

# Dibenzophosphaborin: A Hetero- $\pi$ -conjugated Molecule with Fluorescent Properties Based on Intramolecular Charge Transfer between Phosphorus and Boron Atoms

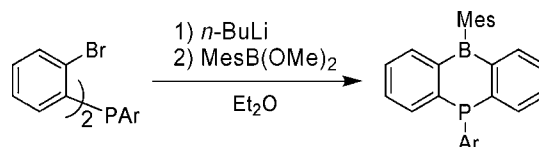
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## ABSTRACT



The first dibenzo-1,4-phosphaborins were synthesized and characterized by X-ray crystallographic analysis. The phosphaborins exhibited UV/vis absorption derived from intramolecular charge transfer from the phosphorus atom to the boron atom. The phosphaborins showed different fluorescent properties depending on the substituents on the phosphorus atom.

Hetero- $\pi$ -conjugated molecules have been paid much attention in recent years because atomic orbitals on heteroatoms can interact electronically with carbon-based  $\pi$ -orbitals, and the resultant hetero- $\pi$ -systems reduce HOMO–LUMO gaps compared to the parent  $\pi$ -system, owing to a rise of HOMO level (N, P) or a decline of LUMO level (B, Si).<sup>1</sup> Heteroatom-substituted cyclopentadienes (heteroles) are the most studied compounds among such molecules due to the interesting electronic and optical properties derived from efficient hyperconjugation between planar extended  $\pi$ -orbital and atomic orbitals on heteroatoms. As for phosphorus-containing  $\pi$ -systems, the electronic and optical properties of phosphorus-containing  $\pi$ -conjugated systems can be changed by the electrochemical or chemical tuning of the lone pair, which is induced by oxidation, coordination to Lewis acids, and complexation with transition metals.<sup>2</sup> On the other hand, only

a few hetero- $\pi$ -conjugated systems featuring six-membered rings have been studied so far.

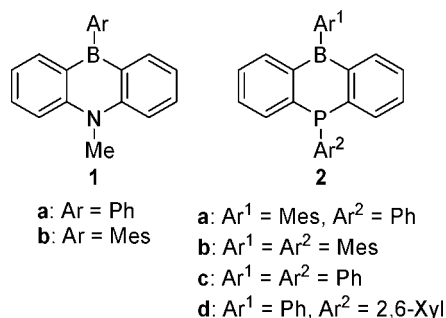
Dibenzo-1,4-dihydro-1,4-azaborine (azaborine) **1** is a nitrogen and boron analogue of 9,10-dihydroanthracene and has a hetero- $\pi$ -conjugated system including the lone pair of the nitrogen atom and the vacant p-orbital of the boron atom (Figure 1).<sup>3</sup> HOMO–LUMO excitation of **1a** ( $\lambda_{\text{max}}$  408 nm) resulted in intramolecular charge transfer (ICT) from the nitrogen atom to the boron atom and fluorescent emission with a high quantum yield ( $\lambda$  420 nm,  $\phi$  0.8) from the zwitterionic excited state.<sup>4</sup> Compound **1** also shows interesting optical properties, such as UV–vis absorption and

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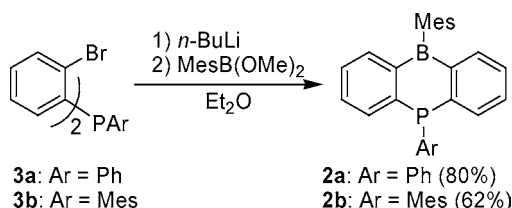
**Figure 1.** Azaborines and phosphaborins.

fluorescence in response to external stimuli (i.e., OH<sup>−</sup>, ROH, or other Lewis bases)<sup>2,3</sup> or the formation of a CT complex with electron acceptors (i.e., TCNQ).<sup>5</sup>

The phosphorus analogue of **1**, phosphaborin, is expected to have electronic and optical properties different from those of **1**. The lone-pair electrons of phosphorus atom make a smaller contribution to conjugation with the  $\pi$ -system than those of nitrogen. In addition, tricoordinated phosphorus compounds take a pyramidal structure unlike tri- and diarylamine, which are usually trigonal planar, so phosphaborin will change the local structure around phosphorus atom upon excitation, resulting in a large Stokes shift in photoluminescence. Despite its potential application for optical devices, phosphaborin has not yet been reported. Here we report the synthesis, structure, and fluorescent properties of the first phosphaborin.

*B*-Mesityl-*P*-phenylphosphaborin **2a** and *B,P*-dimesitylphosphaborin **2b** were synthesized by the reactions of dilithio derivatives prepared from the arylbis(2-bromophenyl)phosphanes, **3a** and **3b**, respectively, with MesB(OMe)<sub>2</sub> in Et<sub>2</sub>O under reflux conditions (Scheme 1). Both

**Scheme 1**

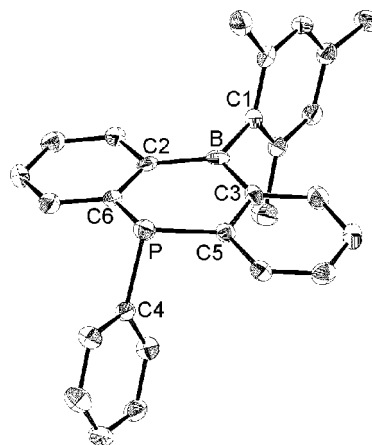


phosphaborins **2a** and **2b** were obtained as crystalline solids, which were stable against air and moisture in the solid state, but **2b** decomposed gradually for several days in solution.

In the <sup>31</sup>P NMR spectra, the signals of **2a** ( $\delta_P$  −13.3) and **2b** ( $\delta_P$  −22.2) shifted upfield compared with those of the parent triarylphosphanes **3**. The magnetic shielding of the

phosphorus nucleus is probably increased by steric congestion around the phosphorus atom because of the rigid fused-ring structure. In the <sup>11</sup>B NMR spectra, the signals of **2a** ( $\delta_B$  65.1) and **2b** ( $\delta_B$  62.3) appeared in the usual region of triarylborane and shifted downfield compared with those of azaborine **1**, indicating the existence of weaker  $\pi_{CC}$ – $2p_B$  interaction in phosphaborins than in **1**.

Single crystals of **2a** suitable for X-ray crystallographic analysis were obtained by recrystallization from benzene/Et<sub>2</sub>O (Figure 2).<sup>6,7</sup> Unlike the azaborine ring, the phos-



**Figure 2.** ORTEP drawing of *B*-mesityl-*P*-phenylphosphaborin **2a** with thermal ellipsoid plot (50% probability). H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): B–C1 1.570(5), B–C2 1.554(5), B–C3 1.553(5), P–C4 1.836(3), P–C5 1.811(3), P–C6 1.819(3); C1–B–C2 120.6(3), C2–B–C3 119.9(3), C3–B–C1 119.3, C4–P–C5 100.33(14), C5–P–C6 103.22(16), C6–P–C4 103.37(14).

phaborin ring of **2a** deviates from planarity due to pyramidalization at the phosphorus atom. The sums of the bond angles around the phosphorus atom (307°) and the boron atom (360°) are similar to those of ordinary triarylphosphanes and triarylboranes.

Single crystals of **2b** were obtained by recrystallization from benzene. Although the crystallographic analysis of **2b**

(6) Crystallographic data for **2a**: C<sub>27</sub>H<sub>24</sub>BP<sup>1/2</sup>/benzene, pale yellow needle, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 8.138(4) Å, *b* = 16.833(9) Å, *c* = 16.975(9) Å,  $\beta$  = 92.835(3)°, *V* = 2323(2) Å<sup>3</sup>, *Z* = 4, *F*(000) = 908, crystal size 0.50 × 0.10 × 0.05 mm<sup>3</sup>, 6.16 ≤ 2 $\theta$  ≤ 54.96. In total, 9578 reflections were collected, of which 2774 were independent (*R*<sub>int</sub> = 0.0355) and employed for refinement: 292 parameters, 0 restraints, *R*<sub>1</sub> (*I* > 2 $\sigma$ (*I*)) = 0.0445, *wR*<sub>2</sub> (all data) = 0.0871. The intensities of reflection were collected at 120 K on a RIGAKU MSC Mercury CCD diffractometer with a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71070 Å) using CrystalClear (Rigaku Corp.). The structure was solved by direct methods (SHELXS) and expanded using Fourier techniques. The structures were refined by full-matrix least-squares methods on *F*<sup>2</sup> (SHELXL-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. CCDC-267794 contains 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](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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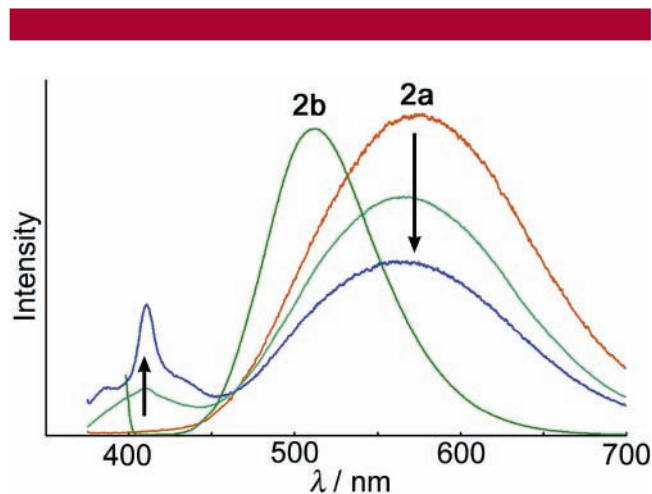
is not good enough for precise discussion due to disorder, nonplanarity of dibenzophosphaborin ring is obviously strengthened compared to that of **2a** derived from steric repulsion of the mesityl group on the phosphorus atom (see the Supporting Information).

Density functional calculations<sup>8</sup> (B3LYP/6-31G(d) level) were performed on model compounds **2c** and **2d**.<sup>9</sup> The optimized structure for **2c** reproduced the molecular structure of **2a** almost completely. The frontier molecular orbitals are delocalized over the phosphaborin rings, but the HOMO and LUMO have the significant coefficients of a lone pair on the phosphorus atom and a vacant 2p orbital on the boron atom, respectively. Natural bond orbital (NBO) analysis was performed on **2c** in order to reveal further insight into the electronic structure of phosphaborin.<sup>10</sup> NBO analysis showed that the highest occupied natural localized molecular orbital corresponds to the phosphorus lone pair and the lowest unoccupied natural localized molecular orbital is the vacant 2p orbital on the boron atom. The electronic excitation of phosphaborin is probably derived from ICT from the phosphorus atom to the boron atom. Second-order perturbation analysis indicates strong electron donation from  $\pi_{CC}$  to  $2p_B^*$ , while the delocalization of the phosphorus lone pair to  $\pi_{CC}^*$  is weak. These data are in contrast to a structural and theoretical investigation on the electronic structure of the azaborine that the donation from the nitrogen lone pair to  $\pi_{CC}^*$  is stronger than the  $\pi_{CC}-2p_B^*$  interaction.<sup>11</sup>

The UV-vis spectra showed absorption maxima in the near-ultraviolet region ( $\lambda_{max}$  368 nm for **2a**, 393 nm for **2b**). These absorptions are derived from the ICT as predicted by TD-DFT calculations on model compounds (**2c**,  $\lambda_{max}$  365 nm; **2d**,  $\lambda_{max}$  382 nm).<sup>12</sup> The red shift of the absorption in **2b** is explained by planarization around the phosphorus atom induced by the bulky mesityl group of **2b** and the consequent elevation of the HOMO level.<sup>13</sup> The UV-vis absorption maxima of azaborine do not depend on the substituent of

the nitrogen atom because the planar structure around the nitrogen atom of azaborine is not widely affected by its substituents.

Phosphaborins **2a** and **2b** showed different fluorescence spectra (Figure 3). The fluorescence spectra of **2a** were



**Figure 3.** Fluorescence spectra of **2a** (298 K, cyclohexane, excitation at 368 nm, (orange)  $1.0 \times 10^{-3}$  M, (green)  $1.0 \times 10^{-4}$  M, (blue)  $1.0 \times 10^{-5}$  M) and **2b** (298 K, cyclohexane,  $8.0 \times 10^{-5}$  M, excitation at 393 nm).

concentration-dependent in the range of 1.0 to 0.010 mM in cyclohexane solution. In the diluted solution, the intensity of the broad emission near 560 nm was weakened and the sharp emission at 410 nm increased. The fluorescence of **2b** ( $\phi_{FL}$  0.16<sup>14</sup>), however, was independent of its concentration. Our interpretation of the broad emission observed near 560 nm is that **2a** forms an excimer upon excitation when in a concentrated solution; **2b** does not appear to form an excimer because of steric repulsion around the phosphorus atom, resulting in monomer-derived emission. In the case of azaborine, the emission is independent of concentration—regardless of the reduced bulkiness of substituents on the nitrogen atom. Thus, the excimer formation of **2a** is considered a specific characteristic to phosphaborin, which has a more active lone pair than azaborine.

The monomer emission of **2a** does not show significant Stokes shift (40 nm), but **2b** exhibits rather large Stokes shift (115 nm). Structural relaxation from excited-state induces Stokes shift, and **2b** should experience greater structural change around phosphorus atom than **2a** upon photoexcitation. Both crystallographic analysis and theoretical calculations indicate the phosphorus atom of **2b** deviates from phosphaborin ring much more than that of **2a**. The phosphorus atom of **2b** seems to move toward the mean plane defined by the five atoms of the phosphaborin ring other than phosphorus atom upon photoexcitation, resulting in a larger Stokes shift.

(14) The fluorescence quantum yield ( $\phi_{FL}$ ) of **2b** was determined at 298 K using 9,10-diphenylanthracene as a standard in cyclohexane. The  $\phi_{FL}$  of **2a** could not be determined due to the excimer formation and weakness of emission.

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(9) To reduce the computational time, **2c** and **2d**, which have phenyl groups instead of mesityl groups on boron atoms, were used. These simplifications rarely affected the structure of phosphaborin rings.

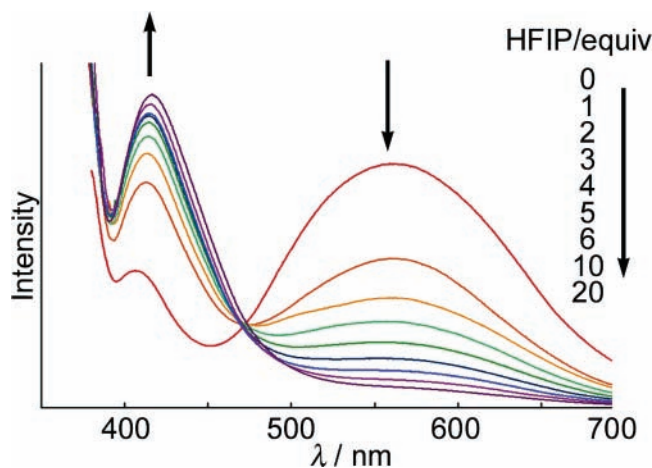
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A similar emission change was observed in response to the addition of a proton source (Figure 4). When 1,1,1,3,3,3-



**Figure 4.** Fluorescence change of **2a** upon addition of HFIP (298 K, cyclohexane,  $1.0 \times 10^{-4}$  M, excitation at 368 nm).

hexafluoro-2-propanol (HFIP) was added to the cyclohexane solution of **2a** as a proton source, the broad emission near 560 nm that was derived from the excimer gradually decreased and the sharp emission at 410 nm increased. In contrast with this finding, the emission maximum of **2b** did not shift, but the emission intensity decreased monotonically when HFIP was added. The origin of the proton-dependent

fluorescence change of **2a** is still unclear, but it is evident that excimer formation is prevented by protonation of the phosphorus atom in the excited state.

In summary, phosphaborin, the first heavy analogue of azaborine, was synthesized. The X-ray crystallographic analysis and theoretical calculations revealed weak delocalization of the phosphorus lone pair electrons into the  $\pi$ -system. The excimer-derived emission as well as Stokes shift of phosphaborin can be controlled by steric factor on the phosphorus atom, judging from the different fluorescent behavior between the two phosphaborins. Such fluorescent behavior is not observed in the case of azaborine, and  $\pi$ -conjugated framework of phosphaborin has an intrinsic potential for constructions of new optical devices.

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**Supporting Information Available:** Experimental procedure for the preparation of **2a,b** and **3a,b** and the X-ray crystallographic data in CIF format for **2a,b**. This material is available free of charge via the Internet at <http://pubs.acs.org>. OL051537Q