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Boron Heterocycles

9-Boraanthracene Derivatives Stabilized by N-Heterocyclic Carbenes**

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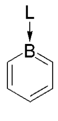
Polycyclic aromatic hydrocarbons (PAHs) are excellent p-type organic semiconductors.[1] In this context, materials based on anthracene, tetracene, and pentacene in particular have been studied extensively. To apply these materials in solar energy conversion devices, effective n-type semiconducting partners are necessary.[2] While progress has been made in the development of such materials by, for example, including highly fluorinated substituents,[3] interest remains high in meeting the considerable challenges faced in discovering a viable n-type material that meets criteria of stability and electron affinity.

Since incorporation of nitrogen into polycyclic aromatic frameworks can enhance p-type semiconducting behavior,[4] it is possible that related boron-containing heterocycles may present an effective strategy towards viable n-type materials.[5] To this end, we have been exploring the properties of "BN" PAHs, in which one or more C=C units in a PAH are substituted with isoelectronic B=N fragments.[6] While promising, the BN strategy is limited by the fact that BN is isoelectronic with CC, and so the systems are not electron-deficient relative to the hydrocarbons. Thus, transposition of one carbon for one boron atom may be more effective.



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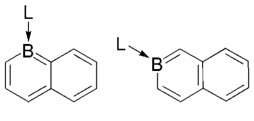

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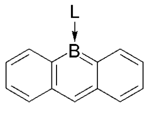
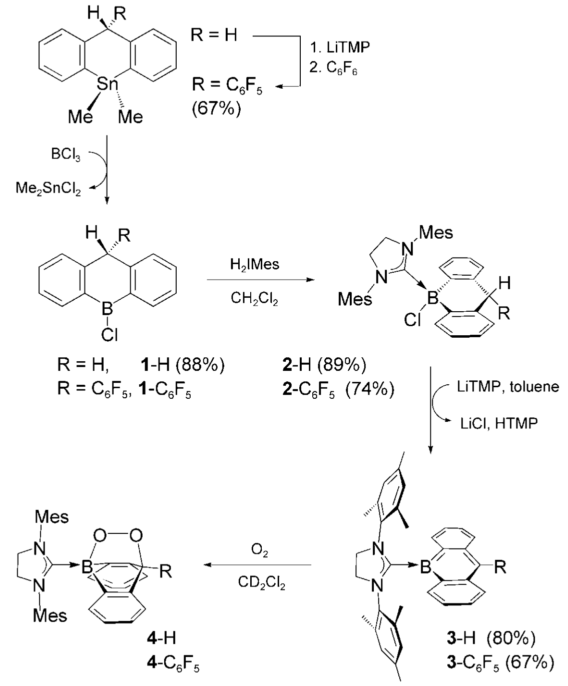


III

Although borabenzenes (**I**, where L is a neutral Lewis base donor) have been known and studied for many years,[7] less is known about higher boraacenes. For example, routes to boranaphthalenes **II** are known,[8] but to our knowledge the 9-boraanthracenes **III** remain unexplored—although the chemistry of the anionic 9-borataanthracenes was explored in some detail by Van Veen and Bickelhaupt in the 1970s.[9] Mention of one 9-boraanthracene (where L = SMe_2) occurs in the literature,[10] although it was characterized only by electronic spectroscopy. We have therefore begun to devise routes to derivatives of **III** with a view towards evaluating their photophysical properties, and we report initial findings herein.

The known stannacycle[11] shown in Scheme 1 (R = H) can be derivatized by deprotonation and quenching with an electrophile, for instance C_6F_6 as shown.[12] The two stannacycles depicted are readily converted into the highly moisture-sensitive haloboranes by a transmetalation reaction with excess BCl_3 in good to excellent yields. The chemical shifts of the ^{11}B nuclei in the NMR spectra of these compounds ($\delta = 55$ and 57 ppm for **1**-H and **1**-C_6F_5, respectively) indicate that they are monomeric, three-coordinate species,[13] which accounts for their high reactivity towards moisture. Borinic anhydrides ("BOB" compounds) are commonly observed contaminants if compounds **1** are not converted into more stable derivatives in a timely fashion.



Scheme 1. Synthesis and reactivity of 9-boraanthracene derivatives stabilized by N-heterocyclic carbenes. LiTMP = lithium 2,2,6,6-tetramethylpiperidide.

Treatment of haloboranes **1** with the saturated N-heterocyclic carbene ligand 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (H_2IMes)[14] led to formation of complexes **2**-H and **2**-

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C_6F_5 essentially upon mixing. For **2**-H, the signal in the ^{11}B NMR spectrum moves upfield to $\delta = -6.4$ ppm, and in the ^{1}H NMR spectrum, the diagnostic singlet for the benzylic protons in **1**-H at 4.48 ppm split into two doublets ($|^2J_{HH}| = 16.4$ Hz) at $\delta = 3.55$ and 3.90 ppm. The NMR spectroscopic characteristics of **2**-C_6F_5 are more complex, but it appears to exist as a single diastereomer in which the H_2IMes and C_6F_5 groups are oriented *trans* to each other across the boracyclic framework, on the basis of observation of NOE crosspeaks between H_2IMes resonances and the benzylic proton of the central boracyclic ring. Deprotonation of these adducts using LiTMP suspended in toluene was indicated by a gradual change from colorless to bright orange suspensions over the course of about one hour. Both **3**-H and **3**-C_6F_5 are only sparingly soluble in toluene and precipitate from the reaction mixture, allowing for easy isolation and purification by filtration. In CD_2Cl_2, the diagnostic AB quartet representing the benzylic protons of **2**-H is no longer present in the ^{1}H NMR spectrum of **3**-H, and the remaining proton resonance shifts downfield to $\delta = 7.27$ ppm. Similarly, the triply benzylic proton of **2**-C_6F_5 is absent in **3**-C_6F_5. The chemical shifts in the ^{11}B NMR spectrum ($\delta = 27$ and 29 ppm for **3**-H and **3**-C_6F_5, respectively) fall within the range typically observed for compounds of type **I** ($\delta = 24$–33 ppm).[7]

X-ray quality crystals of **3**-H were grown from hot bromobenzene; the thermal ellipsoid diagram is shown in Figure 1.[15] The C1–B bond length in **3**-H is the same (within 2σ) as that observed in related borabenzene complexes.[16] The longer B–C bonds to C22 and C34 lead to slight distortions in the boraanthracene region of the molecule, but this moiety remains essentially isosteric with the all-carbon framework. The flanking rings show some degree of bond-length alternation as is observed in the parent hydrocarbon.[17]

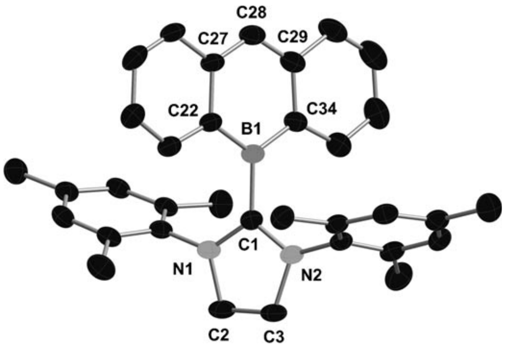


Figure 1. Thermal ellipsoid (50%) diagram of the molecular structure of **3**-H. Selected bond lengths [Å], angles [°], and dihedral angles [°]: C1-B1 1.607(4), C22-B1 1.507(4), C34-B1 1.513(4), C1-N1 1.344(4), C1-N2 1.345(4), C22-C27 1.449(4), C27-C28 1.393(4), C28-C29 1.396(5), C29-C34 1.449(4); C1-B1-C22 120.7(3), C22-B1-C34 118.6(3), C1-B1-C34 120.7(3); N1-C1-B1-C22 59.9(4), N2-C1-B1-C22 −120.7(3).

The electronic spectra of **3**-H and **3**-C_6F_5 were investigated in dilute dichloromethane solution (Figure 2). The absorption spectra of both **3**-H and **3**-C_6F_5 reveal broad absorptions between 410 and 550 nm with maxima at 485 and 489 nm, respectively. From the onset of absorption, the optical gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gap) of **3**-H and **3**-C_6F_5 was estimated to be 2.25 eV (Table 1).[18] DFT modeling (UB3LYP/6-311+G(d,p))[19] of **3**-H revealed a predominantly boraanthracene π-based HOMO and a LUMO which has π* character in addition to density on the carbene moiety (Figure S1 in the Supporting Information), suggesting some degree of charge transfer. The calculated HOMO–LUMO gap of 2.6 eV (475 nm) agrees well with the observed UV maxima. Fluorescence spectra were also acquired for **3**-H and **3**-C_6F_5, both in solution[12] and in the solid state (Figure S2 in the Supporting Information). The excitation and emission profiles of both species are very similar except for a 16 nm bathochromic shift for **3**-C_6F_5 relative to **3**-H. Thus, **3**-H exhibits an emission maximum of 597 nm, while that for **3**-C_6F_5 appears at 614 nm in the solid state. The Stokes shift is 50 nm for both compounds, and the $S_1 \leftarrow S_0$ transition is approximately 2.1 eV on the basis of these measurements.

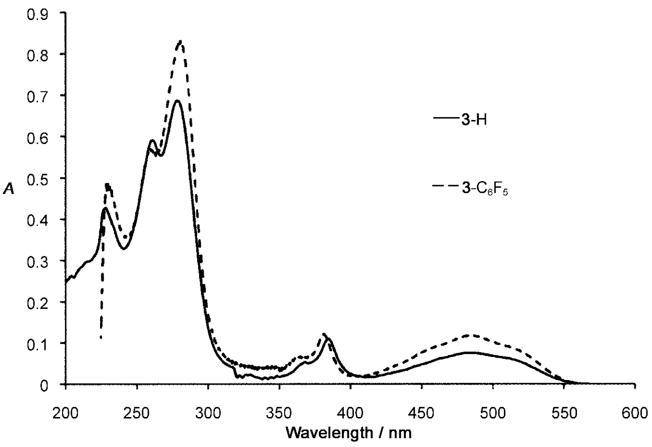


Figure 2. UV/Vis absorption spectra (dichloromethane, 10^{-5} M).

Table 1: Summary of optical and electrochemical data.

Compound	HOMO–LUMO [eV][a]	$E_{1/2ox}$[b] [V]	E.A. [eV][d]	I.P. [eV][d]
3-H	2.25	−0.67[c]	−1.9	−4.1
3-C_6F_5	2.25	−0.28	−2.3	−4.5
anthracene	3.23	0.89	−2.5	−5.7
tetracene	2.56	0.52	−2.8	−5.3

[a] Estimated from the absorption onset of the longest-wavelength UV band in CH_2Cl_2. [b] Test substrate 1 mM in 0.1 M $[NBu_4][PF_6]$, referenced to an internal standard $Fc/Fc^+ = 0$. [c] E_{ox}. [d] Calculated using Fc/Fc^+ as −4.8 eV from vacuum in conjunction with optical band-gap data. E.A. = electron affinity, I.P. = ionization potential.

Cyclic voltammetric measurements of **3**-H and **3**-C_6F_5 in dichloromethane revealed that no reduction waves were found for either molecule, but that each was susceptible to oxidation (Figure S3 in the Supporting Information).[12] In the instance of **3**-H an irreversible oxidation occurred at −0.67 V relative to ferrocene/ferrocenium (Fc/Fc^+).[20] A potential of −0.28 V was measured for **3**-C_6F_5, indicating that the presence of the C_6F_5 group increased the oxidative stability of the framework, as expected on the basis of the electron-withdrawing nature of the C_6F_5 group. Interestingly, for **3**-C_6F_5 the process showed good reversibility when scan rates above 100 mV s^{-1} were employed. The increased stability of **3**-$C_6F_5^{+}$ is attributed to increased steric congestion about the anthracene core, possibly inhibiting dimerization of the radical cation.[21] These data suggest that, with appropriate substitution, compounds **3** may serve as p-type semiconducting materials.

When solutions of either **3**-H or **3**-C_6F_5 are exposed to an O_2 atmosphere, they quickly (within minutes) decolorize, forming the air- and moisture-stable 9,10-endoperoxide adducts **4**-H and **4**-C_6F_5 quantitatively as judged by NMR spectroscopy. In addition to NMR spectral features consistent with endoperoxide formation, the structure of **4**-H was confirmed by X-ray crystallography (Figure 3). The crystal structure of **4**-H shows an elongation of the B–C1 bond by 0.050(5) Å, in accord with rehybridization of the boron atom from sp^2 to sp^3. Despite the increased steric crowding about the molecular core, the ^{1}H NMR spectra of both compounds are indicative of facile rotation about the B–C1 bond.

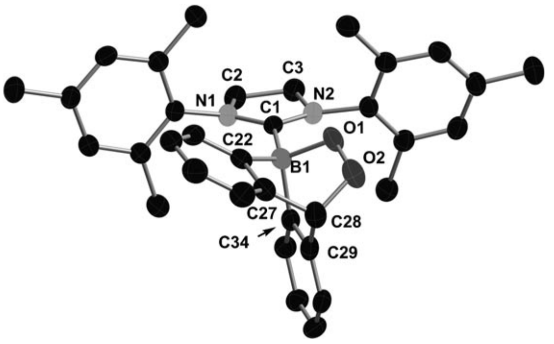
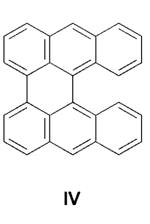


Figure 3. Thermal ellipsoid (50%) diagram of the molecular structure of **4**-H. Selected bond lengths [Å] and angles [°]: C1-B1 1.657(3), C22-B1 1.642(3), C34-B1 1.627(3), C1-N1 1.337(2), C1-N2 1.348(2), B1-O1 1.527(3), O1-O2 1.456(2), C22-C27 1.418(3), C27-C28 1.504(3), C28-C29 1.495(3), C29-C34 1.406(3), C28-O2 1.461(3); C1-B1-C22 125.76(17), C22-B1-C34 106.25(16), C1-B1-C34 107.95(16), C1-B1-O1 105.18(16).

While it is known that anthracene derivatives undergo endoperoxide formation on treatment with dioxygen, generally these reactions require a photosensitizer and therefore involve the addition of singlet oxygen ($^1O_2$).[22] Even then, reaction times are on the order of hours, not the minutes observed for conversion of compounds **3** to **4** upon treatment with oxygen. Indeed, the transformations of **3** to **4** require no added photosensitizer or strong irradiation; furthermore, since the reactions proceed at qualitatively the same rate in the dark, the starting materials **3** are not acting as self-photosensitizers and appear to react directly with triplet oxygen ($^3O_2$). While it has been suggested computationally that a thermal reaction pathway between anthracene and $^3O_2$ is competitive with that involving $^1O_2$,[23] only in the strained helianthracene molecule **IV** has thermal reaction with $^3O_2$ been observed experimentally,[24] and this reaction is exceedingly slow. Higher acenes, such as tetracene and pentacene, are thought to react much more readily with triplet oxygen owing to a greater tendency towards biradical ground-state structures;[1,23,25] these results suggest that 9-boraanthracene derivatives behave more like higher acenes in this regard. That said, low-temperature EPR spectroscopy gives no evidence for any biradical character in compounds **3**, and the triplet state of **3**-H is calculated to be 28.0 kcal mol^{-1} higher in energy than the singlet state. We are considering other reaction manifolds for these reactions with $^3O_2$,[26] but this question remains under investigation. The remarkably rapid reaction of compounds **3** with oxygen points to possible oxygen-sensor applications.[27]



IV

In conclusion, we have developed a concise route to 9-boraanthracene stabilized by an N-heterocyclic carbene, along with the 10-C_6F_5-substituted derivative; this route should be generalizable to other examples with substitution in the 10-position. Our preliminary investigations show that these molecules display chemical and photophysical properties that are strikingly different from that of anthracene and are more akin to higher acenes. This similarity is most apparent in the pronounced reactivity of both **3**-H and **3**-C_6F_5 toward oxygen and in the smaller HOMO–LUMO gap. From these results it would appear that, somewhat counterintuitively, boron incorporation has rendered this anthracene molecule more oxidatively unstable and perhaps a candidate for p-type semiconduction. This effect may be attributable to the lower Pauling electronegativity of boron (2.04) versus carbon (2.55). Work on these and other boron-containing acenes is ongoing and will be reported in due course.

Experimental Section

For full experimental details and spectroscopic data, see the Supporting Information. X-ray crystal data is available from the Cambridge Structural Database.[15] Numbering scheme refers to standard anthracene notation.

Synthesis of **3**-H: 9-bora-9-chloro-9,10-dihydroanthracene 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene adduct (**2**-H, 640 mg, 1.23 mmol) was suspended in toluene (12 mL), and lithium tetramethylpiperidide (156 mg, 1.24 mmol) was added at ambient temperature. The mixture was stirred for one hour, at which time the orange solid was isolated by vacuum filtration and washed with toluene (10 mL), diethyl ether (10 mL), and finally pentane (20 mL). The crude solid was freed of LiCl by dissolving it in dichloromethane and passing the mixture through a 0.2 μm polytetrafluoroethylene (PTFE) filter (480 mg, 0.99 mmol, 80 %). X-ray quality crystals were grown by cooling a supersaturated bromobenzene solution. ^{1}H NMR (Bruker Avance, 400 MHz, CD_2Cl_2): $\delta = 8.01$ (d, 2H, $^3J_{HH} = 8.4$ Hz, $H^{1,8}$), 7.6 (d, 2H, $^3J_{HH} = 8.4$ Hz, $H^{4,5}$), 7.27 (s, H^{10}), 7.09 (td, 2H, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.3$ Hz, $H^{2,7}$), 6.75 (td, 2H, $^3J_{HH} = 6.8$ Hz, $^4J_{HH} = 1.2$ Hz, $H^{3,6}$), 6.68 (s, 4H, *m*-MesH), 4.36 (s, 4H, NCH_2CH_2N), 2.4 (s, 12H, *o*-Mes$(CH_3)_4$), 2.06 ppm (s, 6H, *p*-Mes$(CH_3)_2$); ^{11}B{^{1}H} NMR (128.4 MHz, CD_2Cl_2): $\delta = 27$ ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta =$ 138.9, 138.5, 135.7, 134.4 ($C^{1,8}$), 130.2 (MesCH), 128.9 ($C^{4,5}$), 124.3 ($C^{2,7}$), 115.9 ($C^{3,6}$), 113.2 (C^{10}), 52.8 (NCH_2CH_2N), 21.0 (*p*-Mes$(CH_3)_2$), 19.6 ppm (*o*-Mes$(CH_3)_4$); LRMS (EI): *m*/*z*: 482.5 (M^+, 100 %), 305.3 (H_2IMes^+, 74 %), 177.2 (M^+-H_2IMes, 70 %); HRMS (EI): Calculated $C_{34}H_{35}BN_2$ 482.2893, found 482.2882.

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[15] Crystal data for **3**-H: $C_{34}H_{35}BN_2{\cdot}C_6D_5Br$, MW = 644.46, monoclinic, space group $P2_1/n$, $a = 12.230(5)$, $b = 14.864(4)$, $c = 18.248(7)$ Å, , $\beta = 97.255(15)°$, $V = 3291(2)$ Å^3, $Z = 4$, $\rho = 1.291$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, 5650 measured reflections, 4602 unique, min/max transmission = 0.6629 and 0.8615, $R1$ ($I > 2\sigma$) = 0.0502, $wR2$ = 0.1277, GoF = 1.050, No. of parameters = 403, final difference map within +0.59 and −1.32 e Å^3. Crystal data for **4**-H: $C_{34}H_{35}BN_2O_2$, MW = 514.45, monoclinic, space group $P2_1/n$, $a = 11.5020(3)$, $b = 19.5600(7)$, $c = 13.6530(5)$ Å, $\beta = 114.3910(19)°$, $V = 2797.49(16)$ Å^3, $Z = 4$, $\rho = 1.221$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, 5083 measured reflections, 4037 unique, min/max transmission = 0.9881 and 0.9926, $R1$ ($I > 2\sigma$) = 0.0536, $wR2$ = 0.1332, GoF = 1.054, No. of parameters = 356, final difference map within +0.70 and −0.25 e Å^3. CCDC 721750 (**3**-H) and 721751 (**4**-H) 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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