Synthesis and Properties of Dithieno-fused 1,4-Azaborine Derivatives

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Supporting Information Placeholder

ABSTRACT: The first synthesis of dithieno[3,2-b:2′,3′-e][1,4]azaborinine (DTAB) derivatives has been achieved by Buchwald–Hartwig coupling and subsequent Friedel–Crafts-type C–H borylation. A facile method for further π-extension of DTAB was also developed via stannylation and subsequent Kosugi–Migita–Stille cross-coupling reaction. The fundamental properties of DTAB derivatives were also investigated.

Azaborines, which are benzene ring alternatives that include boron and nitrogen atoms, have received considerable attention since the pioneering work reported by Dewar,1,2 and several new azaborine derivatives have been studied extensively over the past decade due to their unique properties.3 Meanwhile, thienoacenes, acene derivatives that contain thiophene moieties, have also been the focus of research as promising compounds for the synthesis of organic materials.4 The incorporation of main-group atoms into thienoacenes is also a hot topic these days, and several heterothienoacenes have been reported.5 Thienoazaborines, thiophene-fused azaborines, have also been studied.6 For instance, Perepichka and coworkers reported integrated compounds that contained thiophene and 1,2-azaborine units. They synthesized thienothiophenes fused by two 1,2-azaborine rings and found that these compounds exhibited fluorescence (Figure 1 (a)).6d In 2013, Wang, Yuan, and Pei reported the synthesis of BN-substituted tetraphenonaphthalene derivatives and their properties as semiconductors.6e In contrast to thienoacenes, including 1,2-azaborines, there has been no report on the synthesis of thienoacenes including 1,4-azaborines as far as we can tell, although they should be potential candidates for the synthesis of interesting organic materials. We have been interested in the synthesis and properties of heterothienoacenes, and here has been on dithieno[3,2-b:2′,3′-e][1,4]azaborinine (DTAB) (Figure 1 (b)). The syntheses of dibenzo[b,e][1,4]azaborine (DBAB)6 and dithieno[3,2-b:2′,3′-e][1,4]thiaborine (DTTB), analogues of DTAB, have already been reported by Clark6 and Liu.7 At the beginning of our study, we calculated the NICS(1) values of DBAB, DTTB, and DTAB, which have a methyl group on the nitrogen atom and a phenyl group on the boron atom (Figure 1(b)). The NICS(1) value of DTAB (−6.3) was the most negative among them, suggesting that it is highly aromatic. Clark and Liu reported that the boron-containing rings of DBAB and DTTB were almost planar, indicating their aromaticity, and the introduction of a bulky substituent such as a mesityl group conferred stability upon them. We assumed that DTAB would be stable on account of its high aromaticity even without a bulky substituent on the boron atom. Based on this hypothesis, we started to synthesize DTAB derivatives that had a phenyl group on the boron atom.

Figure 1. (a) Representative examples of previously reported thiophene-fused 1,2-azaborines; (b) Structure of dibenzo-1,4-azaborine (DBAB), dithieno-1,4-thiaborine (DTTB), and dithieno-1,4-azaborine (DTAB) with NICS values calculated at the GIAO-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level. NICS values were calculated with the structures (R = Me, Ar = Ph).

Our synthetic strategy is illustrated in Scheme 1. We considered that DTAB 1 could be synthesized by a Friedel–
Crafts-type C–H borylation\(^{10}\) of 3,3′-dithienylamine 2 derived from 3-thienylamine 3 and 3-bromothiophene via a Buchwald–Hartwig cross-coupling reaction. Furthermore, thus-obtained 1 could be transformed to more \(\pi\)-extended derivatives by cross-coupling reactions.

Scheme 1. Our Synthetic Strategy for Dithienoaaborines

While 3,3′-dithienylamines have been known to be useful precursors for dithienopyrroles, there has been only one report on the synthesis of more \(\pi\)-extended 3,3′-dithienylamine derivatives.\(^{11}\) Therefore, we first developed a synthetic method for the construction of 2 by a Buchwald–Hartwig cross-coupling reaction (eqs 1–5). \(N\)-Methyl- and \(N\)-phenyl-3,3′-dithienylamine (2a and 2b) could be synthesized by a similar method reported by Rasmussen and coworkers.\(^{11}\) \(P(\tau\text{-Bu})_3\) was an effective ligand, and 2a and 2b were obtained in respective yields of 75% and 72%. For the synthesis of \(N\)-methyl-3-benzol[b]thiophenyl-3-thienylamine (2c), the use of \(P(\tau\text{-Bu})_3\) was not effective. Optimization of the reaction conditions revealed that RuPhos, a commonly used ligand for Buchwald–Hartwig coupling reactions, was effective. With RuPhos, the reaction of 3a with 3-bromothiophen[b]thiophenyl-3-thienylamine (2c), the use of \(P(\tau\text{-Bu})_3\) was not effective. The packed structure of 1a was illustrated in Figure 2(b). Intermolecular \(\text{N–B} \) interaction was not observed, and the packed structure was mainly affected by \(\pi\)-\(\pi\) interaction.

![Scheme 1](image)

Table 1. Synthesis of Dithienoaaborine 1a by C–H Borylation under Various Conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>(\text{Et}_3\text{N} )(equiv)</th>
<th>time (h)</th>
<th>yield (%)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>48</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>48</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>24</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>48</td>
<td>&gt;99 (96)(^a)</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>48</td>
<td>82(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 2a (0.20 mmol), PhBCl\(_2\) (1.5 equiv), \(\text{Et}_3\text{N} \)(0–2 equiv), PhCl (0.29 M), 135 °C. \(^b\) Determined by \(^1\)H NMR with 1,1,2,2-tetrachloroethane as an internal standard. \(^c\) Isolated yield. \(^d\) Performed with 1.0 mmol of 2a.
Next, we performed C–H borylation of 2b–d under the optimized conditions (Scheme 2). Phenyl(di-3-thienyl)amine (2b) could also be used for this reaction, and the corresponding DTAB 1b was obtained in 66% yield with 3 equiv of PhBCl2. Precursors bearing 3-benzo[b]thienyl and 3-thieno[3,2-β]thienyl groups were efficient for this reaction and the π-expanded DTAB derivatives 1c and 1d were obtained in respective yields of 86% and 84%. Notably, a more π-expanded ladder-type DTAB precursors were all stable, could be easily handled in air under ambient conditions, and could be purified by simple column chromatography on silica gel. This is likely due to their high aromaticity.

Scheme 2. Synthesis of Several Dithienoazaborines via C–H borylation

![ORTEP drawing of 1a](image1)

![Packed structure of 1a](image2)

Next, we performed C–H borylation of 2b–d under the optimized conditions (Scheme 2). Phenyl(di-3-thienyl)amine (2b) could also be used for this reaction, and the corresponding DTAB 1b was obtained in 66% yield with 3 equiv of PhBCl2. Precursors bearing 3-benzo[b]thienyl and 3-thieno[3,2-β]thienyl groups were efficient for this reaction and the π-expanded DTAB derivatives 1c and 1d were obtained in respective yields of 86% and 84%. Notably, a more π-expanded ladder-type DTAB 1e was readily obtained from precursors 2e, which have two reaction sites (61% yield). As expected, 1a–e were all stable, could be easily handled in air under ambient conditions, and could be purified by simple column chromatography on silica gel. This is likely due to their high aromaticity.

Scheme 2. Synthesis of Several Dithienoazaborines via C–H borylation

![ORTEP drawing of 1a](image3)

![Packed structure of 1a](image4)

As expected, 1a–e were all stable, could be easily handled in air under ambient conditions, and could be purified by simple column chromatography on silica gel. This is likely due to their high aromaticity.

Scheme 2. Synthesis of Several Dithienoazaborines via C–H borylation

![ORTEP drawing of 1a](image5)

![Packed structure of 1a](image6)

Thus-obtained 4 was a good precursor of π-extended DTAB derivatives, and several DTAB derivatives were obtained by Kosugi–Migita–Stille cross-coupling (Table 2). In the presence of Pd[P(η-Bu)3]2 (5 mol %), treatment of 4 with iodobenzene (2 equiv) at 80 °C gave phenyl-substituted DTAB 5a in 85% yield (entry 1). Aryl halides bearing electron-donating or -withdrawing groups could be used in the reaction to give the corresponding π-extended DTABs in good to excellent yields (entries 2–7).

Scheme 3. Stannylation of 1c

![Scheme 3](image7)

Table 2. Synthesis of π-Extended DTAB 5 by Kosugi–Migita–Stille Cross-coupling

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>X</th>
<th>5</th>
<th>yield (%)</th>
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<tr>
<td>1</td>
<td>H</td>
<td>I</td>
<td>5a</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>CH3</td>
<td>I</td>
<td>5b</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>CH3O</td>
<td>I</td>
<td>5c</td>
<td>71</td>
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<td>4</td>
<td>Ph2N</td>
<td>Br</td>
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<td>79</td>
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<td>5</td>
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<tr>
<td>7</td>
<td>CN</td>
<td>I</td>
<td>5g</td>
<td>99</td>
</tr>
</tbody>
</table>

* Reaction conditions: 4 (0.20 mmol), aryl halide (2 equiv), Pd[P(η-Bu)3]2 (5 mol %), toluene (0.1 M). b Isolated yield. c Performed in 1 mmol scale.

Next, the fundamental physical properties of DTABs were investigated. UV–Vis absorption spectra of 1a–e are illustrated in Figure 3. The onset of absorbance (λonset) of 1a was 369 nm, which is similar to that of 1b (367 nm). The value of λonset increased with π-extension, and that of 1e was 418 nm, which is the longest among them. These results suggest that the HOMO–LUMO gaps of DTABs become smaller by π-extension, and that of 1e is the smallest among them (2.96 eV).

A similar tendency was observed in the UV–Vis absorption spectra of 5a–g. We also measured fluorescence spectra of DTABs, and found that DTAB 1a–e exhibited weak fluorescence (Φ < 0.1). The fluorescence emission (λem) of 1a–e was observed around 377–417 nm, and the value was increased with their π-extension. Among 5a–g, the fluorescence of 5d was the strongest (Φ = 0.27) probably because the diphenylamino moiety would work as an efficient donor unit.

Cyclic voltammetry (CV) was then carried out for 1a–e and 5a–g. In all of the cyclic voltammograms, irreversible oxidation peaks were observed. In contrast, no clear reduction peak was observed in the range of the electron window. The onset values of oxidation (Eonset) were in the range of 0.55–0.77 V for 1a–e and 0.33–0.59 V for 5a–g (vs. Fe/Fe3+). The combined electrochemical and optical data led to estimated HOMO–LUMO levels for 1a–e and 5a–g (Table 3 and Sup-
Table 3. Electrochemical and Optical Data for DTAB 1a–e

<table>
<thead>
<tr>
<th></th>
<th>λ_{max} (nm)</th>
<th>log ε</th>
<th>E_{onset} (nm/eV)</th>
<th>E_{HOMO} (eV)</th>
<th>E_{LUMO} (eV)</th>
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<tbody>
<tr>
<td>1a</td>
<td>351</td>
<td>4.24</td>
<td>369, 3.36</td>
<td>-5.52</td>
<td>-2.16</td>
</tr>
<tr>
<td>1b</td>
<td>350</td>
<td>4.37</td>
<td>367, 3.38</td>
<td>-5.57</td>
<td>-2.19</td>
</tr>
<tr>
<td>1c</td>
<td>305</td>
<td>4.41</td>
<td>395, 3.14</td>
<td>-5.35</td>
<td>-2.21</td>
</tr>
<tr>
<td>1d</td>
<td>293</td>
<td>4.40</td>
<td>382, 3.24</td>
<td>-5.44</td>
<td>-2.20</td>
</tr>
<tr>
<td>1e</td>
<td>303</td>
<td>4.71</td>
<td>418, 2.96</td>
<td>-5.37</td>
<td>-2.19</td>
</tr>
</tbody>
</table>

α E_{nset} values were determined by the onset of CV in CH2Cl2. All potentials were calibrated with reference to Fe/Fe+. E_{HOMO} and E_{LUMO} values were determined with reference to ferrocene (4.8 eV vs vacuum). Optical band gap: E_{g}^{opt} = 1240/λ_{max}. E_{LUMO} = E_{HOMO} + E_{g}^{opt}.

ASSOCIATED CONTENT
Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/.

Experimental details, photophysical and electrochemical properties of 1a–e and 5a–g, spectral data for all new compounds, data of theoretical calculations (PDF)

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Notes

The authors declare no competing financial interest.

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(7) This property was measured with reference to Fc/Fc+.

Figure 3. UV–Vis spectra of 1a–e measured in o-C6H4Cl2 (1.0 ×10−5 M).


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