

Tuning of the Optical Properties and Lewis Acidity of Dibenzo-*p*-nictogenaborins by Modification on Bridging Main Group Elements

Tomohiro Agou, Junji Kobayashi, and Takayuki Kawashima*

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

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Dibenzophosphaborin **1** and dibenzoazaborine **7** have been synthesized from the corresponding dibromides and MesB(OMe)₂. Dibenzophosphaborin *P*-sulfide **2**, the *P*-selenide **3**, and the phosphonium salt **4** were obtained by the reaction of **1** with S₈, elemental selenium, and benzyl bromide, respectively. Crystallographic analysis of **1–3** and **7** showed that the dibenzophosphaborin framework does not have a planar structure, which is caused by the pyramidalization around the phosphorus atoms, unlike in **7**. Compound **1** showed a blue-shifted and weak UV–vis absorption relative to **7**, indicating a weak electronic interaction between the phosphorus lone pair electrons and the π -orbitals on the dibenzopnictogenaborin framework. The longest absorption bands of **2** and **3** are attributable to the intramolecular electron transfer from the lone pair electrons on the chalcogen atoms to the π^* orbitals on the dibenzophosphaborin framework, and the existence of these electronic transitions is supported by TD-DFT calculations. The UV–vis and ¹¹B NMR spectra of **4** showed a temperature-dependent change due to the coordination of a counter bromide anion to the boron center, indicating a strong Lewis acidity of the boron center. We also investigated the complex formation ability of dibenzopnictogenaborin to fluoride or chloride anions. The complex formation constants increased in accordance with the decrease in LUMO energy levels calculated using the DFT method. Compound **4** exhibited an anomalously high complex formation ability among these compounds, due to the strong electron-withdrawing effect of the phosphonium cation moiety.

Introduction

Main group element substituents confer interesting electronic and optical properties to π -conjugated molecules because the donor or acceptor orbitals of these elements can interact electronically with π -orbitals (hyperconjugation) to decrease the energy gaps between the HOMOs and LUMOs. A number of hetero π -conjugated molecules containing nitrogen or sulfur atom donor centers have been known for several decades and these have been studied extensively, but the use of other main group elements, such as phosphorus, silicon, and boron, as key components to produce an electronic modulator has only been investigated recently.¹ These main group elements have low-lying acceptor orbitals (e.g.: Si, $\sigma^*(\text{Si}-\text{R})$; B, vacant 2p; P, $\sigma^*(\text{P}-\text{R}$ or $\text{P}-\text{P})$), and these lower the LUMO levels of π -systems, in contrast to donor atoms, which raise the HOMO levels. The advantage of using such a new strategy to construct π -conjugated

molecules with small HOMO–LUMO gaps is exemplified by the application of silacyclopentadienes (siloles) to fabricate electron carrier materials for use in organic light-emitting devices (OLEDs), as well as OLEDs constructed from phosphole-based materials.

Recently, boron-containing π -conjugated molecules have been investigated as novel organic materials for optical or

* To whom correspondence should be addressed. E-mail: takayuki@chem.s.u-tokyo.ac.jp.

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electronic applications, because boron has two superior characteristics over other main group elements, including silicon and phosphorus: (1) Boron atoms have vacant 2p orbitals that can act as acceptor orbitals, and the electronic interaction between boron atoms and π -orbitals, constructed from carbon 2p orbitals, is generally strong. (2) Complex formation with Lewis bases transforms the coordination mode of boron atoms from trigonal planar to tetrahedral, and the electronic interaction between the vacant 2p orbitals and the π orbitals no longer occurs. Thus, the electronic state of a boron-containing π -systems can be controlled using an external stimulus (e.g., a Lewis base).² Such properties are the main justification to investigate the properties of novel π -conjugated molecules bearing boron atoms for applications such as fluorescent materials,³ electroluminescence devices,⁴ nonlinear optics,⁵ organic conductors,⁶ and Lewis base sensors.⁷

In addition to the properties described above, phosphorus-containing π -conjugated molecules have another interesting feature: they exhibit electronic modulation by substitution of the phosphorus atoms. Phosphorus atoms usually function as both a weak donor and an acceptor, because they have lone pair electrons and low-lying $\sigma^*(\text{P}-\text{C}$ or $\text{P}-\text{P})$ orbitals,

respectively. Such electron-withdrawing properties can be dramatically enhanced by the oxidation of a phosphorus atom, e.g., as in chalcogenation, alkylation, or complexation with a metal (P-substitution). The modulation of the electronic state of a π -conjugated molecule by P-substitution has been shown to be effective through intensive research into the electronic and optical properties of diarylphospholes.⁸

Dibenzoheteraborins are boron-containing π -conjugated molecules featuring a dihydroanthracene framework. The rigid, planar structure of dibenzoheteraborins is expected to allow for increased electronic interactions between a bridging main group element and the π -orbitals on the benzene rings leading to an enhancement of fluorescence intensity. The optical properties of nitrogen- or oxygen-containing dibenzoheteraborins and dibenzoborin have been reported. The nitrogen-containing molecule (dibenzoazaborine) absorbs violet light strongly and emits a moderately intense fluorescence.^{3c,9} We have also reported on the synthesis, structure, and photophysical properties of dibenzophosphaborins, a new member of the dibenzoheteraborin family containing phosphorus atoms as electron donors.¹⁰ Unlike azaborine, the fluorescence of dibenzophosphaborin is very weak and shows a large Stokes shift (100–200 nm), indicating a substantial structural relaxation around the phosphorus atoms on photoexcitation. However, the optical properties of other heteraborins have not been investigated systematically. In addition, the effect of bridging main group elements on the electronic structure and the Lewis acidity of heteraborins has not been studied, despite the promise of constructing a broad library of boron-containing π -conjugated molecules with a common molecular structure. The electronic state of dibenzophosphaborin can be regulated by the substitution on the phosphorus atom.

Here, we report on the synthesis, structure, optical properties, and the Lewis acidity of dibenzoheteraborins bearing nitrogen or phosphorus atoms as the bridging main group elements. Azaborine has a rigid, nearly planar molecular structure, resulting in a decreased HOMO–LUMO gap and an intense fluorescence.^{3c} In contrast, phosphaborin and its P-derivatives show a weak fluorescence due to pyramidalization around the phosphorus atoms and a lack of molecular rigidity, but a modification on the phosphorus atom sites can change the Lewis acidity of the boron centers dramatically.

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Experimental Section

General Comments. General chemicals were used as received. Cyclohexane and CH_2Cl_2 for spectrochemical or fluorometric grade (Dojindo) were used for optical measurement. All manipulations were carried out using Schlenk technique under an argon atmosphere. Solvents were purified by MBRAUN MB-SPS system (Et_2O , THF, and toluene) or distillation from CaH_2 (CH_2Cl_2). Gel permeation liquid chromatography (GPC) was performed using LC-918 or LC-908 with JAIGEL 1H+2H columns (Japan Analytical Industry) using chloroform or toluene as solvents, respectively. NMR spectra were recorded by a JEOL AL-400 spectrometer (^1H , 400 MHz; ^{13}C , 100 MHz; ^{11}B , 128 MHz) or JEOL ECX-400 spectrometer (^1H , 400 MHz, ^{13}C , 100 MHz). Chemical shifts are reported in δ . ^1H NMR spectra are referenced to residual protons in deuterated solvent, ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent, and ^{11}B NMR spectra are referenced to an external standard of $\text{BF}_3\cdot\text{Et}_2\text{O}$. High-resolution mass spectra were recorded by a JEOL JMS-700P using PEG600 as an internal standard. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F4500 fluorescence spectrophotometer. All melting points were measured with a Yanaco MP-S3 and uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. The syntheses of dibenzophosphaborin **1**⁹ and dibenzozaborine **7**^{3c} have been reported previously.

Preparation of Compounds. (a) Dibenzophosphaborin Sulfide 2. In a 5 mm o.d. NMR tube, to a solution of **1** (30.6 mg, 78 μmol) in toluene (0.5 mL) was added S_8 (10.0 mg, 0.30 mmol as S). After a few freeze-pump-thaw cycles, the tube was sealed in vacuo and heated at 75 °C for 6 h. After confirmation of disappearance of **1** by ^{31}P NMR, the sealed tube was opened. The residual S_8 was filtered off, and the solvent was removed under reduced pressure. The residue was subjected to GPC to give **2** as a pale yellow solid (21.2 mg, 64%).

2: pale yellow solid; mp 198–199 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.93 (s, 3H), 2.01 (s, 3H), 2.40 (s, 3H), 6.91 (s, 1H), 6.95 (s, 1H), 7.27–7.36 (m, 3H), 7.49 (t, J = 7.4 Hz, 2H), 7.62 (dd, J = 13.4, 8.2 Hz, 2H), 7.68–7.73 (m, 4H), 8.34 (dd, J = 14.6, 7.4 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.23 (s), 22.53 (s), 22.83 (s), 126.86 (s), 127.19 (d, J = 11.4 Hz), 128.42 (d, J = 12.2 Hz), 130.66 (d, J = 10.5 Hz), 130.86 (d, J = 2.9 Hz), 131.34 (d, J = 2.9 Hz), 132.57 (d, J = 13.4 Hz), 135.44 (s), 136.24 (s), 137.52 (d, J = 11.4 Hz), 138.59 (brd, J = 9.5 Hz), 139.52 (d, J = 10.5 Hz), 140.38 (s), 141.22 (s); ^{31}P NMR (162 MHz, CDCl_3) δ 8.6; ^{11}B NMR (128 MHz, CDCl_3) δ 65.8 ($h_{1/2}$ = 1700 Hz); HRMS (FAB^+) m/z calcd for $\text{C}_{27}\text{H}_{24}\text{BPS}$ 422.1429, found 422.1433 (M^+); UV-vis (cyclohexane) [λ_{max} (log ϵ)] 353 (3.31), 360 (3.15). Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{BPS}\cdot 0.33\text{H}_2\text{O}$: C, 75.71; H, 5.80. Found: C, 75.80; H, 5.83.

(b) Dibenzophosphaborin Selenide 3. In a 5 mm o.d. NMR tube, to a solution of **1** (28.3 mg, 73 μmol) in toluene (0.5 mL) was added elemental selenium (23.1 mg, 0.29 mmol). After a few freeze-pump-thaw cycles, the tube was sealed in vacuo and heated at 75 °C for 6 h. After confirmation of disappearance of **1** by ^{31}P NMR, the sealed tube was opened. The residual selenium was filtered off, and the solvent was removed under reduced pressure. The residue was subjected to GPC to give **3** as a yellow solid (20.8 mg, 61%).

3: yellow solid; mp 207–209 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.92 (s, 3H), 2.01 (s, 3H), 2.39 (s, 3H), 6.91 (s, 1H), 6.95 (s, 1H), 7.29–7.35 (m, 3H), 7.58 (t, J =

7.6 Hz, 2H), 7.63–7.72 (m, 6H), 8.34 (dd, J = 15.0, 7.4 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.30 (s), 22.61 (s), 22.88 (s), 126.79 (s), 127.14 (d, J = 14.0 Hz), 128.36 (d, J = 12.4 Hz), 130.88 (d, J = 2.5 Hz), 131.13 (s), 131.23 (s), 133.48 (d, J = 14.0 Hz), 134.06 (s), 134.35 (d, J = 14.1 Hz), 134.78 (s), 137.46 (d, J = 9.1 Hz), 138.27 (s), 139.44 (d, J = 10.7 Hz), 140.27 (s); ^{31}P NMR (162 MHz, CDCl_3) δ 17.5 ($^1J_{\text{PSe}}$ = 732 Hz); ^{11}B NMR (128 MHz, CDCl_3) δ 67.6 ($h_{1/2}$ = 1500 Hz); $^{77}\text{Se}\{^1\text{H}\}$ NMR (76 MHz, CDCl_3) δ -268 (d, $^1J_{\text{PSe}}$ = 732 Hz); UV-vis (cyclohexane) [λ_{max} (log ϵ)] 369 (3.10), 391 (3.07). Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{BPSe}$: C, 69.11; H, 5.16. Found: C, 68.90; H, 5.13.

(c) Phosphonium Salt 4. To a solution of **1** (1.0 g, 2.6 mmol) in toluene (20 mL) was added benzyl bromide (BnBr) (1.2 mL, 10 mmol), and the mixture was refluxed for 12 h. After cooling of the mixture to room temperature, resulting precipitates were collected by filtration and washed with pentane to give **4** as a colorless solid (1.2 g, 84%).

4: colorless solid; mp 214–215 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.27 (s, 3H), 1.88 (s, 3H), 2.34 (s, 3H), 5.55 (d, J = 14.4 Hz, 2H), 6.70 (dd, J = 7.2, 2.0 Hz, 2H), 6.82–6.87 (m, 4H), 6.97 (td, J = 7.3, 2.4 Hz, 1H), 7.67–7.75 (m, 7H), 7.95 (brs, 2H), 8.35 (dd, J = 13.0, 7.2 Hz, 2H), 8.58 (dd, J = 13.8, 7.0 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.17 (s), 22.28 (s), 22.75 (s), 32.24 (d, J = 44.8 Hz), 120.32 (s), 121.13 (s), 124.60 (s), 125.45 (s), 126.75 (d, J = 7.6 Hz), 127.29 (s), 127.84 (d, J = 3.8 Hz), 128.43 (d, J = 3.8 Hz), 130.44 (d, J = 12.4 Hz), 130.56 (d, J = 5.7 Hz), 134.07 (d, J = 10.5 Hz), 134.30 (d, J = 1.9 Hz), 134.74 (d, J = 2.9 Hz), 134.94 (d, J = 12.4 Hz), 135.42 (d, J = 13.4 Hz), 137.86 (d, J = 63.9 Hz), 138.09 (s), 140.85 (d, J = 10.5 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 6.5; ^{11}B NMR (128 MHz, CDCl_3) δ 62.3 ($h_{1/2}$ = 2300 Hz); HRMS (FAB^+) m/z calcd for $\text{C}_{34}\text{H}_{31}\text{BP}$ 481.2256, found 481.2279 ($[\text{M} - \text{Br}]^+$); UV-vis (CH_2Cl_2) [λ_{max} /nm (log ϵ)] 381 (2.82), 312 (3.90), 307 (3.88). Anal. Calcd for $\text{C}_{34}\text{H}_{31}\text{BBrP}\cdot\text{H}_2\text{O}$: C, 70.49; H, 5.74. Found: C, 70.71; H, 5.41.

X-ray Data Collection and Structure Refinement. The intensities of reflections were collected at 120 K on a Rigaku MSC Mercury CCD diffractometer with a graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.710 70 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).¹¹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystallographic data are listed in Table 1. Selected bond lengths and angles are given in Table 2. CCDC-605853 (**7**), CCDC-605854 (**2**), and CCDC-605855 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K. Fax: (+44) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

UV-Vis Titration Experiments. A CH_2Cl_2 solution of dibenzophosphonictogenaborins (1.0×10^{-4} M, 2.0 mL) was placed in a quartz cell with a septum cap. To this solution was added a solution of $n\text{-Bu}_4\text{NF}$ in CH_2Cl_2 (0.10 M) by portions, and the absorption change was monitored at λ_{max} of each compound. The collected data were fitted using a reported method.^{7f}

Results and Discussion

Dibenzoheteraborins **1** and **7** bearing a phosphorus or nitrogen atom were synthesized in moderate yields by the

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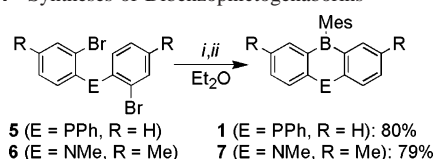
Table 1. Crystal Data and Structure Refinement for **2**, **3**, and **7**

param	2	3	7
empirical formula	C _{27.5} H ₂₆ BO _{0.5} PS	C ₂₇ H ₂₄ PBSe	C ₂₄ H ₂₆ BN
fw	431.34	469.20	339.27
cryst size/mm ³	0.40 × 0.40 × 0.40	0.70 × 0.50 × 0.20	0.20 × 0.20 × 0.20
cryst system	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.304(2)	9.254(3)	16.548(2)
<i>b</i> /Å	14.747(4)	14.834(7)	12.8158(14)
<i>c</i> /Å	17.336(5)	17.483(8)	19.342(3)
α /deg	86.360(8)	86.106(15)	
β /deg	81.222(8)	80.210(14)	108.9558(10)
γ /deg	75.856(7)	76.791(13)	
<i>V</i> /Å ³	2278.5(10)	2301.2(17)	3879.6(9)
<i>Z</i>	4	4	8
<i>D</i> _c /g cm ⁻³	1.324	1.354	1.162
<i>F</i> (000)	960	960	1456
2 θ /deg	6.10–54.96	6.04–54.96	6.10–54.96
reflens collod/unique	17 486/9887 (<i>R</i> _{int} = 0.0199)	15 924/8838 (<i>R</i> _{int} = 0.0241)	29 694/8712 (<i>R</i> _{int} = 0.0567)
params/restraints	570/0	547/0	481/0
goodness of fit on <i>F</i> ²	1.058	1.066	0.911
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0394	0.0333	0.0569
w <i>R</i> ₂ (all data)	0.1215	0.0882	0.1508

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1–3** and **7**

param	1 ^{a,b}	2 ^c (planar)	2 ^c (butterfly)	3 ^d (planar)	3 ^d (butterfly)	7 ^e
B–C1	1.554(5)	1.557(2)	1.563(2)	1.563(3)	1.568(3)	1.522(3)
B–C4	1.553(5)	1.565(2)	1.560(2)	1.565(3)	1.564(3)	1.524(3)
B–C _{Mes}	1.570(5)	1.574(2)	1.570(2)	1.582(3)	1.570(3)	1.584(3)
Pn–C2	1.819(3)	1.8094(16)	1.8062(16)	1.819(2)	1.813(2)	1.392(2)
Pn–C3	1.811(3)	1.8058(16)	1.8111(16)	1.809(2)	1.816(2)	1.395(2)
Pn–C _R	1.836(3)	1.8165(16)	1.8147(15)	1.818(2)	1.820(2)	1.465(2)
P–Ch		1.9535(6)	1.9507(6)	2.1087(9)	2.1004(9)	
C1–B–C _{Mes}	120.6(3)	121.06(13)	120.18(14)	120.68(18)	120.6(2)	123.20(17)
C4–B–C _{Mes}	119.3(3)	117.93(13)	119.88(14)	118.40(19)	119.65(19)	122.16(16)
C1–B–C4	119.9(3)	120.93(13)	119.79(13)	120.88(19)	119.8(2)	114.58(17)
C2–Pn–C _R	103.37(14)	105.18(7)	103.49(7)	105.85(10)	102.74(10)	118.57(15)
C3–Pn–C _R	100.33(14)	103.79(7)	103.39(7)	103.47(10)	103.64(10)	118.77(16)
C2–Pn–C3	103.22(16)	106.74(7)	105.29(7)	106.59(10)	105.42(10)	122.65(15)
C2–P–Ch		113.87(5)	115.02(5)	113.26(8)	115.31(8)	
C3–P–Ch		114.11(6)	115.48(5)	114.39(8)	115.29(8)	
C _{Ph} –P–Ch		112.25(5)	112.80(5)	112.43(8)	113.02(8)	

^a Pn = P and R = Ph. ^b Reference 4. ^c Pn = P, R = Ph, and Ch = S. ^d Pn = P, R = Ph, and Ch = Se. ^e Pn = N and R = Me. Structural data for one of the two independent structures are shown.

Scheme 1. Syntheses of Dibenzopnictogenaborins^a

^a (i) *n*-BuLi (for **5**) or *t*-BuLi (for **6**), 0 °C; (ii) MesB(OMe)₂, reflux.

reaction of the dilithio derivatives prepared from the corresponding dibromides **5** and **6**, respectively, with MesB(OMe)₂ by refluxing in Et₂O (Scheme 1). These molecules were stable against air and moisture both in the solid state and in solution because of the steric protection of the mesityl groups. In addition, the ring structures of these molecules fix the position of the mesityl groups orthogonal to the pnictogenaborin framework, so that the steric protection of the mesityl groups is effective compared to other triarylboranes bearing one mesityl group that are oxidized in air.

Single crystals of **1** and **7** suitable for X-ray crystallographic analysis were obtained by slow evaporation of their C₆H₆ and CHCl₃/EtOH solutions, respectively (Figures 1 and

2).^{10,11} The diheteroanthracene ring of nitrogen-containing **7** deviated slightly from the planar structure due to the twisting of a benzene ring. In contrast, dibenzophosphaborin **1** had a butterfly-type structure owing to the pyramidalization at the phosphorus atom.¹⁰ Such a nonplanar structure suggests that the lone pair orbital is not aligned perpendicular to the dibenzoborin framework, resulting in an inferior electronic interaction compared to that seen in **7**.

The P-derivatives of **1** were synthesized using usual organophosphorus chemistry methods (Scheme 2). The sulfide **2** and selenide **3** were obtained by the reaction of **1** with the elemental chalcogen in toluene. These reactions proceeded quantitatively, judging from the ³¹P NMR spectra, but the moderate solubility of **2** and **3** may decrease the isolated yields. The reaction with BnBr gave the phosphonium salt **4**. These results indicate that the phosphorus atom of **1** has the same reactivity as that of ordinary triarylphosphines. The sulfide **2** and phosphonium salt **4** were pale yellow and colorless solids, respectively, but the selenide **3** was obtained as a yellow solid. We also tried to synthesize the dibenzophosphaborin *P*-oxide from the oxidation of **1** using various oxidants, but the decomposition of the frame-

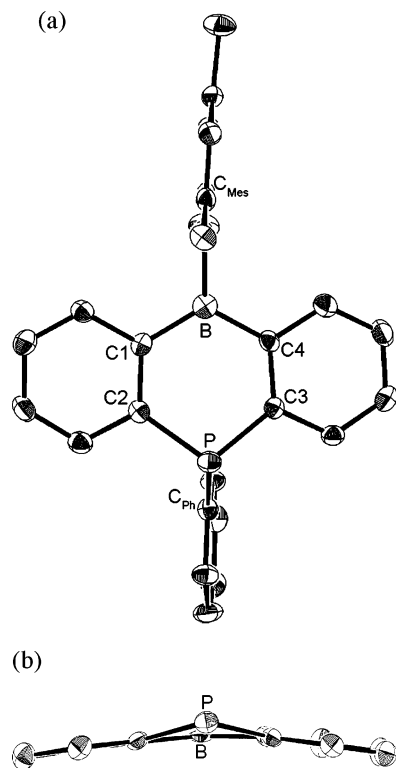


Figure 1. ORTEP drawings of dibenzophosphaborin **1** (50% probability):¹⁰ (a) top view; (b) side view (mesityl and phenyl groups not shown). Hydrogen atoms and a solvent molecule are omitted for clarity.

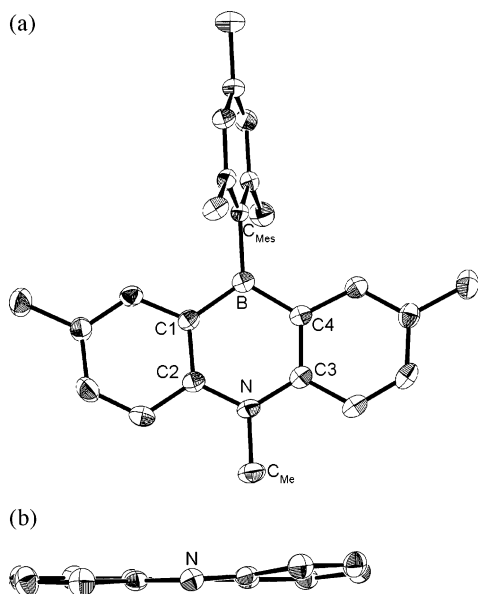
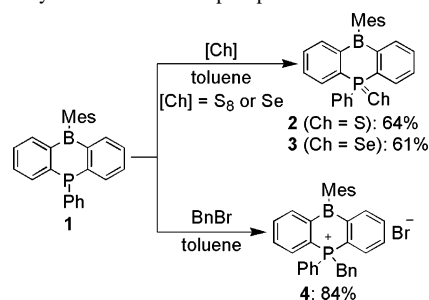


Figure 2. ORTEP drawings of dibenzoazaborine **7** (50% probability): (a) top view; (b) side view (mesityl and methyl groups not shown). One of two independent structures is shown here. Hydrogen atoms are omitted for clarity.

work occurred due to the instability of the triarylborane moiety in the oxidative conditions.

Single crystals of the chalcogenides **2** and **3** were obtained by recrystallization from $\text{CHCl}_3/\text{MeOH}$ and $\text{CHCl}_3/\text{EtOH}$, respectively.¹¹ The crystal structures of **2** and **3** were investigated using X-ray crystallographic analysis, and the molecular structures of **2** and **3** are shown in Figures 3 and 4, respectively. Two independent structures were found in

Scheme 2. Syntheses of Dibenzophosphaborin P-Derivatives



the crystals: one molecule had a near planar structure, but the other had a boatlike distorted ring with a central phosphaborin moiety. One MeOH molecule/two molecules of **2** was included in the unit cell, and a hydrogen bond was formed between MeOH and the boatlike structural isomer of **2**. Although no solvent molecules were found in the single crystals of **3**, there was no significant difference in the crystal structures between these two compounds.

The crystal data for **2**, **3**, and **7** are summarized in Table 1, and selected bond lengths and angles of **2**, **3**, and **7**, as well as **1**, are listed in Table 2.

The UV-vis spectra of the dibenzopnictogenaborins and the dibenzophosphaborin P-derivatives were recorded in CH_2Cl_2 at 298 K (Table 3). Dibenzoazaborine **7** showed an

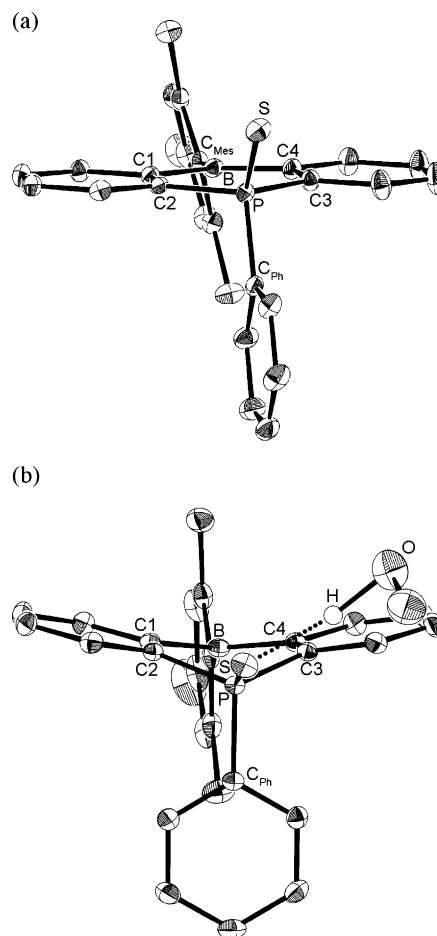


Figure 3. ORTEP drawings of dibenzophosphaborin sulfide **2** (50% probability): (a) isomer with a planar structure; (b) isomer with a butterfly structure. The hydrogen bond between MeOH and the sulfur atom is shown as a dotted line (MeOH-S: 1.92(5) Å).

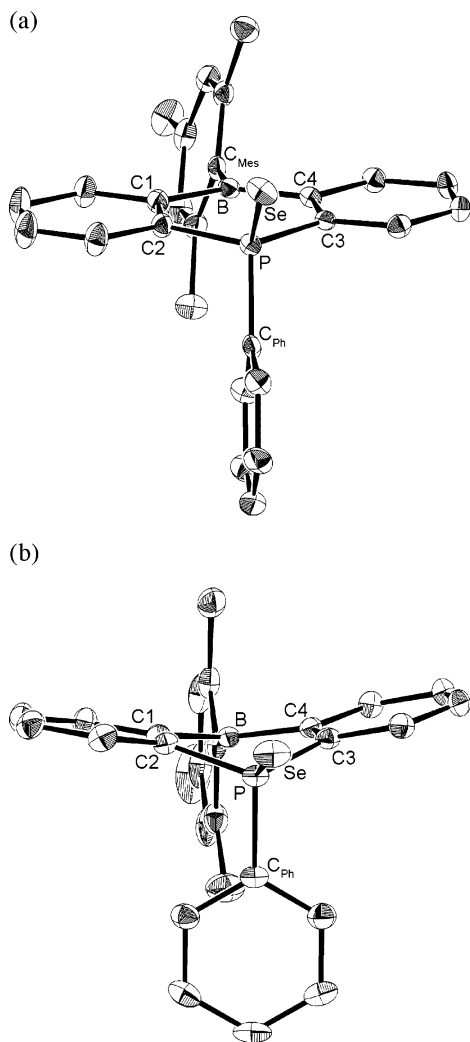


Figure 4. ORTEP drawings of dibenzophosphaborin selenide **3** (50% probability): (a) isomer with a planar structure; (b) isomer with a butterfly structure.

Table 3. UV–Vis Spectral Data for Dibenzophosphaborins in CH_2Cl_2 at 298 K

compd	λ/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)
1	368 (5000)
7	404 (11 600), 385 (9900)
2	353 (2000), 360 (1400)
3	369 (1300), 391 (1200)
4	312 (8000), 307 (7600), 381 (660)

intense and sharp absorption profile in the violet to near UV region, but the UV–vis absorption of the phosphaborin **1** showed a weak and broad absorption, indicating a weaker donor–acceptor interaction between the phosphorus and boron atoms through π -conjugation, which was expected from the crystal structure described above. The phosphonium salt **4** showed an absorption maximum around 300 nm that is close to that of dibenzoborin **8** (λ_{max} 313 nm) and dibenzoxaborine **9** (λ_{max} 321 nm) (Figure 5).⁹ Although the $\sigma^*(\text{P–Ph})$ orbital of **4** potentially works as an electron acceptor orbital, like the $\sigma^*(\text{Si–R})$ orbital of siloles or the $\sigma^*(\text{P–R})$ orbital of phospholes (vide supra), these spectral data suggest that such electronic interactions are very weak in the case of **4**, and the phosphorus atom of **4** effectively functions as a bridging unit, like the carbon or oxygen atoms

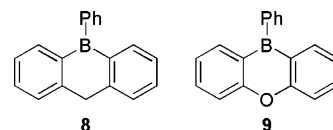


Figure 5. Dibenzoborin **8** and dibenzoxaborin **9**.

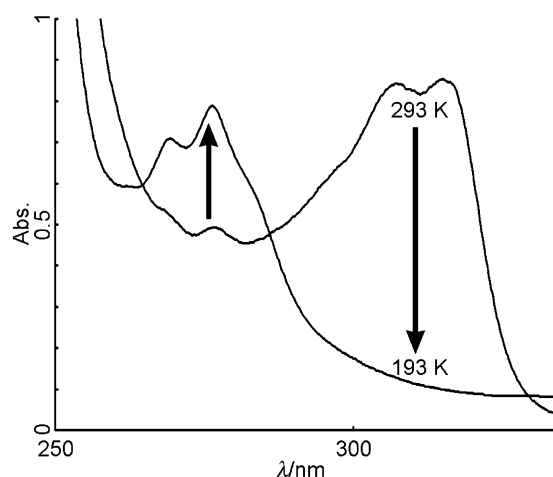


Figure 6. VT UV–vis spectra of phosphonium salt **4** in CH_2Cl_2 ($1.0 \times 10^{-4} \text{ M}$).

of **8** or **9**, respectively. Theoretical calculations on the phosphaborins also suggested that the P–Ph bonds of the phosphaborins do not function as acceptor orbitals (see Supporting Information for the orbital plots of the phosphaborins). The dibenzophosphaborin chalcogenides **2** and **3** showed a weak absorption in near UV region, with intense absorption bands in the UV region. The absorption maximum of the selenide **3** was red-shifted compared to that of the sulfide **2**. These absorptions were assigned to the intramolecular charge transfer from the lone pair orbitals on the chalcogen atoms to the LUMOs that are constructed mainly from the boron 2p orbitals. This idea is supported by TD-DFT calculations (vide infra).

The UV–vis spectra of the phosphonium salt **4** ($1.0 \times 10^{-4} \text{ M}$ in CH_2Cl_2) showed a temperature dependency (Figure 6). The intensity of the absorption band around 300 nm decreased on cooling. This absorption was attributed to the $\pi\text{--}\pi^*$ transition of the dibenzoborin moiety, and no π -conjugation via the vacant 2p orbital on the boron atom occurred due to the coordination of the bromide anion at lower temperatures. The temperature dependence of the coordination of the bromide anion was also shown in the VT ^{11}B NMR spectra of **4** in CD_2Cl_2 ($7.0 \times 10^{-2} \text{ M}$) (Figure 7). Above a temperature of 273 K, a single signal at δ_{B} 56, corresponding to triarylborane, was observed. When the sample was cooled to temperature below 253 K, the signal at δ_{B} 56 decreased in intensity, and a new signal was observed at around δ_{B} 0. This signal was attributed to the bromoborate that is formed by the coordination of the bromide anion to the boron atom.

Dibenzoazaborine **7** exhibited a moderately strong fluorescence in cyclohexane at 298 K (λ_{em} 421 nm, Φ 0.48), with a small Stokes shift ($\Delta\lambda < 20 \text{ nm}$), indicating a retention of the rigid molecular structure in the excited state.¹²

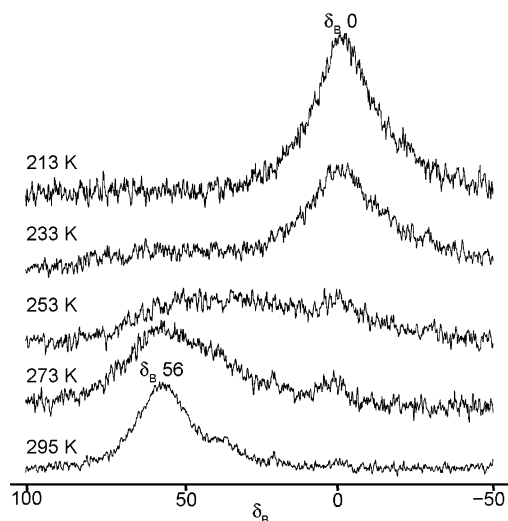


Figure 7. VT ^{11}B NMR of phosphonium salt **4** in CD_2Cl_2 (7.0×10^{-2} M).

However, the fluorescence of dibenzophosphaborin **1** and its P-derivatives was very weak ($\Phi < 0.01$), and the broadened spectral profiles, as well as the large Stokes shift ($\Delta\lambda > 100$ nm), revealed the existence of a substantial structural change after photoexcitation.

Theoretical calculations at the B3LYP/6-31G(d) level of theory were performed to investigate the electronic structure of the dibenzoheteraborins, and the calculated energy levels of the frontier molecular orbitals and excited states estimated using the TD-DFT method are summarized in Table 4.^{13,14} Orbital plots are shown in the Supporting Information. All the LUMOs of these molecules were mainly constructed from the vacant 2p orbitals on the boron atoms. Both the HOMO and LUMO of dibenzoazaborine **7** were relatively high in energy because of the strong electron-donating properties of the nitrogen atom. When the main group element was changed to phosphorus, the energy level of the frontier orbitals decreased by 0.3 eV due to the weaker electron donation. The effect of modification of the phosphorus atom of dibenzophosphaborin was studied for the sulfide **2**, selenide **3**, and phosphonium salt **4**. The HOMOs of **2** and **3** were attributed to the lone pair orbitals on the chalcogen atoms, and the UV-vis absorption bands of these molecules

Table 4. Calculated Frontier Orbital Energy and Excited States^a

compd	HOMO/eV	LUMO/eV	excited states ^b
1	-5.74	-1.78	$\pi^* \leftarrow \pi$
7	-5.40	-1.42	$\pi^* \leftarrow \pi$
2	-5.81 ^c	-2.34	$\pi^* \leftarrow \text{n(Ch)}$
3	-5.42 ^c	-2.34	$\pi^* \leftarrow \text{n(Ch)}$
4 ^d	-9.04	-5.32	$\pi^* \leftarrow \pi(\text{B-Ph})$ $\pi^* \leftarrow \pi$

^a All the calculations were performed at the B3LYP/6-31G(d) level of theory. The mesityl groups on boron atoms were replaced by phenyl groups to reduce computation time. ^b Excited states were estimated by TD-DFT method implemented with the Gaussian 03 program package. ^c HOMO was the lone pair orbital of a chalcogen atom. ^d Only the cation part was calculated.

Table 5. Complex Formation Constants $K(\text{X}^-)$ ($\text{X} = \text{F}, \text{Cl}$) of Dibenzophosphonictogenaborins

compd	$K(\text{F}^-)/\text{M}^{-1}$	$K(\text{Cl}^-)/\text{M}^{-1}$
1	$2.1(3) \times 10^4$	— ^a
7	14(3)	— ^a
2	$1.4(2) \times 10^5$	11(1)
3	$3.3(7) \times 10^6$	14(3)
4	— ^b	$1.7(1) \times 10^4$

^a Complex formation was not observed. ^b The value of $K(\text{F}^-)$ was too large to be determined.

in the near UV region are thought to be intramolecular charge-transfer bands from the lone pair orbitals on the chalcogen atoms to the vacant 2p orbitals on the boron atoms. TD-DFT calculations also reveal that the lowest excited states of **2** and **3** correspond to the $\pi^* \leftarrow \text{n(Ch)}$ transitions. Among the compounds investigated, compound **4** has anomalously low-lying frontier orbitals, reflecting the strong electron-withdrawing property of the phosphonium moiety (Table 4). The longest UV absorption bands of **4** are attributable to the intramolecular charge transfer from the mesityl group on the boron atom to the π^* orbital on the dibenzophosphaborin framework, and the second longest absorption band originates from the $\pi^* \leftarrow \pi$ transition of the dibenzophosphaborin moiety.

The complex formation constants between the dibenzoheteraborins and halide anions were determined from UV-vis titration experiments, and the results are summarized in Table 5. The complex formation constants of dibenzoazaborine **7**, phosphaborin **1**, and its sulfide **2** with fluoride anion increased in this order, reflecting the order of the calculated LUMO levels.¹⁵ The complex formation constant of the phosphonium salt **4** was too large to be determined under the same conditions. Next, we tested the complex formation with chloride anion. It is difficult to capture halide anions with triarylboranes, other than fluoride anion,¹⁶ and the dibenzoheteraborins having relatively high LUMO levels did not form complexes with chloride anion. However, the

(12) Fluorescence quantum yields were determined using anthracene in EtOH (Φ 0.27) as a standard.

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dibenzophosphaborin chalcogenides **2** and **3** formed complexes with chloride anion, and the phosphonium salt **4** showed a high complex formation constant with chloride anion, reflecting the anomalously low LUMO energy level. Although we also tried titration experiments using *n*-Bu₄NBr under the same experimental conditions, complex formation was not observed. However, the VT ¹¹B NMR data indicate that bromide anion can coordinate to the boron atom at low temperatures (vide supra). As described above, the Lewis acidity of dibenzophosphaborin was remarkably enhanced by substitution on the phosphorus atom site.

Conclusions

In summary, we have synthesized dibenzopnictogenaborins bearing a nitrogen or phosphorus atom. These molecules showed different optical properties and Lewis acidity corresponding to the bridging main group element. The azaborine exhibited relatively strong UV–vis absorption bands and fluorescence, with a small Stokes shift, reflecting the rigid, planar structure. On the other hand, the phosphaborin

and its P-derivatives emitted a weak fluorescence due to the lack of rigidity, but titration with halide anions revealed that the Lewis acidity of the P-derivatives is tunable due to the change in substituent on the phosphorus atom site. Among these compounds, the phosphonium salt has the strongest Lewis acidity, and even bromide anion can coordinate to the boron center at low temperatures.

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Supporting Information Available: X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compounds **2**, **3**, and **7** in CIF format and orbital plots of **1–4** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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