Boron-doped Pentacenes: Isolation of Crystalline 5,12- and 5,7-Diboratapentacene Dianions

Joshua E. Barker, Akachukwu D. Obi, Diane A. Dickie, Robert J. Gilliard*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

ABSTRACT: The syntheses, molecular structures, reactivities and computational assessment of dipotassium diboratapentacene isomers are described (**1**-**2**). These compounds represent the first examples of aromatized diboraacenes where the boron atoms are spatially separated in different rings of the acene framework. Both **1** and **2** react with carbon dioxide (CO_2) via diastereoselective carboxylation of the pentacene backbone that likely proceeds by a frustrated Lewis pair-like mechanism. The placement of the boron atoms and the reactivity studies provide a platform for later stage functionalization of diboraacenes beyond the central ring of the polycyclic aromatic hydrocarbon core.

Developing new synthetic methods to selectively dope boron in specific positions of traditional carbonaceous heterocycles has become a key strategy to obtain materials with unusual electronic structures and/or photophysical properties.[1] Boraacenes (BAs) are a versatile class of boron-doped heterocycles which have shown promise for small molecule activation,[2] nanographene synthesis,[3] and the development of organic electronics.[4] Their genesis can be traced to the first reports of anionic boratabenzenes by Herberich[5] and Ashe.[6] Despite a substantial amount of work in this area since then,[7] there have been few examples of BAs with π-extension beyond anthracene. Notably, despite the popularity of their all-carbon analogues,[8] borapentacenes are rare and the only example of a fully aromatized borapentacene was synthesized by Piers and coworkers.[9]

An advantage of synthetically doping boron atoms into conjugated hydrocarbons is the ability to chemically reduce boron due to its vacant p_z orbital.[10] This allows for modulation of the electronic structure of BAs which leads to control over reactivity. The utility of this strategy can be illustrated with 9,10-diboraanthracenes.[2] Unreduced 9,10-diboraanthracenes have a formally antiaromatic central ring due to unoccupied p_z orbitals on boron,[11] however, reduction leads to a fully aromatized electron-rich anthracene motif. Anionic 9,10-diboraanthracenes reported by Wagner (**I**, Figure 1a) show novel reactivity with a variety of small molecules (e.g., CO_2, H_2, alkenes) as a result of cooperative reactivity from both boron atoms.[12] Similarly, neutral carbene-stabilized 9,10-diboraanthracenes synthesized by Harman (**II**)[13] and Braunschweig (**III**)[14] react with CO_2, O_2, CO, and other small molecules. Despite these promising results, diboraacenes (DBAs) beyond 9,10-diboraanthracenes are underexplored, and the overwhelming majority of structures contain both boron atoms in the same ring. There are few examples of π-extended DBAs,[4,11a,15] but none of them contain an aromatized acene motif. Overall, synthetic routes to DBAs with boron atoms separated into different rings are almost non-existent and it has been noted that such targets are synthetically challenging to achieve.[15c] Nevertheless, new DBA structures are important as templates for a wide range of new functional molecules and materials.

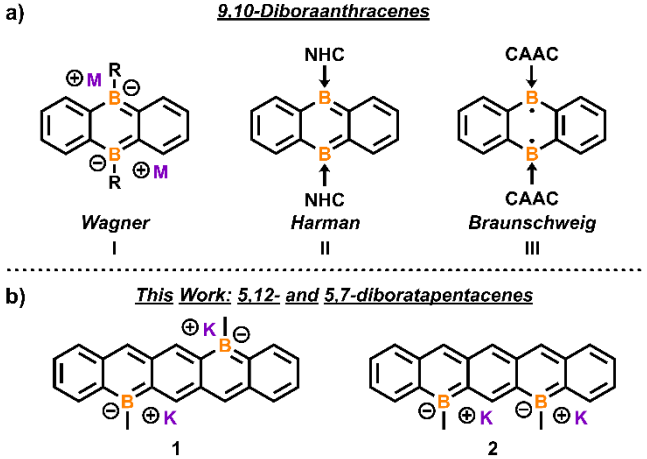
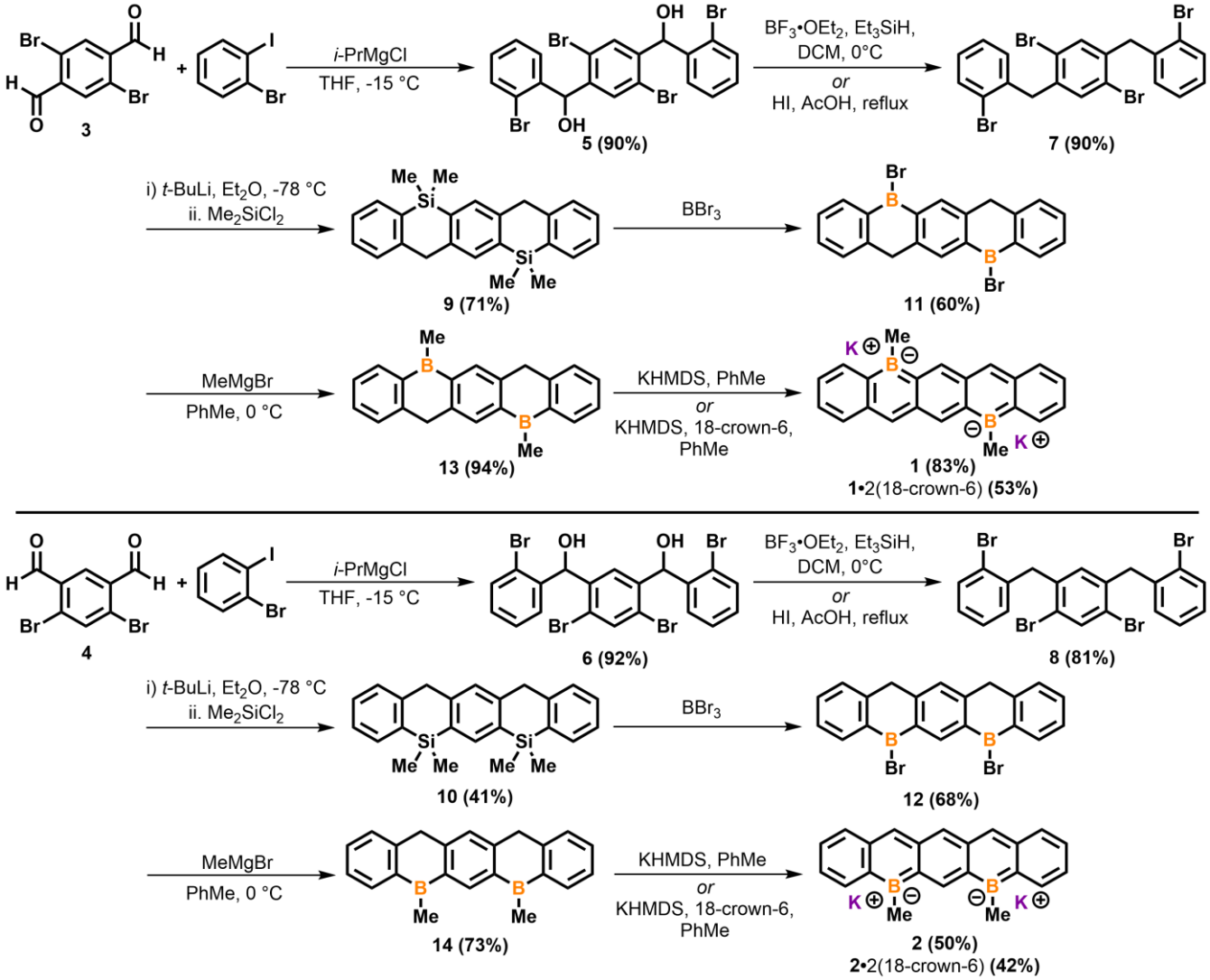


Figure 1. Diboraacenes: a) 9,10-diboranthracenes [NHC = N-heterocyclic carbene, CAAC = cyclic(alkyl)(amino) carbene]; b) anionic diboratapentacenes described in this work.

Considering our established interest in reduced boracycles containing 5- and 7-membered rings,[16] we reasoned that we could apply reduction strategies for the development of π-extended linear acenes. We posited that separation of the boron atoms into different rings would open the door to dual reactivity and functionalization of acenes beyond the central position of the polycyclic aromatic hydrocarbon core. Herein we report the synthesis, molecular structures, computations, and reactivities of 5,12-diboratapentacene (**1**) and 5,7-diboratapentacene (**2**) dianions (Figure 1b). Importantly, these molecules represent the first examples of aromatized DBAs where the two boron atoms are spatially separated in different rings within the acene framework. Moreover, both **1** and **2** readily react with CO_2 to give diastereoselective *syn* or *anti* carboxylation across the boron rings depending on the presence or absence of coordinating 18-crown-6 ethers.

The synthesis of diboratapentacenes (DBPs) **1** and **2** began from 2,5-dibromoterepthalaldehyde (**3**)[17] and 2,4-dibromoisophthalaldehyde (**4**)[18] (Scheme 1). Reaction of *i*PrMgCl with 2-bromo-iodobenzene formed the mono-Grignard, to which solutions of **3** or **4** were added to yield phthalyl alcohols **5** and **6**. The alcohols were reduced to diphenyl-xylenes **7** and **8** in moderate to high yields using either BF_3•OEt_2/Et_3SiH or HI/AcOH conditions. Tetramethyldisilapentacenes **9** and **10**

Scheme 1. Synthesis of 5,12- and 5,7-Diboratapentacene.



were generated following tetralithiation of **7** and **8**, and subsequent quenching with neat Me_2SiCl_2. Silicon-boron exchange with **9** and **10** in neat BBr_3 proceeded readily at room temperature resulting in tetrahydro-dibromoborapentacenes **11** and **12** in moderate yields. Formation of these boracycles was confirmed by X-ray crystallography (Figure S1) as well as the appearance of a broad resonance at 61.5 ppm in the ^{11}B NMR spectra of **11**, indicative of tricoordinate boron species. Due to poor solubility no sufficiently resolved ^{11}B NMR spectrum of **12** could be obtained. Methylation of compounds **11** and **12** was carried out by the addition of MeMgBr to their respective toluene solutions at 0 °C, producing **13** and **14**. Addition of the methyl group led to slight downfield shifts in the ^{11}B NMR spectra (δ 63.6 ppm and 62.6 ppm for **13** and **14**, respectively), typical of tricoordinate arylboranes. Finally, deprotonation with KHMDS yielded the desired dipotassium 5,12-dimethyl-5,12-diboratapentacene (**1**) and dipotassium 5,7-dimethyl-5,7-diboratapentacene (**2**). The addition of 18-crown-6 during deprotonation produces **1**•2(18-crown-6) or **2**•2(18-crown-6) as monomeric complexes. Upon deprotonation with KHMDS and subsequent aromatization of the boron ring, the C-8 protons in **1** (6.98 ppm, for numbering see Figure 2a) and C-7/C-14 in **2** (7.52 ppm, for numbering see Figure 2b) appear far downfield from the analogous shifts in **13** (4.52 ppm) and **14** (4.48 ppm). As a result of increased electron density around the boron atoms, the ^{11}B shifts of both **1** (43.3 ppm) and **2** (42.8 ppm) are upfield-shifted when compared with **13** and **14**. Notably, the ^{1}H NMR spectra are nearly identical between derivatives with or without 18-crown-6. This indicates that there is likely a similar coordination environment of the potassium atoms in solution for both molecules.

DBPs **1** and **2** are dark green both in the solid state and in solution. UV-Vis spectra of dilute THF solutions of **1** and **2** are shown in Figure 2. When compared with reports of substituted all-carbon acenes[19] the characteristics of **1** and **2** are comparable to those of hexacene and heptacene which is consistent with previous observations of boron-doped acenes.[9] Both com-

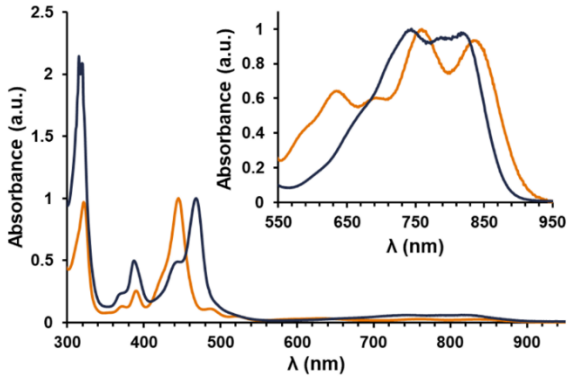


Figure 2. UV-Vis spectra of **1** (Navy) and **2** (Orange) in THF.

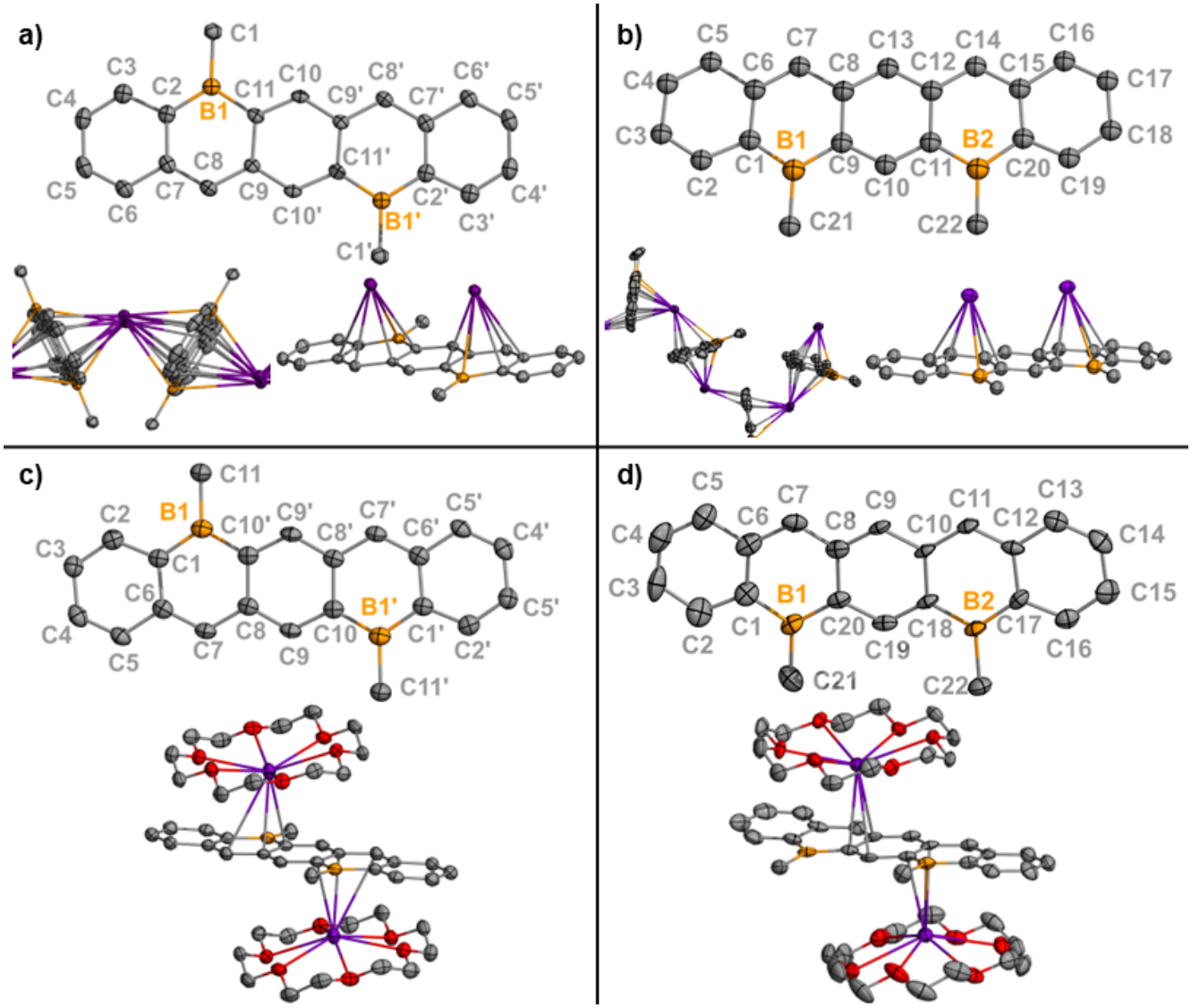


Figure 3. Molecular structures and packing of **1**•3(THF) (a); **2**•3(THF) (b); **1**•2(18-crown-6) (c); **2**•2(18-crown-6) (d). Hydrogens and disordered THF molecules have been removed for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (Å) - **1**•3(THF): C1-B1 1.600(4), B1-C2 1.517(4), C2-C7 1.455(4), C7-C8 1.405(4), C8-C9 1.426(3), C9-C101 1.457(3), C11-B1 1.547(4); **2**•3(THF): C21-B1 1.587(15), B1-C1 1.514(15), C1-C6 1.423(15), C6-C7 1.394(15), C7-C8 1.420(13), C8-C9 1.464(12), C9-B1 1.533(14); **1**•2(18-crown-6): C11-B1 1.601(4), B1-C1 1.518(4), C1-C6 1.453(4), C6-C7 1.386(4), C7-C8 1.425(4), C8-C10' 1.455, C10'-B1 1.544; **2**•2(18-crown-6): C21-B1 1.610(11), B1-C1 1.513(14), C1-C6 1.453(13), C6-C7 1.438(18), C7-C8 1.388(19), C8-C20 1.484(17), C20-B1 1.536(18).

pounds share similar features, with strong high-energy transitions (**1**, λ_{abs} = 468 nm; **2**, λ_{abs} = 445 nm) and a weaker low-energy absorbance (**1**, λ_{abs} = 744, 816 nm; **2**, λ_{abs} = 634, 759, 856 nm) exhibiting the vibronic structure typically seen in acenes. TD-DFT calculations, performed at TD-B3LYP/6-31G(d,p) level of theory, attribute the low-energy absorbance to the HOMO to LUMO transition for both molecules which is consistent with other acenes. Notably, the lowest energy λ_{abs} values for **1** and **2** are red-shifted ~60 nm and ~100 nm, respectively, from unsubstitued heptacene (753 nm)[19b] and in a similar range as silyl-ethynyl substituted heptacenes.[19a]

The molecular structures of **13** and **14** (Figure S2) were obtained from crystals grown from vapor diffusion of hexanes into toluene. Additionally, air and moisture-sensitive single crystals of **1**•3THF and **2**•3THF as well as their crown-ether adducts were grown at -37 °C either by vapor diffusion of hexanes into THF solution (**1**•3(THF)), simple recrystallization from THF (**1**•2(18-crown-6)), or by layering hexanes over a THF solution of the desired dianion [**2**•3(THF), **2**•2(18-crown-6)]. These methods yielded dark green plate [**1**•3(THF), **2**•3(THF), **2**•2(18-crown-6)] or block-like crystals [**1**•2(18-crown-6)] which were suitable for X-ray diffraction. For both **1**•3(THF) and **2**•3(THF), the solid-state crystal structures showed two crystallographically distinct molecules in the unit cell, with co-facially bound potassium atoms stabilized by three THF molecules (Figure 2). The aromatization of the boron-containing rings is observable by the shortening of the C7-C8 (1.405(4) Å) and C2-B1 (1.517(4) Å) bonds in **1** relative to the analogous bonds in **13** (C6-C7 1.5040(13) Å, C1-B1 1.5545(15) Å respectively). Similar evidence for aromatization is seen in the C1-B1 (1.514(15) Å) and C6-C7 (1.394(15) Å) bonds of **2** when compared to C6-C7 (1.486(16) Å) and C1-B1 (1.573(19) Å) in **14**. For **1**•3(THF) and **2**•3(THF), the potassium atoms exhibit η^3-η^6–coordination with metal-centroid distances between 2.8229(12) and 3.0357(12) Å in **1** and 2.765(4) to 3.078(4) Å in **2.** Both compounds crystallize as 1-D

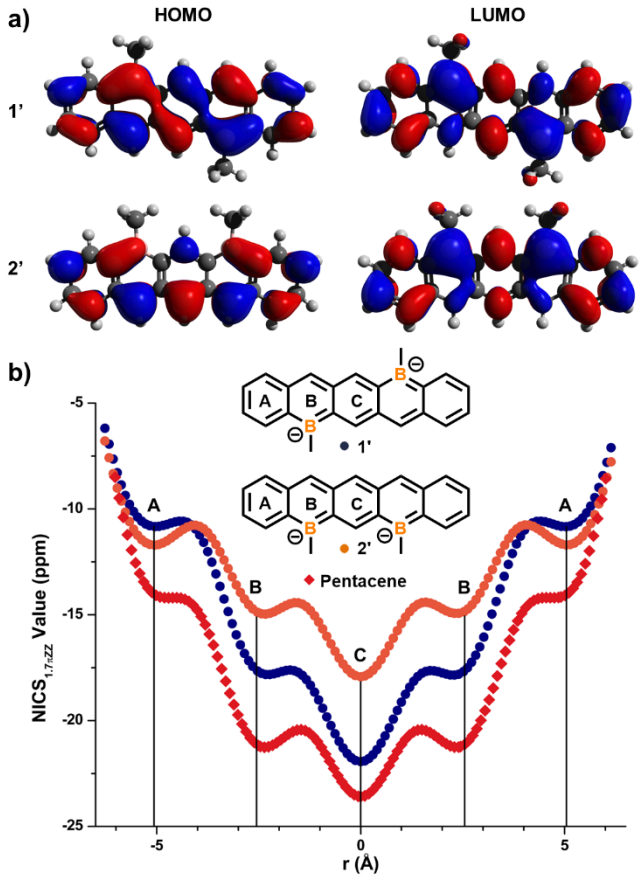
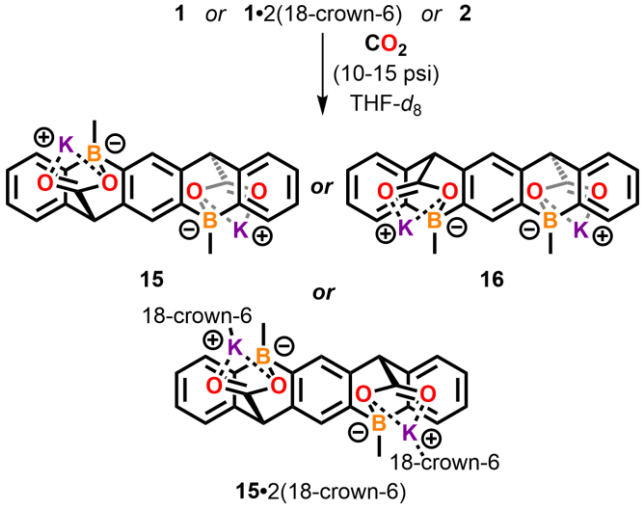


Figure 4. a) HOMO and LUMO plots of **1'** and **2'**; b) NICS-XY scan plots of **1'** and **2'**. All calculations were performed at the B3LYP/6-31G(d,p) level of theory.

coordination polymers where the potassium atoms bound to each boron ring are shared in a face-to-face fashion with the next molecule. Unsurprisingly, crown ether coordination in **1**•2(18-crown-6) and **2**•2(18-crown-6) interrupts this packing motif. For these two structures, the potassium atoms are coordinated on opposite sides of each diboratapentacene unit and are η^2- or η^3-bound to the internal side of each boron ring.

Nucleus independent chemical shift (NICS) calculations were performed to determine the aromaticity of the diboratapentacene structures. NICS X-Y scans[20] were calculated at the B3LYP/6-31G(d,p) level of theory for **1'**, **2'**, as well as pentacene (Figure 3). As is typical for extended acenes, both **1'** and **2'** contain stronger local aromaticity in the central ring (ring C), which is also seen in pentacene. The aromaticity progressively decreases moving to the outer rings. While both **1'** and **2'** are less aromatic than pentacene, **2'** shows the weakest overall aromaticity. The central ring of **2'** is ~3.5 ppm less aromatic than that of **1'** which in turn is only ~1.5 ppm less aromatic than pentacene. It is likely that the weaker aromaticity of **2'** results from decreased delocalization of π-electrons due to the arrangement of the boron atoms within the pentacene framework. This is also reflected in the HOMO plots of **1'** and **2'**.

Scheme 2. Reactions of CO_2 With Diboratapentacenes.



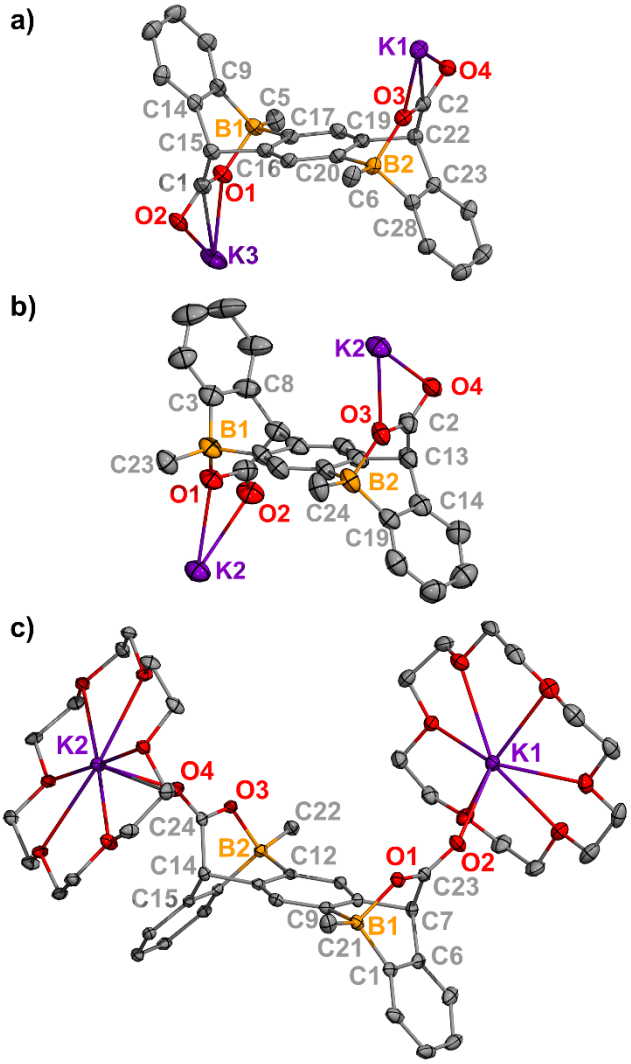


Figure 5. Molecular structures of **15** (a), **16** (b), and **15**•2(18-crown-6) (c). Hydrogens and solvent have been removed for clarity. Ellipsoids are drawn at 50% probability.

In order to examine electronic structure, we also generated HOMO and LUMO plots for **1'**, and **2'**. Based on the work by Wagner[2,12c] and Bickelhaupt[21] we expected that **1** and **2** could potentially activate small molecules with an FLP-like mechanism[2] where the external carbons of the boron ring (C8 for **1'**, C7/C14 for **2'**) and the boron atoms react cooperatively as Lewis bases and Lewis acids, respectively. Calculations of the frontier orbitals of **1** and **2** (calculated as free dianions, **1'** and **2'**, Figure 5a) supported this hypothesis showing that, while the HOMO is distributed more evenly across the molecule, the boron atoms have a much greater contribution to the LUMO.

Charging J-Young NMR tubes containing solutions of **1**, **2**, and **1**•2(18-crown-6) with 10-15 psi of CO_2 (Scheme 2) led to clean conversion to **15**, **16**, and **15**•2(18-crown-6), respectively. NMR spectra showed that the C-8 proton resonance of **15** was shifted upfield to 4.47 ppm (MeCN-*d*3), while the C7/C14 resonance for **16** was shifted to 4.34 ppm (THF-*d*8), both confirming dearomatization of the boron rings. Additionally, the upfield singlet associated with the methyl group was shifted far-upfield at 0.32 ppm for **15** and 0.33 ppm for **16** as a result of the tetracoordinate boron atom. The presence of CO_2 in **15** and **16** was verified by the appearance of a downfield ^{13}C NMR resonance (178.9-181.3 ppm) and the diagnostic C=O stretching band (~1626-1632 cm^{-1}) in IR spectra (Figure S3 and Figure S4). Cooling solutions of **15** (MeCN-d3) or **16** (THF-d_8) to -37 °C yielded single crystals of **15** and **16** suitable for X-ray diffraction. The solid-state crystal structures show that a molecule of CO_2 has reacted across each of the boron rings (Figure 4). The orientation of each carboxylate moiety suggests that the C-8/C-8' carbons in **1** and C-7/C-14 carbons in **2** react as nucleophiles with the carbon of CO_2 with concomitant coordination of an oxygen to the boron atom across the ring. It is possible that this reactivity occurs in a stepwise or concerted fashion. In either case it follows the FLP-type reactivity expected from the HOMO-LUMO plots and seen in some DBA derivatives.[2] Interestingly, only the *anti*-product was observed in both cases. This is consistent with an *anti*-coordination arrangement of the potassium atoms in solution which would facilitate carboxylation on opposite faces of the diboratapentacene scaffold. Consequently, it is surprising that only *syn*-carboxylation is observed when using **1**•2(18-crown-6) to form **15**•2(18-crown-6) (Figure 4). The mechanism for this selectivity is unclear, however this finding indicates that selective late-stage modification of **1** and **2** should be possible. The extended packing of **15** and **16** is also unique as both form 2-D coordination frameworks (see supporting information). This packing is not observed in **15**•2(18-crown-6) which packs as individual molecules.

We have reported the successful synthesis and characterization of DBP isomers **13** and **14** and their conversion to the corresponding diboratapentacene dianions **1** and **2**, which are the first fully-aromatized DBP structures with boron atoms in separate rings. The introduction of these new DBP topologies may serve as chemical synthons for new functionalized DBPs for applications in organic electronics and other functional materials. DFT calculations and the observed activation of CO_2 demonstrated the ability of these molecular scaffolds to serve as a ditopic activator for small-molecules. An unexpected and exciting result was the *anti* vs. *syn* selectivity of the carboxylation dependent on the presence of crown-ethers coordinated to the potassium atoms. Further studies of the reactivity of 5,12- and 5,7-diboratapentacenes as well as exploration of other structures based on these scaffolds will be reported in due course.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

NMR spectra for all compounds; X-ray refinement details; IR spectra; and computational details (PDF)

Accession Codes

CCDC2213825-2213835 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

AUTHOR INFORMATION

Corresponding Author

Robert J. Gilliard, Jr. – Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States; orcid.org/0000-0002-8830-1064; Email: rjg8s@virginia.edu

Author Contributions

Joshua E. Barker – Department of Chemistry, University of Virginia, Charlottesville Virginia, United States; orcid.org/0000-0001-6139-8858

Akachukwu D. Obi – Department of Chemistry, University of Virginia, Charlottesville Virginia, United States; orcid.org/0000-0001-7118-7931

Diane A. Dickie – Department of Chemistry, University of Virginia, Charlottesville Virginia, United States; orcid.org/0000-0003-0939-3309

Notes

The Authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors acknowledge the Arnold and Mabel Beckman Foundation for support of this work through a Beckman Young Investigator Award. The University of Virginia and the National Science Foundation Major Research Instrumentation (CHE-2018870) programs are also acknowledged.

REFERENCES

1. (a) Escande, A.; Ingleson, M. J. Fused Polycyclic Aromatics incorporating Boron in the Core: Fundamentals and Applications. *Chem. Commun.* **2015**, *51*, 6257–6274; (b) Wakamiya, A. incorporation of Boron into π-Conjugated Scaffolds to Produce Electron-Accepting π-Electron Systems. In *Main Group Strategies towards Functional Hybrid Materials*; John Wiley & Sons, Ltd, 2017; pp 1–26; (c) von Grotthuss, E.; John, A.; Kaese, T.; Wagner, M. Doping Polycyclic Aromatics with Boron for Superior Performance in Materials Science and Catalysis. *Asian J. Org. Chem.* **2018**, *7*, 37–53.
2. Prey, S. E.; Wagner, M. Threat to the Throne: Can Two Cooperating Boron Atoms Rival Transition Metals in Chemical Bond Activation and Catalysis? *Adv. Synth. Catal.* **2021**, *363*, 2290–2309.
3. (a) Dou, C.; Saito, S.; Matsuo, K.; Hisaki, I.; Yamaguchi, S. A Boron-Containing PAH as a Substructure of Boron-Doped Graphene. *Angew. Chem. Int. Ed.* **2012**, *51,* 12206–12210; (b) Osumi, S.; Saito, S.; Dou, C.; Matsuo, K.; Kume, K.; Yoshikawa, H.; Awaga, K.; Yamaguchi, S. Boron-Doped Nanographene: Lewis Acidity, Redox Properties, and Battery Electrode Performance. *Chem. Sci.* **2015**, *7*, 219–227.
4. John, A.; Bolte, M.; Lerner, H.-W.; Meng, G.; Wang, S.; Peng, T.; Wagner, M. Doubly Boron-Doped Pentacenes as Emitters for OLEDs. *J. Mater. Chem. C* **2018**, *6*, 10881–10887.
5. Herberich, G. E.; Greiss, G.; Heil, H. F. A Novel Aromatic Boron Heterocycle as Ligand in a Transition Metal π-Complex. *Angew. Chem. Int. Ed.* **1970**, *9*, 805–806.
6. Ashe, A. J.; Shu, P. 1-Phenylborabenzene Anion. *J. Am. Chem. Soc.* **1971**, *93* (7), 1804–1805.
7. (a) Paetzold, P.; Finke, N.; Wennek, P.; Schmid, G.; Boese, R. 2-Boratanaphthalin-Anion als hexahapto-gebundener Ligand. *Z. Naturforsch.* **1986**, *41b*, 167–174; (b) Ashe III, A. J.; Al-Ahmad, S.; Kampf, J. W. Boratabenzene Zirconium(II) Complexes: An Unusual Annulation with Ethynes. *Angew. Chem. Int. Ed.* **1997**, *36*, 2014–

2016; (c) E. Herberich, G.; Cura, E.; Ni, J. A New Synthetic Route to 2-Boratanaphthalenes. *Inorg. Chem. Commun.* **1999**, *2*, 503–506; (d) Braunstein, P.; Cura, E.; Herberich, G. E. Heterometallic Complexes and Clusters with 2-Boratanaphthalene Ligands. *J. Chem. Soc., Dalton Trans.* **2001**, No. 11, 1754–1760. (e) Van Veen, R.; Bickelhaupt, F. The 9-Mesityl-9-Boraanthracene Anion. *J. Organomet. Chem.* **1971**, *30*, C51–C53; (f) van Veen, R.; Bickelhaupt, F. Synthesis of the 9-Mesityl-10-Phenyl-9-Boraanthracene Anion. *J. Organom. Chem.* **1972**, *43*, 241–248; (g) Jutzi, P. Preparation of the 9-Phenyl-9-Boraanthracene Anion. *Angew. Chem. Int. Ed.* **1972**, *11*, 53–54; (h) Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. Zirconium Complexes of 9-Phenyl-9-Borataanthracene. Synthesis, Structural Characterization, and Reactivity. *J. Am. Chem. Soc.* **1998**, *120*, 6037–6046; (i)Kushida, T.; Zhou, Z.; Wakamiya, A.; Yamaguchi, S. Planarized B-Phenylborataanthracene Anions: Structural and Electronic Impacts of Coplanar Constraint. *Chem. Commun.* **2012**, *48*, 10715–10717; (j) Bartholome, T. A.; Kaur, A.; Wilson, D. J. D.; Dutton, J. L.; Martin, C. D. The 9-Borataphenanthrene Anion. *Angew. Chem. Int. Ed.* **2020**, *59*, 11470–11476.

8. Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting π-Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. *Chem. Rev.* **2012**, *112*, 2208–2267.

9. Wood, T. K.; Piers, W. E.; Keay, B. A.; Parvez, M. Synthesis and Comparative Characterization of 9-Boraanthracene, 5-Boranaphthacene, and 6-Borapentacene Stabilized by the H2IMes Carbene. *Chemi. Eur. J.* **2010**, *16*, 12199–12206.

10. Yamashita, M.; Nozaki, K. Boryl Anions. In *Synthesis and Application of Organoboron Compounds*; Fernández, E., Whiting, A., Eds.; Topics in Organometallic Chemistry; Springer International Publishing: Cham, 2015; pp 1–37.

11. (a) Chen, J.; Kampf, J. W.; Ashe, A. J. Syntheses and Structures of 6,13-Dihydro-6,13-Diborapentacenes: π-Stacking in Heterocyclic Analogues of Pentacene. *Organometallics* **2008**, *27*, 3639–3641; (b) Reus, C.; Weidlich, S.; Bolte, M.; Lerner, H.-W.; Wagner, M. C-Functionalized, Air- and Water-Stable 9,10-Dihydro-9,10-Diboraanthracenes: Efficient Blue to Red Emitting Luminophores. *J. Am. Chem. Soc.* **2013**, *135*, 12892–12907.

12. (a) Lorbach, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. Dilithio 9,10-Diborataanthracene: Molecular Structure and 1,4-Addition Reactions. *Organometallics* **2010**, *29* (22), 5762–5765; (b) von Grotthuss, E.; Diefenbach, M.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. Reversible Dihydrogen Activation by Reduced Aryl Boranes as Main-Group Ambiphiles. *Angew. Chem. Int. Ed.* **2016**, *55*, 14067–14071; (c) von Grotthuss, E.; Prey, S. E.; Bolte, M.; Lerner, H.-W.; Wagner, M. Selective CO2 Splitting by Doubly Reduced Aryl Boranes to Give CO and [CO3]2−. *Angew. Chem. Int. Ed.* **2018**, *57*, 16491-16495; (d) von Grotthuss, E.; Nawa, F.; Bolte, M.; Lerner, H.-W.; Wagner, M. Chalcogen–Chalcogen-Bond Activation by an Ambiphilic, Doubly Reduced Organoborane. *Tetrahedron* **2019**, *75*, 26–30; (e) von Grotthuss, E.; Prey, S. E.; Bolte, M.; Lerner, H.-W.; Wagner, M. Dual Role of Doubly Reduced Arylboranes as Dihydrogen- and Hydride-Transfer Catalysts. *J. Am. Chem. Soc.* **2019**, *141*, 6082–6091.

13. (a) Taylor, J. W.; McSkimming, A.; Guzman, C. F.; Harman, W. H. N-Heterocyclic Carbene-Stabilized Boranthrene as a Metal-Free Platform for the Activation of Small Molecules. *J. Am. Chem. Soc.* **2017**, *139*, 11032–11035.

14. (a) Saalfrank, C.; Fantuzzi, F.; Kupfer, T.; Ritschel, B.; Hammond, K.; Krummenacher, I.; Bertermann, R.; Wirthensohn, R.; Finze, M.; Schmid, P.; Engel, V.; Engels, B.; Braunschweig, H. CAAC-Stabilized 9,10-Diboraanthracenes—Acenes with Open-Shell Singlet Biradical Ground States. *Angew. Chem. Int. Ed.* **2020**, *59*, 19338–19343; (b) Dietz, M.; Arrowsmith, M.; Gärtner, A.; Radacki, K.; Bertermann, R.; Braunschweig, H. Harnessing the Electronic Differences between CAAC-Stabilised 1,4-Diborabenzene and 9,10-Diboraanthracene for Synthesis. *Chem. Commun.* **2021**, *57*, 13526–13529.

15. (a) John, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. A Vicinal Electrophilic Diborylation Reaction Furnishes Doubly Boron-Doped Polycyclic Aromatic Hydrocarbons. *Angew. Chem. Int. Ed.* **2017**, *56*, 5588–5592; (b) Radtke, J.; Schickedanz, K.; Bamberg, M.; Menduti, L.; Schollmeyer, D.; Bolte, M.; Lerner, H.-W.; Wagner, M. Selective Access to Either a Doubly Boron-Doped Tetrabenzopentacene or an Oxadiborepin from the Same Precursor. *Chem. Sci.* **2019**, *10*, 9017–9027; (c) Ito, M.; Sakai, M.; Ando, N.; Yamaguchi, S. Electron-Deficient Heteroacenes That Contain Two Boron Atoms: Near-Infrared Fluorescence Based on a Push–Pull Effect**. *Angew. Chem. Int. Ed.* **2021**, *60*, 21853–21859; (d) Mützel, C.; Farrell, J. M.; Shoyama, K.; Würthner, F. 12b,24b-Diborahexabenzo[a,c,Fg,l,n,Qr]Pentacene: A Low-LUMO Boron-Doped Polycyclic Aromatic Hydrocarbon. *Angew. Chem. Int. Ed.* **2022**, *61*, e202115746; (e) Chen, C.; Wang, M.-W.; Zhao, X.-Y.; Yang, S.; Chen, X.-Y.; Wang, X.-Y. Pushing the Length Limit of Dihydrodiboraacenes: Synthesis and Characterizations of Boron-Embedded Heptacene and Nonacene. *Angew. Chem. Int. Ed.* **2022**, *61*, e202200779.

16. (a) Wentz, K. E.; Molino, A.; Weisflog, S. L.; Kaur, A.; Dickie, D. A.; Wilson, D. J. D.; Gilliard Jr., R. J. Stabilization of the Elusive 9-Carbene-9-Borafluorene Monoanion. *Angew. Chem. Int. Ed.* **2021**, *60*, 13065–13072; (b) Wentz, K. E.; Molino, A.; Freeman, L. A.; Dickie, D. A.; Wilson, D. J. D.; Gilliard, R. J. Reactions of 9-Carbene-9-Borafluorene Monoanion and Selenium: Synthesis of Boryl-Substituted Selenides and Diselenides. *Inorg. Chem.* **2021**, *60*, 13941–13949; (c) Hollister, K. K.; Yang, W.; Mondol, R.; Wentz, K. E.; Molino, A.; Kaur, A.; Dickie, D. A.; Frenking, G.; Pan, S.; Wilson, D. J. D.; Gilliard Jr., R. J. Isolation of Stable Borepin Radicals and Anions. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202516; (d) Wentz, K. E.; Molino, A.; Freeman, L. A.; Dickie, D. A.; Wilson, D. J. D.; Gilliard, R. J. Jr. Activation of Carbon Dioxide by 9-Carbene-9-Borafluorene Monoanion: Carbon Monoxide Releasing Transformation of Trioxaborinanone to Luminescent Dioxaborinanone. *J. Am. Chem. Soc.* **2022**, *144*, 16276–16281.

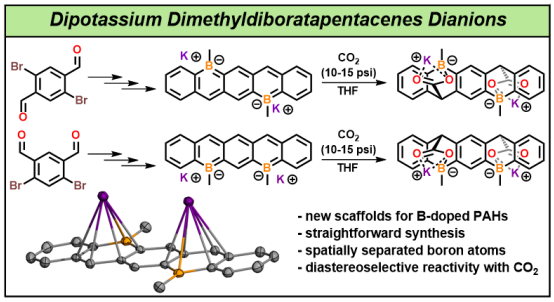
17. Prusinowska, N.; Bardziński, M.; Janiak, A.; Skowronek, P.; Kwit, M. Sterically Crowded Trianglimines—Synthesis, Structure, Solid-State Self-Assembly, and Unexpected Chiroptical Properties. *Chemistry – An Asian Journal* **2018**, *13*, 2691–2699.

18. Bonifacio, M. C.; Robertson, C. R.; Jung, J.-Y.; King, B. T. Polycyclic Aromatic Hydrocarbons by Ring-Closing Metathesis. *J. Org. Chem.* **2005**, *70*, 8522–8526.

19. (a) Payne, M. M.; Parkin, S. R.; Anthony, J. E. Functionalized Higher Acenes: Hexacene and Heptacene. *J. Am. Chem. Soc.* **2005**, *127*, 8028-8029. (b) Einholz, R.; Fang, T.; Berger, R.; Grüninger, P.; Früh, A.; Chassé, T.; Fink, R. F.; Bettinger, H. F. Heptacene: Characterization in Solution, in the Solid State, and in Films. *J. Am. Chem. Soc.* **2017**, *139*, 4435-4442.

20. Gershoni-Poranne, R.; Stanger, A. The NICS- *XY* -Scan: Identification of Local and Global Ring Currents in Multi-Ring Systems. *Chem. Eur. J.* **2014**, *20*, 5673–5688.

21. Veen, R. V.; Bickelhaupt, F. Reactions of the 9-Mesityl-9-Boraanthracene Anion. *J. Organomet. Chem.* **1974**, *77*, 153–165.



Insert Table of Contents artwork here