4-(benzylidenamino)-2,6-dimethylphenyl]borane and tris[2,6-dimethyl-4-(phenylazo)phenyl]borane, respectively. These triarylboranes bear an extended  $\pi$ -conjugated system bridged by a nitrogen-containing  $\pi$ -linker on each of their aryl groups. UV-vis absorption spectra and theoretical calculations revealed that the  $\pi$ -conjugated system of the triarylborane was effectively extended by utilizing the reactivity of the amino groups. © 2013 Elsevier Ltd. All rights reserved.

Organoboron compounds are known as Lewis base sensors, a function rendered by the Lewis acidity of the boron atom. In particular, triarylboranes are highly proficient Lewis-base sensors because they have strong Lewis acidity, and their extended  $\pi$ -conjugated systems, connected by the vacant p orbital of the boron atom, confer dramatic changes in their physical properties upon complexation with a Lewis base. Such strong responses result from structural changes to the  $\pi$ -conjugated system.<sup>1</sup> Reported examples include fluoride- and cyanide-sensing compounds, which can recognize fluoride and/or cyanide ions, they are toxic, and authenticate their existence by converting recognition interactions into physical phenomena, such as color and fluorescence changes.<sup>1,2</sup>

The structure of the  $\pi$ -conjugated system on the aryl groups of triarylboranes is a key factor regulating their physical properties and output behavior as chemosensors, such as color and/or fluorescence changes. Although many triarylboranes bearing various extended  $\pi$ -conjugated systems have been synthesized to tune their properties, the extension of the  $\pi$ -conjugated systems of triarylboranes is not easily accomplished. Utilizing the simple and reliable reactivity of an amino group to afford a nitrogencontaining double bond is one possible approach to readily extend the  $\pi$ -conjugated systems of triarylboranes. Using this approach, a few examples of triarylboranes bearing extended  $\pi$ -conjugated

systems with CH=N<sup>3</sup> or N=N<sup>4</sup>  $\pi$ -linking moieties have been prepared to date. However, all of them have only one aryl group connected to a nitrogen-containing  $\pi$ -linker per boron atom, and no triarylboranes bearing nitrogen-containing double bonds at all of their aryl groups have been reported. Trigonally expanded  $\pi$ -conjugated systems are very appealing owing to their potential as near-infrared dyes,<sup>5</sup> two-photon absorption materials,<sup>6</sup> and nonlinear optical materials.<sup>7,8</sup> Therefore, the extension of the  $\pi$ -conjugated system of a triarylborane at all three of its aryl groups using nitrogen-containing double bonds is expected to be a facile method for accessing sophisticated triarylborane-based chemosensors bearing trigonal  $\pi$ -conjugated systems and for tuning their properties. Here we report the synthesis of tris(4-amino-2,6-dimethylphenyl)borane (1), a triarylborane bearing an unsubstituted



Scheme 1. Compound 1 and extension of its  $\pi$ -conjugated system.



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Scheme 2. Synthesis of amine-substituted triarylboranes 1 and 3-6.

amino group on all of its aryl substituents, and the facile extension of its  $\pi$ -conjugated system by utilizing the reactivity of the amino groups (Scheme 1).

BocNH-substituted triarylboranes **3–5** were synthesized by Ullmann condensation between bromo-substituted triarylborane **2**<sup>9</sup> and *tert*-butyl carbamate (Scheme 2). The number of BocNH groups introduced can be controlled by changing the coupling conditions. Deprotection of the Boc-protecting groups of **3** and **5** gave NH<sub>2</sub>substituted triarylboranes **1** and **6**, respectively, in good yields (Scheme 2). Simple dehydrative condensation of compound **1** with benzaldehyde and nitrosobenzene afforded compounds **7** and **8**, respectively (Scheme 3). Structures of compounds **1** and **3–8** were confirmed by <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR and high-resolution MS.

In their <sup>1</sup>H NMR spectra, symmetrically substituted triaryboranes 1, 3, 7, and 8 showed one singlet which was assigned to the methyl group, indicating their structures have  $D_3$  symmetry at the tris(dimethylphenyl)borane core in CDCl<sub>3</sub>. In contrast, methyl group signals in unsymmetrically substituted triarylboranes 4-6 showed one sharp and two broad singlets with the integral ratio of 6:6:6. These spectral behaviors are consistent with structures having  $C_2$  symmetry with the suppression of rotation about the B-C bonds. To determine the rotation barrier about the B-C bonds, VT-<sup>1</sup>H NMR spectra of compound **6** were acquired (Fig. 1). The Gibbs energy of activation of rotation about the B-C bonds of compound **6** was estimated to be  $68 \pm 1 \text{ kJ/mol}$  on the basis of the temperature of coalescence of the methyl signals (45 °C). The rotations about the B–C bonds in compounds 1, 3–5, 7, and 8 are considered to be suppressed to a similar degree as that in compound 6.

The UV-vis spectra of trigonally substituted triarylboranes **1–3**, **7**, and **8** showed absorption maxima at 334–372 nm in chloroform, which were assigned to the  $\pi$ – $\pi$ \* transition (Fig. 2 and Table 1). Compound **8** has an additional absorption maximum at 442 nm, which was assigned to the n– $\pi$ \* transition.<sup>10</sup> In compounds **7** and **8**, by connecting the  $\pi$ -conjugated moieties to the aryl groups using the N-containing  $\pi$ -linkers, a red shift of their  $\pi$ – $\pi$ \* absorption maxima in comparison with those of compounds **1–3**, bearing the smaller  $\pi$ -conjugated systems, is observed. These spectral behaviors suggest that the  $\pi$ -conjugated systems of compounds **7** and **8** are effectively extended by introducing the N-containing  $\pi$ -linkers. The longer  $\pi$ – $\pi$ \* absorption maxima of compound **8**, in comparison with that of **7**, is considered to result from the planarity of the azo group-connecting  $\pi$ -conjugated systems.



Figure 1. VT-<sup>1</sup>H NMR spectra of compound 6.



Figure 2. UV-vis absorption spectra of compounds 1-3, 7, and 8 in chloroform.

#### Table 1

Absorption wavelengths ( $\lambda_{abs}$ ) in chloroform, and calculated energy levels (*E*) of the HOMO and LUMO of triarylboranes **1–3** and **7–9** 



-6.17

-1.70

<sup>a</sup> Not calculated.

Н

<sup>b</sup> Not measured.

9





Figure 3. Molecular orbital diagrams of compounds 7 and 8. (a and b) HOMO of 7 (degenerated), (c) LUMO of 7, (d and e) HOMO of 8 (degenerated), and (f) LUMO of 8.



**Figure 4.** Energy levels of the frontier molecular orbitals of compounds **1**, **3**, and **7–9**. The upper and lower lines denote the energy levels of the LUMO and HOMO, respectively.

To evaluate the effectiveness of the N-containing  $\pi$ -linkers on the extension of the  $\pi$ -conjugated system of the triarylborane, molecular orbitals of 1, 3, 7, and 8 were calculated by a DFT method at the B3LYP/6-31G(d) level of theory. Those of tris(2,6-dimethylphenyl)borane (9) were also calculated. In the calculations,  $C_3$ symmetry was imposed on the structures of the triarylboranes. In 7 and 8, their HOMOs and LUMOs are delocalized over the entire molecule, indicating that the  $\pi$ -conjugated system of the triarylborane is effectively extended by incorporating N-containing  $\pi$ -linkers at each aryl group (Fig. 3). The calculation of the HOMO/LUMO energy levels for the triarylboranes shows that the energy levels of the LUMO of compounds 7 (-1.96 eV) and 8 (-2.58 eV) are lowered more than those of compounds 1, 3, and 9 (-1.09, -1.48,and -1.70 eV) by the extension of the  $\pi$ -conjugated system, which results in the red shift of the  $\pi$ - $\pi$ <sup>\*</sup> absorption maxima in the UV-vis spectra for **7** and **8** (Fig. 4 and Table 1). The more planar  $\pi$ -linker moiety in compound **8** (dihedral angle (Ph)N=N-C-C in the optimized structure: 1.8°), compared with that of compound 7 (dihedral angle (Ph)C(H)=N-C-C in the optimized structure:  $39.3^{\circ}$ ), results in a greater reduction of the LUMO of **8**, thereby resulting in the longer wavelength of the  $\pi$ - $\pi$ \* absorption maximum.

As a preliminary experiment, complexation of triarylborane **8** with fluoride ion was investigated. Addition of tetrabutylammonium fluoride to a THF- $d_8$  solution of compound **8** gave the solution color change from orange to yellow as a result of formation of fluoroborate, which was confirmed by <sup>1</sup>H and <sup>11</sup>B NMR. This fluoroborate gave back compound **8** upon hydrolysis.

In conclusion, triarylborane **1** bearing an unsubstituted amino group on all of its aryl substituents was synthesized via Ullmann condensation. Additional  $\pi$ -conjugated moieties were connected to each of the aryl groups of **1** by facile dehydration reactions to provide triarylboranes **7** and **8**, bearing N-containing  $\pi$ -linkers. UV-vis absorption spectra and theoretical calculations revealed that the  $\pi$ -conjugated system of the triarylborane was effectively extended by utilizing the reactivity of the amino groups. The method developed in this study to readily expand  $\pi$ -conjugated systems of triarylboranes in a trigonal manner may provide new sophisticated Lewis base sensors. The further extension of  $\pi$ -conjugated systems of triarylboranes based on this study and evaluation of the chemosensing ability of the triarylboranes bearing N-containing  $\pi$ -linkers are currently underway.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013. 03.080.

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