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Boron Materials

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Enforced Planarity: A Strategy for Stable Boron-Containing π-Conjugated Materials**

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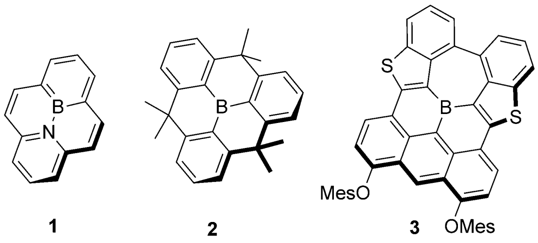
The incorporation of main-group elements into organic materials is an important strategy for modulation of the material's photophysical and electronic properties. The choice of heteroatom has a significant impact on these issues, and while there are several options for adding elements that are more electron rich than carbon (N, O, P, S), the synthesis of electron-deficient materials is largely reliant on trivalent boron.[1] Its empty p orbital can serve as a Lewis base or electron acceptor, and as a conduit for conjugation in an organic π system. To this end, several fascinating and highly functional boron-containing organic materials have been developed, including those with boron incorporated in lateral[2] or in-chain[3] positions of extended and oligomeric conjugated materials. Among the several applications for these materials, selective sensing of hard anions, such as F^-, is a prominent example.[4]

Despite recent advances, these materials do have an Achilles heel that is a direct result of boron's most desired property—electron deficiency. The propensity of boron to react with nucleophiles, and its oxophilicity makes tricoordinate organoboron compounds rather air and (particularly) water sensitive. Three strategies for overcoming this problem can be identified. Perfluorination of aryl groups on boron lowers the nucleophilicity of the carbon atoms attached to boron and perfluoroarylboranes, while extremely Lewis acidic, can be remarkably water tolerant.[5] Substitution of carbon with π-donor atoms, such as N or O, can stabilize tricoordinate boron, but at the expense of the Lewis acid function often demanded from these materials—and water intolerance can still be an issue. The most common strategy is the use of sterically bulky groups (at least one), such as mesityl[6] or triisopropylphenyl, to kinetically stabilize the boron[7] with respect to reactivity with H_2O. While fairly effective, this strategy too can diminish function by hampering reactions with other nucleophiles or preventing packing patterns in the solid state that are desirable for the conduction of charges.

In response to these limitations, two recent papers by Yamaguchi and co-workers introduce an exciting new concept for stabilizing three-coordinate organoboron compounds.[8] Their novel strategy involves encasing the boron in a two-dimensional π scaffold that enforces planarity on the boron by prevention of its pyramidalization through the increased ring strain brought on by this process. While this concept has some precedent in the BN pyrene complex **1**,[9] it has not been explicitly implemented in a true triorganoborane for the purpose of imparting stability. Yamaguchi's compounds **2** and **3** (Scheme 1) are the first molecular designs specifically prepared to test the validity of enforced planarization as a means of stabilizing kinetically naked boron centers.



Scheme 1. Planarized organoboron compounds.

The preparation of compounds **2** and **3** is non-trivial and represents a tour de force in modern organoboron synthesis. Compound **2** can be considered as triphenyl borane that has been rigidified in a planar conformation with three methylene tethers. This compound was prepared from a 9,10-dihydro-9-boraanthracene functionalized with a 2,6-vinyl substituted aryl group on boron using an intramolecular Friedel–Crafts cyclization with $Sc(OTf)_3$ as the Lewis acid catalyst. This planarizes the boron center at an early stage of the synthesis, which is critical, since the following steps require harsh oxidation conditions (CrO_3 in refluxing acetic acid) and methylation with Me_2Zn. This synthesis already emphasizes the high stability of this embedded boron center under rather severe conditions. Compound **3**, anchored with a seven-membered borepin core, is a more extended π-conjugated analogue of **2**, in which all the carbon atoms in the encircling framework are sp^2 hybridized. The key precursor in the synthesis of **3** was an anthryl bis(bromobenzothienyl)borane,

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which underwent a radical-promoted intramolecular reaction using tris(trimethyl silane) ($(\text{TMS})_3\text{SiH}$), followed by an oxidative intramolecular cyclization with FeCl_3. Unlike "normal" triarylboranes, both of these compounds can be purified by column chromatography on silica gel in an open atmosphere, allowing for facile isolation and a high level of purity.

X-ray structural analysis reveals the splendor of these beautiful planar structures (Figure 1). The boron centers have a trigonal planar geometry with the sum of the three C-B-C angles of 360.0°. The B–C bond lengths for **2** (1.519(2)–1.520(2) Å) and **3** (1.508(2)–1.539(2) Å) are comparable, but are considerably shorter than those of trimesityl borane (Mes_3B) (1.573–1.580 Å).[10] This situation is indicative of strong interactions between the empty p-orbital on boron and the π-conjugated framework. Indeed, the π-donating effect of the *ipso*-carbon atoms on boron was reflected in the ^{11}B NMR spectra of **2** and **3**, which show broad signals upfield ($\delta = 48.6$ and 39.5 ppm, respectively) compared to Mes_3B ($\delta = 79.0$ ppm).[11] Compound **2** did not enter into π–π interactions in the solid state, which was attributed to the steric hindrance caused by the peripheral methyl groups. In contrast, because of the completely planar skeleton, compound **3** features close π–π interactions with a distance between the planes of approximately 3.5 Å.

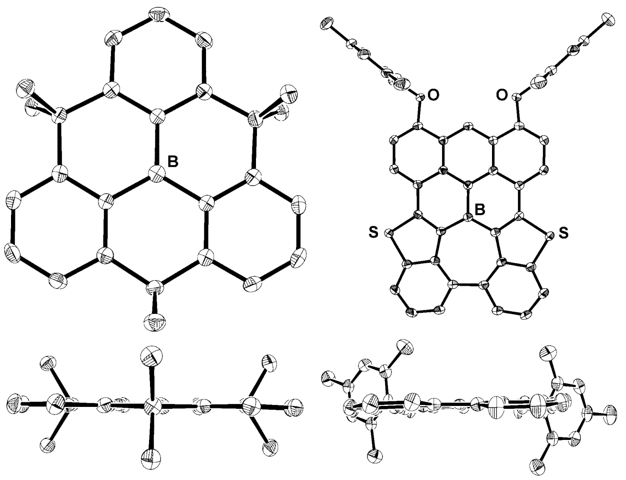

Figure 1. ORTEP diagrams, thermal ellipsoids set at 50% probability, of the molecular structure of **2** (left) and **3** (right). Hydrogen atoms are removed for clarity.

The UV/Vis absorption spectra of compounds **2** and **3** in THF, showed a slight blue shift for **2** compared to Mes_3B, and a much broader, low-energy absorption profile for **3** as a consequence of its extended peripheral conjugation. Both compounds are reversibly reduced by one electron as demonstrated by cyclic voltammetry experiments conducted in THF. Electrochemical experiments on non-planarized boranes in donor solvents can be complicated by the coordination of the solvent to the Lewis acidic borane;[12] not so in this case, because THF does not bind to the boron center. Compound **2** exhibits a half-reduction potential of -2.59 V (vs Fc/Fc^+; $\text{Fc} = [(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]$), whereas **3** has reversible waves for both reduction ($E_{1/2} = -1.37$ V, vs Fc/Fc^+) and oxidation ($E_{1/2} = 0.60$ V, vs Fc/Fc^+). These observations suggest that, despite the lack of steric protection, the radicals generated by these redox processes are stable under the measurement conditions. This opens the door for possible application of these molecules as electron-transporting materials.

While able to accept electrons, the propensity of these compounds to bind Lewis base donors that normally bind strongly to organoboranes is significantly diminished—but not precluded. For example, in THF, both molecules bind the hard, anionic fluoride ion with binding constants of $7.0\times10^5\,\text{M}^{-1}$ and $1.3\times10^5\,\text{M}^{-1}$ for **2** and **3**, respectively. These values are similar to those recorded for Mes_3B ($3.3\times10^5\,\text{M}^{-1}$),[4b] showing that the boron centers still possess significant Lewis acidity towards the F^- ion. Common neutral donors such as pyridine, however, do not bind strongly to these boron centers, if at all. Compound **3** binds pyridine only at low temperatures, as demonstrated by the thermochromic change in color from purple at room temperature to yellow at −80 °C upon coordination.

The physical basis of the remarkable stability and diminished reactivity of these compounds towards Lewis bases is due to a combination of factors. Clearly, the boron center is thermodynamically discouraged from undergoing pyramidalization by the ring strain that would result through the sp^2 hybridized atoms of the C-B-C angles at the cores of the molecules, if these angles should decrease from 120°. The short B–C bonds enforced by the structural framework make these bonds less susceptible to cleavage by protic reagents even if they are able to interact with the boron center. Furthermore, there is a significant entropic barrier to the cleavage of these bonds through the chelate effect. Thus, the two Yamaguchi studies demonstrate that the enforced planarization of the boron centers is an exciting, viable new strategy for introducing the intrinsically useful properties of boron into usable π-conjugated organic frameworks. While the synthetic challenges in preparing such frameworks are not to be taken lightly, advances in synthetic methodology in this rapidly expanding area should allow for many more examples of enforced trigonal planarity in the near future.

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