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

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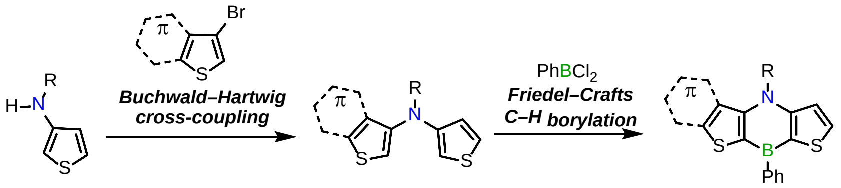
Supporting Information Placeholder



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 terthiophenes 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 tetrathienonaphthalene derivatives and their properties as semiconductors.[6g] 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,[7] and focus 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)[8] and dithieno[3,2-*b*:2',3'-*e*][1,4]thiaborine (DTTB), analogues of DTAB, have already been reported by Clark[8a] and Liu[9]. 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.

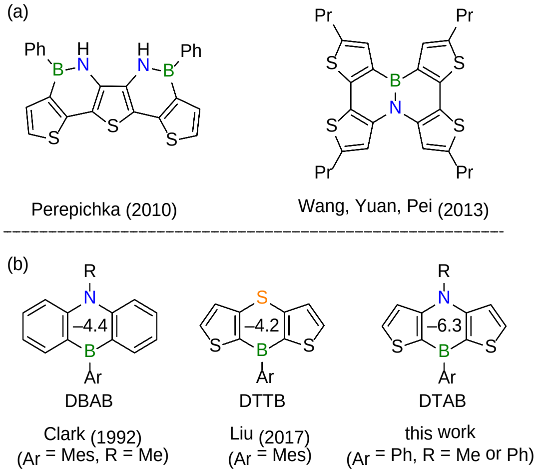
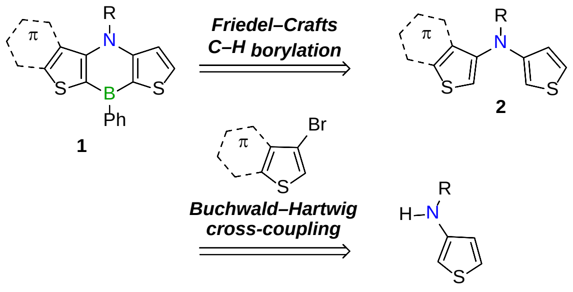


Figure 1. (a) Representative examples of previously reported thiophene-fused 1,2-azaborines; (b) Structure of dibenzo-1,4-azaborine (DBAB), dithieno-1,4-thiaborine (DTTB), and dithieno-1,4-azaborine (DTAB) with NICS(1) calculated at the GIAO-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level. NICS values were 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 π-extended derivatives by cross-coupling reactions.

Scheme 1. Our Synthetic Strategy for Dithienoazaborines



1

2

3

While 3,3′-dithienylamines have been known to be useful precursors for dithienopyrroles, there has been only one report on the synthesis of more π-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(*t*-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-benzo[*b*]thiophenyl-3-thienylamine (**2c**), the use of P(*t*-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-bromobenzo[*b*]thiophene afforded the desired product **2c** in 78% yield. A tandem coupling reaction using 3,6-dibromothieno[3,2-*b*]thiophene was also carried out; the use of Pd[P(*t*-Bu)$_3$]$_2$ gave both the dehalogenated mono-coupling product **2d** and the double-coupled diamine **2e** in respective yields of 21% and 13%. When RuPhos was used as a ligand, the yield of **2e** increased to 58%.[12]

Next, we chose **2a** as a model compound, and C–H borylation was carried out (Table 1). In chlorobenzene, treatment of **2a** with PhBCl$_2$ (1.5 equiv) at 135 °C for 48 h gave the desired azaborine **1a** regioselectively in 40% yield (entry 1). Further optimization revealed that the addition of Et$_3$N increased the yield of **1a**. With 1 equiv of Et$_3$N, the NMR yield of **1a** increased to 61% (entry 2). The reaction proceeded quite efficiently with 2 equiv of Et$_3$N. **1a** was obtained in 88% yield even within 24 h (entry 3), and the reaction proceeded quantitatively within 48 h (entry 4, >99% NMR yield, 96% isolated yield). When the reaction was performed on a 1 mmol scale, **1a** was also obtained in good yield (entry 5).

The structure of **1a** was confirmed by X-ray analysis (Figure 2). The sum of the bond angles around the nitrogen, boron, and carbon atoms that comprised the azaborine ring was 360°, and the sum of the interior angles of the azaborine ring was 720°, indicating that the azaborine ring is completely planar. The packed structure of **1a** is illustrated in Figure 2(b). Intermolecular N–B interaction was not observed, and the packed structure was mainly effected by π–π interaction.

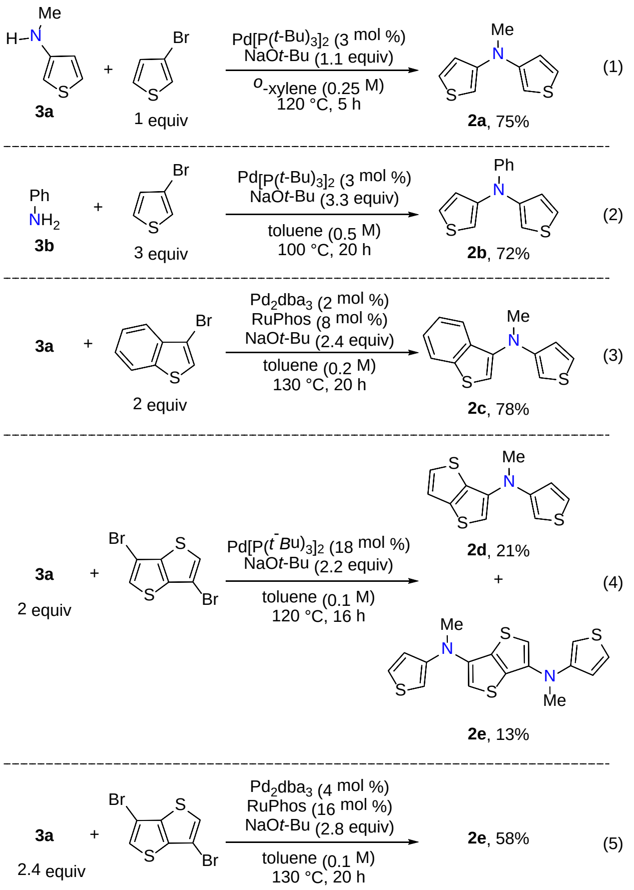
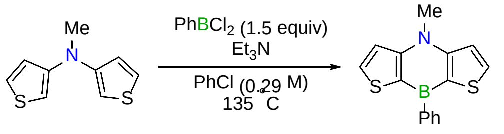


Table 1. Synthesis of Dithienoazaborine 1a by C–H Borylation under Various Conditions [a]



2a

1a

entry	Et$_3$N (equiv)	time (h)	yield (%)[b]
1	0	48	40
2	1.0	48	61
3	2.0	24	88
4	2.0	48	>99 (96)[c]
5	2.0	48	82[c,d]

[a] Reaction conditions: **2a** (0.20 mmol), PhBCl$_2$ (1.5 equiv), Et$_3$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**.

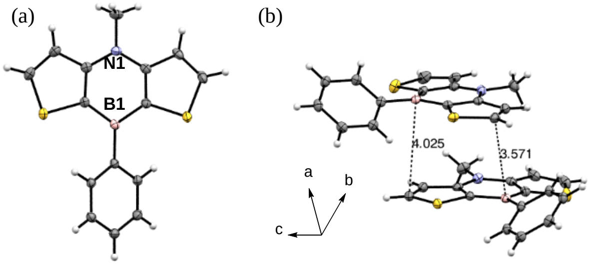
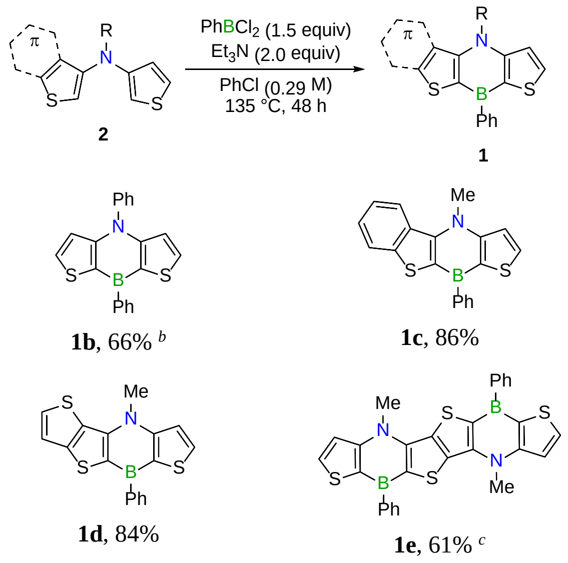


Figure 2. (a) ORTEP drawing of **1a** with 50% thermal ellipsoids. (b) Packed structure of **1a**.

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 $PhBCl_2$. Precursors bearing 3-benzo[*b*]thienyl and 3-thieno[3,2-*b*]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 [a]



[a] Reaction conditions: **2** (0.20 mmol), $PhBCl_2$ (1.5 equiv), Et_3N (2 equiv), PhCl (0.29 M). Isolated yield. [b] Performed with 3 equiv of $PhBCl_2$. [c] Performed with **2e** (0.32 mmol), $PhBCl_2$ (3 equiv), Et_3N (4 equiv) in PhCl (0.07 M).

For further derivatization of the thus-obtained DTABs, a stannyl group was introduced to **1c**.When **1c** was treated with *t*-BuLi (2.2 equiv) and TMEDA (2.6 equiv) at −78 °C, lithiation proceeded smoothly and a subsequent reaction with Me_3SnCl gave the stannylated DTAB **4** in 84% yield (Scheme 3).[13]

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(*t*-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

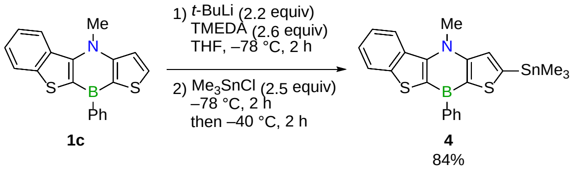
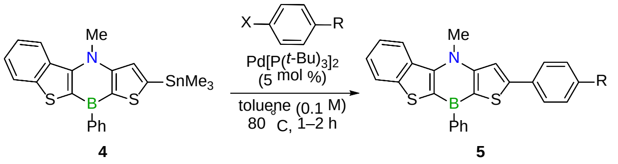


Table 2. Synthesis of π-Extended DTAB 5 by Kosugi–Migita–Stille Cross-coupling [a]



entry	R	X	**5**	yield (%)[b]
1[c]	H	I	**5a**	85
2	CH_3	I	**5b**	92
3	CH_3O	I	**5c**	71
4	Ph_2N	Br	**5d**	79
5	F	I	**5e**	91
6	CF_3	I	**5f**	97
7	CN	I	**5g**	99

[a] Reaction conditions: **4** (0.20 mmol), aryl halide (2 equiv), Pd[P(*t*-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 (λ_{onset}) of **1a** was 369 nm, which is similar to that of **1b** (367 nm). The value of λ_{onset} 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**.[14] We also measured fluorescence spectra of DTABs, and found that DTAB **1a–e** exhibited weak fluorescence ($\Phi < 0.1$). The fluorescence emission (λ_{em}) of 1**a–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 ($\Phi = 0.27$) probably because the diphenylamino moiety would work as an efficient donor unit.[15]

Cyclic voltammetry (CV) was then carried out for **1a–e** and **5a–g**.[14] 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 (E_{onset}) were in the range of 0.55–0.77 V for **1a–e**[16] and 0.33–0.59 V for **5a–g** (vs. Fc/Fc$^+$). The combined electrochemical and optical data led to estimated HOMO–LUMO levels for **1a–e** and **5a–g** (Table 3 and Supporting Information). All of the DTABs have HOMO levels lower than −5.1 eV and deep LUMO levels,[17] suggesting that they would be stable in air and would act as electron-acceptors. Their energy levels are consistent with the results of DFT calculations.

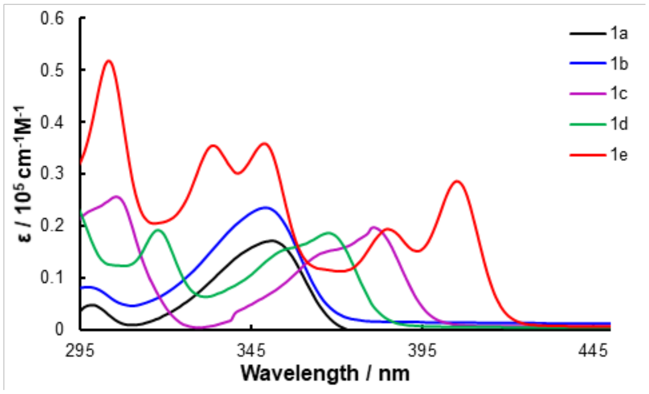


Figure 3. UV–Vis spectra of **1a–e** measured in *o*-$C_6H_4Cl_2$ (1.0×10^{-5} M).

In conclusion, we have achieved the first syntheses of DTAB **1a–e** by Buchwald–Hartwig coupling and subsequent C–H borylation. Further π-extension of **1c** to afford **5a–g** was also achieved. The fundamental physical properties of the DTAB derivatives were also studied. Further investigations of these derivatives are in progress in our laboratory.

Table 3. Electrochemical and Optical Data for DTAB 1a–e[a]

1	λ_{max} (nm)	log ε	$\lambda_{onset}/E_g^{opt}$ (nm/eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
1a	351	4.24	369, 3.36	–5.52	–2.16
1b	350	4.37	367, 3.38	–5.57	–2.19
1c	305	4.41	395, 3.14	–5.35	–2.21
1d	293	4.40	382, 3.24	–5.44	–2.20
1e	303	4.71	418, 2.96	–5.37	–2.19

[a] E_{onset} values were determined by the onset of CV in CH_2Cl_2. All potentials were calibrated with reference to Fc/Fc⁺. E_{HOMO} values were determined with reference to ferrocene (4.8 eV vs vacuum).[18] Optical band gap: $E_g^{opt} = 1240/\lambda_{onset}$. $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

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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