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Boron Heterocycles

Photochemical Synthesis of a Ladder Diborole: A New Boron-Containing Conjugate Material**

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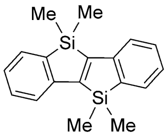
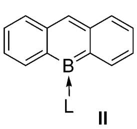
Incorporation of main-group elements into organic frameworks has emerged in the last decade as a promising route to develop new materials.[1] For instance B,[2] Si,[3] P[4] or S[5] impart interesting features to conjugated hydrocarbon frameworks such as effective orbital interactions, change in dipole moments, and diversity in coordination number. In particular, "ladder" compounds[6] are attractive because, as acene analogs, they are planar molecules and possess an extended π-conjugated system, leading to highly desirable photophysical and electronic properties like intense luminescence[7,8] and high carrier mobility.[9] In 2003 Tamao and co-workers reported the synthesis of the bis-silicon-bridged stilbene **I** by an intramolecular reductive cyclization reaction.[10] Compared to its carbon analogue, this compound has an intense blue emission, which is red-shifted by about 60 nm.[10] Several other examples, such as phosphonium borates[11] and bis-phosphorus-bridged stilbenes[12] have also been reported.



I



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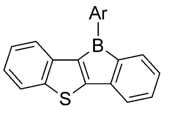

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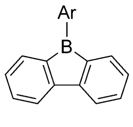

IV

Within the context of heteroacene chemistry, those based on boron are an emerging class of materials that have been used to prepare functional π-conjugated molecules for use as organic light emitting diodes,[13] field effect transistors,[14] and photovoltaics.[15] Arguably the most important characteristic of a three-coordinate boron center situated in a π-conjugated framework is the empty p-orbital, which allows for effective delocalization of electrons throughout the whole system. The transposition of carbon for the more electropositive boron atom can also alter the HOMO–LUMO characteristics of a compound significantly. For example, we found that 9-boraanthracene derivatives **II**, stabilized by N-heterocyclic carbenes,[16] unlike anthracene itself, absorbs in the visible region because the HOMO–LUMO gap is strongly decreased compared to its all-carbon analogue. The same effect was found in the more extended boratetracene and borapentacenes analogues.[17]

Apart from the promising materials that can be prepared with boron-containing molecules, boron heterocycles are of fundamental interest and have been used for decades to probe the basic concepts of aromaticity and antiaromaticity.[18] A multitude of interesting borole derivatives have been reported in the past few years,[19] which include metal-containing,[20] tetrathienyl-substituted,[21] and the highly Lewis-acidic perfluoropentaphenyl boroles.[22] In this context, recent studies by Yamaguchi et al. on heteroarene-fused boroles have provided more insight into the effect incorporation of the borole ring into extended π systems has on the antiaromaticity of boroles.[5a,7] Despite the fact that a lower antiaromatic character and higher stability was predicted for compound **III** based on the electron-donating capability of the thiophene unit, the fused borole showed a surprisingly high antiaromatic character and air and moisture sensitivity.[7] This is in contrast to the observations made for the dibenzoborole derivative **IV**,[23] where the presence of the benzene rings decreased the antiaromaticity of the borole core.

With the remarkable properties of ladder, main group element-containing π-systems and boroles in mind, we focused our attention on the synthesis of hitherto unknown bis-boron-bridged stilbene derivatives. Transmetalation of Group 14 element-based heterocycles with R_nBX_{3-n} is a reliable method for making boracycles.[24] We thus first attempted to synthesize the desired bis-boron-bridged stilbene core by treatment of Tamao's silole derivative **I** with neat BBr_3 (100 °C, 48 h), but this approach failed. Therefore, reductive routes akin to those pioneered by Tamao[10] were employed in an effort to assemble the desired ladder diborole framework. It was envisioned that reduction of the haloborane-functionalized diaryl acetylene **1** would result in a cyclization reaction to yield the targeted diborole.

The route to the precursor **1** is depicted in Scheme 1 and relies on two consecutive boron–metal exchange reactions. First, 2,2′-di-bromophenyl acetylene was lithiated at low temperature with *t*BuLi then quenched with Me_3SnCl. The bis-dichloroborane was synthesized as an orange solid in 85 % yield by treating the distannane with an excess of BCl_3. Incorporation of the bulky aryl group was accomplished by selective transmetalation of one chloro substituent per boron with the 2,4,6-triisopropylphenyl (tipp) copper(I) reagent.[25] Compound **1** was isolated as a colorless solid in 70 % yield and is a moisture-sensitive compound whose ^{11}B NMR spectrum

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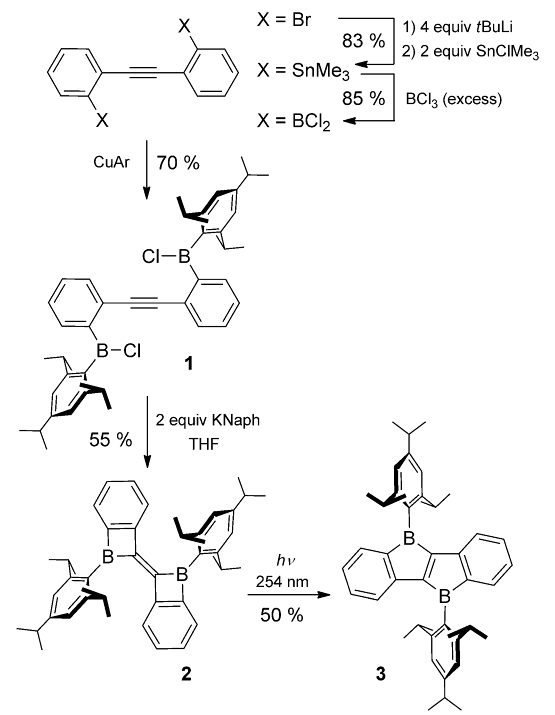


Scheme 1. Synthesis of bis-benzocycloborabutylidene **2** and bis-boron-bridged stilbene **3**.

exhibits a signal at 66.3 ppm, characteristic of a 3-coordinate boron center.[24a,26] Derivatives of **1** in which a less bulky aryl group is incorporated (Ar = C_6H_5, 2,4,6-trimethylphenyl) could also be prepared, but the subsequent reduction chemistry was not clean in comparison to that observed for the tipp-substituted haloborane, so here we only describe the chemistry of **1**.

Dihaloborane **1** was reacted with a freshly prepared solution of potassium naphthalenide in THF at −78 °C. Immediately, the solution changed from colorless to deep purple. The resulting mixture was allowed to reach room temperature over the course of two hours; the solution slowly turned brownish yellow. After evaporation of the solvent and removal of naphthalene by sublimation, a brown solid was left in the flask, which was triturated with hexanes, allowing for isolation of a bright yellow solid in 55 % yield (Scheme 1).

This compound displayed green fluorescence when irradiated under UV light in both solution and solid state and initially was presumed to be the desired ladder diborole **3**. Indeed, the spectral characteristics of the compound are fully consistent with the expected structure. The ^{11}B NMR spectrum shows a broad resonance at $\delta = 70.1$ ppm (in CD_2Cl_2) and the ^{1}H and ^{13}C{^{1}H} spectra are indicative of a C_{2h} symmetric structure, although only two out of three carbons attached to boron were observable in the ^{13}C NMR spectrum due to quadrupole relaxation. However, it was observed that the compound was both air and moisture sensitive and we anticipated that **3** would be at least tolerant of ambient atmosphere due to the steric protection offered by the tipp groups. X-ray crystallographic analysis of single crystals surprisingly revealed the structure to be the thermodynamically less favored bis-benzocycloborabutylidene structural isomer **2** (Figure 1). Despite the fact that the data were collected at 123 K, the B-aryl groups were disordered; nonetheless, the central part of the structure was free of any disorder and the analysis unequivocally establishes the connectivity in the molecular structure of **2** (more details are given in the Supporting Information). The X-ray structure of **2** revealed some interesting features. The dihedral angle C1-C6-C7-C7′ is 179.7(2)° and the sum of the angles around boron is 359.1°, suggesting a coplanar structure. The tipp groups are slightly canted relative to the B_2C_6 plane with a dihedral angle C13-C8-B1-C7 of 67.6(6)°. The trigonal planar geometry about the boron centers is significantly distorted due to the necessarily small C1-B1-C7 angle of 86.6(3)°. The two boracycles are linked by a C=C double bond (1.330(7) Å), and the boron atoms are found in a *trans* arrangement about this double bond. All carbon atoms are sp^2-hybridized, which causes a planar structure and allows conjugation throughout the whole system. Compounds with a boracyclobutene moiety are extremely scarce[27] and the strain associated with the core four-membered rings likely contributes to the observed moisture sensitivity of the compounds, despite the considerable steric protection of the Lewis-acidic boron. Indeed, we were able to characterize the product of hydrolysis of **2** by X-ray diffraction (structure is provided in the Supporting Information), which shows that the B1−C1 bonds are selectively cleaved when **2** reacts with H_2O.

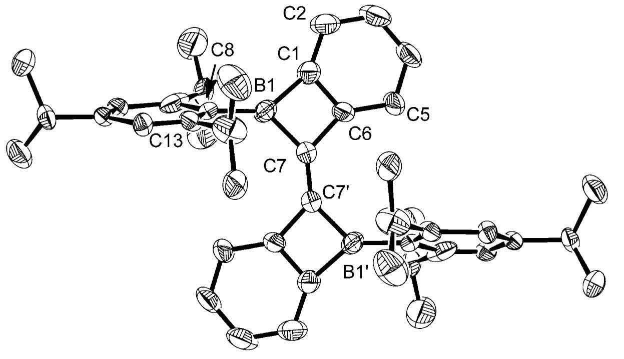


Figure 1. Thermal ellipsoid (50%) diagrams of the molecular structure of **2**. Selected bond lengths [Å], angles [°], and dihedral angles [°]: C1–B1 1.575(5), C7–C7′ 1.330(7), C7–C6 1.485(5), C1–C6 1.416(5), C7–B1 1.581(5), C1-B1-C7 86.6(3), C1-B1-C8 138.3(3), C7-B1-C8 134.2(3), C13-C8-B1-C7 67.6(6), C1-C6-C7-C7′ 179.7(2).

Compound **2** is a structural isomer of the desired ladder diborole **3**, and DFT computations (see below) suggest that it is significantly higher in energy than the fused diborole; therefore, attempts to induce thermal isomerization were made. No change in the ^{1}H NMR spectrum was observed after heating a toluene solution of **2** at 80 °C for 1 h. Conversely, a facile photoisomerization process was observed upon irradiation of solutions of **2** with 254 nm light (quartz tube, CD_2Cl_2, 0.016 mol mL^{-1}); use of higher wavelength light (> 350 nm) did not effect the isomerization. The progress of the photoreaction was monitored by ^{1}H NMR spectroscopy (Figure 2), which revealed the clean formation of a new C_2 symmetrical compound after ca. 10 h during which time the solution changed from yellow to dark green in color.

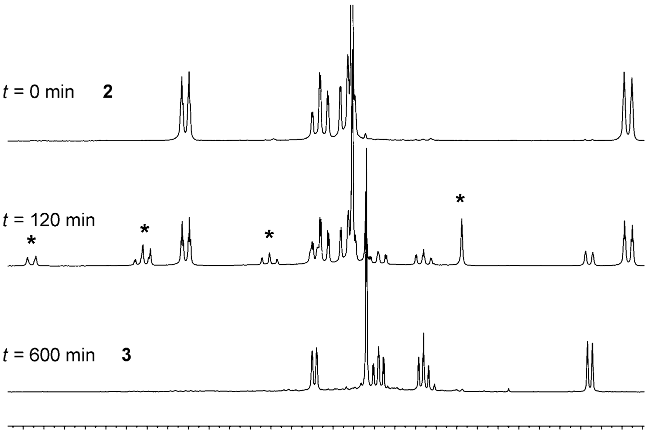


Figure 2. Photochemical reaction of **2** monitored by ^{1}H NMR spectroscopy (irradiated in a quartz NMR tube at 254 nm). The top spectrum corresponds to the ^{1}H NMR spectrum of **2** prior to irradiation; the middle trace is the spectrum at partial conversion, with the peaks marked by the * due to the intermediate; the bottom is the spectrum after full conversion to **3**. For full spectra, see the Supporting Information.

Although the conversion was quantitative by NMR spectroscopy, during the course of the reaction a third species (also with C_2 symmetry) was observed. The ^{11}B NMR resonance at 68.6 ppm, was not significantly different from that observed for **2**. X-ray crystallographic analysis confirmed the final product to be the desired bis-boron-bridged stilbene **3** (Figure 3).

The boron centers in **3** adopt a distorted trigonal planar geometry with a C3-B1-C1 angle of 102.1(2)°. The bis-benzoborole skeleton in **3** is completely planar, which can be appreciated with the dihedral angles C1-C1′-C2-C3, C1′-C1-B1-C3 and C1-C1′-C2-C7, equal to 0.1(4)°, 0.4(2)° and 179.6(3)°, respectively. Unlike **2**, the tipp groups are essentially perpendicular relative to the B_2C_6 plane with a dihedral angle C1-B1-C8-C13 of −90.1(4)°. The bond lengths of the borole ring in **3** differ only slightly compared to heteroarene-fused boroles reported by Yamaguchi and co-workers.[5a,7] Notably, there is a large bond alternation in the butadiene moiety. The C1−C1′ and C2−C3 bond lengths are 1.367(5) and 1.419(13) Å, respectively, while the C1′−C2 bond length is 1.480(4) Å.

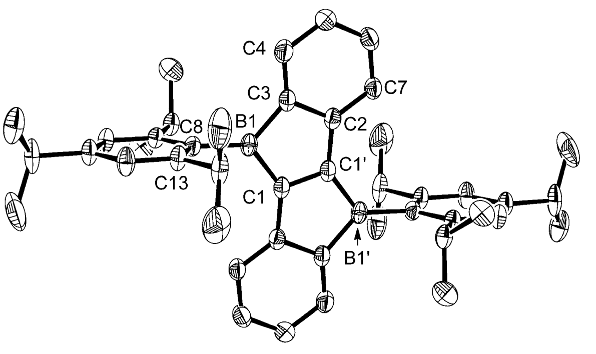


Figure 3. Thermal ellipsoid (50%) diagrams of the molecular structure of **3**. Selected bond lengths [Å], angles [°], and dihedral angles [°]: C1–B1 1.571(4), C1–C1′ 1.367(5), C1′–C2 1.480(4), C2–C3 1.419(3), C3–B1 1.588(4), C3-B1-C1 102.1(2), C8-B1-C1 128.6(2), C8-B1-C3 129.2(2), C1-B1-C8-C13 −90.1(4), C1-C1′-C2-C3 0.1(4).

Both **2** and **3** have 14 π electrons and **3** may be expected to exhibit Hückel aromaticity; however, the borole rings at its core are classical examples of antiaromatic rings. To probe the aromatic/antiaromatic character of the π framework in **3**, we carried out NICS[28] calculations at the B3LYP/6-311+G(d)[29] level of theory. The NICS values for the five-membered rings are indicative of antiaromaticity ($\mathrm{NICS(0)} = 14.9$, $\mathrm{NICS(1)} = 6.3$, and $\mathrm{NICS(1)}_{zz} = 21.8$) and the flanking benzene rings ($\mathrm{NICS(0)} = -3.2$, $\mathrm{NICS(1)} = -6.2$) are less aromatic than benzene itself ($\mathrm{NICS(0)} = -9.7$).[28a] Thus, in this system, which by the Hückel convention is aromatic as a whole, the annulated aromatic benzene rings stabilize its antiaromatic core.

The mechanism of the clean photoconversion of **2** to **3** is not known with precision, but the Vis spectra and TD-DFT calculations provide valuable insight into its character. Compound **2** exhibits major absorptions at 263 nm ($\varepsilon = 25\,400$) and 314 nm ($\varepsilon = 16\,000$) and a weaker band at 459 nm ($\varepsilon = 8200$); notably, selective irradiation of the lower energy absorptions does not result in any conversion of **2** to **3**. Thus, it is the excitation at 263 nm that results in productive photoreaction. TD-DFT calculations (B3LYP/6-31G(d), td = (nstates = 20)) on **2** reproduce the experimental absorption spectrum quite accurately and show that the absorptions are ($\pi \rightarrow \pi^*$) in character. The lower energy transitions are mainly comprised of the HOMO to LUMO transition; both orbitals have large contributions from the π orbitals associated with the central C=C double bond (see Supporting Information). However, the band at 263 nm (calcd 286 nm, oscillator srength $f = 0.2168$) corresponds mainly to $\pi \rightarrow \pi^*$ transitions with contributions from HOMO−6 to LUMO, but also HOMO to LUMO+2 (Figure 4). As can be seen, both of these populate antibonding π orbitals associated with the B−C bonds of the boracyclobutene rings, suggesting that photo-induced homolytic bond cleavage is the key step in the isomerization of **2** to **3**.[30]

Scheme 2 summarizes our proposed mechanism and suggestions for the nature of the observed transient intermediate in the reaction; the numbers in square brackets are the calculated relative energies of the species in kcal mol^{-1}. Not including the $B{-}C_{Ar}$ bond, there are two B−C bonds associated with the strained four-membered boracyclic rings in **2**, labeled **a** and **b** in Scheme 2. Cleavage of bond **a** allows for formation of **3**; unlike the product from homolytic cleavage of bond **b**, which is presumably related to the species formed by reduction of **1** (Scheme 1), the formation of the two five-membered rings in **3** is aided by the presence of a C=C double rather than triple bond. This picture of the reaction also allows for reasonable speculation as to the nature of the minor intermediate observed in the reaction

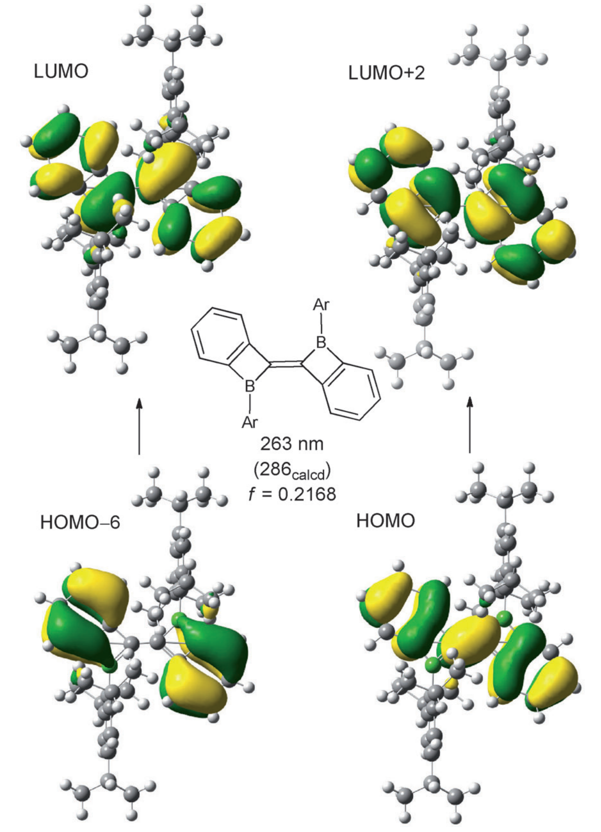
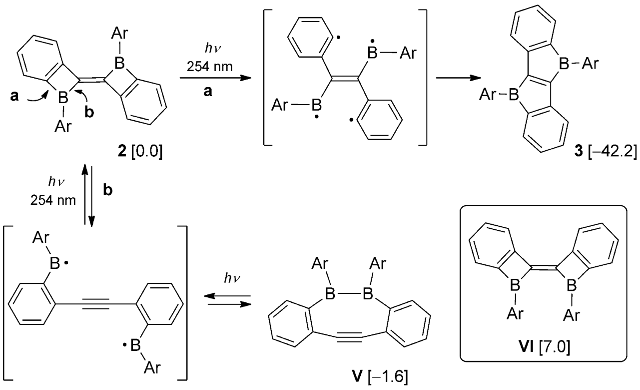


Figure 4. Molecular orbitals relevant for the photoreaction: HOMO−6, HOMO, LUMO, LUMO+2 (isocontour value 0.02). Oscillator strength, and wavelength.



Scheme 2. Proposed mechanism for the formation of **3**: Path **a** involves photocleavage of B−C bond **a**, and path **b** that of bond **b**. Numbers in square brackets indicate the energies (kcal mol^{-1}) of the species shown relative to **2** (SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE).[31]

(Figure 2). The photoproduct of cleavage of bond **b** can reform **2**, or form a B−B bond to give **V** as depicted in Scheme 2. Although such a diboracyclooctyne ring would be expected to suffer from some strain, its computed energy is actually slightly less than that found for **2**. Furthermore, a disilicon analog has been reported to undergo photoconversion to the disilole ladder framework **I**,[6,32] so it would be expected that **V** would eventually convert to **3** as the intermediate does. Another viable possibility for the identity of this intermediate is the *cis* isomer of **2**, **VI** in Scheme 2. Photoisomerization of alkenes is well known and the energy of **VI** is only 7 kcal mol^{-1} higher than that of the isolated *trans* isomer. Both of these structures are consistent with the observed symmetry of the intermediateon the basis of its ^{1}H NMR spectrum and both would be expected to fully convert to **3** upon further irradiation, since the ladder diborole isomer is substantially more stable than all three compounds (**2**, **V** or **VI**).

In summary, we have described the synthesis of the hitherto unknown bis-boron bridged stilbene **3**, which was prepared from the unexpected bis-boracyclobutylidene **2** by a light-driven isomerization. Both compounds represent new classes of boron-containing heterocyclic frameworks, which were fully characterized. Work aimed at further understanding the photochemistry, expanding the generality of the methodology and reducing the ladder diboroles to the dianions isoelectronic to the pentalenes[33] is underway.

Experimental Section

General experimental details, full characterization of all new compounds and computational details are included in the Supporting Information. CCDC 885080 (**2**), 885081 (**3**), and 885085 (hydrolysis product of **2**), 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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Communications

Boron Heterocycles

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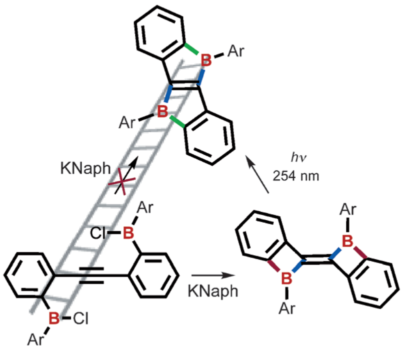
Photochemical Synthesis of a Ladder Diborole: A New Boron-Containing Conjugate Material



Climbing the ladder: Reductive cyclization of alkynyl haloboranes lead to the bis-benzocycloborabutylidene rather than the expected ladder diborole, despite the former being much less thermodynamically favored. Photochemical conversion to the ladder diborole was, however, quite facile upon irradiation at 254 nm.