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Tri-9-anthrylborane and Its Derivatives: New Boron-Containing π-Electron Systems with Divergently Extended π-Conjugation through Boron

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Several extension modes of π-conjugation have been realized in the carbon π-electron systems, as shown in Figure 1. Those involve (a) a linear chain-type, (b) a sheet-type, and (c) a sphere- and tube-type extension, represented by polyacetylene, graphite, and fullerene and carbon nanotube, respectively.[1] In contrast to these structures, (d) a starburst divergent-type extension of π-conjugation seems difficult to achieve in the carbon π-electron systems. Such π-conjugation may be readily realized using Group 13 or 15 elements at the diverging point. Triarylamine derivatives represent one typical example in which π-conjugation through the lone-pair electrons on nitrogen in the HOMO level causes their low ionization potentials and makes them a useful class of hole-transporting materials.[2] As a new family of π-electron systems with such π-conjugation, we now report the trianthrylborane derivatives, where three anthracene π-systems are introduced on a boron atom. In contrast to the amine cases, the π-conjugation would be divergently extended through the vacant p-orbital on boron in the LUMO level,[3−7] thus realizing the high electron-accepting properties.[8]

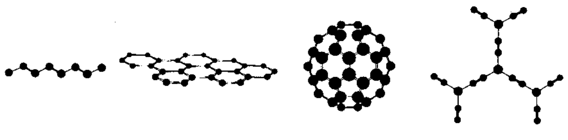
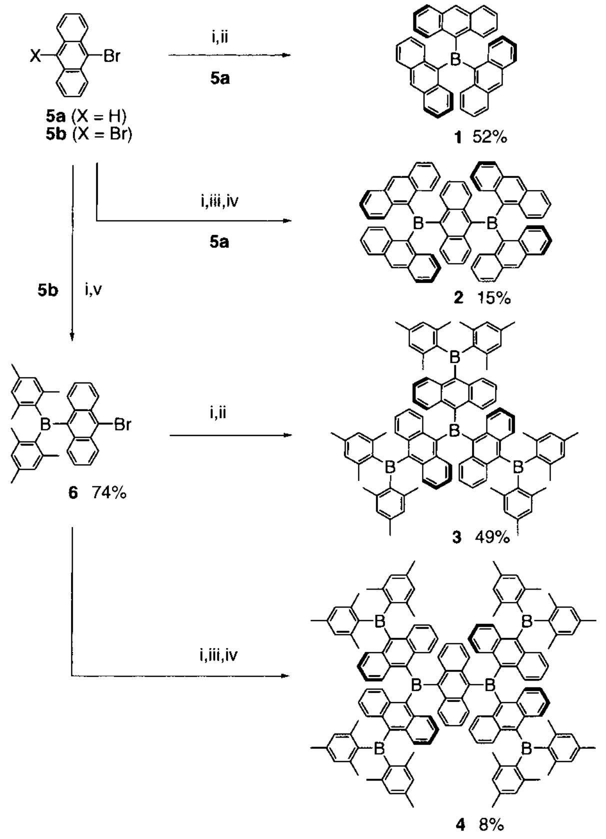

(a) linear (b) sheet (c) sphere (d) starburst

Figure 1. Schematic representations of several extension modes of π-conjugation: Trivalent hetero-elements are postulated as the diverging point for the starburst extension mode.

Scheme 1[a]



[a] Reagents and conditions: (i) *n*-BuLi (1.0−1.2 mol. amt.), Et$_2$O; (ii) BF$_3$·OEt$_2$ (0.3 mol. amt.); (iii) BF$_3$·OEt$_2$ (1.5 mol. amt.); (iv) 9,10-dilithioanthracene (0.25 mol. amt.), generated from **5b** with *n*-BuLi (2.2 mol. amt.) in Et$_2$O; (v) Mes$_2$BF (1.1 mol. amt.). Mol. amt. = molar amount.

Trianthrylborane **1** itself and three more extended derivatives **2**−**4** have been studied. Compound **2** is a dianthrylboryl-substitued trianthrylborane and compounds **3** and **4** are the dimesitylboryl-substituted derivatives of **1** and **2**, respectively. These compounds have been prepared from bromoanthracenes **5** and **6** as the key precursors, as shown in Scheme 1. All the compounds thus prepared have a substantial stability toward air and moisture and can be handled without special care due to the protection of the central boron atom by the bulky anthryl groups.

Among these compounds, the structure of **1** (see the Supporting Information) has been determined by X-ray crystallography, which reveals a completely planar geometry at the boron atom and a propeller-like arrangement of the three anthryl groups with the dihedral angles of about 53° between the central borane plane and anthracene planes. Despite these relatively large dihedral angles, π-conjugation through the central boron seems to still work well in this skeleton, and the color of compound **1** is bright orange and that of compounds **2**−**4** is bright red.

In solution, compounds **1**−**4** actually show unique UV−vis absorption spectra.[9] Their spectra are shown in Figure 2 and the data are summarized in Table 1 together with those for related compounds, di(9-anthryl)mesitylborane (**7**) and (9-anthryl)-

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(6) Corriu, R. J.-P.; Deforth, T.; Douglas, W. E.; Guerrero, G.; Siebert, W. S. *Chem. Commun.* **1998**, 963.

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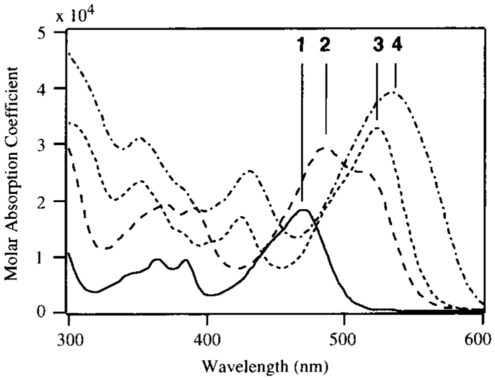

Figure 2. UV−vis absorption spectra of trianthrylborane derivatives in THF.

Table 1. UV−Vis Absorption and Electrochemical Data for Anthrylborane Derivatives

compd	UV−vis[a] λ_{max}/nm (log ϵ)	CV[b] E_{pc} ($E_{1/2}$)/V vs Fc/Fc$^+$
1	470 (4.35)	−1.86
2	485 (4.45)[c]	−1.64 (−1.61), −1.82 (−1.76)[d]
3	524 (4.54)	−1.71 (−1.66), −2.08 (−2.01)
4	535 (4.59)	−1.56 (−1.52), −1.86 (−1.78)
7	448 (4.14)	−2.00
8	420 (4.03)	−2.14

[a] In THF. [b] Measured under the following condition; sample concentrated 1 mM in 0.1 M Bu_4NClO_4 CH_3CN/CH_2Cl_2 1/1 solution, scan rate 100 mV/s, unless otherwise stated. [c] A shoulder peak is observed at 512 nm (log ϵ = 4.37). [d] CH_2Cl_2 was used as a solvent due to the low solubility.

dimesitylborane (**8**),[10] for comparison. Trianthrylborane **1** has absorption bands around 350−390 nm attributed to the $\pi-\pi^*$ transitions of the anthracene moieties and, in addition, *an intense band at 470 nm*. A comparison of **1** with **7** and **8** shows bathochromic shifts of the longest absorption maximum wavelengths as the number of anthryl groups increases, suggesting that π-conjugation is divergently extended to the three anthryl groups in **1**.[11] Furthermore, compounds **2**−**4** have longer absorption maxima than that of **1**. Notably, about 50 nm bathchromic shifts are observed for **3** and **4** in comparison with **1** and **2**, respectively, indicative of the effective extension of the π-conjugation to the external boron moieties in **3** and **4**.

To obtain deeper insights into the electronic structures of the trianthrylborane π-conjugated systems, molecular orbital calculations have been performed for compound **1**.[12] Based on the HF/6-31G(d) level calculation, while the HOMO and HOMO-1 are degenerate to each other and are respectively primarily localized on one anthryl group with significant density on a second anthracene, the LUMO is delocalized over three anthracene moieties via the boron vacant p-orbital, as shown in Figure 3. As a consequence, the LUMO energy level of **1** is about 0.75 eV lower than that of anthracene itself.[12] The ZINDO calculation[13] indicates that the new absorption band observed for **1** consists of two excitations with comparable oscillator strengths: Excitation 1, λ_{calc} 382 nm, f = 0.392 (HOMO → LUMO 63%); Excitation 2, λ_{calc} 377 nm, f = 0.360 (HOMO-1 → LUMO 55%).

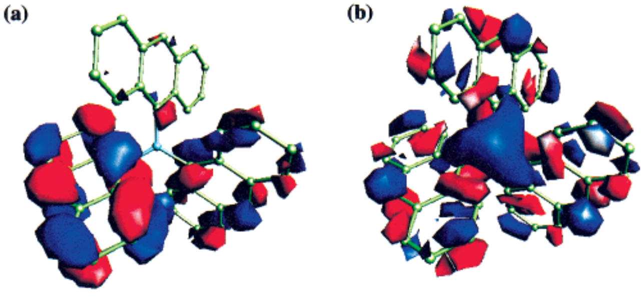

Figure 3. Representation of (a) HOMO and (b) LUMO of trianthrylborane **1** based on the HF/6-31G(d) calculation.

To evaluate the electron-accepting properties, cyclic voltammetry measurements have been carried out for compounds **1**−**4**, **7**, and **8**, the data being included in Table 1. While a series of mono-boron compounds **1**, **7**, and **8** show an irreversible reduction like other triarylboranes,[8c] compounds **2**, **3**, and **4**, containing two, four, and six boron atoms, respectively, show two reversible reductions. In the mono-boron compound series, the reduction peak potential (E_{pc}) steadily becomes more positive (smaller number in negative) from **8** to **7** to **1**, as the number of anthryl groups increases. From a comparison of the trianthrylborane derivatives **1**−**4**, the extension by the additional dianthrylboryl or dimesitylboryl groups also causes to shift the reduction potentials in the positive direction. Thus, compound **2** has an about 0.2 V more positive E_{pc} value relative to that of **1**. Moreover, about 0.1 V positive shifts of the first E_{pc} are observed from **1** and **2** to their dimesithylboryl-substituted derivatives **3** and **4**, respectively. These results are consistent with the UV−vis absorption data, and strongly suggest that the π-conjugation in the LUMO is extended over the molecule in the trianthrylborane derivatives. It should be also noted that their reduction peak potentials are comparable to or lower than those for the π-electron deficient polymeric materials,[14] such as poly(2,2′-bithiazole-5,5′-diyl)[14a] and poly(quinoxaline-2,6-diyl).[14c]

The key point of the present molecular design is *the introduction of three identical π-electron systems onto a planar boron atom*, which makes it possible to extend the LUMO over the three π-systems across the vacant p-orbital of boron.[15] The results demonstrate a new direction for the construction of electron-accepting organic molecules susceptible to n-doping and electron-transporting, which is one of the most important topics for the development of organic electronic devices such as organic light emitting diodes (OLEDs).

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Supporting Information Available: Experimental procedures and data for **1**−**4**, **6**, and **7**, and crystal structural data for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.

[11] As the related compounds, trianthrylsilanes have their absorption maxima at around 400 nm: Yamaguchi, S.; Akiyama, S.; Tamao, K. *Organometallics* **1998**, *17*, 4347.

[12] The calculations were performed using the Gaussian 98 program. Single point calculation of **1** was carried out using the geometry derived from its crystal structure, whereas the geometry of anthracene was fully optimized at the HF/6-31G(d) level. The LUMO energy levels of **1** and anthracene are 1.175 and 1.924 eV, respectively. Notably, the HOMO energy level of **1** (−6.593 eV) is also higher than that of anthracene (−7.008 eV) by 0.42 eV, mainly due to the substituent effect of the electron-positive boron atom. It should be also noted that the LUMO of **1** is about 0.75 eV lower than that of Ph_3B (1.921 eV, HF/6-31G(d)), indicating the significant contribution of the anthryl moieties to the LUMO. However, one of the reviewers suggested the LUMO of **1** is mostly localized on the vacant p-orbital of the boron atom. Further detailed analysis would be necessary for a full understanding of the electronic structure.

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[14] For examples see: (a) Curtis, M. D.; Cheng, H.; Nanos, J. I. *Macromolecules* **1998**, *31*, 205. (b) Yamamoto, T.; Maruyama, T.; Zhou, Z.-h.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (c) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930. (d) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V. E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409. (e) Jandke, M.; Strohriegl, P.; Berleb, S.; Werner, E.; Brütting, W. *Macromolecules* **1998**, *31*, 6434. (f) Wang, Y. Z.; Gebler, D. D.; Fu, D. K.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1997**, *85*, 1179.

[15] In mixed triarylboranes, the LUMO may not be delocalized over the molecule but localized on the aryl-boryl moieties having more π-extended aryl group(s).