## Photochemistry

## Formation of Azaborines by Photoelimination of B,N-Heterocyclic Compounds\*\*

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Organoboron compounds have broad applications in organic synthesis,<sup>[1]</sup> catalysis,<sup>[2]</sup> optoelectronic devices,<sup>[3]</sup> sensors,<sup>[3,4]</sup> and probes.<sup>[5]</sup> Among  $\pi$ -conjugated organoboron compounds, azaborine molecules or B-N-containing aromatic molecules have attracted much research interest and efforts.<sup>[6]</sup> The replacement of a C-C unit in an aromatic molecule with an isoelectronic B-N unit has been shown to impart interesting electronic, photophysical, luminescent, and chemical properties, which are often very distinct from those of the C-Ccontaining aromatic analogues, to the molecule.<sup>[6]</sup> This observation has led to many potential applications of B-Ncontaining aromatic compounds, such as hydrogen storage materials,<sup>[7]</sup> optoelectronic materials,<sup>[8]</sup> sensors,<sup>[9]</sup> and bioactive molecules.<sup>[10]</sup> Nonetheless, examples of polycyclic πconjugated azaborine molecules and derivatives remain rare compared to the vast number of C-C-containing aromatic compounds and heterocyclic aromatic compounds. The syntheses of azaborine compounds are in general very challenging and often involve multi-step reactions or the use of transition-metal catalysts.<sup>[6]</sup> Thus, the development of efficient and simple synthetic methods for B-N-containing aromatic compounds is highly important to advance the chemistry and applications of this important class of compounds.

We herein disclose the discovery of a new and facile synthetic method for B–N-containing aromatic compounds, namely, the photoelimination method (Scheme 1). Although examples of organoboron compounds that display unusual photochemical reactivity have been reported previously,<sup>[11]</sup> the photoelimination reaction presented here is highly unusual and unprecedented because of the breaking of a C– H bond and of a B–C bond. Furthermore, this photoelimination process is a generic reaction for the B,N-heterocyclic compounds shown in Scheme 1, in which the R group can be either an alkyl or an aryl group and the N heterocycle can be either a pyridyl or a benzothiazolyl. Furthermore, this photo-

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**Scheme 1.** Formation of azaborines through photoelimination of B,N heterocycles.

elimination reaction also occurs readily in a polymer substrate. The details are presented herein.

Compound BN-1 was synthesized in good yield by the reaction of *n*BuLi with 2-(2-methylphenyl)pyridine at -78 °C, followed by the addition of BMes<sub>2</sub>F. The dimethyl analogue BN-2 and the benzothiazolyl B,N-heterocyclic compound BN-3 were obtained in good yields using the same procedure. For BN-4, BMes<sub>2</sub>F was replaced by BMe<sub>2</sub>Br in the synthesis. The presence of tetramethylethylenediamine (TMEDA) in the lithiation step is necessary to ensure that the lithiation takes place at the methyl site and not at the H atom in *ortho* position of the phenyl ring, which can lead to the formation of the undesired phenyl–pyridyl or phenyl–benzothiazolyl chelate products that are analogues of B(ppy)Mes<sub>2</sub> (ppy = phenylpyridine) and derivatives.<sup>[11b]</sup> The yield of BN-4 is poor, which may be caused by the reaction of BMe<sub>2</sub>Br with TMEDA.

The B,N-heterocyclic compounds are generally colorless, except BN-3, which is light yellow both in solution and in the solid state. They are stable in air and upon heating and do not show any appreciable change when heated to 110°C in toluene. They were fully characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy, and HRMS/elemental analysis. The crystal structures of BN-1, BN-3, and BN-4 were determined

by single-crystal X-ray diffraction analysis and the structures of BN-1 and BN-3 are shown in Figure 1. The structural data of BN-4 are provided in the Supporting Information. The lengths of the B– $C_{mesityl}$  and B–N bonds in BN-1 and BN-3 are similar to those in B(ppy)Mes<sub>2</sub>.<sup>[11b]</sup> The B1–C1 bond lengths (1.645(3) Å, 1.647(4) Å) in both compounds are however longer than the B– $C_{Ph}$  bond in B(ppy)Mes<sub>2</sub> (1.625 (2) Å) and related compounds.<sup>[11]</sup>



**Figure 1.** Crystal structures of a) BN-1, b) BN-3, and c) BN-3 a, and d) packing diagram showing intermolecular  $\pi$  stacking in the crystal lattice of BN-3a. For BN-1 and BN-3, all H atoms except those on C1 are omitted for clarity. Important bond lengths [Å] and angles [°] for BN-3 a: B1-C1 1.475(4), B1-C16 1.578(4), B1-N1 1.485(4), C1-C2 1.390(4), C2-C3 1.435(4), C3-C4 1.395(4), C4-N1 1.372(3); C1-B1-N1 114.4(3), B1-C1-C2 122.5(3), C1-C2-C3 120.2(3), C2-C3-C4 118.6(3), C3-C4-N1 123.5(3), C4-N1-B1 120.7(2).

When excited at 300 nm in dry toluene or benzene under nitrogen atmosphere, the solutions of BN-1, BN-2, and BN-4 change from colorless to bright yellow. In the UV/Vis spectra, a distinct new absorption band appears in the 360-520 nm region and increases in intensity with longer irradiation time, which accounts for the color change of the solution (see Figure 2 and the Supporting Information). To elucidate the structural change, the photoreaction was monitored by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy. Upon irradiation, a free mesitylene molecule was observed and the <sup>1</sup>H NMR spectra of BN-1 and BN-2 underwent a distinct change to those of BN-1a and BN-2a, respectively (see the Supporting Information.). The most distinct change in chemical shift is observed for the methylene protons, the signal of which shifted from 3.02 ppm in BN-1 and 2.76 ppm in BN-2 to 7.35 ppm in BN-1a and BN-2a, along with the change in total integration from two protons to one. The <sup>11</sup>B chemical shift also experienced a distinct change from 1.6 ppm in BN-1 and 1.2 ppm in BN-2, typical for tetrahedral boron centers, to 35.5 ppm in BN-1a and 35.0 ppm in BN-2a, similar to some of the previously reported <sup>11</sup>B chemical shifts in 1,2-azaborine compounds.<sup>[9b,12]</sup> BN-1a and BN-2a were fully characterized by NMR and HRMS analyses. The <sup>1</sup>H NMR spectral assignments for both compounds were completed with 2D NOESY NMR data, which



**Figure 2.** UV/Vis (top) and fluorescence (bottom) spectra showing the conversion of BN-2 and BN-3 in toluene ( $\approx 1.0 \times 10^{-5}$  M) and BN-2 in a PMMA film ( $\approx 10$  wt%) to their corresponding azaborines ( $\lambda_{ex} = 300$  nm for BN-2 and 350 nm for BN-3). Inset photographs show the color change (top) of BN-2 and BN-3 before and after irradiation, and the fluorescence colors (bottom) of BN-2a and BN-3a in solution, and BN-2a in PMMA film (far right,  $\approx 10$  wt%) on a glass slide patterned with a mask (the dark area is BN-2/PMMA film).

agree well with DFT-calculated <sup>1</sup>H NMR spectral patterns (see the Supporting Information). The quantum efficiency for the conversion of BN- $2 \rightarrow$ BN-2a was determined to be approximately 4.4%, which is fairly efficient for photochemical reactions. The elimination of methane and the formation of BN-4a from BN-4 were confirmed by NMR and HRMS data. However, the reaction of BN-4 is not as clean as that of BN-1 and BN-2. With prolonged irradiation, the presence of side products, which were not fully characterized, was evident in the <sup>1</sup>H NMR spectra.

The benzothiazole compound BN-3 undergoes a similar photoelimination as BN-1 upon irradiation at 350 nm, forming compound BN-3a as the major product with the elimination of one mesityl group. NMR and HRMS data established that BN-3a is an analogue of BN-1a and BN-2a. Bright yellow-orange crystals of BN-3a were obtained and the crystal structure of BN-3a was successfully determined by X-ray diffraction analysis (Figure 1). The mesityl ring is approximately perpendicular to the azaborine ring (the dihedral angle between the two rings is 102.1°). The lengths of the B-N, B-C, and C-C bonds of the azaborine ring in BN-3a from the X-ray data match very well with those of the DFT-optimized structure and are similar to those of the previously reported azaborine compounds.<sup>[6d, 12a, 13]</sup> The molecules of BN-3a form one-dimensional and partially  $\pi$ -stacked columns in the crystal lattice with the shortest atomic separation distance between the two neighboring aryl rings being 3.52 Å (Figure 1).

BN-1a, BN-2a, and BN-3a are stable for days in the solid state and slowly degrade in solution upon exposure to air. In contrast, BN-4a decomposes rapidly in solution and in the solid state under air, presumably because of the reaction with molecular oxygen.<sup>[14]</sup> The greater chemical stability of BN-1a to BN-3a is clearly provided by the bulky mesityl group. Compounds BN-1a, BN-2a, and BN-4a are previously

unknown isomers of B,N phenanthrenes. Three other isomers of B,N phenanthrene and their derivatives (A-C) were reported previously.<sup>[8b, 13b, 15]</sup> The aromaticity of the new B,N phenanthrene compounds are corroborated by the nucleus-



independent chemical shifts (NICS) obtained from DFT computational data (see the Supporting Information).

Most remarkable is the observation that the photoelimination reactions of all four precursors can also occur in the solid state when a polymer film, such as poly(methyl methacrylate) (PMMA) or poly(N-vinylcarbazole) (PVK), are doped with these precursors. The UV/Vis spectra of all four compounds in PMMA films undergo a similar change as those recorded in toluene upon irradiation by UV light, supporting that the same azaborine species are formed. The UV/Vis spectra for BN-2/PMMA with UV irradiation are shown in Figure 2, those of BN-1, BN-3, and BN-4 in PMMA are provided in the Supporting Information.

Unlike the non-emissive precursor compounds, all four azaborine compounds display bright green or yellow-green fluorescence in solution and in the solid state (see Figure 2, Table 1, and the Supporting Information). Thus, the photo-

Table 1: Photophysical properties of BN-1 a to BN-4a.

	$\lambda_{abs}$ [nm] <sup>[a]</sup>	$\lambda_{ m em}^{[b]}$ [nm] ( $\Phi_{ m FL}$ )	PMMA <sup>[c]</sup> $\lambda_{abs}/\lambda_{em}$ [nm]	H→L [nm]// <sup>f<sup>d]</sup></sup>
BN-1a	422, 447, 470	493, 513 (0.27)	447, 470/505	410/0.185
BN- <b>2</b> a	428, 455, 478	500 (1.00)	452, 476/510	421/0.199
BN- <b>3 a</b>	430, 455, 481	524 (0.16)	455, 483/514	425/0.141
BN- <b>4 a</b>	425, 449, 474	509 (1.00)	454, 479/507	422/0.223

[a] In toluene. [b] In toluene,  $\Phi_{FL}$  was determined using Ir(ppy)<sub>3</sub> ( $\Phi = 0.92$ )<sup>[19]</sup> as the standard under N<sub>2</sub> atmosphere. [c] around 10 wt%. [d] From TD-DFT data.

elimination reaction can also be followed conveniently by fluorescence spectroscopy. Compared to the previously reported B,N phenanthrene isomers  $A-C^{[13b,15]}$  and phenanthrene,<sup>[13b,16]</sup> the absorption spectra of BN-1a, BN-2a, and BN-4a are red-shifted by 50-100 nm. The fluorescence spectra of the new B,N phenanthrene isomers are red-shifted by approximately 150–160 nm relative to phenanthrene,<sup>[13b,16]</sup> 170–180 nm to B,N phenanthrene A (R' = H, R = Ph orH),<sup>[13b]</sup> and 40–50 nm to B,N phenanthrene C (R' = H, R = H, nBu, Ph, SiMe<sub>3</sub>).<sup>[13b]</sup> The relatively low absorption and emission energies of the new B,N phenanthrene molecules may be attributed to their greater polarity, compared to isomers A and C. The fluorescent quantum efficiency  $\Phi_{\rm FL}$  was determined to be 0.27, around 1.00, 0.16, and around 1.00 for BN-1a, BN-2a, BN-3a, and BN-4a, respectively. Compounds BN-2a and BN-4a are the brightest emitters among all known B,N phenanthrene compounds. The much greater  $\Phi_{\rm FL}$  of BN-2a and BN-4a compared to that of BN-1a can be attributed to the diminished intermolecular interactions of BN-2a and BN-4a as a result of the presence of two extra methyl groups on the B,N phenanthrene ring. In fact, compound BN-1a shows concentration-dependent fluorescence in solution (see the Supporting Information). In addition, the fluorescence spectrum of BN-1a in a PMMA film is also significantly redshifted and the emission intensity is diminished as the concentration of BN-1a in the film increases (see the Supporting Information), while similar concentration-dependent fluorescence in solution and in PMMA films were not observed for BN-2a, BN-3a, and BN-4a. The relatively low  $\Phi_{\rm FL}$  of BN-3a may be caused by the benzothiazolyl ring. Because of the contrasting non-emissive and emissive properties of the precursor compounds and the azaborine compounds, patterned fluorescent films with a high contrast can be obtained by simply casting the precursor PMMA film on a glass substrate, then covering the film with a mask and exposing it to UV light. One example of such patterned films is shown in Figure 2 (see the Supporting Information for other examples.)

The absorption and fluorescence spectra of BN-1a, BN-2a, and BN-4a are strikingly similar, despite their different substituents, which is an indication that the low-energy electronic transitions in these molecules are most likely dictated by the B,N phenanthrene unit. Photoelimination reactions are known for many organic compounds, such as azo, azide, and ketone compounds.<sup>[17]</sup> They are however rare for organoboron compounds.<sup>[11e]</sup> To understand the unusual photoelimination reaction and the photophysical properties of the new azaborine compounds, time-dependent DFT (TD-DFT) computational studies were performed for the precursors and the azaborine compounds. In addition, computational studies were also performed for BN-5a, an analogue of BN-1a with the mesityl group being replaced by an H atom, and 9-mesitylphenanthrene for comparison (see the Supporting Information).

The computational results show consistently that the HOMO -> LUMO transition has a high oscillator strength and is responsible for the low-energy absorption band of all B,N phenanthrene compounds (Table 1). The HOMO and LUMO levels of BN-1a, BN-2a, BN-4a, and BN-5a are localized on the B,N phenanthrene ring with no or little contributions from the substituents (Figure 3). Similarly, for the benzothiazolyl compound BN-3a, the HOMO and LUMO levels are localized at the B-N-containing arene ring. Thus, the fluorescence of the new azaborine compounds can be attributed to a  $\pi \rightarrow \pi^*$  transition of the  $\pi$ -conjugated azaborine unit. Because of the lack of significant contributions from the R groups to this transition, the calculated energy of this transition displays only small variations for BN-1a, BN-2a, BN-4a, and BN-5a (see Table 1 and the Supporting Information), which is in good agreement with the experimental data. The transition-energy difference of approximately 10 nm between BN-1a and BN-2a can be attributed to the induction effect of the methyl substituents. The HOMO -> LUMO transition of 9-mesitylphenanthrene is also localized on the phenanthrene ring, but at a much higher energy (300 nm) and with a much lower oscillator strength (0.081) relative to BN-1a. Compared to 9-mesitylphenanthrene, the LUMO level of



*Figure 3.* Diagrams of the key orbitals involved in the electronic transitions that are mainly responsible for the low-energy absorption bands of BN-1 and BN-1 a with an isocontour value of 0.04.

BN-1a is stabilized by 0.52 eV, while the HOMO level is destabilized by 0.85 eV. Thus, the key impact of B–N moiety in phenanthrene is to narrow the HOMO–LUMO gap and decrease the  $\pi \rightarrow \pi^*$  transition energy. This result is in agreement with the general trend observed previously for azaborine compounds,<sup>[13b,18]</sup> with the exception of B,N phenanthrene **A** (**R** = **R**' = **H**), which has a higher HOMO–LUMO transition energy than phenanthrene.<sup>[13b,15b]</sup>

In order to achieve efficient conversion to the azaborine compounds, it is necessary to irradiate the precursor compounds near the absorption maximum of the first absorption band of the B,N heterocycles. TD-DFT data indicate that the electronic transitions responsible for this band in the precursor compounds are mainly from the HOMO-4/HOMO- $6 \rightarrow LUMO$  transitions for BN-1 and BN-2, HOMO-4 $\rightarrow$ LUMO transition for BN-3, and HOMO-1/HOMO-2 $\rightarrow$ LUMO transitions for BN-4. The HOMO-x orbitals involved in these transitions all have large contributions from the B- $C_{R}$   $\sigma$  bonds and some contributions from the methylene C-H  $\sigma$  bonds (see Figure 3 and the Supporting Information) while the LUMO level is localized on the phenylpyridine or phenylbenzothiazolyl unit. Hence, it is conceivable that when excited at energies near these absorption bands, the  $B-C_R \sigma$  bonds are significantly weakened, which is likely the key step responsible for the eventual elimination of a mesitylene or a methane molecule from the B,N-heterocyclic compounds. For the previously reported B(ppy)Mes<sub>2</sub> and its the facile photochromism, with the HOMO being dominated by a  $\pi$  orbital of the mesityl group with no contributions at all from the B–C $_{\text{Mes}}$   $\sigma$  bonds, and the LUMO being dominated mainly from the ppy  $\pi^*$  orbitals.<sup>[11a,b]</sup> The contrasting electronic properties of BN-1 to BN-4 and B(ppy)Mes<sub>2</sub> are clearly responsible for their distinct response toward light. Lastly, based on the electronic potential energy at 0 K obtained from DFT computational data, the products of the photoelimination reaction are lower in energy than the B,N-heterocyclic reactants for all four compounds. The photoelimination reaction is therefore thermodynamically favored, and driven mostly by entropy and the aromatization energy.

In summary, an unprecedented photoelimination reaction of B,N-heterocyclic compounds has been discovered, which can be used effectively for the formation of new  $\pi$ -conjugated polycyclic azaborine compounds by eliminating an R–H molecule from a BR<sub>2</sub>–CH<sub>2</sub> unit. The photoelimination is applicable to solid substrates, such as PMMA or PVK films doped with B,N-heterocyclic compounds. This makes it a simple and convenient method for the in situ generation of new polycyclic azaborine compounds in polymer substrates and for creating patterned fluorescent polymer films by light, which may find applications in the fabrication of optoelectronic devices.

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