ORGANOMETALLICS

Benzo[b]thiophene-Fused Boron and Silicon Ladder Acenes

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Supporting Information

ABSTRACT: Synthetic routes to three new heteroacene compounds in which two benzo[b]thienyl units are bridged by dimethylsilyl and/or mesitylboryl units are described. In the Si/Si and Si/B compounds **1**-syn and **3**-syn, respectively, the sulfur atoms of the flanking benzo[b]thiophenes are disposed in *meta* positions on the central six-membered heterocycle, while in the B/B compound **4**-anti, they are para to each other; the reasons for this lie in the synthetic method employed to prepare **4**-anti. All three compounds were crystallographically characterized and their photophysical properties examined. A comprehensive examination of their



photophysical properties shows that they are weakly absorbing and fluorescing materials, with the diborin derivative **4**-anti exhibiting the most red-shifted absorption maxima and largest fluorescence quantum yield.

INTRODUCTION

The use of highly conjugated organic molecules as semiconducting materials in various devices is growing, and as a result there has been an increased interest in developing new materials and new methods for their facile synthesis. While allcarbon acenes have played a significant role in organic electronics,^{1,2} an important strategy for developing new materials with modified electronic properties has involved the incorporation of main-group elements into the structural frameworks of these polycyclic aromatic hydrocarbon (PAH) frameworks.^{1,3} Thus, the application of "ladder" type molecules containing heteroatom elements has been a very active area of research in main-group chemistry in the past decade.⁴

While researchers in this area have utilized the full palette of main-group elements available, we have focused on hetero-cycles containing $boron^{5-12}$ and $silicon^{13}$ in acenes and acene analogues as a means of altering the properties of these conjugated materials. Boron is one of the few (and from a practical perspective, perhaps the only) choices for incorporating an electron-deficient element into a π -conjugated net-work.^{14–16} A contribution from the empty p orbital associated with the three-coordinate boron center to the LUMO surfaces can lower the energy of this orbital,^{17–19} rendering materials incorporating this element potential electron acceptors and sensors for Lewis bases.²⁰⁻²³ Further, mixed heteroacenes in which boron is partnered with a donor atom $(N, P)^{24-28}$ can exhibit strong intramolecular charge transfer absorption bands. These favorable properties are tempered by the need to stabilize the boron centers with sterically large protecting groups, by generally nontrivial synthetic protocols. Integration of silicon into conjugated frameworks, although electronically saturated, also lowers the LUMO level through hyperconjugation of the π^* system with the σ^* orbitals of the

exocyclic Si–C bonds.^{29–31} While the sp³-hybridized Si center can lead to nonplanar conformations,^{13,32} in some instances fully planar structures are observed.³³

Given our interest in boron- and silicon-modified heteroacenes, we targeted the benzothiophene-buttressed π systems shown below in order to assess the effect of the differing B/Si substitution patterns on the properties of the materials. Initial plans focused on the *syn* isomers, where the thiophene sulfur atoms reside on the same side of the molecule. While the Si/Si and Si/B combinations were readily accessed, the B/B compound could be formed only as its *anti* isomer using the methods developed. Herein we describe the synthesis, structures, and properties of these novel heteroacenes.



syn E, E' = Me₂Si or MesB anti

RESULTS AND DISCUSSION

The silicon–silicon fused molecule **1**-syn was prepared in two steps via the sequence shown in Scheme 1 starting from 3-bromobenzo[b]thiophene. Lithiation with *n*BuLi followed by addition of Me₂SiCl₂ efficiently installed the first dimethylsilyl unit. Double deprotonation of this species required Schlosser's base³⁴ in THF solutions at -20 °C to give clean conversion to

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the dilithio species (monitored by quenching with D_2O and following by ¹H NMR spectroscopy). Trapping this dilithio reagent in situ with Me₂SiCl₂ resulted in the formation of **1**-*syn*, which was recrystallized from hot hexanes in an overall yield of 72% yield for the two steps. In addition to the expected resonances in the ¹H and ¹³C NMR spectra, **1**-*syn* showed two sharp peaks in the ²⁹Si NMR spectrum at -15.6 and -19.4 ppm, similar to those measured by Baumgartner and co-workers for 1,4-dihydro-1,4-silaphosphalins³² and indicative of sp³-hybridized silicon atoms.

We did not envision that **1**-*syn* would be a suitable starting material for the preparation of Si/B and/or B/B compounds through treatment with boron trihalides; therefore, we prepared a related Si/Sn heterocycle (Scheme 2) as a compound for which selective halogen exchange reactions with boron

Scheme 2



trihalides might be feasible.²⁰ The dibromo bis-(benzothiophene)-substituted dimethylsilane precursor was prepared by following the method of Baumgartner and coworkers³² using selective lithium-halogen exchange of 2,3dibromobenzo [b] thiophene in the 2-position and trapping in situ with $1/_2$ equiv of Me₂SiCl₂. A second lithiation step followed by trapping with Me₂SnCl₂ yielded the desired Si/Sn compound 2-syn in very good yield; 2-syn was characterized by multinuclear (¹H, ¹³C, ²⁹Si, ¹¹⁹Sn) NMR spectroscopy and mass spectrometry. 2-syn could be converted to the Si/B compound 3-syn using a one-pot procedure in which treatment with BCl_3 resulted in selective transmetalation with only the Me₂Sn unit. The diarylboron chloride was then protected by addition of a mesityl lithium/toluene suspension to give 3-syn in 31% yield. This compound is stable in air, but due to instability on silica gel, crude products were purified by trituration in hexanes, filtration to remove lithium chloride, and recrystallization of the filtrate, manipulations that led to lowered isolated yields. Characterization by multinuclear NMR spectroscopy revealed a singlet at -16.6 ppm in the ²⁹Si NMR spectrum and a broad signal at 56 ppm in the ¹¹B NMR spectrum. This latter signal is characteristic of three-coordinate boron atoms with aryl substituents³⁵ and, more specifically, is near those measured by Kawashima and co-workers for 1,4-heteroborins substituted with pnictogens^{24,26} or chalcogens,²⁵ as well as that measured by Ashe and co-workers¹⁸ for diborapentacene. The resonance is in the upfield end of the range for three-coordinate boron atoms and is indicative of some conjugation between the boron atom and the π framework of the molecule.

In an effort to induce boron-halogen exchange at both the tin and silicon centers in 2-syn, it was treated with the more Lewis acidic BBr₃ reagent. Harsher conditions, including an excess of BBr₃, higher temperatures (50 °C), and a longer reaction time (2 days), were required in order to drive the reaction to one product.³⁶ While both group 14 dimethyl units were replaced, the product isolated upon treatment with MesLi was the *anti* isomer 4-*anti* rather than the expected *syn* isomer.

DFT computations (B3LYP/6-31G**) predict that 4-anti is only 0.1 kcal/mol more stable than the targeted 4-syn isomer, suggesting that the preference for the 4-anti framework may be kinetic in nature. Monitoring the reaction by NMR spectroscopy showed that conversion of 2-syn to the Si/B-Br intermediate upon treatment with BBr3 is facile at room temperature (Scheme 3); this was indicated primarily by the appearance of Me₂SnBr₂ in both the ¹H and ¹¹⁹Sn NMR spectra. Further addition of BBr3 showed no reaction at room temperature, but upon heating, changes in the Me₂Si region of the ¹H NMR spectrum and two new peaks at -17.6 and -19.4ppm in the ²⁹Si NMR spectrum suggested formation of the two Si-Br products that result from bromine-methyl exchange at silicon. This is all that can be gleaned from these experiments, but we speculate that conversion of these intermediates to the (unobserved) 2,3-dibromoborylbenzo[b]thiophene must occur in order to account for the exclusive production of 4-anti in this reaction. Bimolecular condensation of such ortho-disposed dibromoboryl units to form diboraacene frameworks is known.^{18,37-40} In the case of 2,3-dibromoborylbenzo[b]thiophene, the difference in Lewis acidity of the inequivalent -BBr₂ groups (the boryl group in the 2-position is expected to be a weaker Lewis acid) favors the transition state leading to 4anti over that leading to 4-syn, and the former is isolated exclusively. The equivalent boron nuclei in this compound

Scheme 3



resonate at 59 ppm in the 11 B NMR spectrum, near that observed for 3-syn (vide supra).

The structures of the compounds 1-syn, 3-syn, and 4-anti were investigated by X-ray diffraction, and the molecular structures of the compounds are shown in Figures 1–3, respectively, along with selected metrical parameters. Crystals were grown by vapor diffusion of hexanes into saturated dichloromethane/benzene solutions. 1-syn and 3-syn grew as yellow crystals that could be analyzed on a conventional diffractometer, while 4-anti was available only as a red microcrystalline solid that required a synchrotron source for analysis. Compound 1-syn crystallizes with a single molecule in the asymmetric unit, while both 3-syn and 4-anti have two molecules that are essentially identical. For 4-anti, both molecules lie on a crystallographic inversion center, which is not possible for a molecule with a syn configuration.

All three compounds are relatively planar structures with angles between the least-squares planes defined by the five atoms of the flanking thiophene groups measured at 3.30(12), 11.19(19)-12.00(19), and 0° for 1-syn, 3-syn, and 4-anti, respectively. Most remarkably, the central disilin ring of 1-syn is essentially planar even though it contains two sp³-hybridized silicon atoms. As might be expected, however, within the central rings of the three compounds, there is a great deal of bond alternation. In particular, the internal C–C bonds are clearly localized double bonds, the shortest being in the 1,4-dihydro-1,4-disilin 1-syn (1.373(3) and 1.376(3) Å). In the 1,4-



Figure 1. Displacement ellipsoid (50%) diagram of 1-syn. Selected bond distances (Å): Si(1)-C(1), 1.859(2); Si(1)-C(2), 1.852(2); Si(2)-C(3), 1.865(2); Si(2)-C(4), 1.873(2); C(1)-C(4), 1.373(3); C(2)-C(3), 1.376(3); C(3)-C(16), 1.455(3); C(4)-C(5), 1.455(3); C(5)-C(10), 1.408(3); S(1)-C(2), 1.744(2); S(1)-C(11), 1.729(3); S(2)-C(1), 1.742(2); S(2)-C(10), 1.731(2); C(11)-C(16), 1.407(4). Selected bond angles (deg): C(1)-Si(1)-C(2), 105.11(9); C(3)-Si(2)-C(4), 108.45(10); Selected torsion angles (deg): Si(1)-C(2)-C(3)-Si(2), -5.5(3); Si(1)-C(1)-C(4)-Si(2), 1.9(3).

dihydro-1,4-diborin 4-anti these distances are somewhat longer (1.388(2) Å), while the 1,4-dihydro-1,4-silaborin 3-syn exhibits intermediate values (1.371(7)-1.380(8) Å). In the two independent molecules in the unit cell for both 3-syn and 4-anti, the sum of the angles about each boron atom is 360°, with



Figure 2. Displacement ellipsoid (50%) diagram for one of the two independent molecules of 3-*syn*. Selected bond distances (Å): C(1)-C(4), 1.380(8); C(1)-Si(1), 1.867(6); C(2)-C(3), 1.371(7); C(2)-Si(1), 1.856(5); C(3)-B(1), 1.559(8); C(4)-B(1), 1.559(8); C(1)-S(1), 1.728(5); C(4)-C(5), 1.473(8); C(5)-C(10), 1.412(7); S(1)-C(10), 1.718(7); C(2)-S(2), 1.726(5); C(3)-C(16), 1.476(7); C(11)-C(16), 1.4114(8). Selected bond angles (deg): C(3)-B(1)-C(4), 121.1(5); C(3)-B(1)-C(19), 119.8(4); C(4)-B(1)-C(19), 119.1(5); C(2)-Si(1)-C(1), 101.6(2). Selected torsion angles (deg): Si(1)-C(2)-C(3)-B(1), 9.8(8); Si(1)-C(1)-C(4)-B(1), 2.7(8); C(24)-C(19)-B(1)-C(3), 93.2(6); C(20)-C(19)-B(1)-C(3), -83.0(7).



Figure 3. One of the two independent molecules of 4-anti. Selected bond distances (Å): C(1)-C(2), 1.388(2), C(1)-B(1), 1.552(3); C(2)-B(1), 1.556(2); C(2)-C(3), 1.441(2); C(3)-C(8), 1.415(2). Selected bond angles (deg): C(1)-B(1)-C(2), 115.22(14); C(1)-B(1)-C(9), 118.82(14); C(2)-B(1)-C(9), 125.93(16). Selected torsion angle (deg): $B(1)-C(1)-C(2)-B(1_0)$, 2.9(2).

the mesityl units essentially perpendicular to the central sixmembered ring. For 3-syn, the endocyclic B-C bond lengths are both 1.559(8) Å, slightly longer than those measured for 4anti (1.552(3), 1.556(2) Å). 1-syn exhibits internal siliconcarbon bond lengths similar to those of **3**-*syn*, but the C(1)–Si–C(2) angles are slightly larger (by ~4°) in the former compound. Packing interactions in the three compounds are dominated by short S…H interactions^{41–43} between benzo-thiophene sulfur atoms and aromatic C–H hydrogens on adjacent molecules (Figures S1–S3, Supporting Information). While the bulky mesityl substituents on **3**-*syn* and **4**-*anti* tend to disrupt face-to-face interactions in the packing of these molecules, in 1-*syn* such features are observed between adjacent molecules (separation distance of ~3.54 Å), best observed when the crystal packing is viewed down the *c* axis of the unit cell (see Figure S1, Supporting Information).

Given the bond alternation in the central rings and the fact that the central rings contain four π electrons, the antiaromaticity of the central rings was investigated using NICS(1)_{zz} calculations using Gaussian 03⁴⁴ (B3LYP/6-31G**//B3LYP/6-31+G*). The diborin ring in 4-anti can be considered as antiaromatic (+28.46), while the silaborin core of 3-syn (+11.02) and the disilin ring in 1-syn (+9.25) could qualify as weakly antiaromatic (Table S1, Supporting Information). As expected, the NICS(1)_{zz} values become less positive as silicon atoms are incorporated into the central ring; the smallest positive value was calculated for 1-syn.

Photophysical data for the three new compounds are summarized in Table 1, while further data are presented in Figures S4–S6 and Table S2 in the Supporting Information. Both the absorption and emission maxima for the three substituted benzo[b]thiophenes shift to longer wavelengths as more boron atoms are incorporated into the conjugated framework. This is mainly a result of changes to the LUMO energy surfaces. DFT calculations (B3LYP/6-31G**) show the HOMO surfaces are of π character and contain a node through the center of the molecule, while the LUMO orbitals are of π^* character with contributions from the heteroatoms (Figure 4).



Figure 4. Kohn–Sham orbital surfaces for the HOMOs and LUMOs of **1**-*syn*, **3**-*syn*, and **4**-*anti* prepared by Gaussian 03 at the B3LYP/6-31G** level of theory. See Table S3 (Supporting Information) for the calculated energies of these orbitals.

Table 1. Summary of Photophysical Properties of 1-syn, 3-syn, and 4-anti^a

	$\lambda_{ m abs,max} \ ({ m nm}) \ (\log \ arepsilon)$	λ_{onset} (nm)	$\lambda_{\rm em,max}~({\rm nm})$	Φ^b	τ (ns)	$k_{\rm nr}^{\ c} \ (10^7 \ {\rm ns}^{-1})$	$k_{\rm r}^{\ d} \ (10^7 \ {\rm ns}^{-1})$
1-syn	307 (3.74); 296 (3.80); 266 (4.19)	315	327	0.01	3.7	26.8	0.27
3-syn	379 (4.21); 311 (4.27); 270 (4.58); 234 (5.04)	409	425	0.01	0.45	220	2.22
4-anti	427 (3.87); 356 (3.77); 293 (4.65); 281 (4.47)	484	666 (630)	0.15	48.2	1.76	0.31

^{*a*}Absorption and emission were measured in 2.25 × 10⁻⁵ M CH₂Cl₂ solution. ^{*b*}Measured using a calibrated integrating sphere. ^{*c*}Calculated from $k_{\rm nr} = (1 - \phi_{\rm F})/\tau_{\rm F}$. ^{*d*}Calculated from $k_{\rm r} = \phi_{\rm F}/\tau$.

The LUMO surfaces of the two boron-containing molecules are mainly focused on the borin rings and the flanking sulfur atoms. Time-dependent density functional theory (TD-DFT) computations show that the HOMO–LUMO absorptions have low oscillator strengths, and in the case of 4-anti it is symmetry forbidden (Table S3, Supporting Information). Indeed, all major transitions in these compounds have low oscillator strengths (~0.1–0.4), and thus they are weakly absorbing materials. Electrochemical measurements show that quasireversible one-electron reductions occur for each compound, with the disilin being the most difficult to reduce (Figures S7 and S8 and Table S4, Supporting Information). Optical band gaps obtained from the onset of absorption and the reduction potential are in broad agreement with those computed using DFT methods (Table S5, Supporting Information).

The two silicon-containing compounds, 1-syn and 3-syn, exhibit fluorescence quantum yields of nearly 0 (0.01) and relatively short fluorescence lifetimes (0.45 and 3.7 ns, respectively) and have very large rates of nonradiative decay $(k_{\rm nr})$. This may be related to the conformational flexibility imparted by the sp³ silicon centers, which renders these molecules less rigid in comparison to the diborin 4-anti, which exhibits a higher quantum yield of 0.15 and a much longer fluorescence lifetime of 48.2 ns. Furthermore, the compound displays a large Stokes shift of ~230 nm $(4.3 \times 10^4 \text{ cm}^{-1})$. The reasons for this behavior are unclear at this point but do not appear to be related to solvatochromism, since the absorption/ emission profile does not change significantly in solvents of differing polarity²³ (see Figure S4 and Table S2, Supporting Information). One possibility is a lowering of the excited state's energy through orbital overlap between the boron p orbitals and the π system of the molecular framework.²³ The emission profile underwent subtle changes at 173 K (Figure S6, Supporting Information), but fluorescence lifetime measurements at this temperature indicated the presence of two species in solution with lifetimes of 38.5 ns (23.45%) and 54.7 ns (76.55%). Perhaps the former results from a different conformation at low temperature, but the results are not conclusive enough to make firm conclusions.

CONCLUSIONS

In summary, we describe methodology to obtain a family of benzothiophene flanked heteroacenes that contain disilin, diborin, and silaborin six-membered-ring cores. The siliconcontaining compounds are prepared as their *syn* isomers, in which the sulfur atoms of the benzothiophene wings are *syn* to each other across the molecular core. In the case of the diborin structure, the synthetic methodology employed leads to kinetic favoring of the *anti* isomer. Each compound has been fully characterized both structurally and in solution. The compounds are generally poor chromophores, but the diborin species with its electron-deficient, antiaromatic core offers distinctive photophysical features in comparison to the silicon-containing compounds.

EXPERIMENTAL SECTION

General experimental procedures are described in the Supporting Information.

Synthesis of Bis(benzo[b]thiophene)dimethylsilane. *n*-BuLi (1.6 M in hexanes, 0.84 mL) was added to a solution of 3bromobenzo[b]thiophene (285 mg, 1.34 mmol) in diethyl ether (80 mL) at -78 °C, and the solution turned yellow. After 30 min, neat dimethylsilicon dichloride (0.08 mL, 0.67 mmol) was added dropwise and the cold bath was removed immediately. The solution turned light yellow and eventually cloudy. The crude solution was filtered over alumina and the filtrate concentrated in vacuo. The crude product was used without further purification (211.8 mg, 97%) as an off-white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.93 (dd, $J_{\rm HH}$ = 7.8, 0.8 Hz, 2H), 7.78 (dd, $J_{\rm HH}$ = 7.8 Hz, 0.8 Hz, 2H), 7.62 (s, 2H), 7.31 (ddd, $J_{\rm HH}$ = 7.4, 7.5, 1.4 Hz, 2H), 7.27 (ddd, $J_{\rm IHH}$ = 8.1, 7.5, 1.4 Hz, 2H), 0.78 (s, 6H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.2, 141.7, 135.5, 134.5, 124.6, 124.0, 123.9, 122.6, -1.4 ppm. ²⁹Si{¹H} NMR (79 MHz, CDCl₃): δ -24.5 ppm. HRMS (EI): calcd for C₁₈H₁₆SiS₂ [M⁺] 324.0463, found 324.0448.

Synthesis of 1,1,4,4-Tetramethylbis(benzo[b]thieno)[2,3b:3',2'-e][1,4-dihydro-1,4]disilin (1-syn). A suspension of potassium tert-butoxide (229 mg) and n-BuLi (1.6 M in hexanes, 1.28 mL) was stirred for 5 min, and then a solution of bis(benzo[b]thiophene)dimethylsilane (166 mg, 0.51 mmol) in THF (5 mL) was added at -20 °C. The orange-red suspension was stirred for 2 h at this temperature, and neat Me₂SiCl₂ (0.07 mL) was added in one portion. The cold bath was removed immediately and the reaction mixture stirred at room temperature for 16 h. The solvent was removed in vacuo, and the solid crude mixture was triturated in hexanes. Solids were removed by filtration, and the filtrate was concentrated to give 1syn as a yellow solid (80%). X-ray-quality crystals were obtained by recrystallization from hot hexanes. ¹H NMR (400 MHz, CDCl₃): δ 8.08 (ddd, $J_{\rm HH}$ = 8.0, 1.3, 0.80 Hz, 2H), 8.04 (ddd, $J_{\rm HH}$ = 7.8, 1.3. 0.70 Hz, 2H), 7.45 (ddd, $J_{\rm HH}$ = 7.9, 7.0, 1.3 Hz, 2H), 7.40 (ddd, $J_{\rm HH}$ = 7.8, 7.0, 1.3 Hz, 2H), 0.78 (s, J^{29}_{SiH} = 6.8 Hz, 6H), 0.64 (s, J^{29}_{SiH} = 6.8 Hz, 6H) ppm. ${}^{13}C{}^{1}H{}$ NMR (100 MHz, CDCl₃): δ 146.8, 144.9, 144.5, 142.9, 124.5, 124.4, 124.1, 122.6, 1.69, 0.11 ppm. ²⁹Si{¹H} NMR (79 MHz, CDCl₃): δ -15.6, -19.4 ppm. HRMS (EI): calcd for $C_{20}H_{20}Si_2S_2$ [M⁺] 380.0545, found 380.0528.

Synthesis of 1,1,4,4-Tetramethylbis(benzo[b]thieno)[2,3b:3',2'-e][1,4-dihydro-1,4]silastannin (2-syn). This compound was obtained on the basis of a procedure reported by Baumgartner and co-workers.³² n-BuLi (1.6 M in hexanes, 0.69 mL) was added to a solution of bis(3-bromobenzo[b]thiophene)dimethylsilicon³² (0.265 g, 0.55 mmol) in diethyl ether (90 mL) at -78 °C. After 55 min, dimethyltin dichloride (134 mg, 0.61 mmol) in THF (0.5 mL) was added dropwise and the solution was immediately warmed to room temperature. After several hours it turned cloudy white and was stirred at room temperature for a total of 16 h. The crude reaction mixture was filtered through Al2O3 and the solvent removed in vacuo. Evaporation of ether yielded a white foam that gave an off-white solid, **2-syn** (0.207 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 8.04 (dd, J_{HH} = 7.0, 1.4 Hz, 2H), 7.87 (dd, $J_{\rm HH}$ = 7.6, 1.4 Hz, 2H), 7.43 (ddd, $J_{\rm HH}$ = 7.4, 7.4, 1.0 Hz, 2H), 7.39 (ddd, J_{HH} = 7.4, 7.4, 1.4 Hz, 2H), 0.71 (s, 6H), 0.68 (s, J_{119}_{SnH} = 58.5 Hz, J_{117}_{SnH} = 56.0 Hz, 6H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 146.3, 146.0, 143.9, 143.7, 124.7 (¹ J_{119SnC} = 11.1 Hz), 124.6, 124.3 (${}^{1}J_{119}{}_{SnC}$ = 19.5 Hz), 122.6, 2.2, -7.45 (${}^{1}J_{119}{}_{SnC}$ = 375.4 Hz, ${}^{1}J_{117}_{SnC}$ = 360.3 Hz) ppm. ${}^{119}Sn\{{}^{1}H\}$ NMR (149 MHz, CDCl₃): δ -109.9 ppm. ²⁹Si{¹H} NMR (79 MHz, CDCl₃): δ -14.7 ppm. HRMS (EI): calcd for C₂₀H₂₀SiS₂Sn [M⁺] 471.9798, found 471.9795

Synthesis of 1,1-Dimethyl-4-mesitylbis(benzo[b]thieno)[2,3b:3',2'-e][1,4-dihydro-1,4]silaborin (3-syn). BCl₃ gas (714 mg, 6.1 mmol) was condensed into a solution of 2-syn (225 mg, 0.48 mmol) in toluene (45 mL) at $-78\,$ °C. The reaction mixture turned a light brown-yellow and was gradually warmed to room temperature then stirred for 60 min. At this point, solvent was removed in vacuo and the crude mixture was brought into an inert-atmosphere glovebox and redissolved in a minimal amount of toluene (2 mL). A suspension of mesityllithium (239 mg, 1.94 mmol) in toluene (2 mL) was then added dropwise and the reaction mixture stirred for 16 h at room temperature. Toluene was removed in vacuo and the crude mixture filtered over Fluorisil and washed with dichloromethane. After removal of CH₂Cl₂, the crude solid was triturated in hexanes and filtered to yield 3-syn as a yellow solid (66.5 mg, 31%). ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, $J_{\rm HH}$ = 8.0 Hz, 2H), 7.29 (ddd, $J_{\rm HH}$ = 7.4, 7.4, 1.3 Hz, 2H), 7.17 (d, J_{HH} = 8.3 Hz, 2H), 7.11 (ddd, J_{HH} = 7.6, 7.6, 1.3 Hz, 2H), 6.99 (s, 2H), 2.50 (s, 3H), 2.03 (s, 6H), 0.70 (s, 6H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 158.6, 145.9, 144.3, 137.2, 137.0, 127.6, 125.3, 124.8, 124.2, 121.9, 21.8, 21.5, -0.79 (two peaks for carbon atoms bonded to the boron atom were not observed due to quadrupolar relaxation) ppm.¹¹B{¹H} NMR (128 MHz, CDCl₃): δ 56.9 ppm. ²⁹Si{¹H} NMR (79 MHz, CDCl₃): δ -16.6 ppm. HRMS (EI): calcd for C₂₇H₂₅BSiS₂ [M⁺] 452.1260, found 452.1282.

Synthesis of I,4-Dimesitylbis(benzo[b]thieno)[2,3-b:2',3'e][1,4-dihydro-1,4]diborin (4-anti). BBr₃ gas (~3 mL, ~10 equiv) was condensed into a thick-walled glass vessel containing solid 2-syn (149 mg, 0.32 mmol) at -78 °C and gradually warmed to room temperature. The reaction mixture was stirred at 50 °C for 2 days. Excess BBr3 was removed in vacuo, and the crude mixture was brought into a glovebox and redissolved in a minimal amount of toluene (2 mL). A suspension of mesityllithium (81 mg, 0.64 mmol) in toluene (2 mL) was then added dropwise and the reaction mixture stirred for 16 h at room temperature. Toluene was removed in vacuo and the crude mixture filtered through an Acros disk, washing with dichloromethane. After removal of CH2Cl2, 4-anti was obtained as a red solid (75 mg, 45%). X-ray -quality crystals were grown by slow evaporation of hexanes into a concentrated CH2Cl2 solution of 4-anti containing 2 drops of benzene. ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, $J_{\rm HH}$ = 8.0 Hz, 2H), 7.35 (d, $J_{\rm HH}$ = 8.0 Hz, 2H), 7.27 (ddd, $J_{\rm HH}$ = 7.8, 7.6, 1.2 Hz, 2H), 7.15 (dd, J_{HH} = 7.8, 7.6, 1.2 Hz, 2H), 6.97 (s, 2H), 2.44 (s, 3H), 2.23 (s, 6H) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ 162.4, 148.2, 147.6, 146.4, 140.3, 138.6, 138.3, 128.1, 126.32, 126.27, 125.8, 123.2, 22.8, 21.7. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ 58.9 ppm. HRMS (EI): calcd for C₃₄H₃₀B₂S₂ [M⁺] 524.1993, found 524.1975.

X-ray Crystallography. Data were collected at 150 K on an Agilent Technologies Gemini A Ultra diffractometer with Mo radiation $(\lambda = 0.71073 \text{ Å})$ for 1-*syn* and with Cu radiation $(\lambda = 1.54184 \text{ Å})$ for 3-*syn* and with synchrotron radiation $(\lambda = 0.6889 \text{ Å})$ at beamline I19 of the Diamond Light Source for 4-*anti*. Corrections were made for absorption, and structures were solved and refined using Bruker SHELXL software.⁴⁵ All three structures are fully ordered and gave satisfactory refinement with anisotropic displacement parameters and with isotropic H atoms constrained to ideal geometry. The noncentrosymmetric structure of 3-*syn* was found to be twinned by inversion with contributions of 58% and 42(3)% for the two components. Full crystallographic details are provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving general experimental procedures, additional photophysical data, further details on the computations conducted, and crystallographic information for **1**-*syn*, **3**-*syn*, and **4**-*anti*. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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