

Supporting Information for

Synthesis and Reactivity of a Bis(dimesitylboryl)azaborine and Its Fluoride Sensing Ability

Tomohiro Agou, Masaki Sekine, Junji Kobayashi, and Takayuki Kawashima*
takayuki@chem.s.u-tokyo.ac.jp

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

General.

General chemicals were used as received. For optical measurements, commercial spectrochemical or fluorometric grade solvents were used without further purification. All manipulations were performed under argon atmosphere using standard Schlenck technique. Dehydrated Et₂O and THF were purchased from Kanto Chemicals and further purified by MBRAUN MB-SPS system equipped with activated alumina and molecular sieve columns before use. Gel permeation liquid chromatography (GPC) was performed using Japan Analytical Industry LC-918 and LC-908-C60 with JAIGEL 1H+2H columns using chloroform as a solvent. NMR spectra were recorded by a JEOL AL-400 spectrometer (¹H, 400 MHz; ¹¹B, 128 MHz; ¹⁹F, 376 MHz) or a BRUKER DRX-500 spectrometer (¹³C, 125 MHz). Low resolution mass spectra were measured with a Shimadzu QP-5000 (EI). UV-vis spectra were recorded on a JASCO V-670 spectrophotometer, and fluorescence spectra were measured with a JASCO FP-6500 fluorescence spectrophotometer. All melting points were determined on a Yanaco MP-S3 micro melting point apparatus and uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, the University of Tokyo. Bis(2,4-dibromophenyl)methylamine,¹ TipB(OMe)₂,² and Mes₂BOMe³ were prepared according to literatures.

Dibromoazaborine 2.

To an Et₂O (50 mL) solution of bis(2,4-dibromophenyl)methylamine (4.2 g, 8.4 mmol) was added *n*-BuLi (1.6 M in hexane, 11 mL, 17 mmol) at 0 °C, and the mixture was stirred at the temperature for 4.5 h. To the mixture was added TipB(OMe)₂ (2.5 mL, 8.5 mmol) at 0 °C, and the mixture was stirred at rt for 2 d. The reaction was stopped by the addition of aq. NH₄Cl, and the aqueous layer was extracted with chloroform. The combined organic layer was dried on anhydrous MgSO₄, and the solvents were removed under reduced pressure. The crude material was dissolved into chloroform, and to the solution was added hexane to give pure **2** as pale yellow solids (3.4 g, 74%).

2: pale yellow solids. mp 275-277 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.99 (d, *J* = 6.8 Hz, 12H), 1.38 (d, *J* = 7.2 Hz, 6H), 2.25 (sept, *J* = 6.8 Hz, 2H), 3.00 (sept, *J* = 7.2 Hz, 1H), 4.05 (s, 3H), 7.07 (s, 2H), 7.55 (d, *J* = 9.2 Hz, 2H), 7.79 (dd, *J* = 9.2, 2.4 Hz, 2H), 7.96 (d, *J* = 2.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 24.1, 24.3, 34.2, 35.2, 35.8, 113.1, 117.0, 120.1, 130.1, 135.9, 136.2, 139.5, 144.4, 148.4, 150.4; ¹¹B NMR (128 MHz, CDCl₃) δ 54; LRMS (EI): *m/z* 553 (M⁺). Anal. Calcd. for C₂₈H₃₂BBr₂N: C, 60.79; H, 5.83; N, 2.53. Found: C, 60.62; H, 5.92; N, 2.36.

Bis(dimesitylboryl)azaborine 1.

To an Et₂O (40 mL) solution of **2** (0.50 g, 0.90 mmol) was added *t*-BuLi (2.2 M in pentane, 2.1 mL, 4.5 mmol) at -75 °C, and the mixture was stirred at -75 °C for 30 min and rt for 15 min. To the mixture was added Mes₂BOMe (0.56 g, 2.0 mmol) in Et₂O (5 mL), and the mixture was stirred at rt for 2 d. The solvents were removed under reduced pressure, and the crude material was subjected to GLPC. Further purification by re-precipitation from CHCl₃-MeOH gave **1** as pale green solids (0.26 g, 38%).

1: pale yellow green solids. mp 237-239 °C. ¹H NMR (400 MHz, CDCl₃) δ 0.77 (d, *J* = 6.8 Hz, 12H), 1.20 (d, *J* = 7.2 Hz, 6H), 1.91 (s, 24H), 2.14-2.23 (m, 14H), 2.78 (sept, *J* = 7.2 Hz, 1H), 4.08 (s, 3H), 6.68 (s, 8H), 6.69 (s, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.81 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.88 (d, *J* = 1.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 21.1, 23.2, 23.9, 24.2, 34.3, 34.9, 35.5, 114.1, 118.8, 127.9, 136.4, 136.7, 137.3, 138.0, 140.4, 140.9, 141.8, 147.5, 148.3, 148.5, 149.6; ¹¹B NMR (128 MHz, CDCl₃) δ 58, 72. Anal. Calcd. for C₆₄H₇₆B₃N•H₂O: C, 84.49; H, 8.64; N, 1.54. Found: C, 84.34; H, 8.62; N, 1.50.

*X-ray crystallographic analysis of 1.*⁴

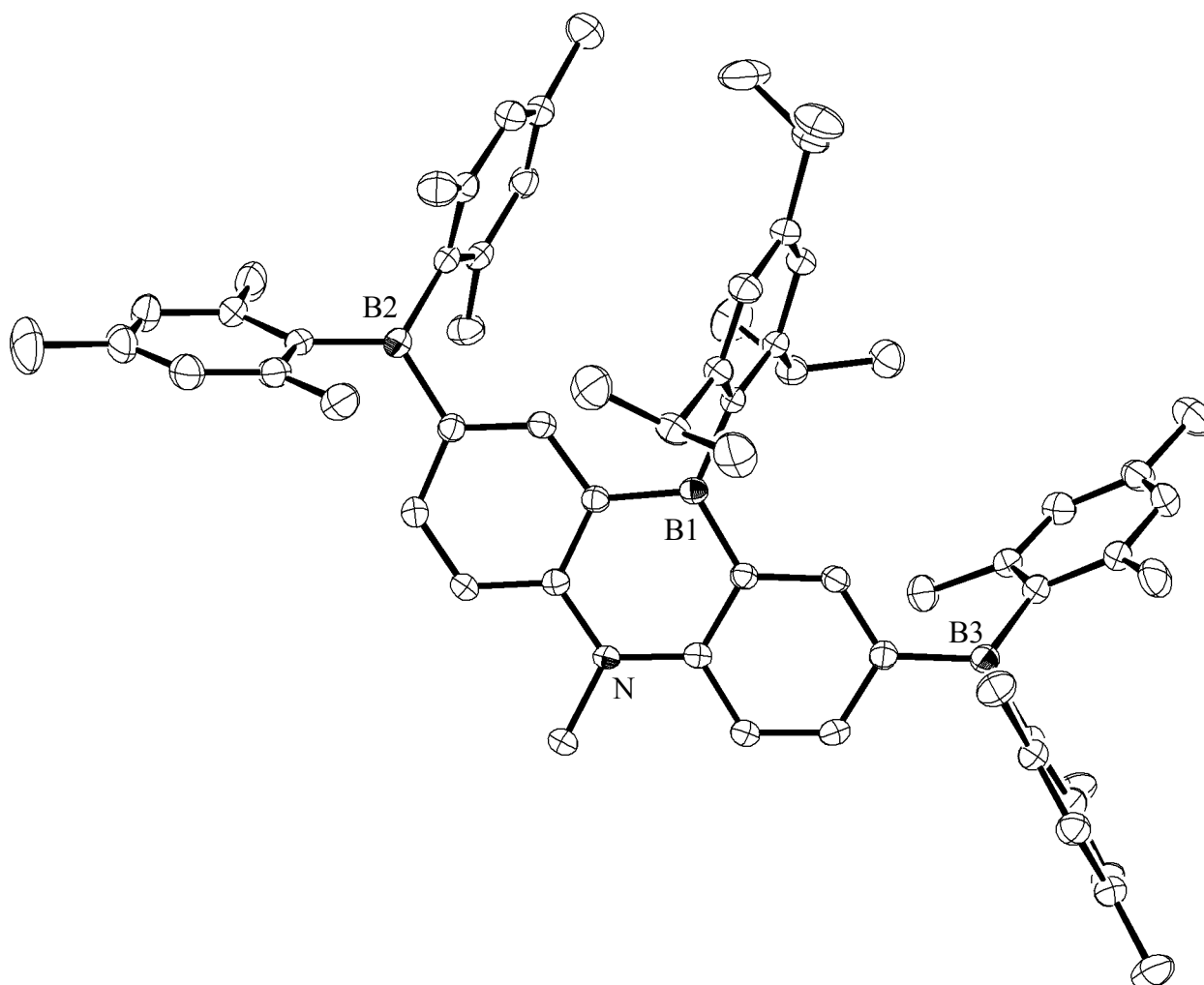
Single crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **1** in CHCl₃-hexane at rt. The intensities of reflections were collected at 120 K on a RIGAKU MSC Mercury CCD diffractometer with a graphite-monochromated Mo K α radiation (λ = 0.71070 Å) using CrystalClear (Rigaku Corp.). The structure was solved by direct methods (SHELXS) and expanded using Fourier techniques. The structure was refined by full-matrix least-squares methods on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

Crystallographic data for **1**: C₆₄H₇₆B₃N, yellow block, monoclinic, space group $P2_1/n$, a = 14.1943(11) Å, b = 23.5686(13) Å, c = 16.7739(11) Å, β = 108.4178(10)°, V = 5324.1(6) Å³, Z = 4, $F(000)$ = 1928, crystal size 0.20 × 0.20 × 0.20 mm³, $3.00 \leq \theta \leq 27.48$. In total, 40560 reflections were collected, of which 11920 were independent (R_{int} = 0.0424), and employed for refinement: 632 parameters, 0 restraints, Goodness of fit on F^2 = 1.081, R_1 ($I > 2\sigma(I)$) = 0.0517, wR_2 (all data) = 0.1544. This data has been submitted to Cambridge Crystallographic Data Centre as supplementary

publication no. CCDC-697739. This data can be obtained via Internet at www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CD21EZ, UK; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

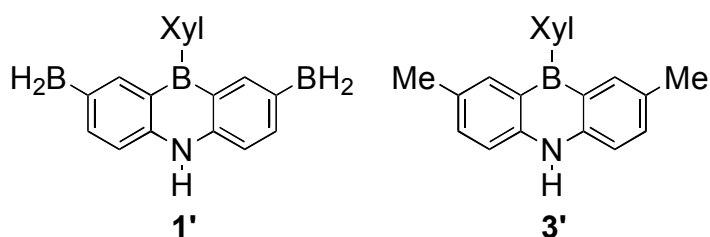
ORTEP drawing of 1 (50% probability)

Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): C(Tip)-B1, 1.578(2); C(Ar)-B1, 1.5324(19), 1.5294(19); C(Mes)-B2, 1.576(2), 1.584(2); C(Ar)-B2, 1.567(2); C(Mes)-B3, 1.582(2), 1.581(2); C(Ar)-B3, 1.555(2); C(Me)-N, 1.4693(17); C(Ar)-N, 1.3967(16), 1.3988(17); $\Sigma(\text{C-B1-C})$, 360; $\Sigma(\text{C-B2-C})$, 360; $\Sigma(\text{C-B3-C})$, 360; $\Sigma(\text{C-N-C})$, 360.



Theoretical calculations of the azaborines and the fluoroborates.

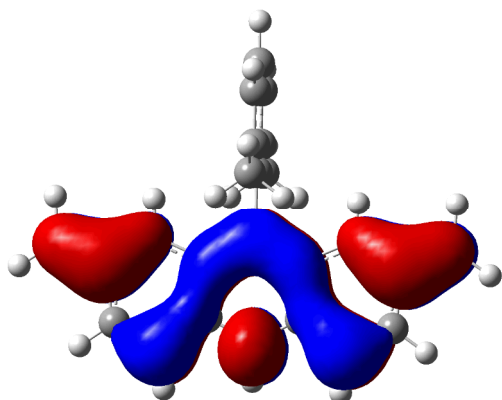
Theoretical calculations were performed by using *Gaussian03* (revision D.02) on a DELL PRECISION 490 workstation or a DELL PRECISION T5400 workstation. B3LYP/6-31G(d) level of theory was chosen for geometry optimizations, single point energy calculations, and frequency calculations. Optimized geometry and molecular orbital surfaces were plotted by *GaussView* (revision 4.1.2).⁵



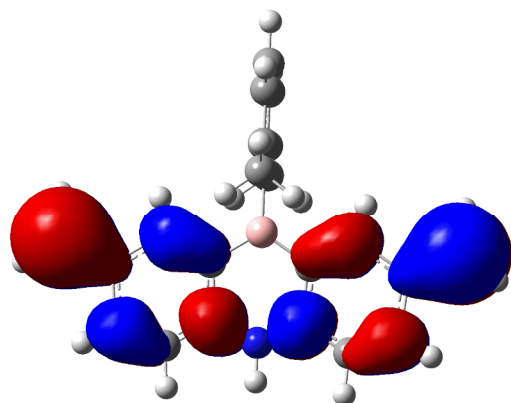
Optimized geometry of 1' (Cartesian coordinates)

Atomic number	X	Y	Z
6	3.636261	-2.377578	0
6	2.397013	-2.986165	0
6	1.229267	-2.188357	0
6	1.304056	-0.767491	0
6	2.596184	-0.203297	0
6	3.782008	-0.959976	0
6	-1.304051	-0.767535	0
6	-1.229197	-2.188407	0
6	-2.396929	-2.986243	0
1	-2.312015	-4.071937	0
6	-3.636194	-2.377697	0
6	-3.781993	-0.960102	0
6	-2.596199	-0.203387	0
1	0.000067	-3.827596	0
1	4.530491	-2.996877	0
1	2.312137	-4.07186	0
1	2.672536	0.88205	0
1	-4.530406	-2.997025	0
1	-2.672582	0.88196	0
6	-0.000025	1.64239	0
6	-0.000029	2.36015	1.220302
6	-0.000029	2.36015	-1.220302
6	-0.000029	3.761503	1.205554
6	-0.000029	3.761503	-1.205554
6	-0.000032	4.462894	0
1	-0.000023	4.305234	2.14827
1	-0.000023	4.305234	-2.14827
1	-0.000031	5.550349	0
5	-5.160106	-0.289403	0
1	-6.15819	-0.952856	0
1	-5.251158	0.904139	0
5	-0.000018	0.061596	0
7	0.000039	-2.814321	0
6	-0.00003	1.627784	-2.547698
1	0.882135	0.98331	-2.655857
1	-0.882313	0.983484	-2.655941
1	0.00008	2.330869	-3.387472
6	-0.00003	1.627784	2.547698
1	-0.882313	0.983484	2.655941
1	0.882135	0.98331	2.655857
1	0.00008	2.330869	3.387472
5	5.160088	-0.289222	0
1	6.158221	-0.952619	0
1	5.251103	0.904332	0

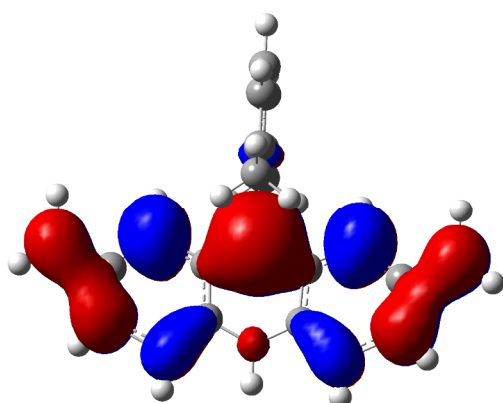
Kohn-Sham orbitals of $1'$



HOMO of $1'$



LUMO of $1'$

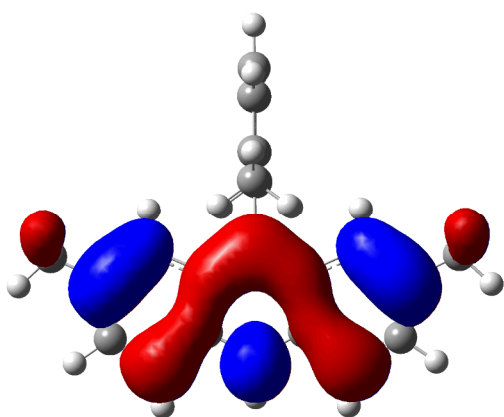


LUMO+1 of $1'$

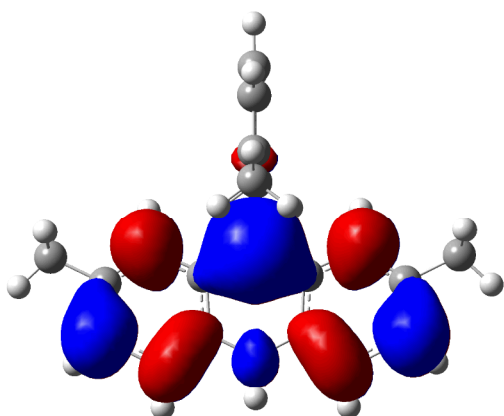
Optimized geometry of **3'** (Cartesian coordinates)

Atomic number	X	Y	Z
6	0	3.643509	2.3473749
6	0	2.404147	2.9675216
6	0	1.229292	2.1872639
6	0	1.3037325	0.7681871
6	0	2.5973779	0.1918459
6	0	3.7697346	0.9409079
6	0	-1.3037325	0.7681871
6	0	-1.229292	2.1872639
6	0	-2.404147	2.9675216
1	0	-2.3370372	4.0544806
6	0	-3.643509	2.3473749
6	0	-3.7697346	0.9409079
6	0	-2.5973779	0.1918459
1	0	0	3.8317548
1	0	4.54117	2.9628503
1	0	2.3370372	4.0544806
1	0	2.6631791	-0.8951837
1	0	-4.54117	2.9628503
1	0	-2.6631791	-0.8951837
6	0	0	-1.6393321
6	-1.2192625	0	-2.3590777
6	1.2192625	0	-2.3590777
6	-1.2053049	0	-3.7608193
6	1.2053049	0	-3.7608193
6	0	0	-4.463033
1	-2.1484369	0	-4.3043339
1	2.1484369	0	-4.3043339
1	0	0	-5.5506876
5	0	0	-0.0546304
7	0	0	2.8195754
6	2.5465248	0	-1.6265431
1	2.6523508	0.8812364	-0.9806707
1	2.6523508	-0.8812364	-0.9806707
1	3.386881	0	-2.3294119
6	-2.5465248	0	-1.6265431
1	-2.6523508	-0.8812364	-0.9806707
1	-2.6523508	0.8812364	-0.9806707
1	-3.386881	0	-2.3294119
6	0	-5.1303531	0.2777697
1	-0.8828842	-5.2671624	-0.3596458
1	0.8828842	-5.2671624	-0.3596458
1	0	-5.9361805	1.0202705
6	0	5.1303531	0.2777697
1	0.8828842	5.2671624	-0.3596458
1	-0.8828842	5.2671624	-0.3596458
1	0	5.9361805	1.0202705

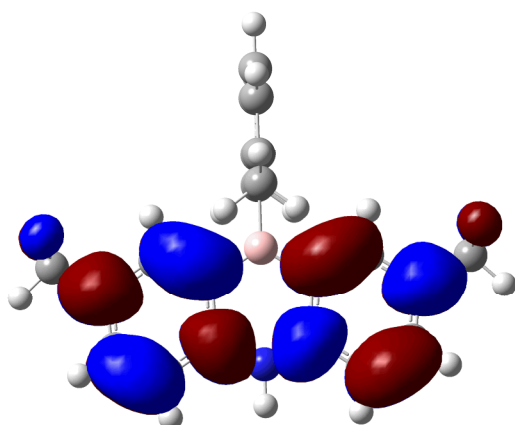
Kohn-Sham orbitals of $3'$



HOMO of $3'$



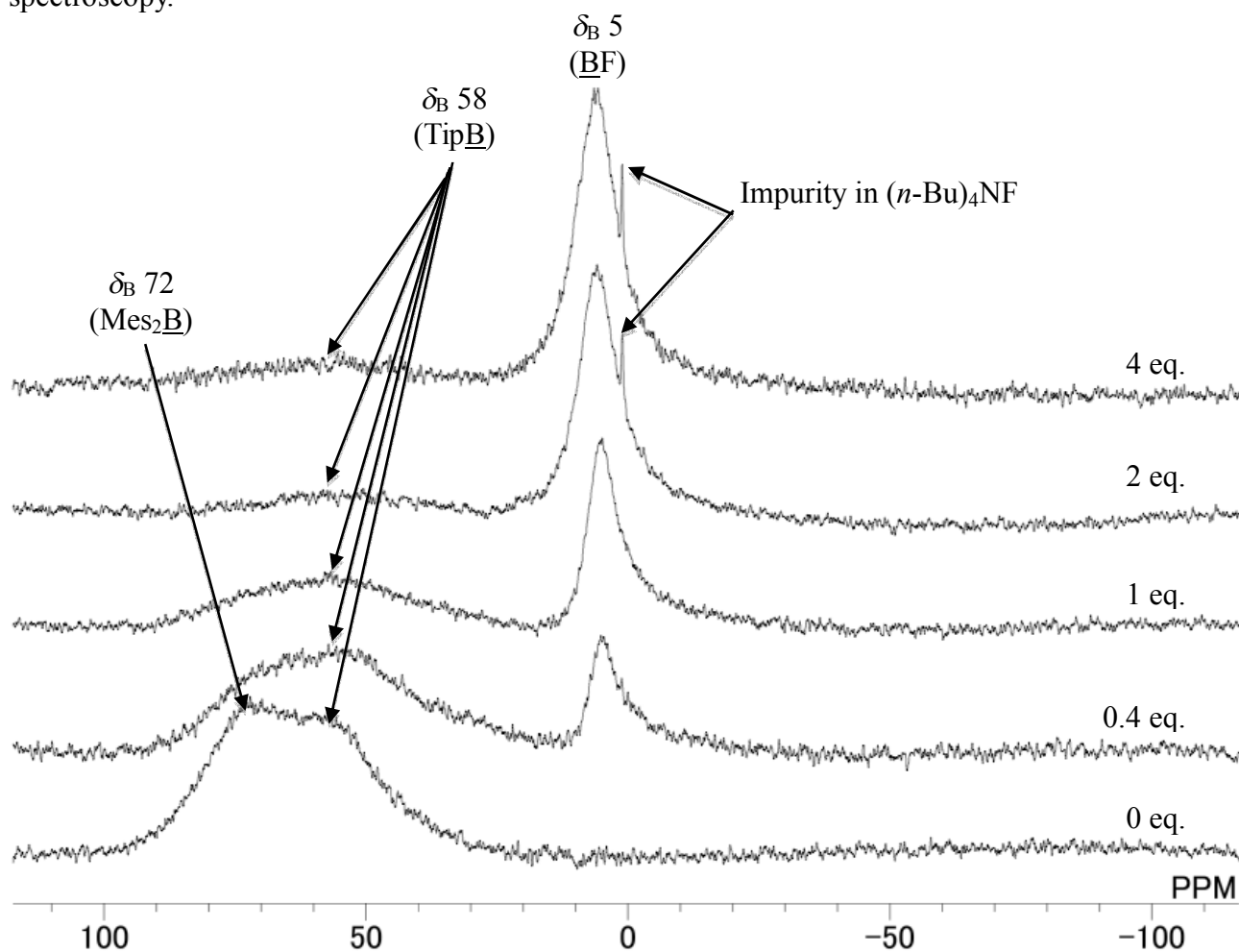
LUMO of $3'$



LUMO+1 of $3'$

Monitoring the formation of fluoroborates from 1 and fluoride ion by NMR spectroscopy.

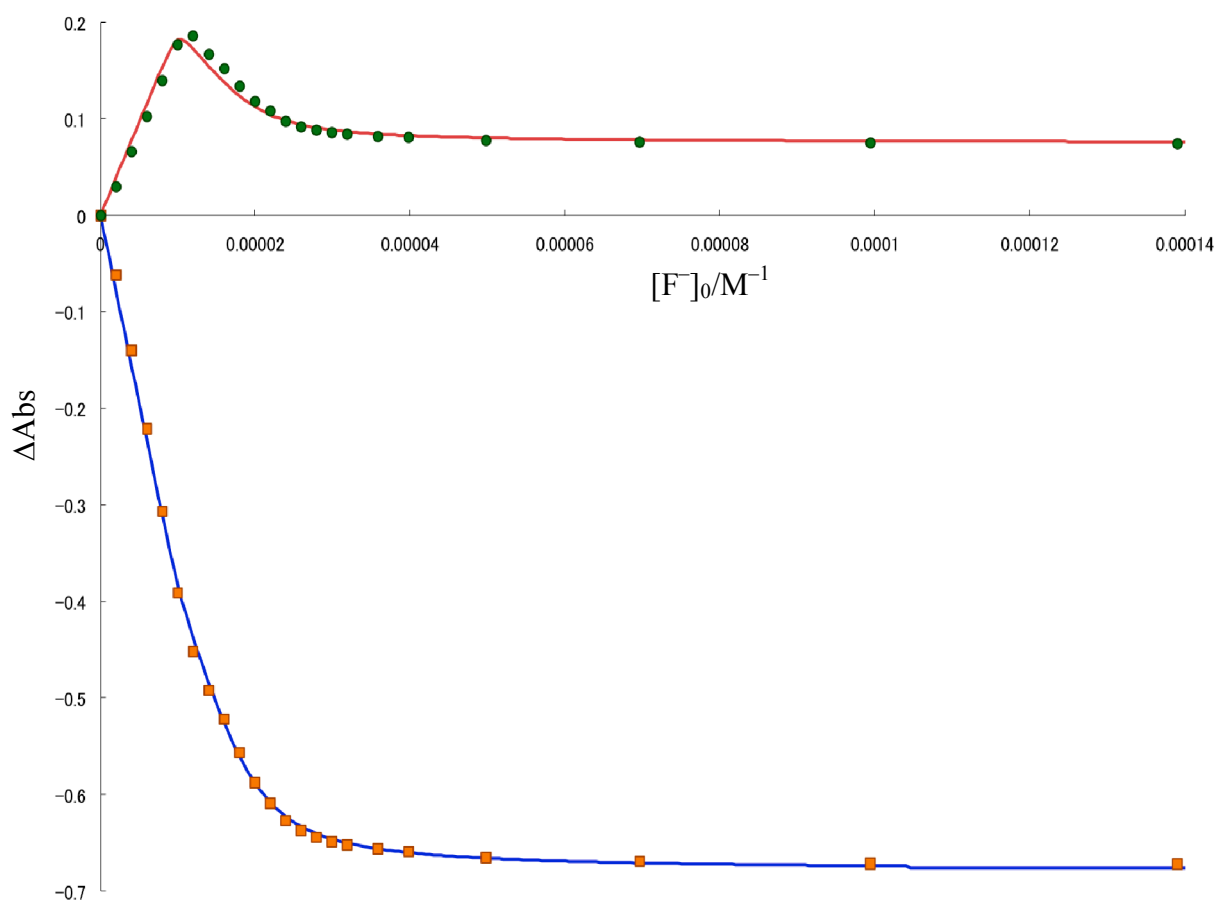
Bis(dimesitylboryl)azaborine **1** (18 mg, 20 μmol) was dissolved in degassed THF (1 mL) under argon atmosphere. In a 5 mm diameter NMR tube, to the above solution of **1** (0.50 mL, 10 μmol of **1**) was added a THF solution of $(n\text{-Bu})_4\text{NF}$ (0.5 M), and the reaction was monitored by ^{11}B NMR spectroscopy.



The ^{11}B NMR spectral change of **1** upon adding $(n\text{-Bu})_4\text{NF}$ in THF at 298 K.

The estimation of the complex formation constants by using a least square fitting method.

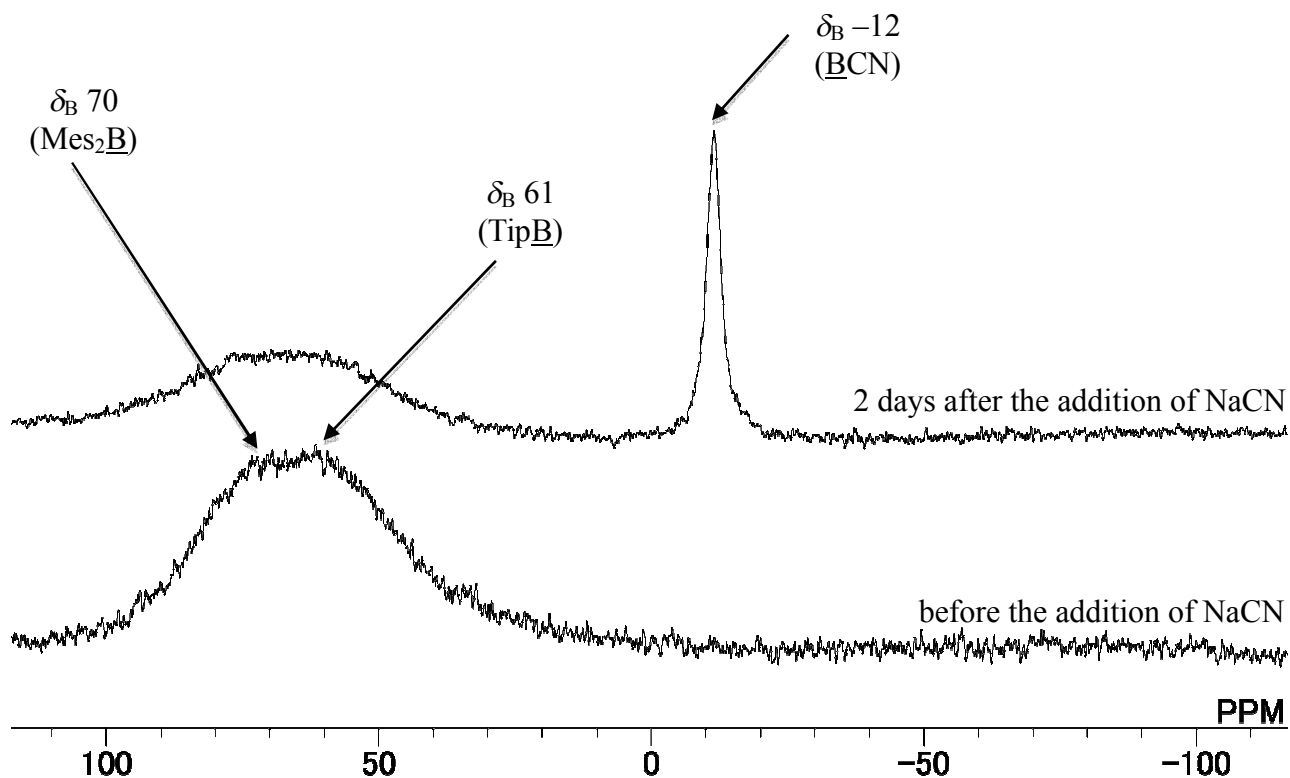
Bis(dimesitylboryl)azaborine **1** (18 mg, 20 μmol) was dissolved in THF (100 mL), and then it was diluted by THF to 1.0×10^{-5} M. In a capped quartz cell, to the above solution (3 mL, 3.0×10^{-8} μmol of **1**) was added a THF solution of (*n*-Bu)₄NF (6.0×10^{-3} M), and the reaction was monitored by UV-vis or fluorescence spectroscopy. From the UV-vis spectral change, the complex formation constants K_1 and K_2 were estimated by using a non-linear least square fitting method.⁶



Plot: experimental values (square: monitored at 383 nm, circle: monitored at 408 nm) and best theoretical fits (line). $\Delta\text{Abs} = \text{Abs} - \text{Abs}_0$.

Monitoring the formation of cyanoborates from 1 and cyanide ion by NMR spectroscopy.

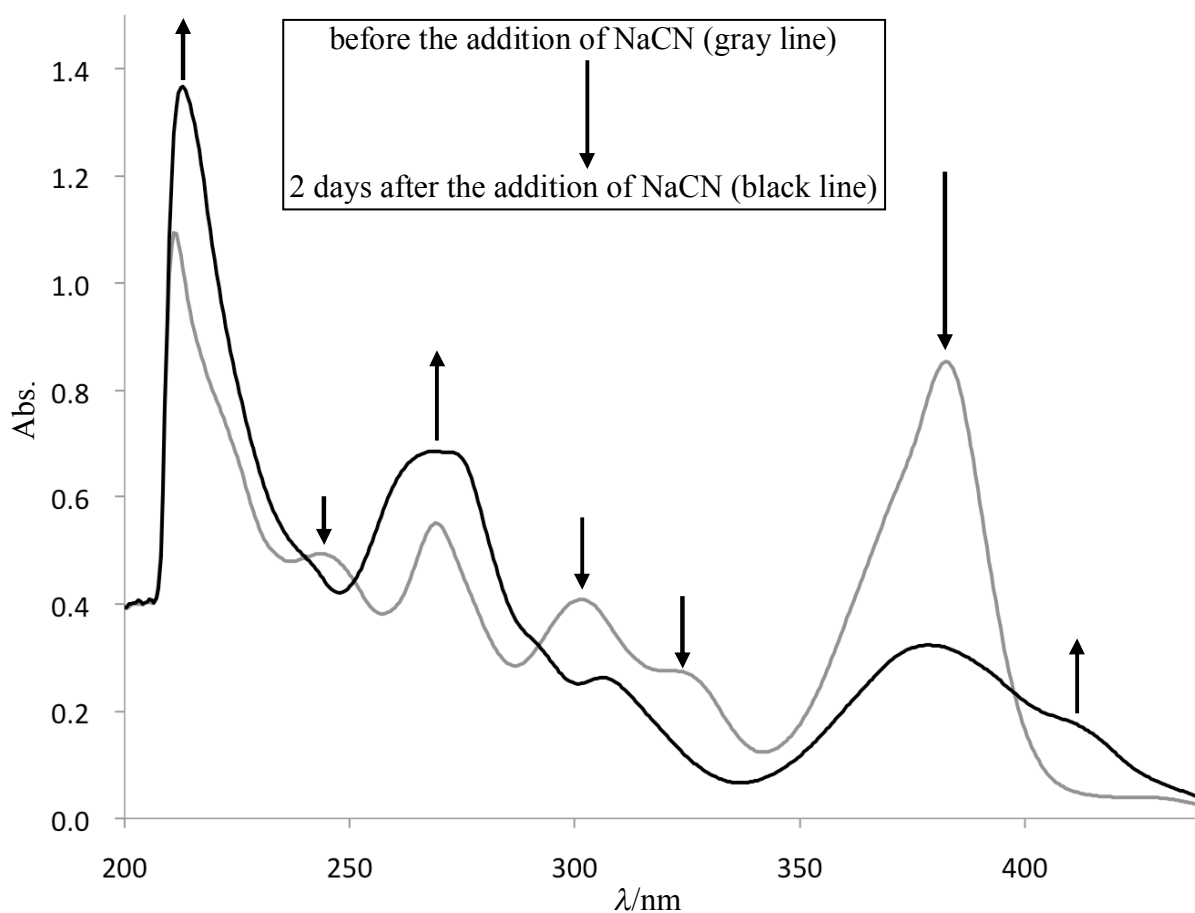
In a 5 mm diameter NMR tube, to the solution of Bis(dimesitylboryl)azaborine **1** (23 mg, 26 μmol) in THF- d_8 (0.5 mL) was added solid NaCN (10 mg, 200 μmol). The reaction was monitored by ^{11}B NMR spectroscopy.



The ^{11}B NMR spectral change of **1** upon the addition of NaCN (solid) in THF- d_8 at 298 K.

Monitoring the formation of cyanoborates from 1 and cyanide ion by UV-vis spectroscopy.

Bis(dimesitylboryl)azaborine **1** (11 mg, 12 μmol) was dissolved in THF (10 mL), and then it was diluted by THF to 1.2×10^{-5} M. In a capped quartz cell, to the above solution (3 mL, 3.6×10^{-8} μmol of **1**) was added solid NaCN (10 mg, 200 μmol), and the reaction was monitored by UV-vis absorption spectroscopy.



UV-vis spectral change of **1** upon the addition of NaCN (solid) in THF at 298 K ($[\mathbf{1}] = 1.2 \times 10^{-5}$ M).

Complete citation of reference 9.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03 (Revision D.02)*, Gaussian, Inc., Pittsburgh, PA, **2004**.

References for the supporting information

- (1) S. Kajigaeshi, T. Kakinami, K. Inoue, M. Kondo, H. Nakamura, M. Fujikawa and T. Okamoto, *Bull. Chem. Soc., Jpn.*, 1988, **61**, 597.
- (2) A. Pelter, K. Smith, D. Buss and Z. Jin, *Heteroat. Chem.*, 1992, **37**, 275.
- (3) M. T. Ashby and N. A. Sheshtawy, *Organometallics*, 1994, **13**, 236.
- (4) A. M. Sheldrick, *SHELX 97-Programs for Crystal Structure Analysis*, Göttingen, Germany, **1998**.
- (5) *GaussView, Version 4.1.2*, R. Dennington, II, T. Keith and J. Millam, Semichem, Inc., Shawnee

Mission, KS, **2007**.

(6) For the program used here: *Prof. Yasuhisa Kuroda, Department of Biomolecular Engineering, Kyoto Institute of Technology, Sakyo-ku, Kyoto 606-8585, Japan. E-mail: ykuroda@kit.ac.jp; Tel & Fax: +81-75-724-7830.*