B,N Heterocycles

DOI: 10.1002/anie.201302660

# Boron-Substituted 1,3-Dihydro-1,3-azaborines: Synthesis, Structure, and Evaluation of Aromaticity**

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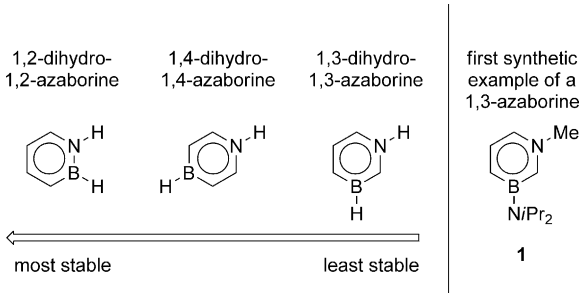
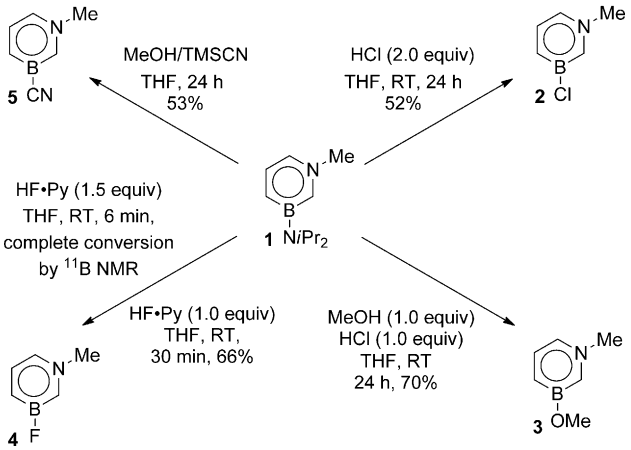
BN/CC isosterism has emerged as an attractive strategy to expand the chemical space of compounds relevant to biomedical research and materials science.[1] Among the three BN isosteres of benzene (i.e., 1,2-dihydrido-1,2-azaborine,[2] 1,3-dihydrido-1,3-azaborine, and 1,4-dihydrido-1,4-azaborine;[3] see Scheme 1), 1,3-dihydro-1,3-azaborine (abbreviated herein as 1,3-azaborine) is thermodynamically the least stable isomer.[4] Not surprisingly, its development has lagged behind that of the other azaborines in the series. The first synthetic example of a 1,3-azaborine was reported in late 2011,[5] and the diversity of synthetically accessible 1,3-azaborines remains very limited to date.




***Scheme 1.*** The three BN isosteres of benzene.

1,3-Azaborines exhibit electronic structures that are very distinct from those of their 1,2-azaborine and carbonaceous analogues.[6] New synthetic tools need to be developed to exploit the unique properties of this family of heterocycles in materials and biomedical applications. Late-stage functionalization strategies are arguably the most efficient approach to generate an array of derivatives from an assembled B,N-heterocyclic core. We envisioned that the boron position in 1,3-azaborines could be utilized as a straightforward point of attachment for a variety of functional substituents at a late stage. For 1,3-azaborines, however, a general method for substitution at boron has yet to be developed. Herein, we describe protocols for the synthesis of a diverse array of B-substituted 1,3-azaborines from the *B*-N*i*Pr$_2$-substituted 1,3-azaborine **1** as a universal precursor. Furthermore, we provide evidence based on structural, magnetic, and energetic considerations that 1,3-azaborines are more aromatic than the corresponding 1,2-azaborines.

Recently, we disclosed that 1,3-azaborine **1** was inert towards anionic and neutral nucleophiles.[5] On the other hand, we showed that the treatment of **1** with acetic acid readily furnished the *B*-OAc-substituted product (Scheme 2).[5,6] Encouraged by this preliminary finding, we envisioned that 1,3-azaborine **1** could be converted into B-substituted derivatives under acidic conditions. The treatment of precursor **1** with HCl (2 equiv) produced the *B*-Cl-substituted 1,3-azaborine **2** in 52% yield (Scheme 2). Full and clean conversion of **1** into **2** was observed by $^{11}$B NMR spectroscopy under the optimized reaction conditions. We believe that the moderate yield of the isolated product is due to loss of the product upon purification by silica-gel chromatography. The relative stability of 1,3-azaborine **2** towards silica gel contrasts starkly with the reactivity of the *B*-Cl substituted 1,2-azaborine, which undergoes complete degradation upon exposure to silica gel.




***Scheme 2.*** Substitution reactions of precursor **1** under acidic conditions. Py = pyridine, TMS = trimethylsilyl.

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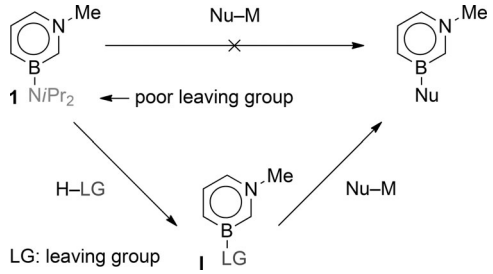
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302660.

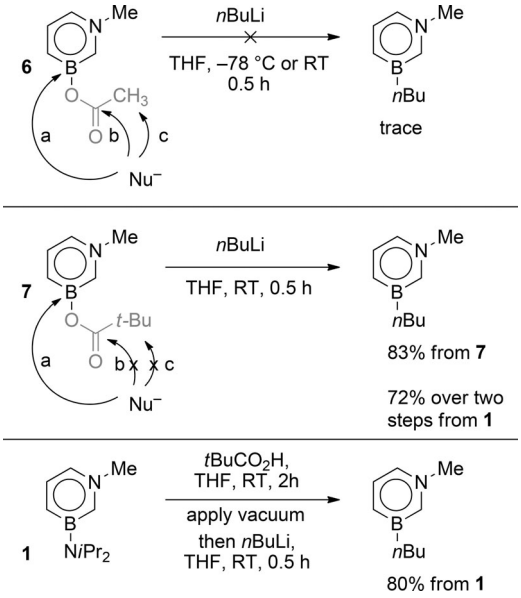
When heterocycle **1** was treated with MeOH, no reaction was observed. However, under acidic conditions, that is, when **1** was treated with a 1:1 mixture of MeOH and HCl, the *B*-OMe-substituted 1,3-azaborine **3** was isolated in 70% yield. Similarly, the treatment of **1** with HF·pyridine (1.0 equiv) gave the fluoride-substituted 1,3-azaborine **4**. When the substitution reaction was carried out with 1.5 equivalents of HF·pyridine, it was complete within 6 min, as determined by $^{11}$B NMR spectroscopy. To the best of our knowledge, compound **4** is the first example of an isolated *B*-F-substituted azaborine.[7] The *B*-CN-substituted 1,3-azaborine **5** was synthesized by the exposure of **1** to a 1:1 mixture of MeOH and TMSCN, presumably through reaction with HCN generated in situ.[8] The *B*-CN connectivity (vs. *B*-NC) in **5** was confirmed by the broad peak at 128.8 ppm (CN) in the $^{13}$C NMR spectrum, which is consistent with the data reported for the *B*-CN-substituted 1,2-azaborine analogue.[9]

Despite the successful examples shown in Scheme 2, the acid–promoted B-substitution has significant limitations. For example, derivatives with carbon-based substituents containing C–H bonds with high p$K_a$ values (e.g., alkyl, aryl, vinyl, alkynyl) cannot be accessed. A method that would enable nucleophilic substitution at boron under neutral or basic conditions would significantly expand the diversity of 1,3-azaborines. We determined previously that heterocycle **1** did not react with a number of anionic nucleophiles owing to the weak leaving-group ability of the diisopropylamino group.[5] Thus, our strategy was to convert **1** into a 1,3-azaborine intermediate **I** with a good leaving group for nucleophilic substitution (Scheme 3).




***Scheme 3.*** Development of a strategy for the nucleophilic substitution of **1**.

With this strategy in mind, we focused our initial attention on developing the *B*-OAc-substituted 1,3-azaborine **6** as a precursor for nucleophilic substitution reactions on the basis of our prior success in using **6** and $LiAlH_4$ to produce *N*-Me-1,3-BN-toluene.[6] However, treatment of **6** with the stronger base *n*BuLi gave only a trace amount of the desired substitution product (Scheme 4, top). We realized that two possible side reactions may compete with the desired nucleophilic attack at boron in compound **6** (path a) when a strong nucleophile/base is used, such as *n*BuLi: 1) attack at the carbonyl carbon atom (path b) and 2) deprotonation (path c). The introduction of a bulky carboxylate as a leaving group with a quaternary α-carbon atom could potentially mitigate the problem. Indeed, when 1,3-azaborine **7**, which



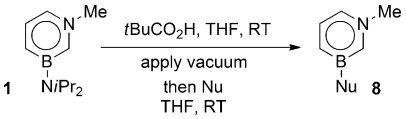

***Scheme 4.*** Optimization of a nucleophilic-substitution protocol.

features the bulky pivalate leaving group at boron, was treated with *n*BuLi at room temperature, the desired *B*-*n*Bu-substituted compound was formed in 83% yield (Scheme 4, middle). The overall yield for the two steps from starting material **1** was 72% owing to the potential loss of material associated with an additional isolation process. To improve the overall efficiency of the substitution protocol starting from 1,3-azaborine **1**, we envisioned that the conversion of **1** into **7** and the subsequent nucleophilic substitution reaction could be performed in one single pot with the only operation between the two reactions being the removal of the diisopropylamine by-product under vacuum. Gratifyingly, the two-step one-pot process gave the *B*-*n*Bu-substituted heterocycle in 80% overall yield (Scheme 4, bottom): an improvement of 8% over that of the step-by-step procedure.

Having established an optimized general protocol, we investigated the scope of the substitution reaction. The one-pot displacement of the diisopropylamino group in **1** occurred readily in the presence of alkyl (Table 1, entry 1), vinyl (entry 2), aryl (entry 3), and alkynyl nucleophiles (entry 4). The substitution reaction also proceeded readily with sterically hindered aryl nucleophiles, such as mesityllithium (Table 1, entry 5). Interestingly, without first converting the diisopropylamino group to B-pivalate-substituted intermediate **7**, phenol and *tert*-butyl alcohol failed to react with 1,3-azaborine **1** even in the presence of HCl. On the other hand, with the optimized one-pot substitution protocol, heteroatom nucleophiles become suitable as reaction partners. The use of phenoxide (Table 1, entry 6) and *tert*-butoxide nucleophiles (entry 7) resulted in the formation of the corresponding products **8f** and **8g** in high yield. The diisopropylamino substituent in **1** can be readily converted into another amino functionality, such as the bis(trimethylsilyl)amino group when $KN(SiMe_3)_2$ is employed as the nucleophile; thus, **8h** was obtained in 69% yield (Table 1, entry 8). Notably, as an alternative to the use of the HF·pyridine reagent, the *B*-F-

***Table 1:*** Synthesis of B-substituted 1,3-azaborines through nucleophilic substitution.




| Entry | Nucleophile (Nu) | Product | Yield [%][a] |
|---|---|---|---|
| 1 | *n*BuLi | **8a** | 80 |
| 2 | $CH_2$=CHMgBr | **8b** | 76 |
| 3 | PhMgBr | **8c** | 94 |
| 4 | Ph−≡−MgBr | **8d** | 89 |
| 5 | mesityllithium | **8e** | 87 |
| 6 | PhOLi | **8f** | 99 |
| 7 | *t*BuOK | **8g** | 99 |
| 8 | $KN(SiMe_3)_2$ | **8h** | 69 |
| 9 | CsF | **4** | 81 |
| 10 | $Et_3N$/MeOH[b] | **3** | 96 |

[a] Yield of the isolated product. [b] A vacuum was not applied after the treatment of **1** with pivalic acid.

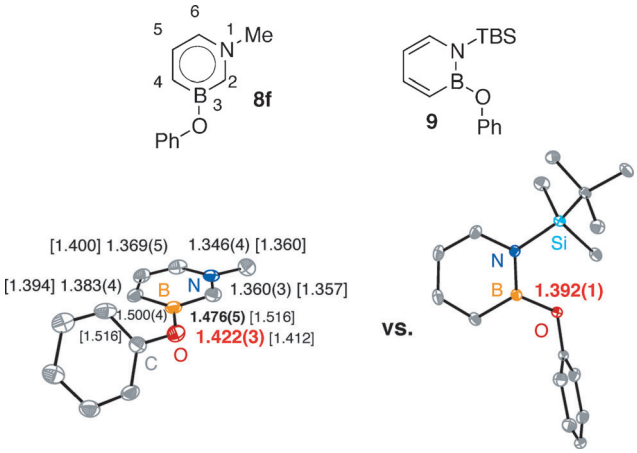
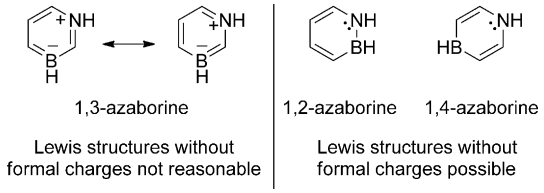



***Figure 1.*** ORTEP illustrations of **8f** and **9**, with thermal ellipsoids drawn at the 35% probability level. The numbers in brackets are optimized gas-phase bond distances calculated at the B3LYP/DZVP2 level. TBS = *tert*-butyldimethylsilyl.

substituted 1,3-azaborine **4** was also formed by a nucleophilic reaction with CsF (Table 1, entry 9). Finally, the one-pot protocol was used to convert 1,3-azaborine **1** into the *B*-OMe derivative **3** with MeOH/$NEt_3$ (Table 1, entry 10).

Within the azaborine series (1,2-, 1,3-, and 1,4-azaborines), the 1,3-isomer is the only family that cannot not be satisfactorily represented by a Lewis structure without invoking formal charges (Scheme 5). Because the chemistry of 1,3-azaborines is just emerging, structural information on




***Scheme 5.*** Lewis structures for the azaborine series.

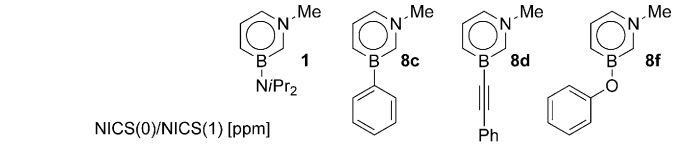
this family of heterocycles is very limited. Compound **1** is the only reported example that has been characterized by single-crystal X-ray analysis.[5] A larger structural database should facilitate the development of a better understanding of the bonding and electronic structure of this family of compounds.

With a library of 1,3-azaborines now readily accessible, we characterized compounds **8c**, **8d**, and **8f** crystallographically.[10] 1,3-Azaborine **8f** is the 1,3-BN isostere of a diphenyl ether (specifically, 1-methyl-3-phenoxybenzene). The observed bonding between the boron and exocyclic oxygen atoms in **8f** is revealing (Figure 1): The exocyclic oxygen atom of **8f** is mostly $sp^2$-hybridized, with a B-O-C bond angle of 123.8(2)°. The C-O-B-C(2) torsion angle of 170.4(2)° and the B–O bond distance of 1.422(3) Å suggest some double-bond character of the B–O bond (sum of single-bond covalent radii: 1.48 Å).[11] However, the observed B–O distance in **8f** is longer (by 0.03 Å) than that of a typical *B*-alkoxide-substituted 1,2-azaborine (B–O 1.389(2) Å)[12] and thus indicates weaker B–O π bonding in a 1,3-azaborine relative to that in a 1,2-azaborine. To enable a more direct comparison of diphenyl ether structures, we prepared 1,2-azaborine **9**[10] and determined its corresponding B–O distance, which is 1.392(1) Å (Figure 1). The weaker B–O π bonding in 1,3-azaborines in comparison to that in 1,2-azaborines is consistent with the electrostatic-potential-map calculations,[6] in which a highly delocalized intraring π-electron system renders the boron atom relatively less capable of accepting π electrons from exocyclic substituents.

Another striking feature of the solid-state structure of **8f** is the short B–C(2) distance of 1.476(5) Å.[13,14] However, the crystallographically determined short B–C(2) distance is not predicted by gas-phase density functional theory (DFT) calculations at the B3LYP/DZVP2[15] level (B–C(2) 1.516 Å).[16] The observed B–C(2) distance for the *B*-diisopropylamino-substituted 1,3-azaborine **1** is 1.525(2) Å, and the corresponding distances in **8c** and **8d** are 1.508(3) and 1.498(2) Å, respectively; the calculated DFT values are consistent with these results (see the Supporting Information). Thus, the observed B-substituent-dependent intraring solid-state B–C(2) bond distances range from 1.476 to 1.525 Å (i.e., a difference of ca. 0.05 Å), which is relatively large and distinct from 1,2-azaborines and arenes.[17]

Overall, the observed intraring bond distances in 1,3-azaborines **1**, **8c**, **8d**, and **8f** are not consistent with a single Lewis structure description. This result corroborates previous theoretical predictions of a significantly electron delocalized structure.[4]

To more quantitatively evaluate the aromatic character of 1,3-azaborines, we calculated the nucleus-independent chemical-shift values NICS(0) and NICS(1)[18] for the B,N-heterocyclic portion of compounds **1**, **8c**, **8d**, and **8f** (Scheme 6). Without exception, the NICS values for the illustrated 1,3-azaborines are more negative than those of the corresponding B-substituted 1,2-azaborines but less negative than those of the corresponding arenes.[19] Thus, on the basis of the NICS values, 1,3-azaborine exhibits aromaticity that is intermediate between that of benzene and that of 1,2-azaborine.

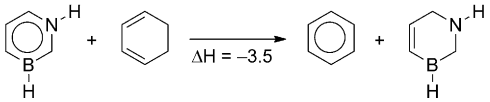



| | | | | | |
|---|---|---|---|---|---|
| increasing aromatic character ↑ | arene | –8.3/–9.0 | –7.8/–9.6 | –8.3/–9.5 | –9.2/–9.5 |
| | 1,3-azaborine | –5.2/–6.6 | –5.9/–7.9 | –6.5/–8.2 | –6.6/–7.6 |
| | 1,2-azaborine | –3.4/–4.5 | –4.4/–6.0 | –5.1/–6.5 | –4.7/–5.4 |

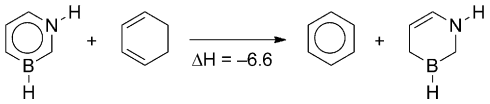
***Scheme 6.*** Calculated NICS(0) and NICS(1) values for 1,3-azaborines **1**, **8c**, **8d**, **8f** and their corresponding 1,2-azaborine and carbonaceous (arene) counterparts.

Finally, we predicted the resonance stabilization energy (RSE) of the parent 1,3-azaborine to be approximately 29 kcal mol$^{-1}$. This value was derived computationally (G3MP2)[20] from Equations (1) and (2), which reveal that the RSE of the parent 1,3-azaborine is approximately 5 kcal mol$^{-1}$ (average of 3.5 and 6.6 kcal mol$^{-1}$) less than that of benzene (RSE = 34.1 kcal mol$^{-1}$). A similar analysis for the parent 1,2-azaborine gave a lower RSE (21 kcal mol$^{-1}$)[21] than that found for the parent 1,3-azaborine. These results are consistent with the structural analysis and NICS calculations.

G3MP2 (298 K), values in kcal mol$^{-1}$




(1)




(2)

Thus, in terms of their structure, magnetism, and resonance energy stabilization, we conclude that 1,3-azaborines should be considered more aromatic than 1,2-azaborines.[22] It appears that the crucial factors governing the relative aromaticity of 1,2- and 1,3-azaborines originate in the extent of π-electron delocalization as well as the lack of a B–N bond in the 1,3-isomer. The greater potential for delocalization of the π electrons in the region of the B–N bond of the 1,2-azaborine[23] may disrupt electron delocalization and result in a less-pronounced aromatic character.

In summary, we have developed the first general method for the synthesis of B-substituted 1,3-azaborines. Our method enabled the synthesis and isolation of the first example of a *B*-F-substituted azaborine. Structural analysis in the solid state revealed a B-substituent-dependent B–C(2) intraring bond distance. The relatively long B–O distance, the calculated NICS values for 1,3-azaborines **1**, **8c**, **8d**, and **8f**, and our evaluation of the resonance stabilization energy suggest that 1,3-azaborines are highly aromatic. In view of the ubiquity and importance of arenes in biomedical research and materials science, the synthetic procedures presented herein represent a significant advance towards harnessing the potential of BN/CC isosterism, and specifically the use of 1,3-azaborines, in these important areas of research.

Received: March 30, 2013
Published online: June 7, 2013

**Keywords:** aromaticity · azaborines · boron · heterocycles · synthetic methods

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[10] Crystallographic data for **8f**: $C_{11}H_{12}BNO$, $M_r = 185.03$, crystal size $0.40 \times 0.19 \times 0.01$ mm$^3$, orthorhombic, space group $Pca2_1$, $a = 11.230(12)$, $b = 11.861(13)$, $c = 7.474(9)$ Å, $V = 995.5(19)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.234$ gcm$^{-3}$, $\mu = 0.077$ mm$^{-1}$, $F(000) = 392$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $2\Theta_{max} = 50.00°$, 7967 reflections measured ($R_{int} = 0.0544$), 1748 reflections observed, 175 refined parameters, $R1 = 0.0485$, $wR2 = 0.1017$, and GOF = 1.072 for reflections with $I > 2\sigma(I)$, $R1 = 0.0660$, $wR2 = 0.1097$, and GOF = 1.072 for all data, max/min residual electron density +0.130/–0.180 e Å$^{-3}$. CCDC 930426 (**8f**), 930428 (**8c**), 930427 (**8d**), and 931041 (**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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[17] A CCDC search (version 2011) of monosubstituted benzenes (> 1900 data points) revealed that $C_{ipso}$–C bond lengths for PhOR, $PhNR_2$, and $PhCR_3$ range from 1.376–1.384, 1.376–1.408, and 1.381–1.400 Å, respectively (i.e., an overall range of 0.032 Å). The B–C distance in reported 1,2-azaborines ranges from 1.486–1.518 Å (i.e., an overall range of 0.032 Å).

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[22] This conclusion is not inconsistent with the fact that 1,3-azaborines are thermodynamically less stable than 1,2-azaborines. The crucial factors that determine the relative thermodynamic stabilities originate in the strength of the σ bonds (see Ref. [4]).

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