



Enhancement of the Lewis acidity by substitution of sulfur-containing hetero aromatics in triarylboranes

Shinji Miyasaka, Junji Kobayashi*, Takayuki Kawashima*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

ARTICLE INFO

Article history:

Received 14 January 2009

Revised 25 February 2009

Accepted 26 February 2009

Available online 4 March 2009

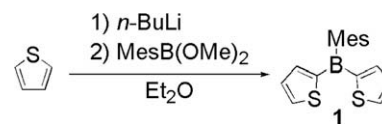
ABSTRACT

Triarylboranes bearing two thiophene, dimethylthiophene, or benzothiophene units were synthesized. X-ray crystallographic analysis revealed the planar structure around the boron atom and non-bonding S–S interaction of the thiophene. They exhibited several intense absorption bands in the UV region. They were stable in the air for months and showed extremely strong Lewis acidities.

© 2009 Elsevier Ltd. All rights reserved.

Fluoride ion recognition and sensing have received considerable attention in recent years because it is a key ionic species in environmental problems and diseases such as caries or osteoporosis. Pyrrole¹, urea², and borane units are often used as fluoride recognition sites of synthetic chemosensors. Among them, π -conjugated triarylboranes are an excellent motif due to drastic changes of UV–vis, or fluorescence spectra upon complexation with fluoride ion. It leads to a drastic change of the frontier orbitals of π -conjugation systems, thereby dramatically altering the photophysical properties. A lot of triarylboranes have been developed and investigated for fluoride ion sensing by taking advantage of the strong B–F bond formation.³ Among them, monothierylboranes showed good fluoride ion recognition ability with the high selectivity, because of a relatively electron-deficient property of thiophene ring.⁴ Introduction of more than two thiophene rings is expected to improve the recognition ability, and dithienyl- and trithienylboranes were indeed reported.⁵ However, the fluoride ion affinities of these compounds were not examined due to their lack of stability against air and moisture. Herein we report the syntheses, structures, optical properties, and fluoride recognition abilities of stable boranes bearing two thiophene, dimethylthiophene, or benzothiophene units on a boron atom.

Dithienylborane **1** was synthesized by the reaction of 2-lithiothiophene, generated by direct lithiation of thiophene, with MesB(OMe)₂ in Et₂O (Scheme 1). **1** was purified by HPLC and obtained as a colorless solid (86%), being stable to air and moisture both in the solid state and solution. Usually triarylborane requires more than two bulky substituents for the kinetic stabilization. However, only one mesityl group on the boron atom was enough for kinetic stabilization of **1**. Dimethylthiophene and benzothiophene were converted to the corresponding boranes **2** (45%) and **3** (80%), respectively, by the similar method, which were also stable in the solid state and solution (Fig. 1).⁶ In CDCl₃, the ¹¹B NMR



Scheme 1. Synthesis of dithienylborane **1**.

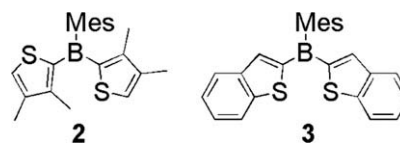


Figure 1. Structural formulas of compounds **2** and **3**.

signals of **1** (δ_B 54.9), **2** (δ_B 58.2), and **3** (δ_B 60.4) appeared in the usual region for triarylboranes.

Single crystals of **1**, **2**, and **3** were obtained by recrystallization from CH₃CN, CHCl₃/hexane, and Et₂O solutions, respectively, and X-ray crystallographic analyses were carried out. The crystal structures of **1** and **2** are shown in Figure 2. **1** had two independent molecules in a unit cell and only one molecule is shown in Figure 2 since they were almost identical. Boron centers of **1**, **2**, and **3** adopted the ideal trigonal planar geometries ($\Sigma_B = 360^\circ$). Dihedral angles between the boron plane of **1** and two thiophene rings ranged from 1° to 9° , meaning the highly planar structure and the effective π -conjugation in **1**. **3** also had a planar structure, in which the corresponding dihedral angles ranged from 1° to 11° . On the other hand, the mesityl ring was almost perpendicular to the boron plane. In contrast, such a co-planarity between the boron plane and thiophene rings was not observed in **2** (dihedral angles were about 30°), because of steric repulsion between a mesityl group and methyl groups of dimethylthienyl groups. Furthermore, it is inter-

* Corresponding authors. Tel.: +81 3 5841 4338; fax: +81 3 5800 6899 (T.K.).
E-mail address: takayuki@chem.s.u-tokyo.ac.jp (T. Kawashima).

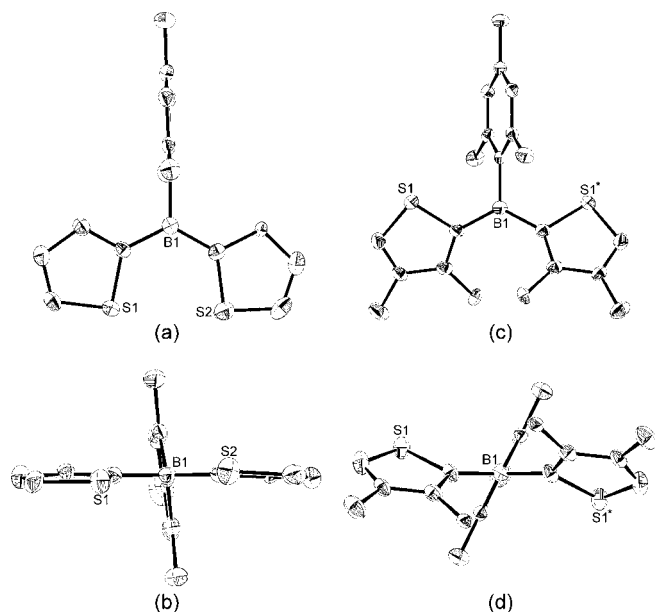


Figure 2. ORTEP drawing of **1** and **2** (50% probability): (a) top view of **1**; (b) side view of **1**; (c) top view of **2**; (d) side view of **2**. Hydrogen atoms are omitted for clarity.

esting to note that the crystal structure of **1** showed an intramolecular S–S non-bonding interaction with 3.26 Å and 3.23 Å, which were shorter than the sum of the van der Waals radii of sulfur atoms (3.6 Å). Such interaction was also observed in the crystal structure of **3** (S...S 3.15 Å).⁷

All compounds **1**, **2**, and **3** exhibited several intense absorption bands including the longest ones at 326 nm, 342 nm, and 361 nm, respectively, in CH₃CN, and 328 nm, 343 nm, and 362 nm in CH₂Cl₂, indicating no significant solvent effects. **2** and **3** showed bathochromic shifts of the longest absorption band compared with that of **1**, due to the increase in HOMO energy level by electron-donating methyl groups for **2** and extended π -conjugation by benzo-fused framework for **3**.

To clarify the sensing ability of fluoride ion, we monitored the absorbance changes of **1**, **2**, and **3** associated with the addition of *n*-Bu₄NF (TBAF). The longer absorption bands of **1**, **2**, and **3** decreased and finally disappeared and a new shoulder band at 235 nm for **1**, 240 nm for **2**, and new bands at 277 and

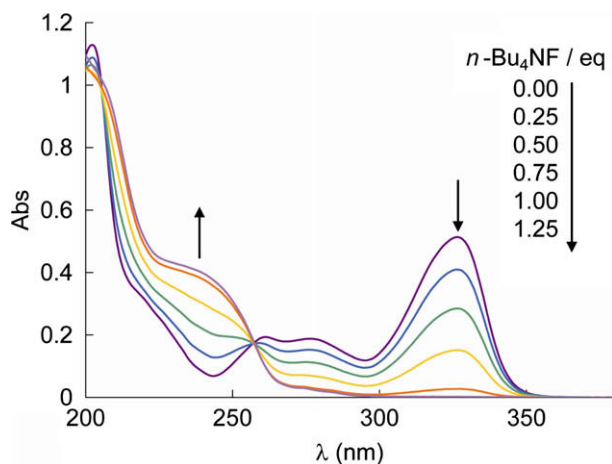


Figure 3. Changes in UV-vis absorption of **1** (20 μM) in CH₃CN upon the addition of TBAF.

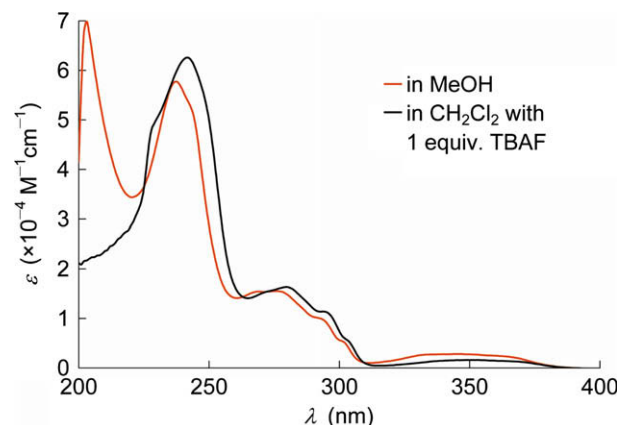


Figure 4. UV-vis spectra of **3** (10 μM) in CH₂Cl₂ with 1 equiv TBAF and in MeOH.

240 nm for **3** arose with the isosbestic point in each spectrum, which indicated the complexation with fluoride ion to form fluoro-borates. For a typical example, the spectral changes of **1** in CH₃CN upon addition of TBAF are shown in Figure 3. The association constants of **1**, **2**, and **3** in CH₃CN were too large to be determined in detail by titration method using UV-vis spectra and were approximately estimated to be more than 10⁸ M⁻¹. However, the association constants could be determined in CH₂Cl₂, which has the larger Acceptor Number than CH₃CN (CH₂Cl₂: 20.4, CH₃CN: 18.9).⁸ The association constants (*K*_a) of **1** was 2.3 × 10⁶ M⁻¹, which was much larger than those of neutral compounds previously reported.^{3a,b,d,4} Compound **2** showed smaller association constant, 4.4 × 10⁵ M⁻¹, due to electron-donating methyl groups. Benzothiophene derivative **3** had the enhanced fluoride ion affinity (*K*_a = 6.2 × 10⁷ M⁻¹) because LUMO energy level of **3** decreased by effective elongation of π -conjugation.⁹ Interestingly, a spectrum of **3** in MeOH was similar to that in CH₂Cl₂ after addition of 1 equiv TBAF (Fig. 4). This result suggests the formation of tetracoordinated boron-MeOH complex, revealing that **3** has the strong Lewis acidity.

In conclusion, mesitylboranes containing two thiophene, dimethylthiophene, and benzothiophene units were synthesized and characterized. Dithienyl borane **1** turned out to have a planar structure and sulfur-sulfur non-bonding interaction determined by X-ray crystallographic analysis. UV-vis spectra of these boranes showed that they had extended π -conjugation systems through a vacant *p*-orbital of the central boron atom. Introduction of thienyl groups to a borane was revealed to raise the Lewis acidity of a borane. Further studies on boranes bearing more π -extended thienyl rings are in progress.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 715341 for **1**, CCDC 715342 for **2**, and CCDC 715343 for **3**. Copies of these informations may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www:http://ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgments

This work was supported in part by Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering), MEXT, Japan. We also thank Tosoh Finechem Corp. for the generous gifts of alkylolithiums.

References and notes

- (a) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438–10439; (b) Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1777–1780.
- (a) Jiménez, D.; Martínez-Mañez, R.; Sancenón, F.; Soto, J. *Tetrahedron Lett.* **2002**, *43*, 2823–2825; (b) Kim, S. K.; Yoon, J. *Chem. Commun.* **2002**, 770–771; (c) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445–3448; (d) Duke, R. M.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 8043–8047.
- (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372–11375; (b) Yamaguchi, S.; Shirasaka, T.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2002**, *124*, 8816–8817; (c) Chiu, C.-W.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2006**, *128*, 14248–14249; (d) Bai, D.-R.; Liu, X.-Y.; Wang, S. *Chem. Eur. J.* **2007**, *13*, 5713–5723; (e) Agou, T.; Kobayashi, J.; Kawashima, T. *Inorg. Chem.* **2006**, *45*, 9137–9144; (f) Agou, T.; Kobayashi, J.; Kim, Y.; Gabbaï, F. P.; Kawashima, T. *Chem. Lett.* **2007**, *36*, 976–977.
- (a) Liu, Z.-Q.; Shi, M.; Li, F.-Y.; Fang, Q.; Chen, Z.-H.; Yi, T.; Huang, C.-H. *Org. Lett.* **2005**, *7*, 5481–5484; (b) Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879–12885.
- (a) Wrackmeyer, B.; Nöth, H. *Chem. Ber.* **1976**, *109*, 1075–1088; (b) Köhler, T.; Faderl, J.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem.* **2002**, 2942–2946; (c) Kim, S.; Song, K.-h.; Kang, S. O.; Ko, J. *Chem. Commun.* **2004**, 68–69; (d) Sundararaman, A.; Victor, M.; Varughese, R.; Jäkle, F. *J. Am. Chem. Soc.* **2005**, *127*, 13748–13749.
- General procedure for the synthesis of dithienylboranes.* To an Et₂O (3 mL) solution of thiophene (2.2 mmol) was added *n*-BuLi (2.2 mmol) dropwise at room temperature. The reaction mixture was stirred at room temperature for 3 h. Then MesB(OMe)₂ (1.0 mmol) was added at room temperature and the reaction mixture was stirred for 10 h. The resulting precipitates were filtered and washed with Et₂O. The crude product was purified by HPLC to afford products. *Spectral data for selected products:* Mesityldi(2-thienyl)borane (**1**): colorless solid. Mp 99–100 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.05 (s, 6H), 2.34 (s, 3H), 6.85 (s, 2H), 7.27–7.29 (m, 2H), 7.81 (d, *J* = 3.5 Hz, 2H), 7.91 (d, *J* = 4.6, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 21.29 (q), 22.62 (q), 126.90 (d), 129.21 (d), 137.06 (s), 137.72 (d), 138.35 (s), 141.56 (s), 142.03 (d), 143.92 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 54.9; UV–vis (CH₃CN) λ/nm (log ε): 326 (4.41), 276 (3.97), 261 (3.99). Anal. Calcd for C₁₇H₁₇BS₂: C, 68.87; H, 5.88. Found: C, 68.92; H, 5.78. Bis(3,4-dimethyl-2-thienyl)mesitylborane (**2**): colorless solid. Mp 177–178 °C. ¹H NMR (500 MHz, CDCl₃) δ 1.95 (s, 6H), 2.00 (s, 6H), 2.17 (s, 6H), 2.29 (s, 3H), 6.78 (s, 2H), 7.42 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 14.89 (q), 14.97 (q), 21.30 (q), 22.42 (q), 127.39 (d), 131.85 (d), 137.29 (s), 137.86 (s), 140.38 (s), 140.82 (s), 143.18 (s), 149.11 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 58.2; UV–vis (CH₃CN) λ/nm (log ε): 342 (4.34), 279 (3.87). Anal. Calcd for C₂₁H₂₅BS₂: C, 71.58; H, 7.15. Found: C, 71.32; H, 7.21. Bis(benzo[*b*]thien-2-yl)mesitylborane (**3**): colorless solid. Mp 120 °C decomp. ¹H NMR (500 MHz, CDCl₃) δ 2.11 (s, 6H), 2.39 (s, 3H), 6.92 (s, 2H), 7.35–7.45 (m, 4H), 7.90–7.95 (m, 4H), 8.11 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 21.37 (q), 22.73 (q), 122.71 (d), 124.50 (d), 125.72 (d), 126.74 (d), 127.08 (d), 137.61 (s), 138.46 (s), 140.38 (d), 140.60 (s), 141.33 (s), 144.36 (s), 146.79 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 60.4; UV–vis (CH₃CN) λ/nm (log ε): 361 (sh) (4.48), 346 (4.52), 299 (4.06), 263 (4.24). Anal. Calcd for C₂₅H₂₁BS₂: C, 75.75; H, 5.34. Found: C, 75.51; H, 5.41.
- Crystal structure of **3** had the disorder on benzothiophene moiety. Two sulfur atoms faced to each other in one disordered structure and one sulfur atom was directed to mesityl group in the other structure.
- Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235–1257.
- Fluoroborates **1-TBAF**, **2-TBAF**, and **3-TBAF** were obtained by the reactions of **1**, **2**, and **3** with TBAF, respectively. Their NMR spectral data are shown below. **1-TBAF**: ¹H NMR (500 MHz, CDCl₃) δ 0.92 (t, *J* = 7.3 Hz, 12H), 1.20–1.30 (m, 8H), 1.30–1.40 (m, 8H), 2.17–2.20 (m, 9H), 2.75–2.85 (m, 8H), 6.61 (br s, 2H), 6.89–6.93 (m, 4H), 7.14 (d, *J* = 4.2 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 13.70 (q), 19.43 (t), 20.94 (q), 23.75 (t), 24.72 (q), 24.77 (q), 57.71 (t), 123.19 (d), 126.27 (d), 127.69 (d), 127.73 (d), 128.37 (d), 132.00 (s), 141.77 (s), 151.23 (s), 163.35 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 2.3; ¹⁹F NMR (376 MHz, CDCl₃) δ –153.07. **2-TBAF**: ¹H NMR (500 MHz, CDCl₃) δ 0.93 (t, *J* = 7.3 Hz, 12H), 1.22–1.31 (m, 8H), 1.36–1.45 (m, 8H), 1.94 (s, 6H), 2.07 (s, 6H), 2.09 (br s, 6H), 2.17 (s, 3H), 2.81–2.88 (m, 8H), 6.57 (s, 2H), 6.65 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 13.70 (q), 14.42 (q), 15.32 (q), 19.51 (t), 20.99 (q), 23.92 (t), 24.48 (q), 24.52 (q), 58.05 (t), 117.76 (d), 128.18 (d), 131.80 (s), 135.51 (s), 137.82 (s), 142.37 (s), 151.16 (s), 157.28 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 2.0; ¹⁹F NMR (376 MHz, CDCl₃) δ –165.52. **3-TBAF**: ¹H NMR (500 MHz, CDCl₃) δ 0.80 (t, *J* = 7.1 Hz, 12H), 0.98–1.12 (m, 16H), 2.21 (s, 3H), 2.27 (br s, 6H), 2.35–2.43 (m, 8H), 6.64 (s, 2H), 7.05–7.09 (m, 2H), 7.13 (s, 2H), 7.14–7.18 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 13.57 (q), 19.29 (t), 20.95 (q), 23.39 (t), 24.77 (q), 24.83 (q), 57.36 (t), 121.16 (d), 121.64 (d), 121.85 (d), 122.51 (d), 123.98 (d), 124.02 (d), 128.48 (d), 132.63 (s), 141.83 (s), 142.26 (s), 142.39 (s), 149.68 (s), 165.52 (s); ¹¹B NMR (160 MHz, CDCl₃) δ 2.5; ¹⁹F NMR (376 MHz, CDCl₃) δ –158.14.