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Authors: Kelsie Krantz, Sarah Weisflog, Nathan Frey, Wenlong Yang, Diane Dickie, Charles Ediwn Webster, and Robert J Gilliard

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Planar, Stair-stepped, and Twisted: Modulating Structure and Photophysics in Pyrene- and Benzene-Fused *N*-Heterocyclic Boranes

Kelsie E. Krantz,^[a] Sarah L. Weisflog,^[a] Nathan C. Frey,^[b] Wenlong Yang,^[a] Diane A. Dickie,^[a] Charles Edwin Webster^{*,[b]} and Robert J. Gilliard, Jr.^{*,[a]}

- [a] Kelsie E. Krantz, Sarah L. Weisflog, Dr. Wenlong Yang, Dr. Diane A. Dickie, Prof. Dr. Robert J. Gilliard, Jr.
 Department of Chemistry, University of Virginia
 409 McCormick Rd./ PO Box 400319, Charlottesville, VA 22904 (USA)
 E-mail: rjg8s@virginia.edu
- [b] Nathan C. Frey, Prof. Dr. Charles Edwin Webster Department of Chemistry, Mississippi State University Box 9573, Mississippi State, MS 39762 (USA) E-mail: ewebster@chemistry.msstate.edu

ABSTRACT: Because of their rigidity, polycyclic aromatic hydrocarbons (PAHs) have become a significant building block in molecular materials chemistry. Fusion or doping of boron into PAHs is known to improve the optoelectronic properties by reducing the LUMO energy level. Herein, we report a comprehensive study on the syntheses, structures, and photophysical properties of a new class of fused *N*-heterocyclic boranes (NHBs), pyrene- and benzene-linked in a "Janus-type" fashion (**2-4**, **6-9**, and **11**). Remarkably, these examples of fused NHBs display fluorescent properties, and collectively their emission spans the visible spectrum. The pyrene-fused NHBs all display blue fluorescence, as the excitations are dominated by the pyrene core. In notable contrast, the emission properties of the benzene-fused analogues are highly tunable and is dependent on the electronics of the NHB fragments (i.e., the functional group directly bound to the boron atoms). Pyrene-fused **2-4** and **11** represent the only molecules in which the K-region of pyrene is functionalized with NHB units, and while they exhibit distorted (twisted or stair-stepped) pyrene cores, benzene-fused **6-9** are planar. The electronic structure and optical properties of these materials were probed by computational studies, including an evaluation of aromaticity, electronic transitions, and molecular orbitals.

INTRODUCTION

The dramatic increase in the synthesis of chemical compounds that contain N-heterocyclic borane (NHB) (C₂N₂B-R, also called diazaborole) moieties may be traced to the seminal discovery of boryllithium.^[1] Since then, anionic NHBs^[2] (i.e., boryl ligands) have been widely used as ligands in main-group^[3] and transition metal chemistry,^[4] particularly in the synthesis of compounds featuring new heteronuclear bonds. Additionally, diazaboroles and their polymeric analogues^[5] have been synthesized for their photoluminescent properties potentially useful for optoelectronic devices.^[6] Fusing multiple NHB units together in a "Janus-type" fashion, and thus adding an element of bifunctionality, has received significantly less attention. These types of compounds are extremely rare, mostly due to synthetic difficulty and thermodynamic instability.^[7] Cowley and coworkers isolated a cationic pyracene-fused NHB that displayed multielectron redox behavior due to the ligand's ability to readily undergo reduction (Figure 1a).^[8] More recently, Kinjo et al. reported boron-based tetraaminoethylene radical cations derived from the boryl-linked tetraazaolefin (Figure 1b).^[9] Last year, Weber et. al isolated and structurally characterized a methylated benzene-fused bis(diazaborole).^[10] Notably, this was the first example of a benzenefused bis(diazaborole) that was characterized structurally by X-ray diffraction. However, photophysical data was unable to be obtained due to rapid decomposition of UV-vis samples. Other examples of fused-NHBs with benzene^[11] and guinone^[12] cores have been incorporated into field effect transistors, but their structural properties were not studied. Despite these

advances, a comprehensive study of both the structural and photophysical properties of fused-

NHBs linked by polycyclic aromatic hydrocarbons (PAHs) is hitherto unknown.



Figure 1. a) Pyracene-fused *N*-heterocyclic borane with redox properties; b) boryl-linked tetraazaolefin that oxidizes to the radical cation; c) methylated benzene-fused bis(diazaborole) d) This work: neutral pyrene-and benzene-fused *N*-heterocyclic boranes featuring structural distortions and luminescent properties.

Owing to boron's empty p_z -orbital, the incorporation of boron into aromatic systems can result in π -conjugation, important for inducing electronic properties useful in optoelectronics,^[13] sensor technology,^[14] and fluorescent dyes.^[15] Pyrene, a blue-chromophore, has served as a ubiquitous building block in electronic devices.^[16] In recent years, boron-doped pyrene-based molecules have become popular with main-group chemists, with the goal of understanding structure-property relationships in new functional materials.^[17] For example, tethering boron to pyrene is known to reduce the LUMO energy and increase the acceptor character by lowering the energy needed for absorption and emission.^[17a, 18] However, studies of compounds containing boron bound to pyrene

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have been limited due to challenging synthetic routes associated with modifying pyrene.^[19] Indeed, functionalization at the K-region of pyrene often requires multi-step syntheses with low overall yields, and electrophilic substitution at the 1-, 3-, 6-, and 8-positions is preferred (i.e, where the HOMO lies).^[16, 20] Recently, we have been exploring doping PAHs with boron,^[21] and attaching main-group element fragments to the K-region of pyrene (Figure S1). This lead to the first pyrenefused *N*-heterocyclic germylenes (NHGe), which display extremely twisted molecular structures.^[22]

Herein we report the syntheses, molecular structures, photophysical properties, and extensive computational studies of pyrene- and benzene-fused NHBs (Figure 1d). Remarkably, the pyrene derivatives **2-4** and **11** are the first examples of compounds in which an NHB moiety is fused to the K-region of pyrene, and they display twisted or stair-stepped structures. In contrast, the benzene-fused compounds **6-9** are planar and possess tunable optical properties based on the electronics of the NHB moieties. It is noteworthy that these are the first fused-NHBs that exhibit fluorescent properties spanning the full visible spectrum.

RESULTS AND DISCUSSION

We began our studies by synthesizing a tetramine with sterically demanding *N*-(2,6diisopropylphenyl) groups. However, due to low yields in the multi-step synthetic route we switched to the less bulky *N*-(*tert*-butyl) tetramine (**1**), prepared using a Buchwald-Hartwig amination (Scheme 1).^[23] Dehydrogenation of **1** and BH₃•THF at 110 °C gave compound **2** as a pale-yellow solid in 77% yield. In the ¹H NMR spectrum, a downfield shift in the resonance (1.26 to 1.66 ppm) assigned to the *N*-(*tert*-butyl) protons represent the decrease in electron density at the nitrogen atoms, where the lone pairs fill the *p*-orbital of boron. A resonance was not observed in the ¹¹B{¹H} NMR spectrum, which was attributed to quadrupolar line broadening.



Scheme 1. Synthesis of pyrene-fused *N*-heterocyclic boranes.

Yellow plate-shaped air- and moisture-sensitive single crystals of **2** suitable for X-ray diffraction studies were obtained from a concentrated toluene solution at -37 °C. An overall twisted structure of **2** was observed, comparable to our pyrene-fused NHGe,^[22] but with smaller "twist angles"^[24] [C2–C2–C2'–C1' (40°) and N2–N1–N2'–N1' (52°)] (Figure 2a). However, the twist angles of **2** are still substantial compared to known pyrene-fused molecules which span two benzene rings (Figure 2b).^[25]



Figure 2. Molecular structure of **2**: a) front view, b) side view. Thermal ellipsoids shown at 50% probability and H atoms (except B-H) were omitted for clarity. Selected bond lengths (Å) and angles (°): B1–H1: 1.15(3); B1–N1: 1.421(7); B1–N2: 1.433(7); C2–C1–C2'–C1': 40; N2–N1–N2'–N1': 52.

Compound **3** was isolated by *in-situ* lithiation of **1** and subsequent salt elimination to give a green solid in 32% yield (Scheme 1). A downfield shift in resonance from 1.26 to 1.79 ppm for the *N*-(*tert*-butyl) protons was observed in the ¹H NMR spectrum. In the ¹¹B{¹H} NMR spectrum, a broad singlet at 25.7 ppm was attributed to the two chemically equivalent boron atoms. In the ¹⁹F NMR spectrum, two broad resonances separated by 0.06 ppm (-125.64 and -125.70 ppm) were observed in approximately 20:80 ratio. These peaks were assigned to both ¹⁰B (*I* = 3) and ¹¹B (*I* = 3/2) coupling to ¹⁹F. However, due to rapid quadrupolar relaxation the coupling constants could not be determined.



Figure 3. Molecular structure of **3**: a) front view, b) side view. Thermal ellipsoids shown at 50% probability and H atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): B1–F1: 1.335(4); B1–N1: 1.419(5); B1–N2: 1.423(5); C1–C2–C1'–C2': 0; N1-N2-N1'-N2': 0, C3–C2–C1–C7: 20.

Pale green plate-shaped air- and moisture-sensitive single crystals of **3** suitable for X-ray studies were obtained from a concentrated toluene/hexane (1:1) mixture at -37 °C (Figure 3a). Unlike the twisted structure of **2**, 0° "twist angles" are observed, and the middle four rings of **3** are

distorted out of plane in a stair-step fashion with a 20° C3–C2–C1–C7 torsion angle (Figure 3b). The 6-membered rings of pyrene not interacting with nitrogen atoms remain coplanar. It is noteworthy that **3** is the first structurally characterized NHB bearing a terminal boron monofluoride unit.

Lithiation and subsequent salt elimination of **1** with PhBCl₂ afforded a light orange solid of **4** in 47% yield (Scheme 1). The ¹H NMR spectrum showed a downfield shift in resonance from 1.26 to 1.61 ppm which integrated to 36, and was attributed to the *N*-(*tert*-butyl) protons. In the ¹¹B{¹H} NMR, a broad singlet at 33.1 ppm was assigned to the two chemically equivalent boron atoms.

Yellow rod-shaped air- and moisture-sensitive single-crystals of **4** suitable for X-ray diffraction studies were obtained from a concentrated hexanes solution at -37 °C (Figure 4a). Compound **4** displayed a distorted pyrene core similar to **3** (Figure 4b), but with a larger torsion angle [28° for C3–C2–C1–C7 plane]. Additionally, the boron-bound phenyl rings are twisted away from the 5-membered rings, yielding a 60° C22–C21–B1–N2 torsion angle, while the geometry around the boron atoms remains trigonal planar.



Figure 4. Molecular structure of **4**: a) front view, b) side view. Thermal ellipsoids shown at 50% probability. H atoms and co-crystallized solvent were omitted for clarity. Selected bond lengths (Å) and angles (°): B1–C21: 1.573(4); B1–N1: 1.453(4); B1–N2: 1.448(5); C1–C2–C1'–C2': 0; N1–N2–N1'–N2': 0, C3–C2–C1–C7: 28; C22–C21–B1–N2: 60.

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We were then interested in obtaining fused boranes in which the entire molecule is planar, to study how the linker and topography of the structure affects the photophysical properties. Due to its tunable pH-dependent colorimetric properties, we targeted fused systems based on an N-alkyl substituted benzene tetramine.^[26] Using the tetramine (5)^[27] and similar reaction conditions used for making compounds 2-4, the benzene-fused compounds 6-8, (Scheme 2) were synthesized in 62, 48, and 50% yields respectively. In the ¹H NMR spectra, a downfield shift from 1.29 to 1.65 (for 6), 1.43 (for 7), and 1.54 ppm (for 8) for the N-tert-butyl protons were consistent with the formation new products. In the ¹¹B{¹H} NMR spectra, chemical shifts of 5.4 (for 7), 28.4 (for 8), 30.0 ppm (for 9) were attributed to the chemically equivalent boron environments. Similar to 2, no ¹¹B{¹H} NMR chemical shift was observed for **6** due to guadrupolar line broadening. In the ¹⁹F NMR spectrum of 7, a standard 1:1:1:1 guartet resonance was observed at -151.8 ppm which was attributed to the presence of two BF₂ units (${}^{1}J_{BF}$ = 56.4 Hz). Compound **7** forms via loss of LiH after the first deprotonation due to the resonance structure that can be obtained when the nitrogen-based electrons are delocalized onto the benzene ring of 5. The loss of LiH prohibits all four deprotonation events occurring, and accordingly, only two equivalents of LiF are eliminated. Though the specific reasons for the mechanistic differences between 3 and 7 are unclear, this underscores the ability of the two linking *π*-systems to facilitate the formation of diverse structural arrangements.



Scheme 2. Synthesis of benzene-fused N-heterocyclic boranes.

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Air- and moisture-sensitive colorless rod-shaped crystals of **6** suitable for X-ray studies were obtained from a concentrated solution in toluene at 110 °C and subsequent cooling to room temperature (Figure 5a). Unlike **2**, compound **6** displayed a completely planar structure (Figure 5b). The B1–H1 [1.140(17) Å] bond lengths were comparable to those in **2** [1.15(3) Å].



Figure 5. Molecular structure of **6**: a) front view, b) view showing planarity of benzene. Thermal ellipsoids shown at 50% probability and H atoms except for boron bound H were omitted for clarity. Selected bond lengths (Å): B1–H1: 1.140(17); B1–N1: 1.426(2); B1–N2: 1.426(2); N1–C2: 1.4166(18); C1–C2: 1.395(2); C1–C3': 1.398(2).

Pink cube-shaped crystals of **7** suitable for X-ray studies were obtained from a concentrated THF solution at room temperature (Figure 6a). Similar to **6**, compound **7** displayed a planar structure (Figure 6b). The system, which indeed contains two BF₂ units, can be best described as a zwitterionic molecule with two positive charges delocalized over the benzene core and a negative charge localized on each boron atom. This interpretation is further supported by the bond lengths of C1–C2 [1.3968(12) Å] and C1–C3' [1.5062(12) Å] which suggest that the π -electrons are delocalized across the N1–C1–C2–C3–N2 atoms and not within the central 6-membered ring. This description is also consistent with reported bis(boron difluoride) complex [(BF₂)₂(µ-4-EtAp)] (Ap = azophenine),^[28] platinum *N'*,*N'*,*N'*,*N''*-diboronazophenine complexes,^[29]

and the $[(ttmgb)(BF_2)_2](BF_4)_2$ (ttmgb = 1,2,3,4-tetrakis(tetramethylguanidinyl)benzene) salt.^[30] Additionally, the B–F bond lengths [1.3906(12) and 1.3853(12) Å] are slightly longer than the B1– F1 bond [1.335(4) Å] in the pyrene complex **3**.



Figure 6. Molecular structure of **7**: a) front view, b) view showing planarity of benzene. Thermal ellipsoids shown at 50% probability and H atoms were omitted for clarity. Selected bond lengths (Å): B1–F1: 1.3906(12); B1–F2: 1.3853(12); B1–N1: 1.5690(13), B1–N2: 1.5678(13), C1–N1: 1.3266(11); C1–C2: 1.3968(12); C1–C3': 1.5062(12).

Colorless plate-shaped single crystals of **8** suitable for X-ray studies were obtained from a concentrated toluene solution at -37 °C (Figure 7a). The molecular structure showed a planar benzene-fused NHB with orthogonal phenyl groups bound to boron (Figure 7b). In contrast to **4**, the phenyl groups in compound **8** are perpendicular to the boron plane, with a C13–C12–B1–N1 torsion angle of 93°.



Figure 7. Molecular structure of **8**: a) front view, b) view showing planarity of benzene. Thermal ellipsoids shown at 50% probability and H atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): B1–N1: 1.4436(19), B1–N2: 1.440(2), B1–C12: 1.609(6); C13–C12–B1–N1: 93.

Probing the acidity of compound **6** was then of interest, and we explored this by the addition of a strong base (Scheme 3). Two equivalents of *n*-butyllithium were added to a mixture of **6** in THF. The absence of a resonance in the ⁷Li NMR spectrum supported the elimination of LiH rather than the formation of a tetracoordinate Li borate salt. Further analysis of the reaction revealed that the B–*H* substituent on **6** is more hydridic than acidic, and thus compound **9** was isolated as a white crystalline solid (50% isolated yield). A broad resonance at 30.0 ppm was observed in the ¹¹B{¹H} NMR spectrum which was very similar to the shift of **8** (28.4 ppm).

Plate-shaped colorless single crystals of **9** suitable for X-ray analysis were grown from a concentrated toluene solution at -37 °C (Figure 8a). Compound **9** exhibited a planar structure with the *n*-butyl groups oriented trans to each other (Figure 8b). The B1–C12 bond length [1.589(8) Å] was comparable to the B1–C12 bond [1.609(6) Å] of **8**.



Figure 8. Molecular structure of **9**: a) front view, b) view showing planarity of benzene. Thermal ellipsoids shown at 50% probability and H atoms were omitted for clarity. Selected bond lengths (Å): B1–N1: 1.439(7), B1–N2: 1.460(7), B1–C12: 1.589(8).

To gain insight into the photophysical properties of **2-4** and **6-9**, UV-vis and fluorescence studies were performed. Absorption maxima of **2-4** were exhibited at 395, 377, and 405 nm,

respectively, assignable to $\pi - \pi^*$ transitions (Figure 10a). Emission maxima for the pyrene-fused NHBs (2-4) were shown at 442, 456, and 457 nm, respectively (Figure 10b), which were all hypsochromically shifted with respect to the tetramine starting material (1). Due to the high contribution of the pyrene core in these excitations, they all emit blue fluorescence under UV-light. The benzene-fused molecules (6-9) have absorption maxima at 326, 384, 387, and 320 nm, respectively, which were all assignable to $\pi - \pi^*$ transitions (Figure 10c). Emission maxima for the benzene-fused NHBs (6-9) were shown at 346, 415, 489, and 350 nm, respectively, and were attributed to π^* - π transitions (Figure 10d). Compounds **7** and **8** were bathochromically shifted with respect to the tetramine starting material (5) while compounds 6 and 9 were hypsochromically shifted. In addition to the experimental studies, the electronic structure and transitions of the fused-NHBs were investigated by DFT calculations (B3LYP/BS1 level of theory), which supported the aforementioned assignments. (see SI for details including natural transition orbitals). In the benzene-fused NHBs, the color of emission varies significantly based on the substituent bound to boron. This major difference is due to the NHB rings contributing more hole to particle (6, 88%-30%, see Figure S78), while the NHB rings in the pyrene-fused compounds contribute much less (2, 49%-24%). Notably, 6-9 all emit in the NIR region which is promising for optoelectronic materials, specifically fluorescent probes.^[31]



Figure 10. a) UV-vis absorption of **1-4**; b) emission of **1-4**; c) UV-vis absorption of **5-9**; d) emission of **6-9**. All samples were dissolved in toluene and ran at room temperature. Compounds **1-4** were excited at 380 nm and **5-9** were excited at 310 nm.

We then desired to explore the photophysical properties of a planar pyrene-fused NHB to test if the fluorescence could be tuned in a manner similar to the benzene-fused NHBs. Therefore, we replaced the *N*-(*tert*-butyl) substituents with less bulky *N*-methyl groups to limit steric interactions with the pyrene-C-*H*. Compound **10** was isolated in 45% yield via Buchwald-Hartwig amination (see SI for experimental details). Lithiation of **10** and successive salt elimination with PhBCl₂ gave **11** as a yellow solid in 66% yield (Scheme 3).





Scheme 3. Synthesis of pyrene-fused N-heterocyclic borane (N-methyl).

Yellow rod-shaped single crystals of **11** were obtained from a concentrated toluene/THF (10:1) mixture at room temperature (Figure 9a). As expected, the overall structure revealed a more planar pyrene core, albeit not completely flat (Figure 9b). Examination of the space-filling model (Figure S29) clearly shows that the methyl protons still interact with the hydrogen atoms on pyrene to yield a slight distortion from planarity. The C3-C2-C1-C7 torsion angle in **11** (11°) is significantly smaller than that in **4** (28°). The decrease in steric bulk at nitrogen also impacts the rotation of the B-Ph group. Consequently, compound **11** displayed the smallest torsion angle for the C20-C15-B1-N2 plane (49°) compared to the same angle in **4** (60°) and benzene-fused **8** (93°).



Figure 9. Molecular structure of **11**: a) front view, b) side view. Thermal ellipsoids shown at 50% probability and H atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): B1–C15: 1.5669(19); B1–

N1: 1.4291(18); B1–N2: 1.4272(18); C1–C2–C1'–C2': 0; N1–N2–N1'–N2': 0, C3–C2–C1–C7: 11; C22–C21–B1–N2: 49.

The absorption (366 nm) and emission maxima (487 nm) of **10** were comparable to that of **1** $(\lambda_{abs} = 369 \text{ nm}, \lambda_{em} = 493 \text{ nm})^{[22]}$ (Figure 11). Conversely, a significant difference in the appearance of the absorption and emission features of **11** $(\lambda_{abs} = 392 \text{ nm}, \lambda_{em} = 419 \text{ nm})$ was observed in contrast to **4**. Additionally, the emission maximum was substantially blue-shifted from **4**. Since the blue emission color of **11** is not drastically different from **2-4**, it supports the use of pyrene-based molecules as blue emitters in organic light emitting diodes. However, this also highlights the benefit of the benzene-fused materials (i.e., in terms of tunable optical properties by eye).



Figure 11. a) UV-vis absorption of **10** and **11**; b) emission of **10** and **11**. Samples were dissolved in toluene and run at room temperature. Compound **10** was excited at 365 nm and **11** was excited at 380 nm.

In the pyrene-fused molecules, the HOMO and LUMO are all delocalized throughout the pyrene core with minimal electron density at boron (Figure 12). However, benzene-fused **6**, **8**, and **9** all have HOMOs that are localized on boron and the benzene core (Figure 13). Nodal planes pass directly through the middle of the compounds, parallel to the boron atoms. In contrast, the HOMO and LUMO of compound **7** are delocalized on the carbon and nitrogen backbone with

no localization on boron, which is consistent with its zwitterionic structure. Unlike **6** and **9**, the LUMO of compound **8** is localized on the outer phenyl rings rather than the boron atoms and benzene core. These results validate the boron-dependent electronics and the substantial difference in emission colors observed under UV light. In the pyrene-fused NHBs (**2-4**, and **11**) the frontier orbitals are only pyrene-based whereas the HOMO/LUMOs of the benzene-fused NHBs (**6-9**) include the 5-membered boron heterocyclic rings. Notably, the LUMO of compound **8** is the only example where the frontier orbitals are extended to the boron-bound substituent outside of the ring (phenyl groups). Additionally, the fused NHBs possess large HOMO-LUMO gaps that cover a broad range of energies (2.88-4.84 eV) that could be promising for materials applications that require wide band gaps.^[32]



Figure 12. Frontier orbitals of pyrene-fused NHBs 2-4 and 11.



Figure 13. Frontier orbitals of benzene-fused NHBs 6-9.

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To further investigate the electronic contributions to aromaticity in the fused NHBs and how this was affected by structural distortions, Nucleus Independent Chemical Shifts (NICS(0)) were computed for each ring (Table 1). For the pyrene-fused NHBs, the NICS(0) values for B/B' and C/C' rings in the pyrene core are consistent across all compounds. As expected, the C/C' rings are the most aromatic in the pyrene core, and maintain their status as π -electron sextets as supported by Clar's theory.^[33] However, the NICS(0) values for ring A/A', the 5-membered boron containing rings, change dramatically throughout all molecules. These changes can be attributed to the differences in the electronic and geometric structures influenced by nitrogen-alkyl group, boron-functional group, and the fused aromatic core. An overall trend of more negative values for the A/A' rings in the benzene-fused NHBs is observed in comparison to the pyrene-fused analogues (with the exception of 7). This can be attributed to the electronic contribution and delocalization of the HOMO on the NHB in 6, 8, and 9 unlike 2-4, and 11. Notably, the NICS(0) values for ring A/A' in 7 are significantly higher than those found in the other compounds due to the borate drastically altering the electronics and removing all aromatic character from the center 6-membered ring (E). Consequently, the NICS(0) value for ring E in 7 is positive, a major contrast from any other molecule in this study. Compounds 6, 8, and 9 all retain aromaticity in ring E as justified by the negative values.

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Table 1. NICS(0) values (B3LYP/BS2 level of theory) of

Compound	A/A'	B/B'	C/C'	D/D'	Е
2	-6 30	_/ 95	-10.47		
2	-0.00	-4.00	40.70		
3	-5.80	-5.29	-10.78	_	_
4	-4.84	-4.44	-10.56	-7.09	_
6	-7.98	-	-	-	-11.77
7	-1.70	-	-	-	4.08
8	-7.56	-	-	-7.33	-11.44
9	-7.87	-	-	-	-11.51
10	-	-5.07	-11.65	-	_
11	-4.84	-4.44	-10.56	-7.09	_

Conclusion

In conclusion, we have isolated, fully characterized, and investigated the photophysical properties of the first pyrene-fused NHBs, which display unique twisted or stair-stepped structures. We have also compared them to structurally related benzene-fused materials, which are all planar. The tunable optical properties of the benzene-fused NHBs make them promising candidates for functional materials due to their emission in the near-infrared region. The structural properties of the fused-NHBs confirm that the aromatic core (pyrene vs. benzene) plays a significant role in the overall electronic structure of the molecules. We believe that these new synthetic routes to molecules that would otherwise be challenging to access, as well as the tunability of this system, will spark new research efforts regarding the use of these compounds as main-group functional materials. Moreover, similar strategies may be successful for unraveling

the chemistry of distorted aromatic systems that incorporate other *p*-block elements and these efforts are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Information. All manipulations involving air- and moisture-sensitive compounds were carried out under inert atmosphere of purified argon using an MBRAUN LABmaster glovebox equipped with a -37 °C freezer, or standard Schlenk line techniques. All solvents were purified by distillation over sodium and benzophenone. Deuterated benzene was purchased from Cambridge Isotope Laboratories, purified by distillation over sodium, and degassed via several freeze-pumpthaw cycles. Glassware was oven-dried at 190 °C overnight. The NMR spectra were recorded at room temperature on a Bruker Advance 600 MHz spectrometer. Proton and carbon chemical shifts are reported in ppm and are referenced using the residual proton and carbon signals of the deuterated solvent (¹H; C₆D₆, δ 7.16; ¹³C; δ 128.1 ppm). Boron and fluorine chemical shifts are reported in ppm and referenced using external standards (¹¹B; BF₃•Et₂O, δ 0.0; ¹⁹F; C₆F₆, δ -164.9 ppm). The UV-visible and fluorescence spectra were recorded on a Cary 60 UV-vis Spectrophotometer and a Cary Eclipse Fluorescence Spectrophotometer. Sample solutions were prepared in toluene in 1 cm square air-free quartz cuvettes. Due to rapid decomposition at the low concentrations needed for obtaining accurate quantum yield data, we were unable to report these values for the fused-NHBs (this was also observed in Weber's compounds).^[34] Elemental analyses were performed on a Perkin Elmer 2400 Series II analyzer. Similarly to other reported fused-NHBs,^[34] we were unable to obtain C,H,N-values for **3**, **4**, **8**, and **11** due to air- and moisturesensitivity. All chemicals were purchased from commercial sources and used directly unless noted otherwise. The 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr•HCl)^[35], 4,5,9,10tetrabromo-2,7-ditert-butylpyrene^[36], and compound **1**^[22-23] were prepared according to the literature procedures.

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Compound 2. To a solution of compound **1** (0.300 g, 0.501 mmol) in toluene (15 mL), BH₃•THF (1 M in THF, 1.75 mL, 1.75 mmol) was added under argon. The yellow slurry was heated to 110 °C for 2 days until a yellow solution was observed. The reaction was cooled to room temperature and the pale-yellow solid was collected via filtration and washed with hexanes (5 mL) and the remaining solid was dried under reduced pressure to leave compound **4** (0.239 mg, 77% yield). Compound **4** can also be isolated from reaction of **2** with 2 eq. of BH₃•THF in toluene. ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 8.83 (s, 4H, CH_{pyr}), 1.88 (s, 36H, N(C(CH₃)₃)), 1.66 ppm (s, 18H, C(CH₃)₃). Unable to observe the BH due to the quadrupolar effect. ¹³C{¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 132.3, 129.3, 125.7, 125.2, 117.5, 54.5, 34.8, 32.6, 30.2 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): No shift was observed. Anal. Calcd for C₄₀H₆₀B₂N₄: C, 77.67; H, 9.78; N, 9.06%. Found: C, 77.18; H, 9.75; N, 9.02%.

Compound 3. To a -78 °C solution of compound **1** (0.200 mg, 0.334 mmol) in Et₂O (20 mL), *n*-BuLi (2.5 M in hexanes, 0.56 mL, 1.40 mmol) was added slowly. The orange solution was slowly warmed to room temperature and stirred for 20 hrs. The reaction mixture was cooled to -78 °C, and BF₃• Et₂O (0.08 mL, 0.668 mmol) was added. The reaction was slowly warmed to room temperature and the light green solution was stirred at room temperature for 22 hrs. The solvent was removed under reduced pressure, and the product was extracted from the green residue with toluene (30 mL). The mixture was filtered over celite to remove LiF salt. The solvent was removed from the filtrate to leave a crude green solid. The solid was washed with hexane (3 x 5 mL) to leave compound **3** as a light green solid (0.0698 g, 32% yield). Single crystals were obtained via 1:1 mixture of toluene/hexane at -37 °C. ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 8.57 (s, 4H, CH_{pyr}), 1.79 (s, 36H, N(C(CH₃)₃)), 1.60 ppm (s, 18H, C(CH₃)₃). ¹³C(¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 144.0, 131.0, 125.5, 117.2, 116.8, 55.1, 36.1, 33.2, 32.4 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): δ 25.7 ppm. ¹⁹F NMR (C₆D₆, 564.69 MHz): δ -125.7 ppm (d, *J* = 33.9 Hz, 1F).

Compound 4. To a -78 °C solution of compound **1** (500 mg, 0.835 mmol) in Et₂O (20 mL), *n*-BuLi (2.5 M in hexanes, 1.40 mL, 3.51 mmol) was added slowly. The orange solution was slowly warmed to room temperature and stirred for 17 hrs. The solvent was removed under reduced pressure and the orange residue was dissolved in toluene (50 mL), and PhBCl₂ (0.218 mL, 1.67 mmol) was added slowly. The reaction was stirred at room temperature for 21 hrs. The red mixture was filtered over celite to remove LiCl salt, and the solvent was removed from the filtrate to leave a crude red solid. The solid was washed with hexane (3 x 5 mL) to leave compound **4** as a pale orange solid (303.8 mg, 47% yield). ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 8.65 (s, 4H, *CH*_{pyr}), 7.96 (d, 4H, *o*-Ph*H*), 7.37 (t, 4H, *m*-Ph*H*), 7.29 (t, 2H, *p*-Ph*H*), 1.64 (s, 18H, C(*CH*₃)₃), 1.61 ppm (s, 36H, N(C(*CH*₃)₃))). ¹³C{¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 144.1, 134.6, 134.3, 126.4, 116.7, 116.0, 56.4, 36.2, 35.2, 32.4 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): δ 33.1 ppm.

Compound 5. Synthesis of compound **5** was modified from the reported literature.^[27] In a Schlenk tube 1,3-bis(2,6-diiso-propylphenyl)imidazolium chloride (IPr•HCI, 0.189 g, 0.444 mmol), [Pd(OAc)₂] (0.0513 g, 0.229 mmol), and NaO*t*Bu (0.0646 g, 0.673 mmol) were stirred in toluene (30 mL) at room temperature until a clear orange solution was observed. 1,2,4,5-tetrabromobenzene (5.00 g, 12.7 mmol) and NaO*t*Bu (5.98 g, 62.2 mmol) were then added to the orange solution. Under positive argon pressure, *tert*-butylamine (5.61 mL, 53.3 mmol) was added, and the resulting orange mixture was heated to 110 °C for 15 hrs. The mixture was cooled to room temperature and filtered over celite to remove NaBr salt. The solvent was removed from the filtrate to leave a brown solid. The crude solid was washed with hexane (3 x 20 mL) to leave compound **5** as a tan solid (3.93 g, 85% yield). ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 6.68 (s, 2H, CH_{benz}), 3.61 (s, 4H, NH), 1.29 ppm (s, 36H, N(C(CH₃)₃).

Compound 6. To a solution of compound **5** (1.00 g, 2.76 mmol) in toluene (100 mL), BH₃•THF (1 M in THF, 5.79 mL, 5.79 mmol) was added dropwise. The resulting yellow mixture was heated to

110 °C for 2 days. The mixture was then cooled to room temperature and the product was collected via filtration. The solid was washed with hexane (3 x 5 mL) to leave compound **5** as a white crystalline solid (0.650 g, 62% yield). Single crystals suitable for X-ray studies were grown from a refluxing toluene solution and slow cooling to room temperature. ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 7.66 (s, 2H, CH_{benz}), 1.65 ppm (s, 36H, N(C(CH₃)₃). Unable to observe the BH due to quadrupolar effect. ¹³C{¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 130.7, 100.6, 67.8, 52.4, 30.9 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): No shift was observed. Anal. Calcd for C₂₂H₄₀B₂N₄: C, 69.14; H, 10.55; N, 14.66%. Found: C, 68.64; H, 10.62; N, 14.54%.

Compound 7. To a -78 °C solution of compound **5** (0.200 g, 0.552 mmol) in THF (40 mL) *n*-BuLi (2.5 M in hexanes, 0.927 mL, 2.32 mmol) was added slowly. The red solution was slowly warmed to room temperature and stirred for 20 hrs. The solution was cooled to -78 °C, and BF₃• Et₂O (0.136 mL, 1.10 mmol) was added. The dark purple solution was stirred at room temperature for 24 hrs. The solvent was removed under reduced pressure, and the product was extracted from the purple solid residue with toluene (40 mL). The mixture was filtered over celite to remove LiF salts. The solvent was removed from the filtrate to leave a crude purple solid. The solid was recrystallized from a concentrated THF solution at room temperature to leave compound **7** as a purple crystalline solid (120 mg, 48% yield). ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 5.43 (s, 2H, CH_{benz}), 1.43 ppm (s, 36H, N(C(CH₃)₃). ¹³C{¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 155.9, 128.9, 55.2, 29.0, 28.3 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): δ 5.4 ppm. ¹⁹F NMR (C₆D₆, 564.69 MHz): δ -151.8 ppm (q, *J* = 56.4 Hz, 2F). Anal. Calcd for C₂₂H₃₈B₂F₄N₄: C, 57.92; H, 8.40; N, 12.28%. Found: C, 58.03; H, 8.46; N, 11.84%.

Compound 8. To a -78 °C solution of compound **5** (0.500 g, 1.38 mmol) in Et₂O (40 mL), *n*-BuLi (1.6 M in hexanes, 3.62 mL, 5.79 mmol) was added slowly. The red solution was slowly warmed to room temperature and stirred for 20 hrs. The solvent was removed under reduced pressure

and the red solid residue was dissolved in toluene (40 mL), and PhBCl₂ (0.365 mL, 2.76 mmol) was then added. The reaction was stirred at room temperature for 24 hrs. The reaction mixture was filtered over celite to remove LiCl salt. The solvent was removed from the filtrate to leave a crude pink solid. The solid was washed with hexane (3 x 5 mL) to leave compound **8** as a light pink solid (0.373 g, 51% yield). Single crystals suitable for X-ray studies were obtained from a concentrated toluene solution at -37 °C. ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 7.81 (s, 2H, CH_{benz}), 7.56 (d, 4H, *o*-PhH), 7.20 (m, 6H, *m*-PhH/*p*-PhH overlapped), 1.54 ppm (s, 36H, N(C(CH₃)₃)). ¹³C{¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 133.9, 130.1, 127.3, 127.0, 102.8, 54.5, 32.4 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): δ No shift was observed, hidden behind probe.

Compound 9. To a -78 °C mixture of compound **6** (0.200 g, 0.5233 mmol) in THF (20 mL), *n*-BuLi (1.6 M in hexanes, 0.719 mL, 1.15 mmol) was added slowly. The resulting green mixture was warmed to room temperature and stirred for 4 hrs. The solvent was removed under reduced pressure to leave a green residue. The product was extracted with toluene (5 mL) and recrystallized at -37 °C to leave compound **9** as a white crystalline solid (0.130 g, 50% yield). ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 7.64 (s, 2H, CH_{benz}), 1.77 (s, 36H, N(C(CH₃)₃), 1.73 (t, 4H, CH₂CH₂CH₂CH₃), 1.68 (m, 4H, CH₂CH₂CH₂CH₃), 1.50 (m, 4H, CH₂CH₂CH₂CH₃), 1.02 ppm (t, 6H, CH₂CH₂CH₂CH₃). ¹³C{¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 129.9, 103.0, 54.4, 32.1, 31.8, 26.6, 14.3 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): 30.0 ppm. Anal. Calcd for C₃₀H₅₆B₂N₄: C, 72.88; H, 11.42; N, 11.33%. Found: C, 72.41; H, 11.42; N, 11.16%.

Compound 10. In a Schlenk tube 1,3-bis(2,6-diiso-propylphenyl)imidazolium chloride (IPr•HCl, 0.0861 g, 0.202 mmol), [Pd(OAc)2] (0.0227 g, 0.101 mmol), and NaO*t*Bu (0.0292 g, 0.304 mmol) were stirred in toluene (40 mL) at room temperature until a clear orange solution was observed. 4,5,9,10-tetrabromo-2,7-ditert-butylpyrene (0.914 g, 1.45 mmol) and NaO*t*Bu (0.667 g, 6.94 mmol) were then added to the orange solution. Under positive argon pressure, methylamine (2 M

in THF, 3.47 mL, 6.94 mmol) was added, and the resulting tan mixture was heated to 110 °C for 18 hrs. The mixture was cooled to room temperature and filtered over celite to remove NaBr salt. The solvent was removed from the filtrate to leave a brown solid. The crude solid was washed with hexane (3 x 5 mL) to leave compound **10** as an orange solid (0.281 g, 45% yield). ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 8.43 (s, 4H, CH_{pyr}), 4.02 (q, 4H, NH), 2.28 (d, 12H, NCH₃), 1.60 ppm (s, 18H, C(CH₃)₃). ¹³C{1H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 147.8, 137.0, 129.0, 120.6, 116.5, 37.4, 35.6, 32.3 ppm.

Compound 11. To a -78 °C solution of compound **10** (200 mg, 0.464 mmol) in Et₂O (40 mL), *n*-BuLi (1.6 M in hexanes, 1.22 mL, 1.95 mmol) was added slowly. The dark red solution was slowly warmed to room temperature and stirred for 20 hrs. The solvent was removed under reduced pressure and the red residue was dissolved in toluene (40 mL), and PhBCl₂ (0.121 mL, 0.929 mmol) was added slowly. The reaction was stirred at room temperature for 27 hrs. The dark yellow mixture was filtered over celite to remove LiCl salt, and the solvent was removed from the filtrate. The crude yellow-green solid was washed with hexanes (3 x 5 mL) to leave compound **11** as a yellow solid (184 mg, 66% yield). Single crystals suitable for X-ray studies were obtained from a concentrated toluene/THF mixture (10:1) at room temperature. ¹H NMR (600 MHz, C₆D₆, 298 K) δ = 9.05 (s, 4H, CH_{pyr}), 7.73 (d, 4H, *o*-Ph*H*), 7.46 (t, 4H, *m*-Ph*H*), 7.38 (t, 2H, *p*-Ph*H*), 3.94 (s, 12H, NCH₃), 1.63 ppm (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (150.90 MHz, C₆D₆, 298 K) δ = 146.1, 136.0, 135.1, 129.7, 128.8, 128.4, 126.1, 117.8, 113.4, 35.8, 35.7, 32.2 ppm. ¹¹B NMR (C₆D₆, 192.55 MHz): δ 29.8 ppm.

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Robert J. Gilliard, Jr. obtained his bachelor's degree in chemistry at Clemson University working with Rhett C. Smith. He earned his doctorate at The University of Georgia with Gregory Robinson. Gilliard was a UNCF-Merck Postdoctoral Fellow and a Ford Foundation Postdoctoral Fellow at the ETH Zürich with Hansjörg Grützmacher and at Case Western Reserve University with John Protasiewicz. He began his independent career at the University of Virginia in 2017, where the Gilliard laboratory is engaged in materials-relevant main-group synthesis, as well as the structure and reactivity of novel s-block complexes.