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Multiple C−H Borylation of Phenylhydrazones to Boron-Nitrogen Analogues of Benzopentalene

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One-pot multiple borylation of phenylhydrazones to a series of novel boron-nitrogen analogues of benzopentalene by the cleavage of C-H bonds with PhBBr$_2$ mediated by NEt$_3$ has been established. The resulting BN benzopentalenes feature unique electronic structures and are luminescent both in solution and solid state.

There is increasing interest in polycyclic conjugated systems in which some of the C=C bonds in hydrocarbons are replaced by isosteric BN pairs.[1] Potential applications of these novel compounds have been demonstrated in the context of materials and biological chemistry due to their unique electronic properties arising from the polarized B−N bonds.[2] On the other hand, the comparison of the BN polycyclic systems with the analogous hydrocarbon systems has been an active topic for several decades, with a particular focus on their reactivity, electronic structures and aromaticity.[1, 2a] The vast majority of these molecules have been based on six-membered azaborine rings, while BN polycyclic compounds based on five-membered conjugated rings have remained largely unexplored.

Pentalene is an antiaromatic bicyclic hydrocarbon with two ortho-fused cyclopentadiene rings. Its stable derivatives can be accessed by either bulky substituents or annulation to aromatic rings. Their dianions are aromatic and have been widely used as ligands in organometallic chemistry.[3] Benzoannulated pentalenes are attractive molecular materials in optical and electronic device applications because of their intriguing electronic properties.[4, 5] Driven by these exciting results, we became interested in the exploration of their BN analogues. However, much less attention has been paid to the five-membered polycyclic BN systems and the electronic properties of them have been virtually unexplored.[6] Herein, we report the facile synthesis of the first BN benzopentalenes containing two BN pairs by reactions of phenylhydrazones with dibromophenylborane (Scheme 1). The reaction formally involved the successive cleavages of one N–H and three C–H bonds with the formation of BN analogues of benzopentalenes fused by an N–N bond. The electronic structures of these novel molecules were studied by UV-vis and fluorescence spectroscopies as well as DFT calculations.

Hydrazones have been widely employed for the construction of heterocyclic organic compounds because of their ease preparation

and relatively high stability.[7] Synthesis of the BN-benzopentalenes **1-3** was accomplished in one-step as shown in Scheme 1. Reactions of the three phenyl-substituted hydrazones **a-c** with two equivalents of PhBBr$_2$ in refluxing toluene in the presence of four equivalents of NEt$_3$ for 8 h led to the formation of **1-3**, respectively, as yellow crystals in modest to good yields (40-70%). The reaction can also be accomplished with two equivalents of PhBBr$_2$(NEt$_3$) in the presence of two equivalents of NEt$_3$. It is noted that more than four equivalents of NEt$_3$ have a negative effect on the yields of **1-3**. The molecular structures of **2** and **3** have been established by X-ray single crystal analysis, which confirmed the BN benzopentalene structure (Figure 1).
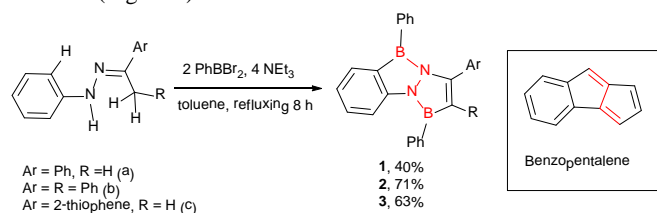
Scheme 1 Multiple C−H borylation strategy for the synthesis of BN benzopentalenes **1-3**.

Similarly, reactions of phenylhydrazones **d-g** with para-F, Cl, Br and Me-substituents on the phenyl rings with PhBBr$_2$ in refluxing toluene yielded the corresponding BN benzopentalenes **4-7** as yellow crystals in good yields (Scheme 2).
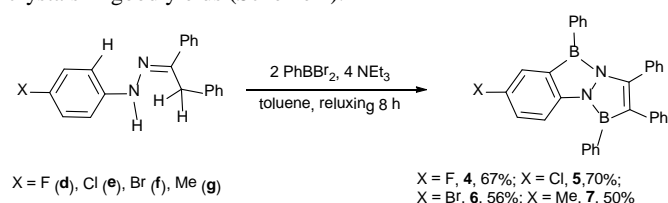

Scheme 2 Synthesis of BN benzopentalenes **4-7**.

In order to clarify the reaction sequence, reaction of phenylhydrazone **a** with one equivalent of PhBBr$_2$ at various temperatures has been investigated. It was found that the reaction at 80 °C resulted in the formation of the monocyclic 1,2-diaza-3-borole

8 as a white solid (Scheme 3) in 32% yield, indicating the initial borylation of the amine N−H bond and one of the sp[3] C−H bonds on the imine functionality. As expected, further reaction of **8** with PhBBr$_2$ in the presence of NEt$_3$ in refluxing toluene yielded the tricyclic product **1** in good yield. However, the similar reaction of 2,6-dimethylphenylhydrazone **h** with PhBBr$_2$ at 80 °C led to the recovery of **h**, indicating that the bulky 2,6-dimethylphenyl group significantly suppressed the borylation of the N−H bond. In addition, the same reaction in refluxing toluene proved to be sluggish and only a very small amount of the corresponding monocyclic product can be observed by the proton NMR spectrum but cannot be isolated. However, monocyclic **9** can be isolated in ca 20% yield in refluxing toluene if the strong base 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) was used instead of NEt$_3$ (Scheme 3).

Compounds **8** and **9** represent rare examples of 1,2-diaza-3-borole derivatives.[1a] The ^{11}B NMR spectra of **8** and **9** exhibited a singlet at 43.8 and 44.5 ppm. The ^{1}H NMR spectra of **8** and **9** display a singlet at δ 4.17 and 2.30 ppm, attributed to the proton resonances of the C*H*Ph and C*H*$_2$ groups in the five-membered rings, respectively. The two compounds can be viewed as pyrrole analogues and are isomeric with well-documented 1,3-diazaboroles.[8]
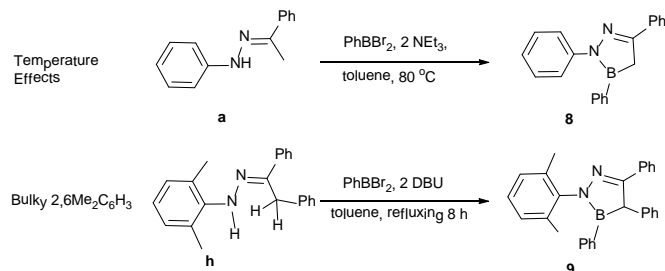
Scheme 2 Synthesis of monocyclic diazaboroles **8** and **9**.

The borylation of aromatic C−H bond promoted by a Lewis acid, so called bora-Friedel-Crafts cyclization typically mediated by AlCl$_3$, has been originally reported by Dewar.[9] This approach has been modified for the synthesis of BN-polyaromatic compounds.[10, 11] However, these reactions, in general, proceeded at high temperatures (150-180 °C) and required a large excess of Lewis acid in the most of cases.[10, 11] We demonstrated that the borylation with a B−Br bond in the presence of a simple base proceeded under the relatively mild conditions.

The solutions of **1-9** in toluene turned brown in 15 min in the air, indicating they are air and moisture-sensitive. However, the solid samples of **1-7** could be exposed to the air for 2 d without detectable decomposition as indicated by the ^{1}H NMR analysis. Hydrolysis of **7** in THF led to the rapid disappearance of yellow color. Compounds **1-9** have been fully characterized by multiple NMR spectroscopy and elemental analysis. The ^{11}B NMR spectra of **1-7** exhibited only one singlet in the range of δ 36.4-37.2 ppm because of the broadness of the signal that cannot be resolved. The molecular structures of BN-benzopentalenes **2** and **3** have been confirmed by X-ray single crystal analysis and are shown in Figure 1 with the relevant bond parameters. The structures of **2** and **3** have a very similar co-planar fused tricyclic core. The sum of the bond angles around the boron atoms ranges from 359.0 (18) to 359.88 (8)°, indicating the almost planar geometry of the boron atoms. The N−N bond lengths of 1.422(2) Å in **2** and **3** are in the typical range for an N−N single bond. The short B−N bond lengths (in the range from 1.429 to 1.441(3) Å) in **2** and **3** indicated the pronounced π interactions between boron and the nitrogen atoms. The molecular structure of **8** and **9** were also determined by X-ray single crystal analysis. The structures are given in Figure S1 with selected bond parameters. The

structures of **8** and **9** feature an almost planar five membered C$_2$N$_2$B ring with the very short B−N bond distances of 1.422(4) and 1.403(2) Å in **8** and **9**, respectively. The C−N bond lengths of 1.293(3) and 1.291(2) Å in **8** and **9** indicate the double bond character. The solid state structures of **8** and **9** are in accordance with the NMR data in solution
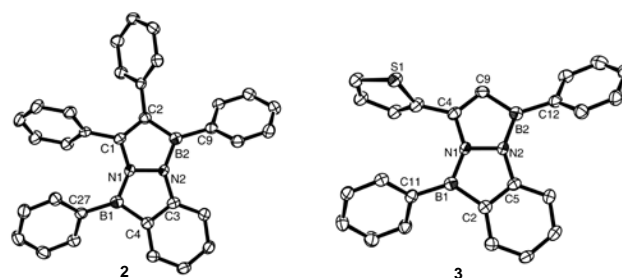

Fig. 1 Single crystal structure view of **2** and **3** (thermal ellipsoids shown at 50% probability, hydrogen atoms excluded for clarity). Selected bond lengths (Å) for **2**: N1−N2 1.422(2), B1−N1 1.441(3), B2−N2 1.433(3), B1−C4 1.550(3), B2−C2 1.548(3), N2−C3 1.419(2), N1−C1 1.398(2), C1−C2 1.368(3), C3−C4 1.396(3). **3**: N1−N2 1.422(2), B1−N1 1.433(3), B2−N2 1.429(3), B1−C2 1.556(3), B2−C9 1.531(3), N1−C4 1.407(3), C5−N2 1.410(3), C2−C5 1.396(3), C4−C9 1.350(3).

The Electronic properties of **1-7** were studied by UV-*vis* and fluorescence spectroscopies. The UV-vis absorption spectra of **1-7**, measured in *n*-hexane, exhibit the broad absorptions with the λ$_{max}$ values in the range from 300 to 344 nm (Figure 2, also see Table S2 in the Supporting Information). These absorptions are significantly high-energy shifted compared to those reported for the analogous phenyl-substituted benzopentalenes (600-660 nm).[4c] TD-DFT calculations at RB3LYP/6-311+G(d,p) level for **2** and **3** indicated that the absorption maxima observed for **2** and **3** are associated with the transitions from the HOMO-1 to LUMOs (See the SI). The HOMO-LUMO transitions in the spectra measured experimentally cannot be observed because of the broad absorptions which are overlapped with those resulted from HOMO-1 to LUMO transitions.
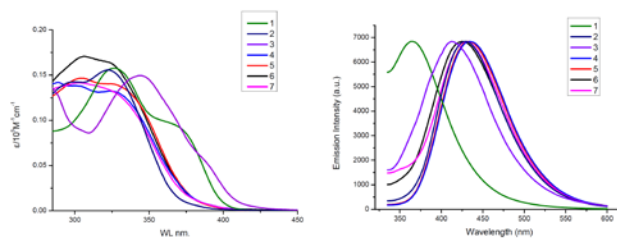

Fig. 2 UV-vis (left) and Emission Spectra (right) of **1-7** in *n*-hexane.

Compounds **1-7** are luminescent in solution. The emission maxima for compounds **1** and **3** (R = H in Scheme 1) in *n*-hexane was observed at 382 and 412 nm (Φ$_F$ = 11 and 26%), respectively, while the maxima for **2** and **4-7** (R = Ph) were in the violet purple range from 425 to 434 nm with the quantum yields Φ$_F$ = 19-60% (Figure 3, also see Table S2). This indicated that the phenyl group at the R position (Scheme 1) has the noticeable electron interactions with the planar tricyclic core, leading to red-shifted emission maxima observed for **2** and **4-7**.

The monocyclic compound **8** is not luminescent in solution and in the solid state. However, compound **9** exhibits a weak luminescence in solution. The emission maxima for **9** in *n*-hexane was observed at 418 nm (Φ$_F$ = 2%). **9** is not luminescent in the solid state. The weak

luminescence of **9** may be related to the bulky 2,6-dimethylphenyl group, which restricts the rotation of the two neighboring phenyl rings to some extent.[12]

DFT calculations have been performed on **2** and **3** at RB3LYP/6-311+G(d,p) level of theory. The calculated structural parameters for **2** and **3** are well-correlated with those determined experimentally (Figures S4 and S5 in the SI). The calculated HOMO and LUMOs of **2** and **3** are given in Figure S6 in the Supporting Information. The HOMOs of **2** and **3** are mainly located in the fused tricyclic ring and the aryl groups on the ring C2 and C4 atoms, respectively. It appears that **2** and **3** have very similar frontier orbital surfaces with the analogous benzopentalenes.[4c] However, the calculated HOMO-LUMO gaps for **2** (3.81 eV) and **3** (3.91 eV) are much greater than the analogous benzopentalenes (ca 2.1 eV).[4c] In addition, the calculated Nucleus-Independent Chemical Shifts (NICS), which have been widely used to estimate the aromaticity of conjugated ring systems,[13] for the two five-membered rings in **2** (see Figure S4 in the Supporting Information, NICS(0) = -0.56 and NICS(1) = 0.39 and 0.03 ppm for the ring containing B41 atom; NICS (0) = 0.21, NICS(1) = -0.34, -0.42 ppm for the ring fused to the phenyl ring) indicated that the BN benzopentalene is non-aromatic.

Conclusions

In summary, we have developed a rapid synthesis of the first BN analogues of benzopentalene based on a cascade borylation of phenylhydrozane C–H bonds with dibromophenylborane in the presence of a simple organic base. The reaction yielded a series of aryl-substituted BN benzopentalenes in good yields. The UV-*vis* and fluorescence spectroscopies as well as DFT calculations revealed that these BN analogues possess much larger HOMO-LUMO gaps as well as higher energy absorption and emission maxima than the analogous phenyl-substituted benzopentalenes. These differences reflect the significant effects of the BN pairs on the electronic structures of the polycyclic conjugated rings. In addition, the non-aromatic character of **2**, as disclosed by DFT calculations, is also distinct from antiaromatic benzopentalene derivatives. The results indicated that replacement of C=C bonds in polycyclic conjugated hydrocarbons with BN pairs may significantly change their electronic structures, leading to unique physical properties. The employments of this strategy for the synthesis of stable BN-conjugated compounds and their electronic effects of BN units in polycyclic systems are currently in progress in our laboratory.

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Notes and references

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† CCDC-1018810 (**2**), CCDC-1018811 (**3**), CCDC-1018812 (**8**) and CCDC-1018813 (**9**) 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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