Synthesis and reactivity of a bis(dimesitylboryl)azaborine and its fluoride sensing ability[†]

Tomohiro Agou, Masaki Sekine, Junji Kobayashi and Takayuki Kawashima*

Received (in Cambridge, UK) 20th October 2008, Accepted 15th January 2009 First published as an Advance Article on the web 20th February 2009 DOI: 10.1039/b818505k

An azaborine bearing two dimesitylboryl groups on its periphery showed very strong light absorption and moderate photoluminescence emission; the reaction of the title compound with fluoride ion resulted in multi-step fluoride ion complexation on the boron atoms of the dimesitylboryl groups, producing mono- and bisfluoroborates.

Triarylborane-based optical materials and anion sensors have been extensively investigated. Because of its property as a strong π -acceptor, as well as the switching of its optical properties upon complex formation with Lewis bases, triarylborane is one of the most powerful candidates for organic functional materials.¹

A synergic electronic interaction between several borane units through π -orbitals is expected to achieve a further decrease in the LUMO energy levels, resulting in effective electron- and Lewis base-accepting materials that are useful for n-type organic semiconductors and sensors.^{2,3} In particular, the reaction of such oligoboryl π -conjugated compounds with anions is interesting, because they can react with anions in a multi-step fashion to give oligoanions, and the absorption and emission colour can be changed by varing the amount of guest anions.

We have reported the syntheses, optical properties, and reactivity of azaborines and their extended analogues (Fig. 1).⁴ The introduction of various functional groups around azaborines was achieved by taking advantage of dibromoazaborine as a common intermediate. Donors (amino groups) and electronically neutral functional groups (carbon substituents) were successfully introduced. Azaborines bearing a strong σ -acceptor, such as ammonio or phosphonio groups were also synthesized recently, and these cationic azaborines showed enhanced Lewis acidity and water solubility that are useful for anion sensing in aqueous media.⁵ Azaborines bearing strong π -acceptors, however, have not previously been synthesized.

The introduction of a strong π -acceptor, such as the dimesitylboryl (Mes₂B) group should be worth investigating



Fig. 1 Azaborine and its periphery-functionalized analogue (FG = functional group).



because it is expected to have dual functions. First, the Mes₂B group can improve the Lewis acidity of azaborine because of its property as a π -acceptor that decreases the LUMO energy level. Second, another donor–acceptor interaction between the nitrogen atom and Mes₂B groups is possible in addition to that between the nitrogen atom and the central boron atom, and the coordination of Lewis bases to the boron atoms can switch the direction of donor–acceptor interactions, resulting in multicolor sensing of Lewis bases.^{3c} Here we report the

synthesis, structure, optical properties, and fluoride ion complexation ability of a bis(dimesitylboryl)azaborine.
Bis(dimesitylboryl)azaborine 1 was synthesized from dibromo-azaborine 2 as a pale yellow solid in moderate yield (Scheme 1). 1 was stable towards air and moisture, because of the effective steric protection of the three boron centres by

bulky groups, as shown by X-ray crystallographic analysis.⁶ The optical data of **1** and other azaborines are summarized in Table 1. When electron-donating groups were introduced on the periphery of the azaborine core, a substantial bathochromic shift in λ_{max} was observed (from 405 nm for **3** to 453 nm for **4**), but there was little change in the extinction coefficient (ε).^{4c} In contrast, the introduction of dimesitylboryl groups resulted in a hypsochromic shift (from 405 nm for **3** to 377 nm for **1**), and the value of ε increased by a factor of approximately 10 compared with other azaborines. To shed light on such differences between the azaborine derivatives, the electronic structures of azaborines were investigated by theoretical calculations.

Theoretical calculations were performed on model azaborines using the Gaussian 03 program package at B3LYP/6-31G(d) level of theory.⁷ In the case of azaborine 3', the LUMO is attributed to the π^* orbital of azaborine, mainly constructed from the vacant 2p orbital of the boron

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan. E-mail: takayuki@chem.s.u-tokyo.ac.jp; Fax: +81-3-5800-6899; Tel: +81-3-5800-6899

[†] Electronic supplementary information (ESI) available: Synthesis, characterization and X-ray crystallographic analysis of **1**, Cartesian coordinates and molecular orbital diagrams for **1**' and **3**', ¹¹B NMR spectra of the reaction mixture of **1** with (*n*-Bu)₄NF, the UV-Vis titration curve, and ¹¹B NMR and UV-Vis spectra of the reaction mixture of **1** and NaCN. CCDC 697739. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b818505k

Table 1	Optical properties of azaborines in cyclohexane at 298 K		
	$\lambda_{max}/nm \ (\log \varepsilon)$	$\lambda_{\rm em}/{\rm nm}~(\Phi)$	Stokes shift/cm
1	377 (4.96)	402 (0.21)	$1.65 \times 10^{3}_{2}$
3 ^{<i>a</i>}	405 (4.02)	421 (0.48)	0.94×10^{3}
4 ^b	453 (3.80)	501 (0.51)	2.12×10^{3}
M	Mes	Tip	
		(n-Hex)NH	
	Me	(n-Hex)	
	3	4	
^a Ref. 4	a. ^b Ref. 4c.		

atom in the azaborine core. In contrast, the LUMO of 1' is distributed over the H₂B groups and benzene rings, and the atomic orbitals of the boron or nitrogen atom in the azaborine core are not involved. In contrast, the HOMO and LUMO + 1 of 1' are π and π^* orbitals of azaborine, respectively, and thus the photo-excitation of 1' is attributable to the intramolecular charge transfer (ICT) from the nitrogen atom to the H₂B groups, which is quite different from the excited states of other azaborines that are similar to the π - π^* excited state of anthracene.

The calculations also indicated that the energy levels of HOMO, LUMO and LUMO + 1 of 1' decreased compared with the energy levels of the corresponding orbitals of 3'because of the electronic effect of the H₂B groups (Fig. 2). The decrease of HOMO level (0.85 eV) is bigger than that in the LUMO level (0.65 eV), resulting in the increase in HOMO-LUMO energy gap (+0.20 eV), which is correlated with the blue-shift of the absorption maximum of 1 (vide supra). Due to the decreased LUMO level, 1 is expected to have enhanced Lewis acidity and exhibit strong complexation ability against Lewis bases. In addition, as 1 has three boron atoms that are capable of acting as Lewis acid centres, stepwise complexation of fluoride ion up to three centres can be possible, resulting in multi-step fluoride ion sensing. The strong light-absorption and emission properties of 1 are also useful for optical sensing, and thus the detection of a Lewis base by 1 was investigated.[‡]



Fig. 2 Calculated energy diagram of model azaborines 1' and 3'.



1 was treated with an excess amount of (n-Bu)₄NF in THF, and the reaction mixture was analyzed by negative-mode FAB mass spectroscopy to show the formation of monofluoroborate 5a or 5b as well as bisfluoroborate 6a or 6b (Scheme 2). This reaction was also monitored by ¹¹B NMR spectroscopy. First, a broad signal around δ_B 72 corresponding to the Mes₂B groups was diminished rapidly and completely disappeared after the addition of more than 2 equivalents of fluoride ion, accompanied by the appearance of a new signal at δ_B 5 due to the formation of fluoroborates. On the other hand, another signal around $\delta_{\rm B}$ 58, which is the resonance of the boron nucleus in the azaborine core, remained throughout the reaction. Judging from these data, fluoride ion is thought to attack the Mes₂B groups selectively to form fluoroborate 5a and bisfluoroborate 6a. The formation of 6a can be explained by considering electrostatic repulsion between the two fluoroborate moieties. 6b has two closely located anionic centres and should be more unstable than 6a. However, the main reason of the formation of 5a rather than **5b** is more obscure. The LUMO of **1** is distributed over the two Mes₂B groups (vide supra), and thus fluoride ion may attack these groups kinetically, but we do not have information about the thermodynamic stability balance between 5a and 5b. Precise theoretical investigation on the stability of these fluoroborates is now under way.

The UV-Vis titration of **1** with $(n-Bu)_4NF$ was carried out in THF at 298 K, and the absorption spectra were gradually changed with two sets of isosbestic points, indicating the stepwise formation of **5** and **6** (Fig. 3). The complex formation constants K_1 and K_2 were determined by using a non-linear least square fitting method.⁸ Although the value of K_1 is too high to be determined exactly, it was estimated to be $> 10^8 \text{ M}^{-1}$. This value is quite high for a triarylborane without any additional effect to enhance Lewis acidity, such as chelation or electrostatic effects (*cf.* Mes₃B: $K = 3.3 \times 10^5 \text{ M}^{-1}$ in THF⁹). The value of K_2 (= 7(1) × 10⁵ M⁻¹) was much lower than that of K_1 , indicating that the formation of the borate ion in **5** may assist charge transfer from the nitrogen to the remaining boryl group, resulting in decreasing Lewis acidity of the boryl group.

The complex formation could also be monitored by fluorescence spectroscopy (Fig. 4). When 2 equivalents of fluoride ion was added, the fluorescence maximum around 400 nm disappeared, and a new broad emission band developed, indicating the quantitative formation of fluoroborate 5. Further addition of fluoride ion resulted in the blue-shift of the emission band on accordance with the conversion of 5 to 6. Because of much smaller value of K_2 than that of K_1 as well as



Fig. 3 UV-Vis spectral change of **1** upon the addition of $(n-Bu)_4NF$ in THF at 298 K ([**1**] = 1.0×10^{-5} M).



Fig. 4 Fluorescence spectra of 1 upon the addition of $(n-Bu)_4NF$ in THF at 298 K ([1] = 1.0×10^{-6} M).

low concentration of 1, a large excess amount of fluoride ion was necessary for this step. Because of its good optical properties (intense light-absorption and emission) as well as strong complexation ability, the detection of fluoride ion under a submicromolar condition can be accomplished easily. These results revealed that the introduction of Mes_2B groups into an azaborine framework is a powerful strategy to enhance both the Lewis acidity and the detection ability.

In conclusion, a new azaborine bearing two Mes_2B groups as a strong π -acceptor has been synthesized from the corresponding dibromoazaborine. The bis(dimesitylboryl)azaborine exhibited quite strong light-absorption and moderate photoluminescence in the near UV to violet region. Theoretical calculations indicated that the LUMO of the bis(dimesitylboryl)azaborine is mainly constructed from vacant 2p orbitals on Mes_2B groups unlike other azaborines. Therefore, its lightabsorption originates from an intramolecular charge transfer from the nitrogen atom to the Mes_2B groups. Theoretical calculations also indicated the enhanced Lewis acidity of the bis(dimesitylboryl)azaborine, as revealed by the complexation titration with fluoride ion monitored by UV-Vis and fluorescence spectroscopy.

Notes and references

‡ Cyanide ion complexation was also investigated by the reaction of **1** and NaCN in THF- d_8 or THF, and the formation of the corresponding cyanide complex was confirmed by ¹¹B NMR and UV-Vis spectroscopy. See ESI† for details.

- 1 (a) C. D. Entwistle and T. B. Marder, *Chem. Mater.*, 2004, **16**, 4574; (b) S. Yamaguchi and A. Wakamiya, *Pure Appl. Chem.*, 2006, **78**, 1413.
- 2 (a) H. Kobayashi, N. Sato, Y. Ichikawa, M. Miyata, Y. Chujo and T. Matsuyama, *Synth. Met.*, 2003, **135–136**, 393; (b) A. Sundararaman, M. Victor, R. Varughese and F. Jäkle, *J. Am. Chem. Soc.*, 2005, **127**, 13748.
- 3 (a) S. Yamaguchi, S. Akiyama and K. Tamao, J. Am. Chem. Soc., 2001, **123**, 11372; (b) A. Sundararaman, K. Venkatasubbaiah, M. Victor, L. N. Zakharov, A. L. Rheingold and F. Jäkle, J. Am. Chem. Soc., 2006, **128**, 16554; (c) G. Zhou, M. Baumgarten and K. Müllen, J. Am. Chem. Soc., 2008, **130**, 12477; (d) J. K. Day, C. Bresner, N. D. Coombs, I. A. Fallis, L.-L. Ooi and S. Aldridge, Inorg. Chem., 2008, **47**, 793.
- 4 (a) T. Agou, J. Kobayashi and T. Kawashima, Org. Lett., 2006, 8, 2241; (b) T. Agou, J. Kobayashi and T. Kawashima, Chem.-Eur. J., 2007, 13, 8051; (c) T. Agou, J. Kobayashi and T. Kawashima, Chem. Commun., 2007, 3204.
- 5 (a) T. Agou, J. Kobayashi and T. Kawashima, *Inorg. Chem.*, 2006, 45, 9137; (b) M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima and F. P. Gabbaï, *Chem. Commun.*, 2007, 1133; (c) T. Agou, J. Kobayashi, Y. Kim, F. P. Gabbaï and T. Kawashima, *Chem. Lett.*, 2007, 36, 976; (d) T. Agou, M. Sekine, J. Kobayashi and T. Kawashima, *Chem.-Eur. J.*, in press.
- 6 Crystallographic data for 1: C₆₄H₇₆B₃N, M = 891.69, monoclinic, space group $P2_1/n$, a = 14.1943(11), b = 23.5686(13), c = 16.7739(11) Å, $\beta = 108.4178(10)^\circ$, V = 5324.1(6) Å³, T = 120 K, Z = 4, μ (Mo-Kα) = 0.062 mm⁻¹, 40 560 reflections measured, 11 920 unique ($R_{int} = 0.0424$) which were used in all calculations. The final R_1 ($I > 2\sigma(I)$) and w R_2 (all data) were 0.0517 and 0.1544, respectively. GOF = 1.081.
- 7 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, Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, 0 H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, Pomelli, J. 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. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03 (Revision D.02), Gaussian, Inc., Wallingford, CT, 2004.
- 8 The analysis was carried out by using a program developed by Prof. Yasuhisa Kuroda. Prof. Yasuhisa Kuroda, Department of Biomolecular Engineering, Kyoto Institute of Technology, Sakyo-ku, Kyoto 606-8585, Japan. E-Mail: ykuroda@kit.ac.jp; Tel and Fax: +81-75-724-7830.
- 9 S. Solé and F. P. Gabbaï, Chem. Commun., 2004, 1284.