

# Synthesis, Characterization, and Properties of Bis-BN Ullazines

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**Supporting Information** 



**ABSTRACT:** A series of bis-BN ullazine derivatives, including the parent species, were synthesized in a small number of steps from commercially available materials. X-ray crystallographic analysis revealed that bis-BN ullazines have rigid and planar frameworks. Most of the bis-BN ullazines are stable toward air and moisture. In addition, the absorption and emission bands of these ullazines are blue-shifted, compared to those of their carbonaceous ullazine analogs.

**P** olycyclic aromatic hydrocarbons (PAHs) have captured the attention of the scientific community. Notably, the formal replacement of a C=C bond with an isoelectronic and isostructural B–N bond can generate novel PAHs with different properties.<sup>1</sup> These unique characteristics of BNaromatics make their application in materials chemistry quite interesting. The synthesis and properties of a variety of BNaromatics, including BN-naphthalenes,<sup>2</sup> BN-phenanthrenes,<sup>3</sup> BN-anthracenes,<sup>4</sup> BN-pyrene,<sup>5</sup> BN-helicenes,<sup>6</sup> BN-indene,<sup>7</sup> BN-coronenes and nanographene,<sup>8</sup> and higher BN-doped PAHs,<sup>9,10</sup> have been well documented. BN-containing PAHs have been explored as promising components for organic lightemitting diodes (OLEDs),<sup>9</sup> organic field-effect transistors (OFET),<sup>10a,b</sup> and organic photovoltaics (OPVs).<sup>10c</sup> BNaromatics are predicted to be uniquely able to serve as singlet fission materials.<sup>11</sup>

Ullazine, which is isoelectronic with pyrene, is a type of PAH that contains a conjugated  $16\pi$ -system with one nitrogen atom in the center. Balli and Zeller synthesized the first ullazine in 1983.<sup>12</sup> In the past two decades, several synthetic protocols have been reported, and most of them are Lewis acid catalyzed or transition-metal-catalyzed annulation reactions.<sup>13</sup> Ullazines are of great interest in the field of optoelectronics and, particularly, in dye-sensitized solar cells (DSCs).<sup>13a,b</sup> and<sup>14</sup> Surprisingly, BN isosteres of ullazines remain completely unexplored; thus, the present study describes, to the best of our knowledge, the first synthesis of BN ullazines, including the parent compound. Our synthesis is based on a simple, highly efficient, dual Friedel–Crafts-type electrophilic borylation

reaction in which two boron atoms are bonded to a central pyrrole. Structures with multiple boron atoms attached to a simple aromatic ring has been reported in the literature.<sup>15</sup> In addition, BN-aromatics based on pyrrole are rare.<sup>16</sup> We envisioned that replacing C=C units with B–N units will cause this new class of BN-heterocycles to have interesting photophysical properties (Figure 1).





BN-pyrrolo[1,2-*a*]quinoline, which can be considered "half" of the bis-BN ullazine, was synthesized first. The starting material, 1-(2-nitrophenyl)-1*H*-pyrrole (1), was prepared through a Clauson–Kaas reaction between 2-nitroaniline and 2,5-dimethoxytetrahydrofuran.<sup>17</sup> Subsequently, reduction of compound 1 using NaBH<sub>4</sub> with BiCl<sub>3</sub> gave 2-(1*H*-pyrrol-1-yl)aniline (2) in good yield. Gratifyingly, electrophilic borylation of 2 with PhBCl<sub>2</sub> produced BN-pyrrolo[1,2-*a*]quinoline (3b) in moderate yield (Method B, Scheme 1).

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Scheme 1. Synthetic Route to "Half" of the Bis-BN Ullazines (BN-pyrrolo[1,2-a]quinolines) 3 and Bis-BN Ullazines 6



The B-Mes and B-Me analogs (**3a** and **3c**) could be prepared via the corresponding two-step sequence: first, borylative cyclization of **2** with BCl<sub>3</sub> and, then, nucleophilic substitution of the B–Cl moiety by the appropriate Grignard reagent (Method A, Scheme 1). Alternatively, parental BN-pyrrolo[1,2a]quinoline **3d** could be produced by treating the initial cyclized intermediate with LiAlH<sub>4</sub> instead of a Grignard reagent (Method C, Scheme 1). We noticed that BN-pyrrolo[1,2a]quinolines **3a**–**3c** can be purified by chromatography on silica gel, but the parental analog **3d** gradually decomposed during chromatography. Pure **3d** was obtained by recrystallization. X-ray structures of **3b**, **3c**, and **3d** were obtained (Figure S7 and Table S11).

The successful synthesis of BN-pyrrolo[1,2-*a*]quinoline **3** encouraged us to synthesize bis-BN ullazines. The synthesis of bis-BN ullazine **6** began with the Clauson–Kaas reaction between 2,5-dimethoxytetrahydrofuran and commercially available 2,6-dinitroaniline followed by the reduction of the NO<sub>2</sub> group to afford 2-(1*H*-pyrrol-1-yl)benzene-1,3-diamine **5a**,<sup>18</sup> which can be alkylated to give compound **5b** in good yield. Bis BN-ullazines **6a–6g** were obtained by 2-fold borylative cyclizations of **5a** or **5b** in good yields in the absence of a catalyst (Method B, Scheme 1). Notably, the yield of the borylation reaction in the presence of aluminum chloride in Dewar's synthesis of BN-pyrene was only 21%.<sup>15</sup> This reactivity difference is probably due to the more electron-rich nature of the pyrrole ring.

We found parental bis-BN ullazine **6d** was extremely unstable to chromatography on silica gel, and it slowly decomposed during recrystallization. Similar reports have shown that substitution at the 3 or 9 position of carbonaceous ullazine can improve its stability.<sup>12b</sup> The <sup>1</sup>H NMR chemical shifts of the N–H protons in bis-BN ullazines **6a–6d** are in the 6.94–7.40 ppm range, which suggests the compound is aromatic. The chemical shift of the B–H proton in **6d** is at approximately 5.21 ppm (doublet), which is similar to the peaks reported for other unsubstituted BN-aromatics bearing B–H bonds.<sup>2a,19</sup> The nucleus-independent chemical shift (NICS) values are important magnetic criteria of aromaticity.<sup>20</sup> The NICS (1) value of the sub-BN ring in **6d** (–1.35) is larger than that of the sub-BN ring in carbonaceous ullazine **6d'** (–3.24), which indicates that **6d** is less aromatic than **6d'** (Figure 2). Density



Figure 2. NICS (1) values, frontier orbital maps and energy levels of bis-BN ullazine 6d and carbonaceous ullazine 6d'.

functional theory (DFT) calculations revealed that there is significant HOMO density on the peripheral nitrogen atom, but none on the boron atom. The calculations also showed significant LUMO density on the boron atom and that the LUMO is less delocalized on the benzene ring and partially resides on the pyrrole ring of bis-BN ullazine **6d**. The position of the LUMO of bis-BN ullazine **6d** is different from its isoelectronic carbonaceous ullazine **6d**' for which the LUMO primarily resides on the central ring, less on the pyrrole ring and none on the bottom half of the molecule. The replacement of a C==C unit with the B=N in ullazine **6d**' resulted in a lower HOMO level and a slightly higher LUMO level. A similar trend was observed for **3d** and its all-carbon analog **3d'** (Figure S1).

We were able to obtain crystals of bis-BN ullazines 6a-6dsuitable for X-ray analysis by slow diffusion of hexane into a solution of **6** in dichloromethane. The structures of bis-BN ullazines 6a-6d are shown in Figure 3, and selected bond distances are presented in Table S10. All four bis-BN ullazines 6a-6d had perfectly flat structures. The dihedral angles between the top pyrrole ring and the bottom benzene ring are very small  $(1.1^\circ-6.7^\circ, Table S10)$ . Parental bis-BN ullazine 6d showed the smallest dihedral angle  $(1.1^\circ)$ , which indicates it had the highest planarity. The aryl substituents on boron (mesityl in 6a; phenyl in 6b) are out of the plane with dihedral angles of approximately  $80^\circ$  for 6a and  $40^\circ$  for 6b, which limits their conjugation with the polycyclic ullazine core. X-ray structures of "half" bis-BN ullazines 3b-3d showed planar frameworks as well (see Figure S7, Table S11).

The B–N bonds in bis-BN ullazines **6a** and **6b** are much shorter than typical B–N single bonds (1.58 Å) and slightly longer than a localized B=N double bond (1.403(2) Å) (Table S10), confirming that these bonds have noticeable double-bond character. The B–N bonds in bis-BN ullazines **6c** and **6d** are comparable to localized B=N double bonds (Table S10), which indicates they have very strong double-bond character (Table S10). Furthermore, the inner ring B–C bonds (1.45–1.54 Å) are shorter than the B–C single-bond covalent radius of 1.6 Å. The B–C bonds of **6c** (~1.49 Å) and **6d** (~1.51 Å)



**Figure 3.** Solid state structures of bis-BN ullazines **6a–6d** with views parallel and perpendicular to the polycyclic planes. Thermal ellipsoids are set at the 35% probability level. H atoms have been omitted for clarity.

are significantly short. The short N–C bonds (1.38-1.42 Å) in bis-BN ullazines **6a–6d** are similar to those reported in the literature for other BN-aromatics.<sup>2–8</sup>

The UV/vis absorption spectra of bis-BN ullazines 6a-6d in  $CH_2Cl_2$  are presented in Figure 4, and their absorption band



Figure 4. Normalized absorption (left) and emission spectra (right) of 6a-6d in  $CH_2Cl_2$  at a concentration of  $10^{-5}$  M.

#### Table 1. Photophysical Properties of 6a-6d

compd	$\lambda_{ m abs} \ ( m nm)$	$\lambda_{ m onset}$ (nm)	$\lambda_{\rm em} \ ({\rm nm})$	$\Phi_{ m pl}$	Stokes shift $(10^3 \text{ cm}^{-1})^a$	$E_{\rm G}^{\rm opt}$ (eV) <sup>b</sup>
6a	318	354	382	0.18	1.22	3.28
6b	331	376	408	0.14	2.70	3.04
6c	309	341	369	0.10	5.26	3.64
6d	316	360	385	0.38	5.26	3.44
<sup>a</sup> Stokes shift = $1/\lambda_{abs} - 1/\lambda_{em}$ . <sup>b</sup> Optical band gap $E_{G}^{opt} = 1240/\lambda_{onset}$ .						

maxima are presented in Table 1. Bis-BN ullazines 6a-6dshowed absorption bands below 380 nm, which can be attributed to the  $\pi,\pi^*$  transitions of the aromatic core. This assignment was further supported by TDDFT calculations (Tables S5–S8 and Figures S2–S5). The observation of a minor solvent effect also supports this assignment (Figure 5 for 6c, Figure S11 for other compounds). The absorption onset of bis-BN ullazine 6b showed a bathochromic shift (376 nm) relative to 6a (354 nm), indicating that the B-Ph moiety in 6bwas in better conjugation with the main plane than the B-Mes moiety in 6a, which was consistent with their X-ray structures.



Figure 5. Normalized UV-vis absorption (left) and emission spectra (right) of 6c in different solvents.

The low energy band of bis-ullazine **6c** (309 nm) was blueshifted, compared to the low energy bands of the other three bis-BN ullazines (**6a**, 318 nm; **6b**, 331 nm; **6d**, 316 nm). The parental bis-BN ullazine **6d** showed an absorption maxima of 316 nm in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{abs} = 315$  nm in MeOH, Figure S11), which is substantially blue-shifted, compared to its carbonaceous ullazine analog **6d**' ( $\lambda_{abs} = 374$  nm in EtOH).<sup>12a</sup> Similarly, the absorption band of **6b** ( $\lambda_{abs} = 331$  nm) is also blue-shifted, compared to its carbonaceous ullazine **6b**' ( $\lambda_{abs} = 392$  nm) (Figure S10 and Table S35).

The emission spectra of bis-BN ullazines 6a-6d are shown in Figure 4. Emission maxima of 6 decrease in the order 6b > b $6d \approx 6a > 6c$ . This trend is consistent with that observed in their absorption spectra. The red shift of the emission band of 6b (408 nm) relative to that of 6a (382 nm) indicated the B-Ph was in better conjugation with the ullazine scaffold. The emission band of **6b** ( $\lambda_{em}$  = 408 nm in CH<sub>2</sub>Cl<sub>2</sub>) was blueshifted relative to that of its carbonaceous ullazine **6b**' ( $\lambda_{em}$  = 518 nm) as well (Figure S10 and Table S35). The emission band of 6c, bearing a methyl substituent on the boron atom, was blue-shifted relative to that of parental bis-BN ullazine 6d. However, the solution state fluorescence quantum yields of bis-BN ullazines 6a-6d are moderate (0.10-0.38). The small Stokes shifts of bis-BN ullazines 6a-6d ( $10^3$  cm<sup>-1</sup>, Table 1) indicate that the structural relaxations are small presumably due to the structural rigidities of 6. The absorption and emission spectra of BN-pyrrolo[1,2-a]quinoline 3 were also recorded (Figure S8 and Table S33).

Unlike the limited solvent effect observed for the absorption spectra, we found a clear positive solvatochromic effect in the emission spectra of bis-BN ullazines 6 (Figure 5 for 6c, Figure S11 for the other compounds). Bis-BN ullazine 6c showed a vibronic structure in low-polarity solvents with a vibronic spacing of approximately 1300 cm<sup>-1</sup>, which corresponds to the breathing mode of the aromatic ring. Therefore, the emitting state of **6c** in low-polarity solvents is dominated by the  $\pi,\pi^*$ state. In contrast, the emission band of 6c becomes structureless and red-shifted in more polar solvents, which might be caused by solvent-induced vibrational relaxation.<sup>21</sup> Similar phenomena were also found in other bis-BN ullazines (Figure S11). The alkyl substituents on the nitrogen atoms of bis-BN ullazines 6e-6g did not substantially affect the photophysical properties of these compounds (Figures S9 and S12 and Table S34).

The electrochemical properties of bis-BN ullazines **6** were investigated using cyclic voltammetry (Figure S13 and Table S36) and differential pulse voltammetry (Figure S14). Bis-BN ullazines **6** exhibited irreversible oxidation and reduction waves. The HOMO levels of bis-BN ullazines **6a**–**6d** calculated from their oxidation onset potentials are comparable (**6a**, –4.83 eV; **6b**, –5.24 eV; **6c**, –4.82 eV, **6d**, –4.87 eV). The LUMO energy

levels were calculated from the HOMO energy levels and the optical band gaps (6a, -1.55 eV; 6b, -2.20 eV; 6c, -1.19 eV, 6d, -1.43 eV) (Table S36).

Tricoordinate boron species are commonly used to detect fluoride ions due to the Lewis acidity of boron.<sup>22</sup> However, we found that the addition of excess tetrabutylammonium fluoride (TBAF) to solutions of bis-BN ullazines **6** caused slight changes, except for **6d**, in their absorption and emission spectra (Figure S15). These phenomena are in stark contrast to the shifts observed for other BN-aromatics.<sup>23</sup> However, we found the boron signal of bis-BN ullazines **6** was diminished after adding an excess of TBAF (Figure S16). It should be noted that the <sup>11</sup>B NMR was recorded at a much higher concentration of bis-BN ullazines **6** than the photophysical studies.

In summary, we have synthesized a series of bis-BN ullazines including an unsubstituted parent species. The obtained set of X-ray structures elucidated the solid-state structures of these bis-BN ullazines. The aromaticity of the parental bis-BN ullazine was quantified by computational and experimental studies. The absorption and emission spectra of the bis-BN ullazines were blue-shifted relative to those of the carbonaceous ullazine analogs. In addition, bis-BN ullazines are stable toward air and moisture. The high stability and rich photophysical properties suggest that bis-BN ullazines are promising candidates for use in organic electronic materials.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b00554.

Full details on the synthesis of all BN-pyrrolo[1,2-a]quinolines 3 and bis-BN ullazines 6, NMR spectra, UV-vis and photoluminescence data, electrochemical data, X-ray crystallographic data, and theoretical calculations (PDF)

#### **Accession Codes**

CCDC 1823295–1823301 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

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