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Luminescent Materials

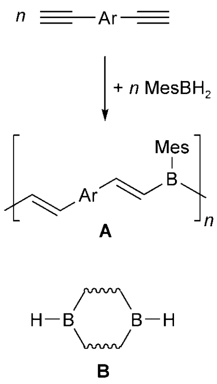
9,10-Dihydro-9,10-diboraanthracene: Supramolecular Structure and Use as a Building Block for Luminescent Conjugated Polymers**

Andreas Lorbach, Michael Bolte, Haiyan Li, Hans-Wolfram Lerner, Max C. Holthausen, Frieder Jäkle,* and Matthias Wagner**

The use of organoboranes in preparative chemistry has been established for decades.[1] In contrast, research on boron-containing materials is still at an early stage, but numerous exciting perspectives are already emerging.[2–6] The incorporation of boron into conjugated π systems leads to similar electronic states as oxidative doping but gives neutral materials because of the isoelectronic relationship between three-coordinate boron atoms and carbocations. Moreover, the ability of boron atoms to form Lewis acid–base pairs and thereby to disrupt the π-conjugation pathway can be exploited for the development of molecular switches because adduct formation is reversible in many cases.

Among the multiple applications that can be envisaged for boron-doped macromolecules, their use in organic light-emitting devices (OLEDs) holds particular promise, since properly designed organoboranes are useful not only as electron transporters but also as light emitters.[7–10] The realization that classical inorganic solid-state materials can be replaced by lightweight and highly tunable organoelement compounds has sparked a vibrant interest in the subject, as well as an intense quest for novel and stable boron-containing functional groups.

One focus of our research is conjugated polymers that contain three-coordinate boron atoms as integral parts of their main chain and exhibit photo- or electroluminescent behavior (see Refs. [11–14] for examples of luminescent polymers with boron-functionalized side chains). To date, only a few synthetic pathways to such compounds have been developed, for example polycondensation approaches[15–20] and the hydroboration polymerization.[21–24] Chujo and co-workers have reported that the hydroboration of (hetero)aromatic diynes with mesitylborane leads to stable π-conjugated organoboron polymers **A** (Scheme 1).[21,22] Depending on the nature of the arenediyl bridge, these compounds exhibit strong green, blue, and even white photoluminescence. However, a possible disadvantage of the mesitylborane component lies in the fact that both reactive hydrogen atoms are attached to the same boron atom. As a result, the first hydroboration event ($\mathrm{MesBH_2 + HCCR \rightarrow MesB(H)R'}$) occurs under steric and electronic conditions that are significantly different to those of the second addition reaction ($\mathrm{MesB(H)R' + HCCR \rightarrow MesBR'_2}$; $\mathrm{R' = C(H)C(H)R}$). An alternative might be the choice of appropriate ditopic derivatives **B** with two spatially separated but chemically related H–B functionalities (Scheme 1).



Scheme 1. Hydroboration polymerization of (hetero)aromatic diynes with mesitylborane to give neutral boron-doped materials **A**; schematic representation of ditopic diorganoboranes **B**. Mes = mesityl.

We came to the conclusion that the following conditions should be met when considering the design of suitable candidates: 1) the ditopic building block itself should already possess an extended π-conjugated electron system, 2) a rigid framework guarantees maximum π overlap between the boron atoms and the aromatic substituents, and 3) a cyclic structure should be more stable than an open-chain derivative. We report herein the realization of this concept, that is, the successful synthesis of 9,10-dihydro-9,10-diboraanthracene ($(\mathbf{2})_n$; Scheme 2). Compound $(\mathbf{2})_n$ possesses an unprecedented polymeric solid-state structure and exhibits high reactivity towards terminal alkynes. We therefore propose this compound as a highly attractive building block for the preparation of both molecular and polymeric organoboron materials.

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[*] Dipl.-Chem. A. Lorbach, Dr. M. Bolte, Dr. H.-W. Lerner,
Prof. Dr. M. C. Holthausen, Prof. Dr. M. Wagner
Institut für Anorganische Chemie, Goethe-Universität Frankfurt
Max-von-Laue-Strasse 7, 60438 Frankfurt am Main (Germany)
Fax: (+49) 69-798-29260
E-mail: max.holthausen@chemie.uni-frankfurt.de
matthias.wagner@chemie.uni-frankfurt.de

H. Li, Prof. Dr. F. Jäkle
Department of Chemistry, Rutgers University Newark
73 Warren Street, Newark, NJ 07102 (USA)
E-mail: fjaekle@andromeda.rutgers.edu

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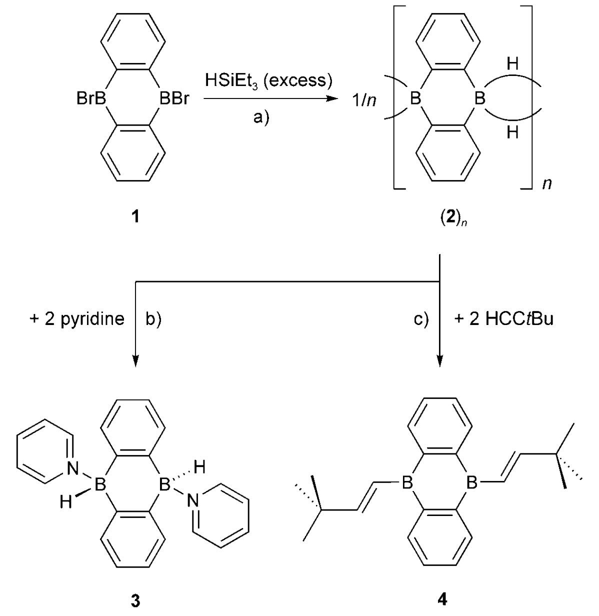
Supporting information for this article (experimental procedures, X-ray crystal structure analysis of **3**, photophysical characterization of **8**, MALDI-TOF spectrum of **8**, and the results of quantum chemical calculations on monomeric **2**, the monoadduct **2**·pyridine, and the diadduct **3** in *syn* and *anti* configuration) is available on the WWW under http://dx.doi.org/10.1002/anie.200901226. CCDC 708349 ($(\mathbf{2})_n$) and 708348 (**3**) 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.



Scheme 2. Synthesis of 9,10-dihydro-9,10-diboraanthracene ($(\mathbf{2})_n$), its pyridine adduct **3**, and its hydroboration product **4**. a) Ultrasonication, RT; b) C_6H_6, RT; c) C_6D_6, RT.

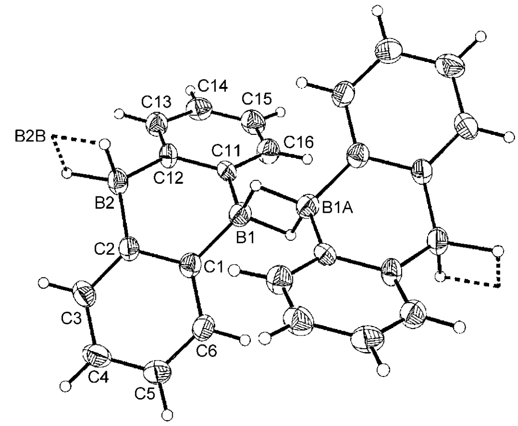


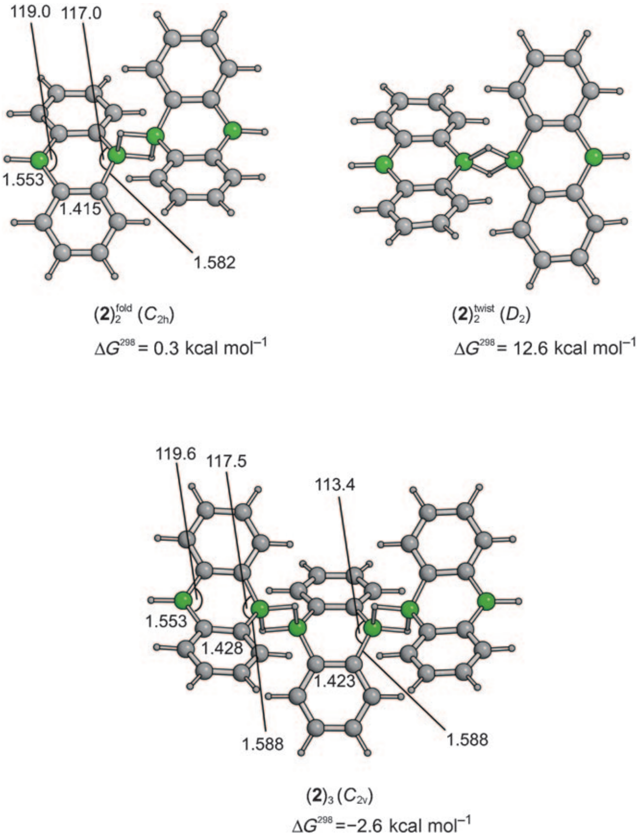
Figure 1. Molecular structure and numbering of $(\mathbf{2})_n\cdot 2n\,C_6H_6$; displacement ellipsoids shown at the 50% probability level; C_6H_6 omitted for clarity. Selected bond lengths [Å], atom···atom distances [Å], bond angles [°], and dihedral angles [°]: B(1)–C(1) 1.577(7), B(1)–C(11) 1.580(7), B(2)–C(2) 1.577(8), B(2)–C(12) 1.599(7), B(1)···B(1A) 1.819(11), B(2)···B(2B) 1.817(12); C(1)-B(1)-C(11) 114.6(4), C(2)-B(2)-C(12) 114.9(4); Ar(C(1))//Ar(C(11)) 133.8. Symmetry transformations used to generate equivalent atoms: A: $-x+1$, $-y+2$, $-z+1$; B: $-x$, $-y+2$, $-z+1$.

For the synthesis of $(\mathbf{2})_n$, 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene ($\mathbf{1}$[25]) was suspended in excess neat $HSiEt_3$ and the mixture was agitated under ultrasonication (Scheme 2). The resulting colorless solid was only slightly soluble in all common inert solvents, which prevented its characterization by liquid-phase NMR spectroscopy. However, $(\mathbf{2})_n$ can easily be converted into its chloroform-soluble pyridine diadduct **3** (Scheme 2). The NMR spectra and the X-ray crystal structure analysis of **3** as well as quantum chemical calculations are in accord with the proposed *anti* diadduct structure (see the Supporting Information).

Single crystals of 9,10-dihydro-9,10-diboraanthracene were grown by layering a solution of **1** in C_6H_6 with a solution of $HSiEt_3$ in hexane. The X-ray crystal structure analysis revealed a polymeric structure $(\mathbf{2})_n$ that occurs through three-center two-electron (3c-2e) B–H–B bonds and is the reason for the poor solubility of the compound (Figure 1).

The intermonomer B···B distances are B(1)···B(1A) 1.819(11) Å and B(2)···B(2B) 1.817(12) Å. These values are about the same as in the B–H–B-bridged dimer $[(C_6F_5)_2BH]_2$ (1.799(7) Å[26]), but shorter than the B···B distance in the sterically congested compound $[Mes_2BH]_2$ (1.851(3) Å[27]). Each of the individual $C_{12}H_8B_2$ fragments in $(\mathbf{2})_n$ adopts a folded boat conformation with a dihedral angle between the two aryl rings of $\phi = Ar(C(1))//Ar(C(11)) = 134°$. We note that the related 9,10-dihydroanthracene ($C_{14}H_{12}$) has a similarly folded shape with a value of $\phi = 145°$.[28] Theoretical studies indicate that the potential energy versus ϕ curve for the 9,10-dihydroanthracene molecule is rather flat over the range of $140° < \phi < 180°$;[28] the same is probably true for $(\mathbf{2})_n$.

To establish the thermochemistry of the formation of $(\mathbf{2})_n$ (from monomeric **2**), we carried out quantum chemical calculations[29] on the dimeric and trimeric models $(\mathbf{2})_2$ and $(\mathbf{2})_3$. For $(\mathbf{2})_2$, we identified two minima, that is, $(\mathbf{2})_2^{fold}$ and $(\mathbf{2})_2^{twist}$ (Figure 2). Somewhat surprisingly, the results indicate that dimerization of **2** is endoergic in both cases ($(\mathbf{2})_2^{fold}$: $\Delta G^{298} = 0.3$ kcal mol^{-1}; $(\mathbf{2})_2^{twist}$: $\Delta G^{298} = 12.6$ kcal mol^{-1}).



$(\mathbf{2})_2^{fold}$ (C_{2h})
$\Delta G^{298} = 0.3$ kcal mol^{-1}

$(\mathbf{2})_2^{twist}$ (D_2)
$\Delta G^{298} = 12.6$ kcal mol^{-1}

$(\mathbf{2})_3$ (C_{2v})
$\Delta G^{298} = -2.6$ kcal mol^{-1}

Figure 2. Optimized molecular structures $(\mathbf{2})_2^{fold}$, $(\mathbf{2})_2^{twist}$, and $(\mathbf{2})_3$; Gibbs free energy differences (298 K, kcal mol^{-1}) are given relative to two or three independent monomers (SCS-MP2/cc-pVTZ//M05-2X/6-31G* data; see the Supporting Information).

While a ΔG^{298} value of 0.3 kcal mol^{-1} might be outside the limits of accuracy of the applied theoretical method, we feel safe in excluding $(\mathbf{2})_2^{\mathrm{twist}}$ as the dimerization product and to rule out the twisted structural motif as an alternative to the folded motif in polymers $(\mathbf{2})_n$. Assembly of three monomer units to form $(\mathbf{2})_3$ (Figure 2) results in an exoergicity of $\Delta G^{298} = -2.6$ kcal mol^{-1}. The central unit of the computed structure $(\mathbf{2})_3$ exhibits essentially identical key geometric parameters as the repeating unit of the experimentally determined solid-state structure $(\mathbf{2})_n$.

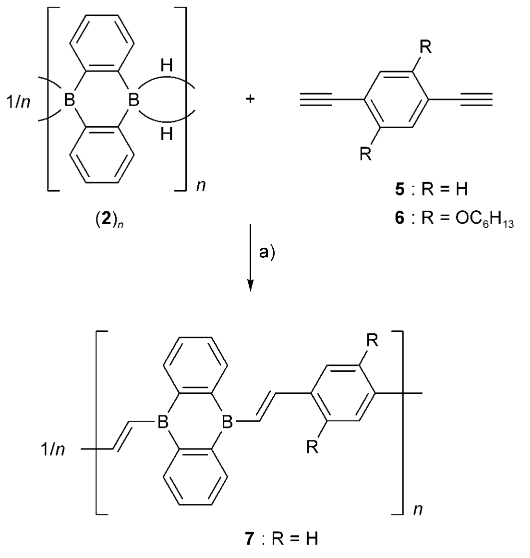
In view of the binding energy difference of −2.9 kcal mol^{-1} between dimerization and trimerization of **2**, a positive binding cooperativity is indicated upon formation of larger aggregates $(\mathbf{2})_n$. In contrast to this behavior, coordination of pyridine to **2** clearly shows negative binding cooperativity ($\mathbf{2}$ + pyridine$\rightarrow$$\mathbf{2}$·pyridine: $\Delta G^{298} = -13.3$ kcal mol^{-1}; **2**·pyridine + pyridine$\rightarrow$**3**: $\Delta G^{298} = -9.0$ kcal mol^{-1}, see the Supporting Information. Experiments have shown qualitatively the same situation to occur for pyridine binding to the bifunctional Lewis acid B,B′-diphenyldiboradiferrocene[30]).

We suggest the following as an explanation for the positive binding cooperativity in $(\mathbf{2})_n$: The simultaneous presence of three- and four-coordinate boron centers in $(\mathbf{2})_2^{\mathrm{fold}}$ results in a puckering of the central six-membered ring (torsion angle B-C-C-B 10.4°) and a relatively small degree of folding ($\phi((\mathbf{2})_2^{\mathrm{fold}} = 151°$). This not only results in intramonomer angle strain but also in comparatively short repulsive arene···arene contacts between the two monomers. Upon addition of a third monomer, puckering of the B_2C_4 ring in the bridging moiety is remediated ($(\mathbf{2})_3$: B-C-C-B 0.0°) and its folding simultaneously increases ($\phi = 134°$), which leads to a release of angle strain and a decrease of intermonomer repulsion. We therefore postulate that extended polymers with numerous repeating units that feature structural motifs related to that of the central unit in $(\mathbf{2})_3$ are favored over short oligomers because the relative proportion of strained end groups is lower.

The results obtained so far suggest that 9,10-dihydro-9,10-diboraanthracene could be used for hydroboration reactions either in pure form ($(\mathbf{2})_n$; cf. $[\text{9-BBN}]_2$[31]) or as more soluble donor complex (**3**-type adducts; cf. 9-BBN·NMe_3[31]). However, when boron-doped π-conjugated materials are the target compounds, it is essential that, after hydroboration, the resulting triorganoborane contains exclusively three-coordinate boron atoms. Thus, in this case, donor-free $(\mathbf{2})_n$ is preferable to a **3**-type adduct compound as a hydroboration reagent.

We first tested the reactivity of $(\mathbf{2})_n$ towards *tert*-butylacetylene (room temperature, C_6D_6) because the bulky alkyl substituent is likely to warrant a high degree of regioselectivity. The reaction was complete within less than 1 minute; its progress was easily monitored by the gradual disappearance of the insoluble borane. The transformation of $(\mathbf{2})_n$ into the vinylborane **4** (Scheme 2) was quantitative (monitored by NMR spectroscopy). The ^{11}B NMR spectrum of **4** shows a broad signal at $\delta(^{11}\mathrm{B}) = 61.7$ ppm that lies in a similar range as Ph_3B ($\delta = 67.9$ ppm) and $(H_2C{=}CH)_3B$ ($\delta = 56.4$ ppm[32]). We observe two signals that are assignable to vinyl protons (δ = 6.74, 6.99 ppm) with a coupling constant typical of *E*-configured olefins[33] (^3J(H,H) = 18.1 Hz). As anticipated, the reaction is completely regioselective.

Initial attempts at the hydroboration polymerization of 1,4-diethynylbenzene (**5**) with $(\mathbf{2})_n$ in C_6H_6 led to the immediate formation of a bright yellow solution and a yellow precipitate (**7**; Scheme 3). The poor solubility of **7** in all common inert solvents prevented an investigation of its chemical and physical properties. Thus, the polymerization reaction was repeated with the dialkyne **6**,[34] which possesses two solubilizing hexyloxy side chains. The reaction of $(\mathbf{2})_n$ with **6** in toluene led to a slightly turbid orange solution that could be passed through a G4 frit to give a clear filtrate. Polymer **8** was isolated as a fluorescent gumlike material from the filtrate by precipitation into hexane. The precipitate could, however, not be redissolved. Since such behavior might be interpreted as an indication of cross-linked polymer chains, we attempted to modify the reactivity of the borane by using THF instead of toluene as the reaction solvent. In this case, crude **8** could be purified by repeated reprecipitation into hexane and was finally freeze-dried to yield a bright yellow substance. Concentrated solutions of **8** in toluene, THF, or $CHCl_3$ are highly viscous and even diluted solutions tend to transform into gels upon standing for several days under an inert atmosphere. Notably, upon shaking, the gels transform back into clear liquids. This behavior is likely due to alignment of the alkyl side chains and a similar observation has recently been made by Chujo and co-workers in the case of BODIPY-functionalized conjugated polymers bearing long alkyl groups on the chromophore (BODIPY: boron dipyrromethene).[35] When solutions of **8** were evaporated to dryness in vacuo, a yellow-orange colored and green luminescent film formed on the glass walls of the vessel.



Scheme 3. Hydroboration polymerization of 1,4-diethynylbenzenes with $(\mathbf{2})_n$. a) R = H: C_6H_6, RT; R = OC_6H_{13}: toluene or THF, RT.

All resonances (except the residual solvent peak, $CDCl_3$) in the ^{1}H NMR spectrum of **8** are severely broadened, which is a typical feature of polymer samples. Signals in the ranges $\delta = 6.2$–6.0 ppm and $\delta = 5.2$–5.0 ppm (overall integral ratio 1:1) are tentatively assigned to olefinic protons. We observe no signals between $\delta = 3.5$–3.0 ppm, which confirms the absence of alkyne protons (which appear at $\delta = 3.33$ ppm in $CDCl_3$ in the ^{1}H NMR spectrum of **6**). Consistent with this observation, no alkyne stretch band is visible in the IR spectrum of **8** (KBr; $\tilde{\nu}(C\equiv C) = 3273\ \mathrm{cm^{-1}}$ (s) in the IR spectrum of **6**). As expected, the ^{11}B NMR resonance of **8** at $\delta \approx 38$ ppm is also strongly broadened.[36] The successful hydroboration with formation of the target polymeric structure was further confirmed by MALDI-TOF mass spectrometry. The pattern observed is consistent with the molecular weight of the expected individual repeating unit (see the Supporting Information).[37]

Solutions of compound **8** in toluene display absorption maxima at $\lambda_{abs} = 410$, 349, and 290 nm and emit green light at $\lambda_{em} = 518$ nm upon excitation at the longest-wavelength absorption band (Figure 3). Similar data were also obtained for thin films. However, a distinct bathochromic shift of the emission was observed with increasing solvent polarity, which suggests a significant polarization of the excited state (see the Supporting Information). The apparent intensity of the luminescence increases along the following sequence: THF solution < toluene solution < thin film < freeze-dried material. A quantum efficiency of approximately 9% was determined for the toluene solution. In air, solutions of **8** undergo rapid hydrolysis with complete loss both of the absorption band at 410 nm and the emission band at 518 nm. In contrast, the luminescence of solid **8** persists in air for up to 30 minutes (Figure 3).

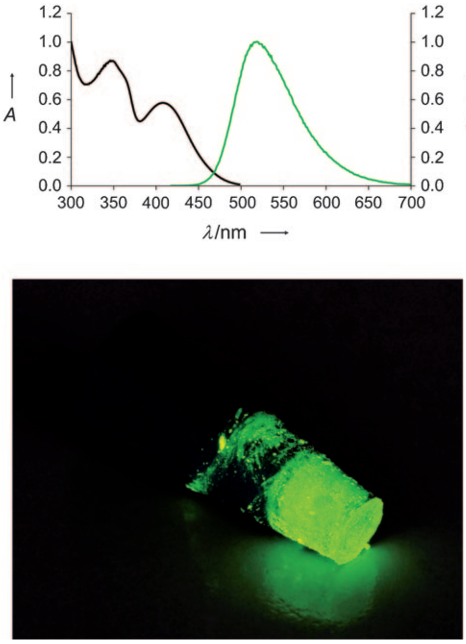


Figure 3. Absorption (black) and emission (green) spectra of **8** (toluene solution) and photograph illustrating the luminescence of solid **8** in air ($\lambda_{ex} = 366$ nm).

In summary, we suggest the diorganoborane $(\mathbf{2})_n$ as a lead structure for the design of ditopic building blocks of new boron-containing organic materials. Not only can they form hitherto inaccessible classes of macromolecules by B–H–B three-center two-electron bonds but can also be employed as efficient reagents for the hydroboration polymerization of diynes, thus giving rise to new luminescent materials.

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[36] To further prove the presence of 9,10-diboraanthracene moieties in the reprecipitated material, we added one drop of water to the solution in the NMR tube and thereby generated 9,10-dihydroxy-9,10-dihydro-9,10-diboraanthracene by hydrolysis of the polymer backbone. The diborinic acid was unambiguously identified by comparison of its ^{11}B, ^{1}H, and ^{13}C NMR spectroscopic data with those of an authentic sample.

[37] The nature of the polymer end groups could not be determined conclusively.