Fluorescent BN-Heterocycles

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1,2-Azaborine Cations**

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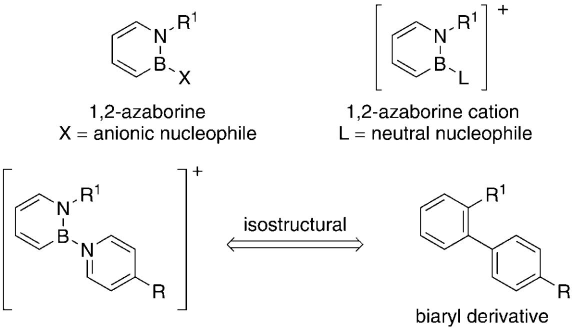
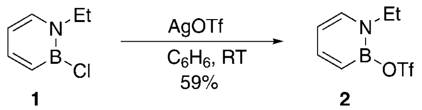
1,2-Dihydro-1,2-azaborine is a six-membered aromatic heterocycle that is isoelectronic with benzene through the replacement of a C=C unit in benzene with an isoelectronic B−N unit.[1,2] Since the pioneering work by Dewar et al.,[3,4] significant advances have been made in the synthesis and reactivity studies of this family of heterocycles.[5–7] Our continued exploration of the 1,2-azaborine motif[8–15] has led us to consider the synthesis of cationic 1,2-azaborines, for which no examples have been reported. In particular, we envisioned that substitution of 1,2-azaborine on the boron atom with pyridine derivatives would furnish cationic biaryl-type structures[16] having the potential for use in materials applications (Scheme 1). Herein we report the synthesis, structural characterization, and optoelectronic properties of pyridine-substituted 1,2-azaborine cations, including a cationic heterocyclic analogue of *para*-terphenyl.



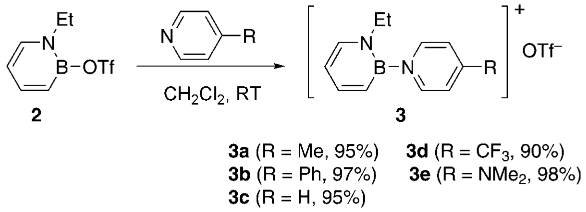
Scheme 1. 1,2-Azaborine cations.

We have previously established nucleophilic substitution of the B−Cl bond in 1,2-azaborines by anionic nucleophiles (with Cl^- serving as the leaving group).[8] Less reactive neutral nucleophiles did not displace the chloride from the boron atom. We hypothesized that a better leaving group on the boron atom (e.g., OTf) could render it susceptible to nucleophilic attack by weaker neutral nucleophiles. In the course of our studies, we discovered that silver reagents facilitate the ligand exchange at the boron position in 1,2-azaborines.[13] We were thus pleased to discover that treatment of 1,2-azaborine **1** with AgOTf produced the substituted 1,2-azaborine **2** in 59 % yield as an extremely moisture-sensitive liquid (Scheme 2). The 1,2-azaborine **2** was characterized by ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy as well as IR spectroscopy.



Scheme 2. Synthesis of **2**. Tf = trifluoromethanesulfonyl.

Heterocycle **2** readily reacts with *para*-substituted pyridines to form the desired cationic 1,2-azaborines **3**. As can be seen from Scheme 3, the substitution reaction is independent of the electronic nature of the nucleophile. Excellent yields have been obtained with both electron-rich and electron-poor pyridines.



Scheme 3. Synthesis of 1,2-azaborine cations **3**.

The 1,2-azaborine cations **3** are highly crystalline solids that fluoresce under UV light. We thus explored the solid-state fluorescence of the pyridine-substituted 1,2-azaborine cations **3**. The solid-state fluorescence and quantum yields of aromatic hydrocarbons, including *para*-terphenyl, have been reported using an integrating sphere.[17] We have recorded the fluorescence spectra of crystalline samples of **3a–e** (Figure 1), all of which were freshly recrystallized prior to making the fluorescence measurements. The solid-state fluorescence of **3a** (R = Me) shows a peak at $\lambda_{em} = 436$ nm ($\Phi_{PL} = 0.03$) and is visibly less fluorescent than samples of **3b** and **3c** under a UV lamp ($\lambda = 365$ nm; see Figure 1, right). The solid-state emission spectrum of **3b** (R = Ph) showed a relatively narrow band at $\lambda_{em} = 448$ nm ($\Phi_{PL} = 0.86$). The high quantum yield observed for **3b** is quite similar to the values obtained for

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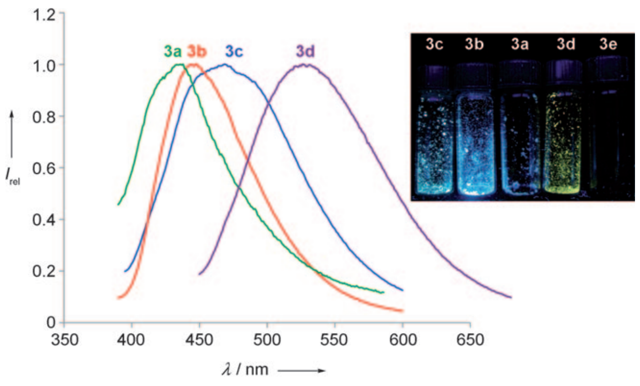


Figure 1. Normalized solid-state fluorescence spectra and images (under UV irradiation) of 1,2-azaborine cations **3**.

para-terphenyl, though the emission maximum of the cationic **3b** is bathochromically shifted relative to the all-carbon *para*-terphenyl by approximately 75 nm.[17] We found that solid samples of **3c** (R = H) were blue-green fluorescent (see Figure 1) with a relatively broad emission maximum at λ_{em} = 469 nm (Φ_{PL} = 0.30). Compound **3d** (R = CF_3) exhibits yellow-green emission at λ_{em} = 527 nm (Φ_{PL} = 0.11), which contrasts the blue emission observed for geometrically similar **3a**. The data illustrated in Figure 1 suggest that the *para* substituent on pyridine has a substantial effect upon the emissive properties of 1,2-azaborine cations. DMAP-substituted **3e** (R = NMe_2;DMAP = 4-dimethylaminopyridine) does not fluoresce in the solid state (Figure 1, right), which is consistent with the reported fluorescence quenching by the presence of a nitrogen lone pair of electrons.[18]

We also determined the absorption properties of 1,2-azaborine cations **3** in solution. The absorption maximum of **3a** (R = Me) in CH_2Cl_2 was found at λ = 287 nm with an extinction coefficient of ε = 12713 $\text{M}^{-1}\text{cm}^{-1}$. The absorption spectrum of **3b** showed a broad, featureless peak at λ = 292 nm (ε = 21869 $\text{M}^{-1}\text{cm}^{-1}$), which is close to that observed for **3a**, but is slightly bathochromically shifted from the absorption maximum of *para*-terphenyl (observed at λ = 280 nm in CH_2Cl_2).[19] The absorption spectrum of **3c** (R = H) also showed a broad peak at λ = 286 nm (ε = 8624 $\text{M}^{-1}\text{cm}^{-1}$). The observed absorption peaks of **3d** at λ = 285 nm (ε = 8126 $\text{M}^{-1}\text{cm}^{-1}$) and **3e** at λ = 283 nm (ε = 21303 $\text{M}^{-1}\text{cm}^{-1}$) are relatively unchanged from the other derivatives of **3**.

Interestingly, of the prepared cationic derivatives, only terphenyl analogue **3b** was found to be fluorescent in solution. The fluorescence spectrum of **3b** in CH_2Cl_2 showed an emission peak at λ_{em} = 360 nm (Φ_{PL} = 0.06), and the absorption maximum was found at λ = 292 nm in CH_2Cl_2 (Figure 2). The large Stokes shift of 68 nm for **3b** is indicative of considerable reorganization between the ground and the excited state. We also observed a bathochromic shift in the emission peak when MeCN was used as the solvent (λ_{em} = 382 nm, Φ_{PL} = 0.17) instead of CH_2Cl_2. Furthermore, the fluorescence of **3b** in MeCN was quenched upon the addition of NaI,[20] highlighting the potential of these materials in sensing applications.

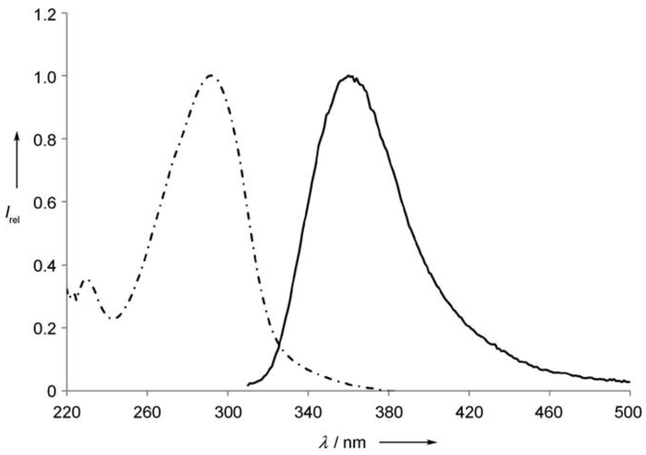


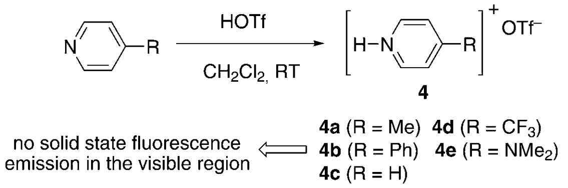
Figure 2. Normalized absorption (dashed line) and emission (solid line) spectra of **3b** in CH_2Cl_2.

Table 1 summarizes the photophysical properties of pyridine-substituted 1,2-azaborine cations **3a–e**. To assess whether the extended conjugation provided by the 1,2-azaborine ring is critical for the observed optoelectronic properties of the 1,2-azaborine cations **3**, we prepared the corresponding protonated pyridinium species **4a–e** (Scheme 4). We determined that under the same conditions for **3**, pyridinium triflate salts **4a–e** do not exhibit solid-state fluorescence emission in the visible region. This is consistent with a critical role of the 1,2-azaborine moiety in the observed emission properties of 1,2-azaborine cations **3**.

Table 1: Photophysical data for **3a–3e**.

Compound	Absorbance [nm][a]	ε [$\text{M}^{-1}\text{cm}^{-1}$][a]	Emission [nm]	Φ_{pl}
3a	287	8126	436[b]	0.03[b]
3b	292	21869	448[b]	0.86[b]
			360[a]	0.06[a]
			382[c]	0.17[c]
3c	286	8624	469	0.30[b]
3d	287	12713	527	0.11[b]
3e	283	21303	N/A	N/A

[a] In CH_2Cl_2 (10^{-5} M). [b] Solid-state emission. [c] In MeCN (10^{-5} M). N/A = not applicable.



Scheme 4.

We have obtained the X-ray crystal structures of 1,2-azaborine cations **3** (except for **3c**), thus unambiguously establishing their structural identity. As a representative example, the solid-state structure of **3b** is illustrated in

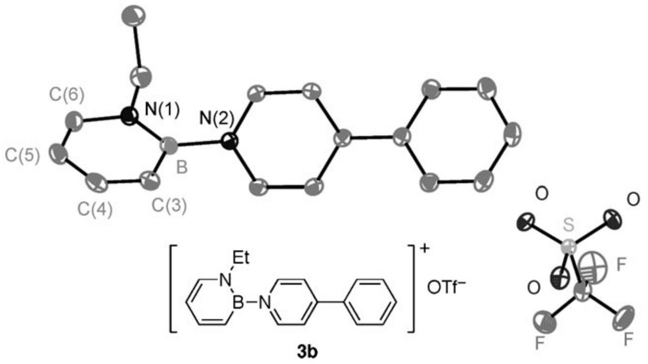


Figure 3. ORTEP illustration of **3b**, with thermal ellipsoids drawn at the 35% probability level (hydrogen atoms have been omitted for clarity). Bond distances (in Å): B-N(1) 1.413(2), B-N(2) 1.531(2), B-C(3) 1.496(2), C(3)-C(4) 1.369(2), C(4)-C(5) 1.408(3), C(5)-C(6) 1.358(2), C(6)-N(1) 1.3736(19); Torsion angles: 1,2-azaborine-pyridine = 50.5°; pyridine-phenyl = 18.0°.

Figure 3 and reveals that the pyridine nitrogen atom is bound to the boron atom with the triflate group serving as a noncoordinating anion.[21] As expected, the dative exocyclic B–N bond (B-N(2) = 1.531(2) Å) in **3b** is significantly longer than the covalent exocyclic B–NPh$_2$ bond in a 1,2-azaborine recently reported in our group (B-N(2) = 1.486(2) Å).[9] The exocyclic B–N bond in cationic **3b** is slightly shorter than the B–N bond in the charge-neutral borabenzene-4-phenylpyridine adduct (B-N = 1.551(3) Å) reported by Fu and coworkers.[22] The 1,2-azaborine ring in **3b** is completely planar and is twisted by approximately 50° relative to the pyridine ring. In contrast, the phenyl ring of **3b** is only slightly twisted relative to the pyridine ring (18°).

We were also interested in examining the structural features of the 1,2-azaborine ring in **3b**.The intra-ring B–N bond is short (B-N(1) = 1.413(2) Å), as is the intra-ring B–C bond (B-C(3) = 1.496(2) Å), which is consistent with bond distances observed for electron-deficient 1,2-azaborines.[13]

Selected bond parameters for 1,2-azaborine cations **3** are given in Table 2. The *para* substituent in the pyridine ring has little influence on the observed bond lengths, which are virtually identical for all derivatives. The torsion angles between the pyridine and 1,2-azaborine ring are similar for derivatives **3a**, **3b**, and **3d**, although in **3e** (R = NMe$_2$) the 1,2-azaborine ring is nearly perpendicular to the pyridine ring. It noteworthy that the 1,2-azaborine cations **3** represent a new family of borenium cations for which only a few members have been structurally characterized by single-crystal diffraction.[23]

Table 2: Selected bond distances [in Å] and angles [°] for 1,2-azaborine cations **3**.

Compound	B-N(1) [Å]	B-C(3) [Å]	B-N(2) [Å]	Ring torsion[a]
3a	1.418(5)	1.481(5)	1.528(5)	57.1°
3b	1.413(2)	1.496(2)	1.531(2)	50.5°
3d	1.416(4)	1.489(4)	1.526(4)	58.0°
3e	1.423(5)	1.489(6)	1.527(5)	77.8°

[a] Torsion angle between the 1,2-azaborine and pyridine ring.

In summary, we prepared the first examples of 1,2-azaborine cations through a nucleophilic substitution reaction between pyridine nucleophiles and the highly Lewis acidic 1,2-azaborine **2**. 1,2-Azaborine cations **3a**–**3d** exhibit solid-state fluorescence that is distinct from the neutral all-carbon analogues. Furthermore, 4-phenylpyridine-substituted 1,2-azaborine cation **3b**, an analogue of terphenyl, displays solution-phase fluorescence in addition to solid-state emission. Control experiments establish the 1,2-azaborine ring as an essential component for the observed optoelectronic properties. This study highlights the unique properties of 1,2-azaborine cations and underscores the potential utility of these complexes in materials applications.

Experimental Section

3b: In a glove box, a solution of 4-phenylpyridine (0.073 g, 0.47 mmol in 1.0 mL CH_2Cl_2) was added to a stirred solution of **2** (0.100 g, 0.392 mmol in 1.0 mL CH_2Cl_2). The mixture was stirred for 1 h at room temperature. At the conclusion of the reaction, the solution was cooled to −20 °C and left at that temperature for 24 h. The desired product precipitated out of the solution as a crystalline solid. The supernatant was decanted and the crystallized product was washed with *n*-pentane (3 × 5 mL). Residual solvents were removed under reduced pressure to provide **3b** as clear, colorless crystals (0.155 g, 97%). ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 8.82$ (d, $^3J_{HH} = 6.9$ Hz, 2H), 8.44 (d, $^3J_{HH} = 6.9$ Hz, 2H), 8.02 (dd, $^3J_{HH} = 9.8$, 6.6 Hz, 1H), 7.97 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.7$ Hz, 2H), 7.68 (m, 3H), 7.55 (d, $^3J_{HH} = 6.6$, 1H), 6.85 (app t, $^3J_{HH} = 7.5$ Hz, 2H), 3.83 (q, $^3J_{HH} = 7.3$ Hz, 2H), 1.38 ppm (t, $^3J_{HH} = 7.3$ Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta =$ 158.1, 149.5, 145.8, 139.6, 134.3, 133.2, 130.5, 128.7, 125.7, 124 (br), 115.7, 47.7, 18.2 ppm. ^{11}B NMR (192.5 MHz, CD_2Cl_2): $\delta = 31.0$ ppm. FTIR (thin film) 3220, 3138, 3078, 2915, 1638, 1612, 1513, 1488, 1474, 1442, 1412, 1377, 1349, 1292, 1233, 1218, 1174, 1151, 1029, 833, 765, 736, 693 cm^{-1}. HRMS (EI) calcd for $C_7H_9BNO_3SF_3$ [M^+] 255.03484, found 255.03528.

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[21] Crystallographic data for **3b**: $C_{18}H_{18}BF_3N_2O_3S$, $M_r = 410.21$, crystal size $0.36 \times 0.31 \times 0.24$ mm^3, monoclinic, space group $P21/n$, $a = 9.3812(9)$, $b = 14.3671(13)$, $c = 14.2217(13)$ Å, $\beta = 110.940(1)°$, $V = 1882.0(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.448$ g cm^{-3}, $\mu = 0.223$ mm^{-1}, $F(000) = 848$, Mo$_{K\alpha}$-radiation $\lambda = 0.71073$ Å, $T = 173(2)$ K, $2\Theta_{max} = 54.00°$, 17178 reflections measured [$R_{int} = 0.0255$], 4101 reflections observed, 325 refined parameters, $R1 = 0.0376$, $wR2 = 0.1050$ for reflections with $I > 2\sigma(I)$, $R1 = 0.0451$, $wR2 = 0.1131$, and GOF = 1.024 for all data, max/min residual electron density $+0.439/-0.201$ e Å^{-3}. CCDC 782514 (**3b**) 782515 (**3a**), 782517 (**3d**), and 782516 (**3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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