

# Syntheses and Structures of 6,13-Dihydro-6,13-diborapentacenes: $\pi$ -Stacking in Heterocyclic Analogues of Pentacene

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**Summary:** 6,13-Dibromo-6,13-dihydro-6,13-diborapentacene (**1**) has been prepared by the reaction of 2,3-bis(trimethylsilyl)naphthalene with  $\text{BBr}_3$ . The reaction of **1** with  $\text{Me}_4\text{Sn}$  or mesityllithium afforded the dimethyl derivative **2** or the dimesityl derivative **3**, respectively. In the solid state compounds **1** and **2** form cofacial  $\pi$ -stacks along the a crystal axes, albeit in slightly different ways.

Organic semiconductors have potential applications as components of light-emitting diodes,<sup>1</sup> photovoltaics,<sup>2</sup> and field-effect transistors (OFETs).<sup>3</sup> Intense research efforts have centered on the use of polycyclic aromatic hydrocarbons (PAHs),<sup>3</sup> e.g. pentacene, and their electron-rich heterocyclic relatives<sup>4</sup> as p-type semiconductors for OFETs. In the solid state many PAHs adopt a herringbone packing,<sup>5</sup> which has less optimal intermolecular orbital overlap than a cofacial  $\pi$ -stacking packing.<sup>6</sup> Although many of the factors which influence solid-state packing are not well understood, it has been observed empirically that some substituted PAHs adopt a favorable cofacial stacking.<sup>7</sup> The search for other  $\pi$ -stacking materials continues. Improved n-type semiconductors structurally similar to PAHs but complementary in the type of charge carriers would also be highly desirable.<sup>8</sup> Promising preliminary investigations on PAHs with electron-withdrawing substituents, particularly fluorine, have been reported.<sup>9</sup> The use of boron heterocycles has also been

proposed.<sup>10</sup> Trivalent boron has a formally vacant 2p orbital which might serve as an electron acceptor. Most of the prior work has involved compounds with bulky B substituents.<sup>11</sup> Although these bulky substituents generally enhance the kinetic stability of boron compounds, they are also likely to prevent any possible intermolecular  $\pi$ -stacking important for high charge mobility in OFETs.

We hypothesize that derivatives of the previously unknown 6,13-dihydro-6,13-diborapentacene ring system with small substituents at boron might circumvent these difficulties. Furthermore the antiaromatic four- $\pi$ -electron character of the central heterocyclic ring<sup>12</sup> should facilitate electron transfer to these compounds, as has been found for the related 5,10-dihydro-5,10-diboraanthracenes.<sup>13</sup> We report here on the first syntheses of 6,13-dihydro-6,13-diborapentacenes (**1–3**), the  $\pi$ -stacking structures of **1** and **2**, and electrochemical data for **3**.

Our synthesis of **1** relies on the known facile B/Si exchange of arylsilanes with boron halides.<sup>14</sup> The reaction of the readily available 2,3-bis(trimethylsilyl)naphthalene<sup>15</sup> with  $\text{BBr}_3$  in toluene at 110 °C gave 22% of **1** as a yellow crystalline solid (Scheme 1). Like most organoboron bromides, **1** is quite moisture sensitive but can be handled using standard Schlenk techniques. It is thermally stable to at least its melting point, 282 °C. 6,13-Dibromo-6,13-dihydro-6,13-diborapentacene (**1**) has been fully characterized by <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectroscopy, high-resolution mass spectroscopy, elemental analysis and X-ray diffraction.<sup>16,17</sup> The bromo groups of **1** can be readily substituted for nucleophiles. Reaction of **1** with  $\text{Me}_4\text{Sn}$  gave the crystalline yellow dimethyl derivative **2** in 33% yield. The reaction of **1** with mesityllithium afforded the dimesityl derivative **3**, which like other mesitylboranes is much less sensitive to water and oxygen than **1** and **2**. It seems likely that

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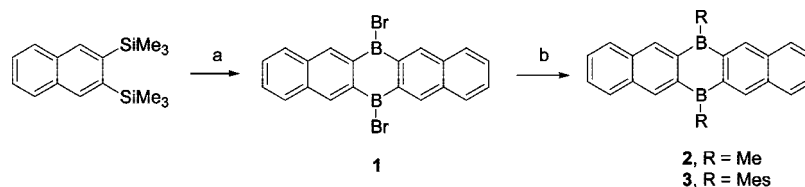
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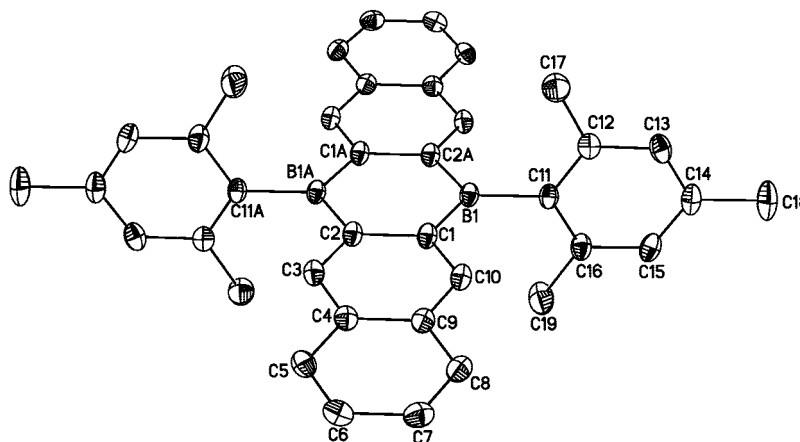
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Scheme 1. Syntheses of 6,13-Dihydro-6,13-diborapentacenes<sup>a</sup>

<sup>a</sup> Conditions: (a) BBr<sub>3</sub>/toluene, 110 °C; (b) for **2** SnMe<sub>4</sub>/toluene, 110 °C, for **3** mesityllithium/THF, 0 °C.



**Figure 1.** Solid-state structure of **3** (ORTEP). Thermal ellipsoids have been set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): B–C( $\alpha$ ), 1.558(2); B–C( $\alpha'$ ), 1.558(2); B–C(exo), 1.584(2); C( $\alpha$ )–C( $\alpha'$ ), 1.450(2).

**1** could also be converted to a variety of other derivatives using the well-honed methods of organoboron chemistry.<sup>18</sup>

Single crystals of **1–3** were grown from toluene solutions. The molecular structures show that the 6,13-dihydro-6,13-diborapentacene core is planar for **1–3**.<sup>17</sup> For **3** the two mesityl groups are inclined to the core plane by approximately 85°

(16) Experimental procedure and characterization of **1**: 2,3-bis(trimethylsilyl)naphthalene (0.55 g, 2.0 mmol) and toluene (5 mL) were added to a Teflon screw-stoppered thick-walled glass reaction tube. After the mixture was cooled to 0 °C, BBr<sub>3</sub> (0.6 mL, 6.3 mmol) was added with magnetic stirring and the valve was then closed. The mixture was next heated to 110 °C for 40 h, affording bright yellow crystals and a brown solution. After the mixture was cooled to room temperature, the liquid was removed by cannula filtration. The solid residue was washed with toluene (2 mL) and dried in vacuo for 1 h to obtain analytically pure product **1** (yield 0.168 g, 22%; mp 282–284 °C). X-ray-quality crystals were obtained by recrystallization from toluene. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.14 (s, 4H, H-5,7,12,14), 7.58, 7.17 (satisfactory computer simulation of AA'XX' pattern was achieved using  $\delta_1$  7.588,  $\delta_2$  7.174,  $J_{AB} = 8.1$  Hz,  $J_{BB'} = 6.4$  Hz,  $J_{AB'} = 1.8$  Hz, 8H, H-1,2,3,4,8,9,10,11). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  142.9, 136.5, 130.6, 129.8, C–B not observable. <sup>11</sup>B NMR (160.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  57.5. UV–vis (C<sub>6</sub>D<sub>6</sub>):  $\lambda_{\max}$  423, 400, 380, 338 nm. HRMS (EI,  $m/z$ ): calcd for C<sub>20</sub>H<sub>12</sub><sup>11</sup>B<sub>2</sub><sup>79</sup>Br<sub>2</sub> (M<sup>+</sup>), 431.9492; found, 431.9501. Anal. Calcd for C<sub>20</sub>H<sub>12</sub>B<sub>2</sub>Br<sub>2</sub>: C, 55.38; H, 2.79. Found: C, 55.24; H, 2.76.

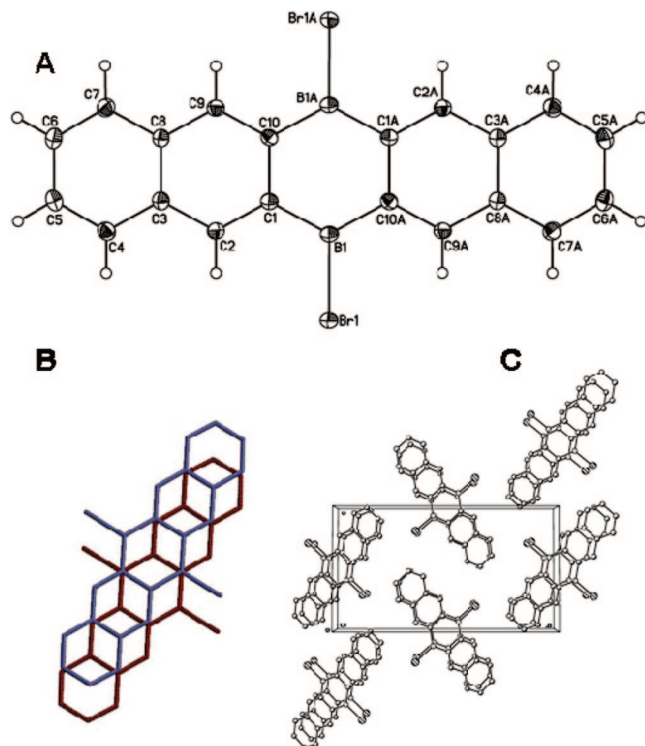
(17) Crystal data for **1**: C<sub>20</sub>H<sub>12</sub>B<sub>2</sub>Br<sub>2</sub>, monoclinic,  $P2_1/c$ ,  $a = 3.932(2)$  Å,  $b = 19.055(7)$  Å,  $c = 10.609(4)$  Å,  $\beta = 92.275(5)^\circ$ ,  $V = 794.2(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.814$  g cm<sup>-3</sup>,  $T = 123(2)$  K,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å. Data were collected on a Siemens SMART CCD instrument. Final  $R$  indices ( $I > 2\sigma(I)$ ):  $R1 = 0.0182$ ,  $wR2 = 0.0461$ .  $R$  indices (all data):  $R1 = 0.0209$ ,  $wR2 = 0.0472$ . GOF on  $F^2 = 1.042$ . Crystal data for **2**: C<sub>22</sub>H<sub>18</sub>B<sub>2</sub>, monoclinic,  $P2_1/c$ ,  $a = 3.968(1)$  Å,  $b = 10.318(3)$  Å,  $c = 19.103(6)$  Å,  $\beta = 91.268(4)^\circ$ ,  $V = 781.8(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.291$  g cm<sup>-3</sup>,  $T = 108(2)$  K,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å. Data were collected on a Siemens SMART CCD instrument. Final  $R$  indices ( $I > 2\sigma(I)$ ):  $R1 = 0.0436$ ,  $wR2 = 0.1252$ .  $R$  indices (all data):  $R1 = 0.0593$ ,  $wR2 = 0.1356$ . GOF on  $F^2 = 1.065$ . Crystal data for **3**: C<sub>38</sub>H<sub>34</sub>B<sub>2</sub>; trigonal,  $R\bar{3}$ ,  $a = b = 30.219(1)$  Å,  $c = 8.4832(7)$  Å,  $V = 6709.0(7)$  Å<sup>3</sup>,  $Z = 9$ ,  $D_c = 1.141$  g cm<sup>-3</sup>,  $T = 85(2)$  K,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å. Data were collected on a Siemens SMART CCD instrument. Final  $R$  indices ( $I > 2\sigma(I)$ ):  $R1 = 0.0494$ ,  $wR2 = 0.1315$ .  $R$  indices (all data):  $R1 = 0.0554$ ,  $wR2 = 0.1385$ . GOF on  $F^2 = 1.043$ .

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(Figure 1). As had been anticipated, the large pendant mesityl groups of compound **3** prevent it from stacking in the solid state. For all three compounds the ring C–C bond distances range from 1.37 to 1.45 Å, quite similar to those of pentacene (1.34–1.46 Å).<sup>5</sup> However, the core B–C bond distances (1.54–1.56 Å) are longer than those found for neutral aromatic boron compounds (range 1.48–1.52 Å),<sup>19</sup> which is consistent with the antiaromatic character of the heterocyclic ring. None of the compounds pack in the familiar herringbone arrangement of pentacene. The packing of **1**, illustrated in Figure 2, shows that the molecules form cofacial  $\pi$  stacks along the  $a$  axis. The intermolecular face-to-face distance is 3.459 Å, and the molecules are inclined to the  $a$  axis by 29.0°. Viewed perpendicularly to the molecular plane (Figure 2B), the molecular packing is slipped along the long molecular axis by about 0.5 ring and along the short molecular axis about 0.25 ring. This brings the boron atom of one molecule vertically close (3.46 Å) to the  $\alpha$ -carbon of its neighbor in the column. Figure 3 illustrates that the molecules of **2** also form  $\pi$ -stacks along the  $a$  axis, but in a somewhat less efficient manner. The intermolecular face-to-face distance is 3.50 Å and the molecules are inclined to the  $a$  axis by 29.2°. Viewed perpendicularly to the molecular plane (Figure 3B), the molecular packing is slipped along the short molecular axis by about 0.75 ring. Since a smaller portion of each ring overlaps vertically, the  $\pi$ -interaction is less efficient.

Dihydrodiborapentacenes **1–3** are all yellow solids. The UV–vis spectrum of **1** in benzene shows a low-energy maximum centered at 400 nm which has a marked vibronic fine structure. The UV–vis spectrum of **3** in cyclohexane had a low-energy maximum at 407 nm with emission at 410 nm. This very small Stokes shift is consistent with minimal geometric

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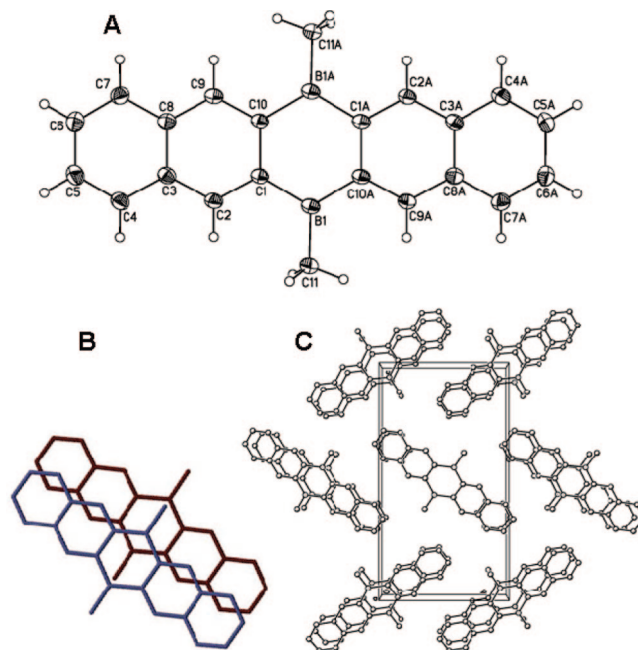


**Figure 2.** (A) Molecular structure of **1** (ORTEP). Thermal ellipsoids have been set at the 50% probability level. Selected bond distances (Å): B–C( $\alpha$ ), 1.549(2); B–C( $\alpha'$ ), 1.543(2); B–Br, 1.950(2); C( $\alpha$ )–C( $\alpha'$ ), 1.454(2). (B) View along the axis perpendicular to the molecular plane, showing slippage. (C) View of the packing along the *a* axis, showing  $\pi$ -stacking.

distortion of the rigid planar core in the excited state. The HOMO–LUMO gaps obtained from the onset of absorption, 2.8 eV for **1** (440 nm) and 3.0 eV for **3** (415 nm), are significantly larger than the 2.07 eV for pentacene. Electrochemical measurements on **3** show the first reduction peak at  $-1.23$  V in acetonitrile. As expected, the reduction peak is shifted positively relative to pentacene ( $-1.87$  V).<sup>9b</sup> It is comparable in magnitude with the reduction of perfluoropentacene ( $-1.13$  V)<sup>9b</sup> and C<sub>60</sub> ( $-1.14$  V),<sup>20</sup> which are excellent n-type semiconductors.

In summary, the novel 6,13-dihydro-6,13-diborapentacene ring system is easy to prepare. These compounds have molecular structures which are similar to that of pentacene but with two fewer  $\pi$ -electrons, which makes them better electron acceptors. In the solid state compounds **1** and **2** each form structures with cofacial  $\pi$ -stacks, but in a somewhat different manner. Thus, the details of the packing are sensitive to B-substituents. Existing

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**Figure 3.** (A) Molecular structure of **2** (ORTEP). Thermal ellipsoids have been set at the 50% probability level. Selected bond distances (Å): B–C( $\alpha$ ), 1.564(2); B–C( $\alpha'$ ), 1.558(2); B–C(exo), 1.578(2); C( $\alpha$ )–C( $\alpha'$ ), 1.446(2). (B) View along the axis perpendicular to the molecular plane, showing slippage. (C) View of the packing along the *a* axis, showing  $\pi$ -stacking.

synthetic methodology should allow preparation of a variety of B-substituted dihydrodiborapentacenes.<sup>21</sup> In general, boron atoms of boraheterocycles interact strongly with their exocyclic substituents;<sup>21</sup> thus, electron density in the ring should also be tunable in a manner which is not as readily achievable in pentacenes. We believe that 6,13-dihydro-6,13-diborapentacenes may find innovative applications as n-type organic semiconductors that complement those of the p-type PAHs.

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**Supporting Information Available:** Text and figures giving experimental procedures and characterization data for all new compounds and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>. OM8005068

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