Communication

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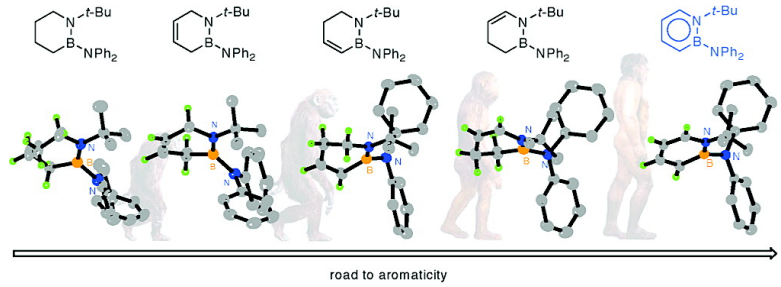

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Crystal Clear Structural Evidence for Electron Delocalization in 1,2-Dihydro-1,2-azaborines

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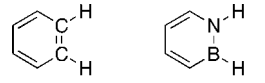
The isolation and structural description of benzene marked the birth of the concept of aromaticity.[2,3] Since this important discovery more than a century ago, derivatives of benzene, that is, arenes, have been playing a pivotal role not only in the field of chemistry but also in other scientific disciplines.[4,5] 1,2-Dihydro-1,2-azaborine (from now on abbreviated as 1,2-azaborine) is related to benzene by substitution of a single CC bond unit of benzene with an isoelectronic BN bond.[6]



Despite its seemingly simple structure, relatively little is known about this family of heterocycles compared to their isoelectronic analogues. Dewar[7,8] and White[9] pioneered the chemistry of 1,2-azaborine and its ring-fused *polycyclic* derivatives in the 1960s.[10] Recent contributions by Ashe,[11–18] Piers,[19–24] and Paetzold[25] have facilitated the preparation of novel BN-heterocycles and sparked a renewed interest in these compounds. As part of a program directed toward the development and application of 1,2-azaborines as versatile arene surrogates, we recently addressed a limitation associated with existing synthetic methods for *monocyclic* 1,2-azaborines, that is, the narrow scope with respect to the boron substituent, by presenting the first general solution for the synthesis of B-substituted 1,2-azaborines.[26]

Because of the similarity between 1,2-azaborine and the quintessential aromatic compound, benzene, the characterization of its aromaticity has been of substantial interest. In the past, assertions of aromaticity of 1,2-azaborines have heavily relied on computational studies.[27–30] Recent synthetic achievements have provided experimental data to supplement the theoretical calculations. For instance, Ashe has demonstrated that 1,2-azaborines can undergo electrophilic aromatic substitutions.[17] The ^{1}H NMR chemical shifts of 1,2-azaborines are consistent with the presence of aromatic ring current effects.[11b]

The geometrical structure of conjugated compounds (i.e., their bond length equalization due to delocalization) provides another crucial criteria of aromaticity.[31] For instance, geometry-based indices of aromaticity have been developed to quantify the extent of aromaticity in carbo- and heterocycles.[32] To date, only five X-ray crystal structures of non-π-bound 1,2-azaborines have been reported.[14,17,18,26] All of these structures exhibit a planar geometry, with intra-ring C−C, C−B, C−N, and B−N bond lengths ranging from 1.35−1.41, 1.50−1.53, 1.37−1.39, and 1.43−1.45 Å, respectively. While these bond distances are consistent with a delocalized picture of this six-membered heterocycle, the lack of structural data of directly comparable reference compounds renders this description somewhat arbitrary and ambiguous. We envisioned that the synthesis of reference heterocycles **A**−**D** (Figure 1) and their direct

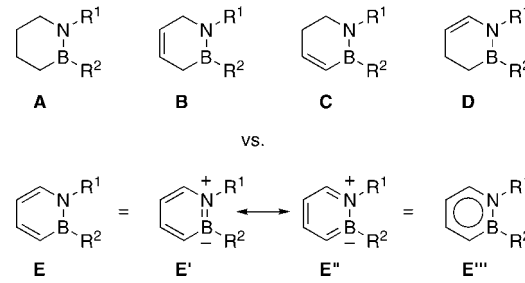
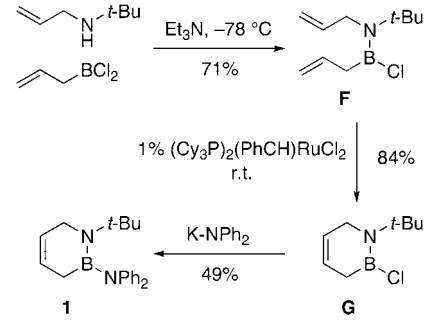


Figure 1. Strategy for determining electron delocalization in 1,2-azaborines: direct structural comparison.

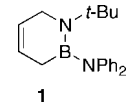
Scheme 1. Synthesis of BN-Heterocycle Precursor **1**



structural comparison with the presumed delocalized structure **E** would provide an unambiguous picture of electron delocalization in 1,2-azaborines.

To the best of our knowledge, no structural data are currently available for monocyclic aminoboranes **A**−**D** illustrated in Figure 1.[33] Furthermore, there are no examples of heterocycles **C** and **D** in the literature. In this Communication, we present the synthesis and structural characterization of a complete set of compounds described in Figure 1 (**A**−**E**; R^1 = *t*-Bu, R^2 = NPh_2). Direct comparison of these structures unambiguously reveals localized bonding in heterocycles **A**−**D** and delocalized bond distances in the aromatic molecule **E**.

In our early work on B-substituted 1,2-azaborines, we noticed that heterocycle **1** containing *N*-*t*-Bu and *B*-NPh_2 substituents furnishes highly crystalline solids suitable for single crystal X-ray diffraction. Thus we chose this substitution pattern for our comparative structural investigation.



The synthesis of **1** is described in Scheme 1. Condensation of *tert*-butylallylamine with allylboron dichloride produced the diene precursor **F**. Ring-closing metathesis[34] of this intermediate using

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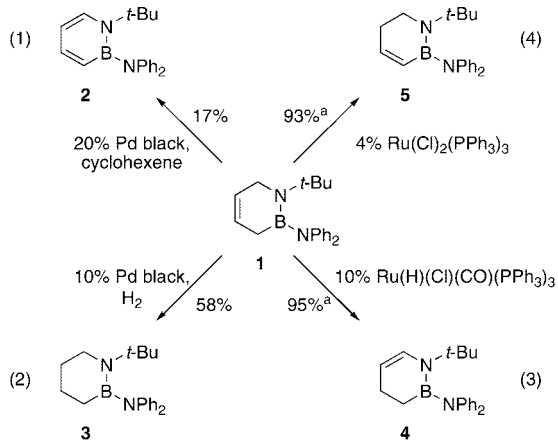
Scheme 2



the first generation Grubbs catalyst gave product **G** in 84% isolated yield. Nucleophilic attack at the B−Cl bond in **G** with potassium diphenylamide furnished the desired heterocycle **1**.

We envisioned that heterocycle **1** could serve as a universal precursor toward the four remaining target structures (**2**−**5** in Scheme 2). Indeed, dehydrogenation of **1** using Pd black[26] generated structure **2** (eq 1). Conversely, compound **1** could be hydrogenated using the same catalyst to furnish **3** (eq 2). Prior to our studies, no methods were available to synthesize heterocycle **4** and **5**. Recognizing that precursor **1** contains an allylamine fragment, we thought that we could take advantage of existing isomerization methods to produce the enamine isomer **4**. Ruthenium complexes have been shown to transform *N*-allylamines and *N*-allylamides into their corresponding isomers in a catalytic fashion.[35−37] Thus, we began to investigate the use of commercially available ruthenium catalysts for the synthesis of **4**. We were surprised to discover a striking difference in reactivity between two of the surveyed ruthenium complexes. While $Ru(H)(Cl)(CO)(PPh_3)_3$ generated the desired *N*-vinyl isomer **4** selectively (eq 3), we were delighted to observe that attempts at the same transformation with $Ru(Cl)_2(PPh_3)_3$ provided the *B*-vinyl isomer **5**, also with high selectivity (eq 4).

The synthetic access to compounds **1**−**5** in Scheme 2 paves the road for their structural analysis. Gratifyingly, we were able to obtain structural data for all five heterocycles via single crystal X-ray diffraction. Selected structural parameters are summarized in Figure 2 and Table 1.[38] Analysis of the data reveals the following trends without exception: (1) all nonaromatic structures (i.e., **1**, **3**, **4**, and **5**) have B−N bond distances consistent with significant double bond character (∼1.41 Å), which lengthen to 1.45 Å after oxidation to **2** (red entries, Table 1); (2) formal C═C double bonds in **1**, **4**, and **5** lengthen significantly upon aromatization (blue entries, Table 1); (3) all formal single bonds shorten upon delocalization (Table 1); (4) the puckered conformations in nonaromatic heterocycles **1**, **3**, **4**, and **5** become planar upon formation of 1,2-azaborine **2** (Figure 2, and Table 1, entry planarity).

Heterocycle **3** serves as a good reference point for structural comparisons. The C−C, C−B, and C−N bond distances in **3** are consistent with formal single bonds (Figure 2, and Table 1).[39] The B−N bond distance of 1.403(2) Å is consistent with a strong double bond character (sum of covalent radii = 1.56 Å). Thus, **3** is isoelectronic and isostructural with a 1,2-disubstituted cyclohexene. Structural comparisons in the Cambridge Crystallographic Database (CCD) indicate that the half-chair conformation of **3** is also adopted by many 1,2-disubstituted cyclohexenes.[40]

Compound **1** is analogous to a 1,2-disubstituted 1,4-cyclohexadiene. It is more planar than **3**, with a root-mean-square deviation

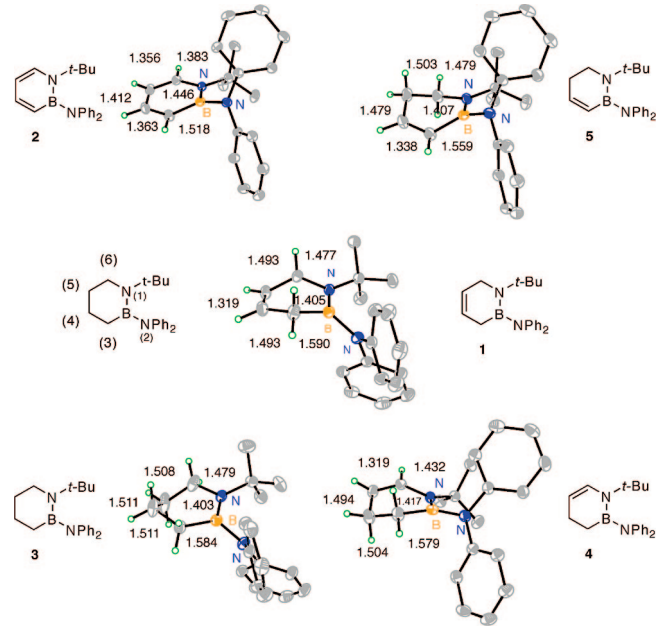
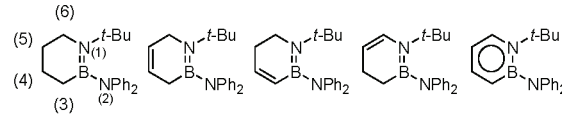


Figure 2. ORTEP illustrations, with thermal ellipsoids drawn at the 35% probability level, of BN-heterocycles **1**−**5**.

Table 1. Selected Bond Distances and Deviations from Planarity (Å) for BN-Heterocycles **1**−**5**



	3	**1**	**5**	**4**	**2**
N(1)–B	1.403(2)	1.405(2)	**1.407(2)**	**1.417(3)**	**1.446(2)**
B–C(3)	1.584(3)	1.590(2)	**1.559(2)**	1.579(4)	**1.518(2)**
C(3)–C(4)	1.511(3)	1.493(2)	**1.338(2)**	1.504(4)	**1.363(2)**
C(4)–C(5)	1.511(3)	1.319(2)	1.479(2)	1.494(4)	1.412(2)
C(5)–C(6)	1.508(3)	1.493(2)	1.503(2)	**1.319(3)**	**1.356(2)**
C(6)–N(1)	1.479(2)	1.477(2)	1.479(2)	**1.432(3)**	**1.383(2)**
B–N(2)	1.488(2)	1.478(2)	1.483(2)	1.480(3)	1.486(2)
planarity[a]	0.226	0.164	0.199	0.183	0.048

[a] Root mean square deviation of intra-ring atoms from the least-squares plane (in Å).

from planarity of 0.164 Å compared to 0.226 Å in **3** (Table 1). However, it is less planar than 1,2-disubstituted 1,4-cyclohexadiene structures, which are almost completely planar.[41] The twisting observed in **1** might be due to steric interactions between the relatively bulky *N*-*t*-Bu and the *B*-NPh_2 substituents. The bond lengths in **1** (in Å) N(1)−B = 1.405(2), and C(4)−C(5) = 1.319(2) are consistent with localized double bonds. The slight shortening of the formal single bonds C(3)−C(4) and C(5)−C(6) in **1** compared to **3** (1.493 Å vs 1.511 and 1.508, respectively) is consistent with a contraction due to a change in hybridization from sp^3 to sp^2.

Partially conjugated **4** and **5** represent the two possible BN-heterocyclic isomers equivalent to 1,3-cyclohexadiene. The bond distances in **5** (in Å) N(1)−B = 1.407(2), B−C(3) = 1.559(2), C(3)−C(4) = 1.338(2) indicate a localized short−long−short "diene" bond sequence. The torsion angle between the double bonds of this "diene" ∠N(1)−B−C(3)−C(4) is −30.9(2)°, indicating a nonplanar geometry. Similarly, the structural parameters in **4** (in Å) C(5)−C(6) = 1.319(3), C(6)−N(1) = 1.432(3), N(1)−B = 1.417(3), are also consistent with a localized "diene" moiety. The value of the torsion angle of −25.2(3)° shows that the C(5)−C(6)−N(1)−B fragment in **4** is nonplanar as well.

Direct comparison of partially conjugated "dienes" **4** and **5** with fully delocalized 1,2-azaborine **2** highlights the clear contrast between *localized* bonding in "dienes" **4** and **5** and *delocalized* bonding in **2** (Table 1, bold entries). Upon forming the six π-electron species **2**, the N(1)−B bond lengthens, and both the B−C(3) and C(6)−N(1) bonds shorten. This observation is consistent with both resonance structures **E′** and **E″** (Figure 1) contributing to the overall structure of 1,2-azaborine **E**, which is indicative of aromatic delocalization (**E‴**).

Structures **1**−**5** reveal with unprecedented detail the geometrical changes that occur from saturated **3** on its transition to the aromatic heterocycle **2** via partially unsaturated **1**, **4**, and **5**. The trends described above are consistent with those seen when comparing nonaromatic cyclohexene, and cyclohexadiene structures with the delocalized aromatic benzene structure.

The boron in boron-containing heterocycles has been shown to accept π-electrons from exocyclic amine substituents to varying degrees, depending on the electronic properties of the heterocycle.[42] The exocyclic nitrogen atom N(2) in **1**−**5** adopts a trigonal planar structure (sum of the angles = 360 ± 1°). The B−N(2) bond distances in **1**−**5** remain constantly ~1.48 Å (Table 1), consistent with some π-bonding.[43] However, as illustrated in Figure 2, the orientation of the nitrogen lone pair in **1**−**5** permits only minimal interaction with the boron atom. We believe that this distortion from coplanarity results from unfavorable steric interactions between the bulky *N*-*t*-Bu and *B*-NPh_2 substituents.

In summary, we have successfully structurally characterized the first examples of "pre-aromatic" 1,2-azaborine heterocycles, enabling the direct comparison of delocalized bonds of 1,2-azaborines to their corresponding formal double and single bonds in nonaromatic systems. The comprehensive data presented in this study provide an unprecedented look into the structural changes that occur in six-membered BN-heterocycles on their road to aromaticity, and they establish with little ambiguity that 1,2-azaborines such as **2** possess delocalized structures consistent with aromaticity.

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Supporting Information Available: Experimental procedures for the synthesis of compounds **1**−**5**, compound characterization data, CIF files for structures **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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