

Electron-Donating Tetrathienyl-Substituted Borole**

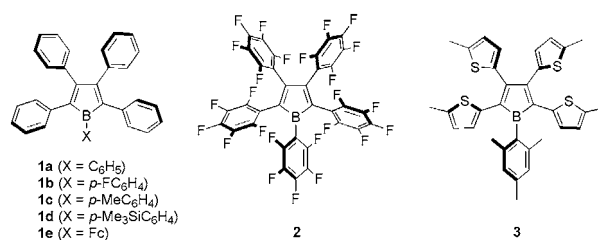
Takafumi Araki, Aiko Fukazawa, and Shigehiro Yamaguchi*

Borole is a boron-containing unsaturated five-membered ring with 4 π electrons, and is isoelectronic to a cyclopentadienyl cation ($C_5H_5^+$).^[1] The unusual electronic structures of borole-based π -electron-containing materials have been predicted by theoretical studies.^[2,3] After the first synthesis of a borole derivative, 1,2,3,4,5-pentaphenylborole (**1a**, Scheme 1), by Eisch and coworkers,^[4,5] only few reports on boroles have appeared for almost four decades, and the crystal structure of **1a** has only quite recently been determined by X-ray crystallography.^[6,7] Thereupon, the interest in this chemistry has been dramatically revived.^[6–16] Various intriguing borole derivatives have been reported within the past several years, including fused boroles,^[8–11] ferrocenylborole,^[6,12] haloboroles,^[13] borole–metal complexes,^[14] carbene-coordinated boroles,^[15] and the highly Lewis-acidic perfluorinated boroles.^[8,16]

The most notable electronic feature of the borole skeleton in comparison to other heteroles is its significantly low-lying LUMO.^[1,2] Therefore, borole-based π -conjugated compounds have been widely recognized as electron-accepting systems. The low-lying LUMOs of these compounds in combination with their antiaromaticity allow them to undergo various reactions, such as the formation of adducts with Lewis acids and bases,^[4c,13a,c,15] B–C bond cleavage,^[4] Diels–Alder reactions with alkynes,^[4,16c] and reduction to a radical anion^[12] or dianion.^[7,12,13b] Recently, the activation of H_2 without any transition metal has also been demonstrated by the use of borole derivatives.^[16b] The Lewis acidity of the perarylated boroles **1** can be significantly enhanced by modification of the peripheral aryl groups by introducing electron-withdrawing substituents, as exemplified by perfluorophenylborole **2** described by Piers and co-workers.^[16] The utilization of the borole skeleton as an electron-accepting unit in the extended π -conjugated system has been also demonstrated.^[9b]

In our studies, we noticed the other important feature of the borole ring, its relatively high-lying HOMO compared with other electron-accepting heteroles, such as silole and phosphole.^[2] This difference might be due to the inductive effect that results from the σ -donating character of the boron

atom, because boron is a more electron-positive element than carbon. In order to highlight this feature, we designed a thienyl-substituted borole **3** (Scheme 1) with a pronounced electron-donating character as a new example of borole-

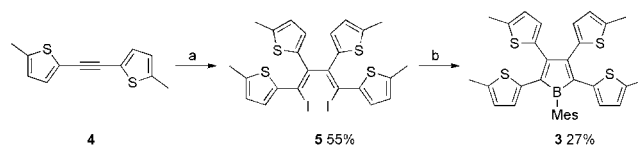


Scheme 1. Various pentaarylboroles. Fc = ferrocenyl.

based π -conjugated compounds. In a theoretical study, Ma and co-workers suggested the unusual electronic structures of borole/thiophene-alternating co-oligomers with a significant contribution of a quinoid structure as well as a distinct biradical character.^[3] Herein, we report the synthesis of the tetrathienyl-substituted borole **3** as the first example of a heteroaryl-substituted borole. The study on the crystal structure and fundamental properties of **3** demonstrated several characteristic features of the borole as an electron-donating building unit.

1-Mesityl-2,3,4,5-tetrakis(2-methylthienyl)borole **3** was successfully obtained by a straightforward two-step synthesis from bis(5-methyl-2-thienyl)acetylene **4** (Scheme 2). Alkyne **4** was first converted to 1,4-diiodobutadiene **5** via a zirconacyclopentadiene intermediate followed by treatment with I_2 in the presence of CuCl, according to the method described by Takahashi and co-workers.^[17] Diiodide **5** was successively treated with $nBuLi$ and a 1.0 M solution of MesBCl₂ in toluene to give a dark green solution. Purification by recrystallization from hexane under an argon atmosphere afforded **3** in 27% yield as an air- and moisture-sensitive green solid.^[18]

The single crystals of the tetrathienylborole **3** were obtained by slow evaporation of a solution of **3** in hexane, and the structure was verified by X-ray crystallography



Scheme 2. Synthesis of **3**. Reagents and conditions: a) Cp_2ZrCl_2 , $nBuLi$, THF, $-78^\circ C \rightarrow RT$, then I_2 , CuCl, $-78^\circ C \rightarrow RT$; b) $nBuLi$, toluene, RT, then MesBCl₂, $-78^\circ C \rightarrow RT$. Cp = cyclopentadienyl, Mes = 2,4,6-trimethylphenyl.

[*] T. Araki, Dr. A. Fukazawa, Prof. Dr. S. Yamaguchi
Department of Chemistry
Graduate School of Science, Nagoya University
Furo, Chikusa, Nagoya 464-8602 (Japan)
E-mail: yamaguchi@chem.nagoya-u.ac.jp
Homepage: <http://orgreact.chem.nagoya-u.ac.jp/en/Home.html>
Prof. Dr. S. Yamaguchi
CREST (Japan) Science and Technology Agency (JST)
Furo, Chikusa, Nagoya 464-8602 (Japan)

[**] This work was supported by a Grant-in-Aid (No. 19675001) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and CREST (JST).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201201156>.

(Figure 1). There is no noticeable intermolecular interaction around the boron center in the packing structure. This packing structure is different from that of pentaphenylborole **1a**^[6] (see the Supporting Information). The borole ring in **3**

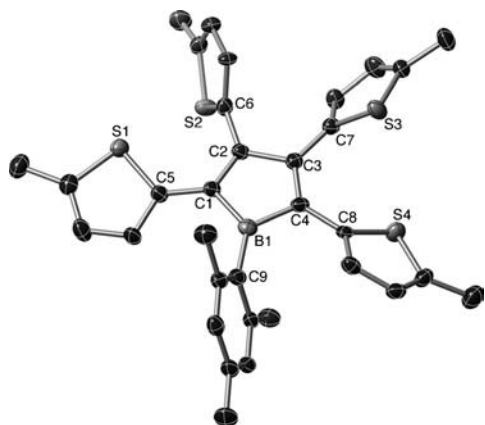


Figure 1. Thermal ellipsoid plots of **3** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

adopts a planar geometry, in which the bond lengths within the butadiene moiety show a large alternation: C1–C2: 1.363(6) Å, C2–C3: 1.524(6) Å, C3–C4: 1.369(6) Å. The alternation of the bond lengths within the butadiene moiety of the borole ring is comparable to that observed for the already reported 1-aryl-2,3,4,5-tetraphenylboroles **1b–e** (C1–C2: 1.358–1.362 Å, C2–C3: 1.518–1.529 Å, C3–C4: 1.353–1.362 Å),^[7] thus indicating the significant antiaromatic character of the borole ring in **3** (see below).

The other notable feature in the crystal structure of **3** is the conformation of the peripheral thienyl groups. While the dihedral angles between the borole ring and the aryl groups at the 1, 3, and 4 positions are large (74.1°, 71.2°, and 43.4°, for the 1-mesityl, 3-thienyl, and 4-thienyl groups, respectively), the dihedral angles between the borole ring and the thiophene rings at the 2 and 5 positions are much smaller (10.7° and 38.2°, respectively). These small dihedral angles at the 2 and 5 positions indicate the effective expansion of π conjugation over the 2,5-dithienylborole framework. In line with this point, the C–C bonds between the borole and the aryl groups at the 2 and 5 positions in **3** are shorter than those in **1b** (**3**: 1.448(6) and 1.467(6) Å, **1b**: 1.486(2) Å). This difference might reflect the stronger interaction between the borole and thiophenes in **3** compared with **1b**. In addition, in **3** the sulfur atoms of the thiophene rings at the 2 and 3 positions and the 4 and 5 positions, respectively, are facing each other, and are in close proximity to each other, with interatomic distances of 3.432 Å (2–3) and 3.495 Å (4–5), respectively, which are slightly smaller than the sum of the van der Waals radii of two sulfur atoms (3.70 Å).

Regarding the effect of the peripherally substituted thienyl groups in **3** compared with the phenyl-substituted analogues **1**, we were interested 1) in the effect on the aromaticity and the singlet–triplet energy difference, and 2) in the electronic perturbation on the orbital levels and thereby

on the photophysical and electrochemical properties. To assess these issues, DFT calculations for **3** in both the singlet and triplet ground states were conducted at the B3LYP/6-31G(d) level of theory. The structural parameters of the X-ray crystal structure are in good agreement with those of the optimized geometry in the singlet state, and not the triplet state. In addition, the NMR signals of **3** at 25 °C did not show any signal broadening (see Figure S5 in the Supporting Information), thus suggesting that **3** exists in the singlet ground state at this temperature. The nucleus-independent chemical shift (NICS) calculations were also conducted at the HF/6-31 + G(d,p)//B3LYP/6-31G(d) level to evaluate the antiaromaticity of the borole ring.^[19] The NICS(0) value of the borole ring of **3** in the singlet state is +12.7 ppm, which is almost comparable with that calculated for pentaphenylborole **1a** (+12.9 ppm). The incorporation of thienyl groups does not affect the antiaromaticity of the borole ring, which is consistent with the fact that the alternation of the bond lengths in the borole ring in **3** is comparable to that in **1b**. Notably, this result is in contrast to the fact that the thiophene-fused borole has an enhanced antiaromaticity, which we have revealed recently.^[11] On the other hand, the calculated singlet–triplet energy difference (ΔE_{S-T}) was only 7.2 kcal mol^{−1} for **3**, which was significantly smaller than that of pentaphenylborole **1a** (15.4 kcal mol^{−1}).^[7] This striking effect on the ΔE_{S-T} is presumably attributable to the difference in the HOMO–LUMO gap. The lower aromaticity of thiophene compared with that of benzene might give rise to the contribution of quinoid structure to some extent.

The tetrathienylborole **3** exhibits a bright green color in toluene (Figure 2). This green color is noticeable, because all the known pentaarylboroles **1** and **2** are dark blue. In the UV/Vis/NIR absorption spectrum, **3** shows a weak absorption band with the λ_{max} of 735 nm ($\epsilon = 1710$). This maximum wavelength is red-shifted by 175 nm and the molar absorption coefficient is about five times larger than those of the pentaphenylborole **1a** ($\lambda_{\text{max}} = 560$ nm, $\epsilon = 360$).^[6] These differences demonstrate the significant perturbation on the electronic structure of borole by the peripheral thiophene rings.

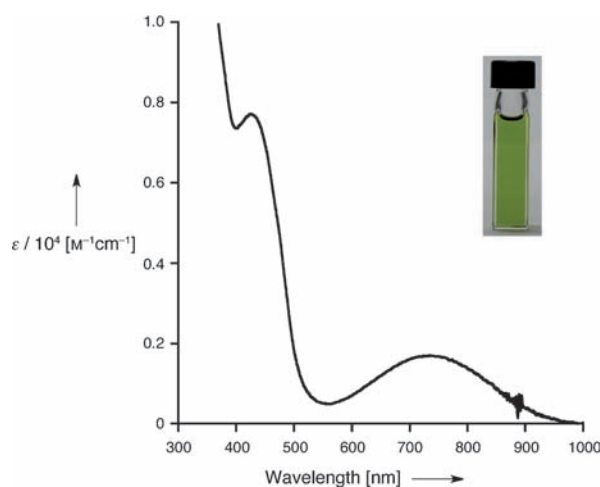


Figure 2. UV/Vis/NIR absorption spectrum of **3** in toluene. Inset: photograph of **3** in toluene.

To gain insights into the difference between **1** and **3**, we compared their electronic structures based on the DFT calculations. Figure 3 shows the comparison of the HOMO and LUMO energy levels for **1a** and **3** together with those of the tetrathienylheterole model compounds **6** and **7**. While the

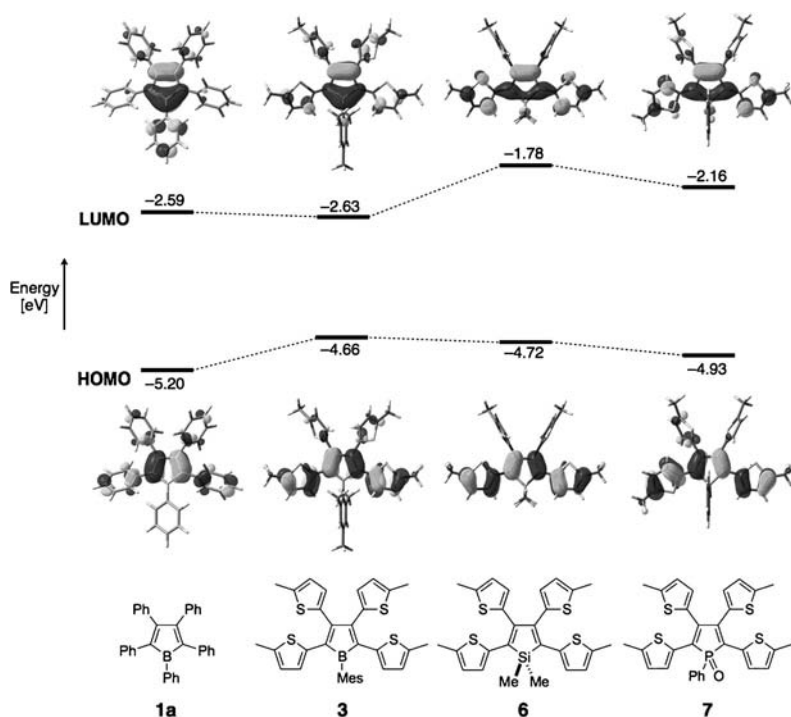


Figure 3. Pictorial representations of the Kohn-Sham HOMOs and LUMOs and their energy levels for a series of pentaarylboreles, calculated at the B3LYP/6-31G(d) level of theory.

LUMO of **3** is only 0.04 eV lower than that of **1a**, **3** has a much higher-lying HOMO than **1a**. This difference in the HOMO level, which amounts to 0.54 eV, is obviously the origin of the significantly red-shifted λ_{max} of **3**. We confirmed by the TD-DFT calculation that the absorption band at 735 nm can indeed be assigned to the HOMO–LUMO transition. This difference in the HOMO level reflects the highly electron-donating character of the thiophene rings as well as the higher coplanarity of the 2,5-diarylborole moiety in **3**.

More importantly, the tetrathienylborole **3** can be recognized as a highly electron-donating π -conjugated system that also possesses a highly electron-accepting character. Even compared with the phosphole oxide congener **7**, which contains the highly electron-withdrawing P=O group, borole **3** has a much lower-lying LUMO by 0.53 eV. Moreover, the HOMO level of **3** is also slightly higher than that of a silole derivative **6**, which is a congener with an electron-positive silicon atom. As a consequence, the λ_{max} of **3** is significantly longer than those of the known analogous silole and phosphole oxide derivatives **6'** (1,1-dimethyl-2,5-dithienylsilole; λ_{max} 415 nm)^[20] and **7'** (1-phenyl-2,3,4,5-tetrathienylphosphole oxide; λ_{max} 434 nm).^[21] These comparisons clearly demonstrate the uniqueness of the borole skeleton as the building unit for π -conjugated systems.

The unusual electronic structure of **3** can be experimentally confirmed by cyclic voltammetry. We successfully conducted the measurement by using inert $n\text{Bu}_4\text{N}[\text{B}(\text{C}_6\text{F}_5)_4]$ as the supporting electrolyte (Figure 4).^[22,23] Compound **3** shows a reversible redox wave that corresponds to one-electron reduction at the low reduction potential of $E_{1/2} = -1.57$ V (vs Fc/Fc⁺). This potential is more positive than that of ferrocenylborole **1e** ($E_{1/2} = -1.96$ V) described by Braunschweig and co-workers,^[12] thus demonstrating the high electron-accepting character of the tetrathienyl derivative. Notably, **3** also shows a reversible redox wave that corresponds to one-electron oxidation at the significantly low oxidation potential of $E_{1/2} = -0.04$ V (vs. Fc/Fc⁺). It is remarkable that the π -conjugated skeleton without any electron-donating groups, such as an NR₂ group, can have such a low oxidation potential as **3**.

In summary, we have succeeded in the synthesis and characterization of the tetrathienyl-substituted borole **3**, which is the first example of a heteroaryl-substituted borole derivative. The combination of the electron-deficient and antiaromatic borole ring with the electron-donating aromatic thiophene rings produced a new type of borole-based π -conjugated system with an unusual electronic structure. The incorporation of the electron-donating thienyl groups on the borole skeleton accentuates the electron-donating character of the borole ring, and leads to the narrow HOMO–LUMO gap and thus the characteristic absorp-

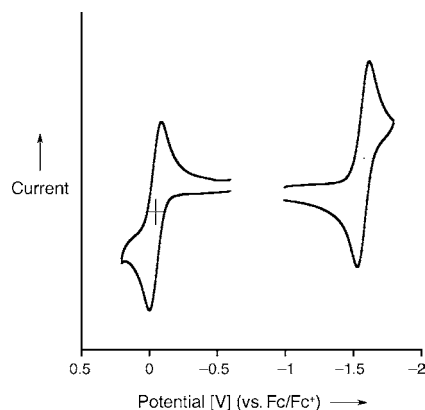


Figure 4. Cyclic voltammogram of **3** in CH_2Cl_2 (1.0 mM), measured with $n\text{Bu}_4\text{N}[\text{B}(\text{C}_6\text{F}_5)_4]$ (0.1 M) as a supporting electrolyte at a scan rate of 100 mVs^{-1} .

tion and electrochemical properties, which are significantly different from those of the known phenyl-substituted boroles. This result has shed light on the hidden nature of boroles, which are electron-accepting as well as electron-donating heteroles. These findings should provide an important guide-

line for the design of more fascinating boron-based π materials.

Received: February 11, 2012

Published online: April 12, 2012

Keywords: antiaromaticity · borole · boron · conjugation · thiophene

- [1] H. Braunschweig, T. Kupfer, *Chem. Commun.* **2011**, 47, 10903.
- [2] U. Salzner, J. B. Lagowski, P. G. Pickup, R. A. Poirier, *Synth. Met.* **1998**, 96, 177.
- [3] H. Cao, J. Ma, G. Zhang, Y. Jiang, *Macromolecules* **2005**, 38, 1123.
- [4] a) J. J. Eisch, N. K. Hota, S. Kozima, *J. Am. Chem. Soc.* **1969**, 91, 4575; b) J. J. Eisch, J. E. Galle, *J. Organomet. Chem.* **1977**, 127, C9; c) J. J. Eisch, J. E. Galle, S. Kozima, *J. Am. Chem. Soc.* **1986**, 108, 379; d) J. J. Eisch, J. E. Galle, B. Shafii, A. L. Rheingold, *Organometallics* **1990**, 9, 2342.
- [5] P. J. Fagan, W. A. Nugent, J. C. Calabrese, *J. Am. Chem. Soc.* **1994**, 116, 1880.
- [6] H. Braunschweig, I. Fernández, G. Frenking, T. Kupfer, *Angew. Chem.* **2008**, 120, 1977; *Angew. Chem. Int. Ed.* **2008**, 47, 1951.
- [7] C.-W. So, D. Watanabe, A. Wakamiya, S. Yamaguchi, *Organometallics* **2008**, 27, 3496.
- [8] P. A. Chase, W. E. Piers, B. O. Patrick, *J. Am. Chem. Soc.* **2000**, 122, 12911.
- [9] a) S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2002**, 124, 8816; b) A. Wakamiya, K. Mishima, K. Ekawa, S. Yamaguchi, *Chem. Commun.* **2008**, 579.
- [10] S. Kim, K. Song, S. O. Kang, J. Ko, *Chem. Commun.* **2004**, 68.
- [11] A. Iida, S. Yamaguchi, *J. Am. Chem. Soc.* **2011**, 133, 6952.
- [12] H. Braunschweig, F. Breher, C.-W. Chiu, D. Gamon, D. Nied, K. Radacki, *Angew. Chem.* **2010**, 122, 9159; *Angew. Chem. Int. Ed.* **2010**, 49, 8975.
- [13] a) H. Braunschweig, T. Kupfer, *Chem. Commun.* **2008**, 4487; b) H. Braunschweig, C.-W. Chiu, J. Wahler, K. Radacki, T. Kupfer, *Chem. Eur. J.* **2010**, 16, 12229; c) H. Braunschweig, C.-W. Chiu, A. Damme, K. Ferkinghoff, K. Kraft, K. Radacki, J. Wahler, *Organometallics* **2011**, 30, 3210.
- [14] H. Braunschweig, C.-W. Chiu, K. Radacki, P. Brenner, *Chem. Commun.* **2010**, 46, 916.
- [15] a) H. Braunschweig, C.-W. Chiu, K. Radacki, T. Kupfer, *Angew. Chem.* **2010**, 122, 2085; *Angew. Chem. Int. Ed.* **2010**, 49, 2041; b) H. Braunschweig, C.-W. Chiu, T. Kupfer, K. Radacki, *Inorg. Chem.* **2011**, 50, 4247.
- [16] a) C. Fan, W. E. Piers, M. Parvez, *Angew. Chem.* **2009**, 121, 2999; *Angew. Chem. Int. Ed.* **2009**, 48, 2955; b) C. Fan, L. G. Mercier, W. E. Piers, H. M. Tuononen, M. Parvez, *J. Am. Chem. Soc.* **2010**, 132, 9604; c) C. Fan, W. E. Piers, M. Parvez, R. McDonald, *Organometallics* **2010**, 29, 5132.
- [17] a) C. Xi, S. Huo, T. H. Afifi, R. Hara, T. Takahashi, *Tetrahedron Lett.* **1997**, 38, 4099; b) A. J. Ashe, J. W. Kampt, S. Pilotek, R. Rousseau, *Organometallics* **1994**, 13, 4067; c) U. Bankwitz, H. Sohn, D. R. Powell, R. West, *J. Organomet. Chem.* **1995**, 499, C7–C9; d) W. P. Freeman, T. D. Tilley, O. M. Liabe-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **1996**, 118, 10457.
- [18] The reaction of di(2-thienyl)acetylene without methyl groups resulted in formation of a complex mixture, thus demonstrating the importance of the methyl group for the isolation of the tetrathienylborole.
- [19] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, 118, 6317; b) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, 8, 863.
- [20] M. Katkevics, S. Yamaguchi, A. Toshimitsu, K. Tamao, *Organometallics* **1998**, 17, 5796.
- [21] C. Hay, C. Fischmeister, M. Hissler, L. Toupet, R. Réau, *Angew. Chem.* **2000**, 112, 1882; *Angew. Chem. Int. Ed.* **2000**, 39, 1812.
- [22] All attempts for the cyclic voltammetry (CV) measurement with $n\text{Bu}_4\text{NPF}_6$ as electrolyte were unsuccessful because of the decomposition of **3** under the applied conditions. The use of $n\text{Bu}_4\text{NB}(\text{C}_6\text{F}_5)_4$ (see Ref. [23]) with its less nucleophilic anion as electrolyte was essential.
- [23] R. J. LeSuer, W. E. Geiger, *Angew. Chem.* **2000**, 112, 254; *Angew. Chem. Int. Ed.* **2000**, 39, 248.