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Synthesis, Structure, and Properties of a Dinaphthoazaborine

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A 1,4-azaborine derivative fused by two naphthalene rings, a dinaphthoazaborine was synthesized, and its molecular structure was revealed by X-ray crystallographic analysis. UV–vis absorption and fluorescence spectra of the dinaphthoazaborine indicated a decrease in the HOMO–LUMO energy gap compared with that of dibenzoazaborines. Electrochemical measurements elucidated the enhanced electron-accepting characteristics of the dinaphthoazaborine.

Boron-containing π-conjugated molecules are an interesting class of compounds because of their various optical, electronic, or chemical properties, such as photoluminescence, electron-accepting ability, and chemosensing of anions.[1] Therefore, recently the development of π-extended boron compounds with novel characteristics has been extensively investigated, and from such a viewpoint we have also reported new functional triarylboranes based on dibenzoazaborine **2** (Figure 1).[2,3] Owing to donor–acceptor interaction between the nitrogen and boron atoms as well as a rigid framework, dibenzoazaborines and their π-extended derivatives exhibit strong light absorption and emission, indicating the potential of a 1,4-azaborine as a good building unit for organic functional materials. The introduction of larger aromatic systems, such as naphthalene or higher acenes to the azaborine ring should further decrease the HOMO–LUMO energy gap and improve the optoelectronic properties. In this communication, we describe the synthesis and optical properties of new azaborine derivative **1**.[4]

Scheme 1 shows the preparation of the precursor **3** of **1**. The coupling reaction of known naphthalene derivatives **4**[5] and **5**[6] under standard palladium-catalyzed amination conditions gave dinaphthylamine **6** in 77% yield. The nitrogen atom of **6** was methylated under phase-transfer conditions to give precursor **3**.

Dinaphthoazaborine **1** was synthesized in 56% yield by the reaction of the dilithio derivative of **3** with MesB(OMe)$_2$ at low temperature (Table 1, Entry 1). When the temperature was raised soon after the addition of MesB(OMe)$_2$, carbazole derivative **7**,[7] a formal oxidative coupling product of the dilithio derivative, was obtained as a major product (Entry 2).[8] Under these conditions, some boron-containing compounds would work as oxidants to promote the C–C coupling reaction of the dilithio derivative.

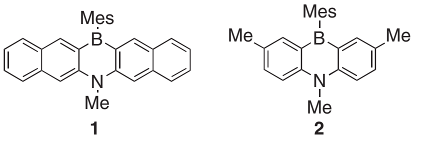
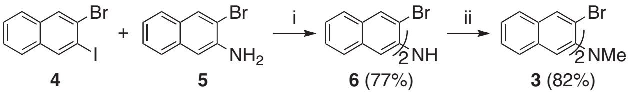
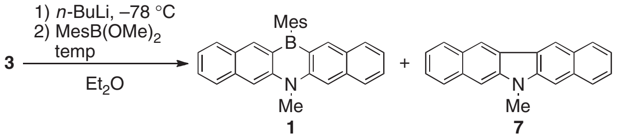


Figure 1. Dinaphthoazaborine **1** and dibenzoazaborine **2**.



Scheme 1. Reagents and conditions: (i) Pd(dba)$_2$, DPPF, *t*-BuONa, toluene, 100 °C; (ii) MeI, KOH, (*n*-Bu)$_4$NI, THF, 55 °C.

Table 1. Synthesis of dinaphthoazaborine **1**



Entry	Temp	Product (yield/%)
1	–78 °C (3 h), then –78 °C to rt	**1** (56)
2	–78 °C to rt	**1** (26), **7** (36)

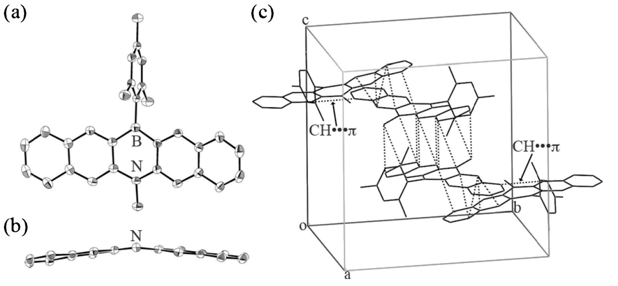


Figure 2. Molecular structure of **1**. Thermal ellipsoid plots are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. (a) Top view. (b) Side view. Mes and Me groups are omitted. (c) Packing diagram. Short contacts (≤3.6 Å) are indicated with dashed lines.

Dinaphthoazaborine **1** was obtained as air-stable red solid, and its molecular structure was elucidated by X-ray diffraction analysis of single crystals obtained from a saturated toluene/hexane solution (Figure 2).[9,10]

The dihedral angle between the Mes group and the azaborine ring of **1** (87°) is slightly larger than that of dibenzoazaborine **2** (79°, an averaged value of two independent molecules in the single crystals).[3a] As shown in Figure 2b, the dinaphthoazaborine skeleton of **1** is butterfly-like, and the angles between the two naphthalene rings is 15°, which is larger than the bent angle between the two benzene rings of **2** (9°, an averaged value of the two independent molecules). These differences between the molecular structures of **1** and **2** may come from the crystal packing, because DFT calculations predicted almost the same geometries around the central azaborine rings in the two compounds.[11,12] In the crystal structure of **1**, two molecules of **1** formed a dimeric structure through the short contacts between the peripheral parts of the naphthalene rings. In addition, the dimeric motif was capped

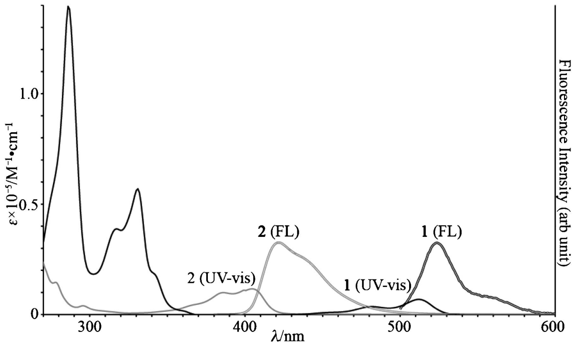


Figure 3. UV–vis and fluorescence spectra of **1** (black) and **2** (gray) in cyclohexane.

Table 2. Optical properties of azaborine derivatives

	λ_{max}/nm ($\log \varepsilon$)^a	λ_{em}/nm (Φ)^a	λ_{calcd}/nm (f)^b
1	519 (3.88)	524 (0.29)	486 (0.0434)
	331 (4.76)		343 (0.2027)
	286 (5.11)		283 (1.8397)
2	405 (4.02)	421 (0.48)	368 (0.1033)

^{a}In cyclohexane at 298 K. ^{b}Calculated at B3LYP/6-31+G(d) level of theory on model compounds **1′** and **2′**.

with two molecules of **1** via π–π interactions between the naphthalene rings and the azaborine rings as well as CH–π interactions between the mesityl groups and the naphthalene rings. Compound **2** and its sulfur analog, a dibenzothiaborine did not show such extended intermolecular short contacts in the solid state,[3a,3b] and thus the introduction of the naphthalene rings affected the intermolecular interactions in the solid state of **1**. Such strong intermolecular interactions were expected to affect its solid-state fluorescence properties (vide infra).

The UV–vis absorption and fluorescence spectra of **1** were measured in cyclohexane (Figure 3). The absorption and emission spectra of dibenzoazaborine **2** are also shown for comparison, and the optical data are summarized in Table 2. **1** showed the longest absorption maximum due to HOMO–LUMO excitation at 519 nm, which is red-shifted from that of **2** (405 nm) by 114 nm, indicating the elongation of the π-system and a decrease in HOMO–LUMO energy gap in **1**. **1** also exhibited intense absorption bands in the UV centered at 331 and 286 nm. Based on the TD-DFT calculation, these absorptions are attributed to the π–π^* excitations of the naphthalene rings mixed with the n(N)–π^*(naphthalene) and π(naphthalene)–2p*(B) excitations.

Emission maximum of **1** was red-shifted by 103 nm from that of **2**, which corresponds to the bathochromic shift of the absorption maximum. The small Stokes shift of **1** (448 cm^{-1}) indicates that the influence of the structural relaxation upon photoexcitation is relatively small. However, despite the rigid molecular skeleton, the fluorescence quantum yield of **1** was lower than that of **2**. Because the calculated oscillator strength for the lowest excited state of **1** (0.0434) is smaller than that of **2** (0.1033), the decreased fluorescence quantum yield of **1** may originate from its smaller rate constant of radiative deactivation.

Unlike the dibenzoazaborine derivatives, **1** did not show detectable solid-state fluorescence emission. Judging from the crystal structure, there can be many intermolecular short contacts between the molecules of **1** in the solid state. Such intermolecular interactions are thought to enhance nonradiative decay via intermolecular energy transfer and quench the solid-state fluorescence.

In THF, **1** showed a one-electron reversible reduction wave at $E_{1/2} = -2.1$ V (vs. Cp_2Fe/Cp_2Fe^+), which was shifted anodic by 1.0 V from that of **2** (-3.1 eV), indicating the improved stability of the radical anion in the case of **1**.[13] **1** also showed a quasi-reversible one-electron reduction wave corresponding to the generation of the dianion at $E_{peak} = -2.9$ V. These results revealed the high electron-accepting ability of **1** and indicate the potential of **1** as a platform for high-performance electron-acceptors and anion sensors.

In conclusion, a new azaborine derivative fused by two naphthalene rings was synthesized. This compound exhibited red-shifted absorption and emission compared with those of dibenzoazaborines. Electrochemical analyses revealed that the dinaphthoazaborine forms a stable radical anion at relatively low potential, indicating its utility as an electron-acceptor and an anion sensor.

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