主論文

Chemistry of Planarized Triphenylboranes: Effects of Structural Constraint and Derivatization

平面固定トリフェニルボランにおける
構造固定の効果および誘導体合成に関する研究

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Preface

The studies in this thesis have been carried out under the direction of Professor Shigehiro Yamaguchi at Nagoya University during April 2010 – August 2013. The studies are concerned with chemistry of planarized triphenylboranes.

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General Introduction

The molecular functions of organic compounds, such as color, luminescence, conductivity, carrier transportation, and magnetism, are all relevant to the π electrons. Organic π-electron systems play important roles not only in life activity, but also in materials science. The living beings take advantage of the π-electron systems for photosynthesis, bioluminescence, and so forth. The natural molecules, which are involved in such biological events, are highly sophisticated. On the other hand, the development of the artificial π-conjugated molecules has attracted much attention, because of their possible applications to dyes, sensing/imaging materials, organic electronic devices, *etc*., which enrich our lives. The organic materials have some advantages, such as lightness, flexibility, and fine-tunability of their properties, compared to the conventional inorganic materials. Although a huge number of designed organic π-electron systems have been synthesized and investigated to date, it is yet difficult to produce novel π-electron materials with desirable and ultimate electronic properties and functions at will. Therefore, the continuous efforts to develop a new class of functional molecules and the full investigation of its characteristic features are important and necessary to accumulate the knowledge of the molecular design concepts. From this point of view, the studies presented in this thesis should provide some important guidelines for the development of unprecedented molecular functional materials.

π-Electron Systems with Structural Constraint

One of the promising strategies to modify the properties of the π-electron systems is to give a structural constraint in a certain conformation. The restricted structure would define the degree of the π conjugation. In addition, a response to external stimuli, associated with a structural change, may occur in a different manner from that in the non-constrained congeners. Alkylene tethers are useful to this end, because they can fix the molecular structure without significant electronic perturbation. Based on this concept, a number of fascinating π-electron materials with structural constraint have been developed.

Poly(*p*-phenylene)s are an interesting class of π-conjugated polymers. A drawback of this type of polymer is the significant torsion angles between the adjacent benzene rings, which decrease the degree of the π conjugation. Müllen and co-workers first synthesized the ladder polymer, in which the poly(*p*-phenylene) framework was fixed in

a planar fashion. The ladder polymers showed a set of intriguing properties, such as red-shifted absorption and fluorescence with a small Stokes shift due to the rigid planar structures (Figure 0-1a).[1] It was also suggested that this type of ladder poly(*p*-phenylene)s exhibits high intra-chain hole mobility.[2] These results clearly demonstrated that the planarization of the skeleton effectively enhances the π conjugation, making the molecules more attractive. This pioneering work triggered the development of various type of ladder π-conjugated polymers, such as planarized poly(*p*-phenylene-2,5-thenylene)s, poly(phenylene sufide)s, and poly(*p*-phenylene-*alt*-9,10-anthrylene)s (Figure 0-1b).[3]

Figure 0-1. (a) Planarization of poly(*p*-phenylene)s and (b) representative examples of planarized π-conjugated polymers.

The structural constraint with alkylene tethers is also powerful enough to distort the inherent molecular structure. Bodwell and co-workers synthesized an alkylene-tethered pyrene. In this molecules, the alkylene tether forces the rigid pyrene skeleton into a curved form (Figure 0-2a).[4] X-ray crystallographic analysis revealed that the pyrene core is largely distorted with the bent angle of 87.8°. Applying this methodology to a more π-extended system, they also succeeded in synthesizing an alkylene-tethered curved teropyrene, which can be regarded as a segment of the single-walled carbon nanotube (Figure 0-2b).[5] The curved teropyrene showed a blue-shifted absorption compared to that of the planar teropyrene. These results demonstrated that the rigid π frameworks could be enforced to have an inherently unfavorable structure, which led to altering their electronic structures and properties.

Figure 0-2. Formation of distorted (a) pyrene and (b) teropyrene skeletons.

The structural constraint by the alkylene tether affects the excited state behavior in diphenylacetylene derivatives. The diphenylacetylenes without structural constraint usually have a copalanr conformation in the ground state, and exhibit a fluorescence from the lowest excited singlet (S_1) state, in which the molecular geometry is not significantly changed. However, by the introduction of a malonate bridge the diphenylacetylene skeleton is constrained to a twisted conformation in the ground state. X-ray crystal structure analysis determined that the twist angle between the two benzene rings is 79.3° (Figure 0-3).[6] The UV-vis absorption spectrum of the compound is significantly blue-shifted compared to those of the non-constrained derivatives. In contrast, the fluorescence properties were similar to each other, indicating that the compound undergoes the large structural relaxation from the twisted conformation to a coplanar conformation in the S_1 state. In addition, the twisted compound also showed a phosphorescence at 77 K. The results indicated that the structural constraint by the malonate tether results in maintaining the twisted structure in the excited triplet state, which emits the phosphorescence.

Figure 0-3. Twisting of diphenylacetylene.

Boron-Containing π Electron Systems

Introduction of main group element into the π-conjugated skeleton is a powerful methodology to modify the electronic and structural features.[7] Among various elements, boron is particularly useful because of its electron-deficiency with a vacant p orbital, which gives several characteristics, such as Lewis acidity and electron-accepting ability.[8] Taking advantage of these features, various types of boron-containing functional materials have been developed to date.

One of the representative applications of triarylboranes is the anion sensors.[9] Yamaguchi et al. first demonstrated that a significant change in the photophysical properties can be attained by the coordination of anions like a fluoride ion to the central boron atom. Gabbaï et al. reported that triarylboranes bearing a trimethylammonio group can be applicable to anion sensing in the aqueous media (Chart 0-1).[10] The cationic moiety not only improves the solubility to the aqueous media, but also significantly enhances the Lewis acidity, enabling the selective sensing of a fluoride or cyanide ions even in the aqueous media.

Chart 0-1. Structures of triarylborane-based anion sensors.

Marder et al. reported the nonlinear optical properties of a series of π-conjugated compounds bearing a triarylborane moiety as an electron-accepting group together with an electron-donating amino group at the termini. The π-electron systems have a large dipole moment and show the large first molecular hyperpolarizability (Chart 0-2a).[11] Fan et al. demonstrated that a π-conjugated compound with two boryl groups at the termini shows the two-photon absorption (TPA) property. For example, the compound shown in Chart 0-2b showed the large TPA cross section of 1340 GM at 775 nm.[12] These results demonstrated the potent use of the electron-accepting triarylborane moieties from the application point of view, particularly for producing the donor-acceptor type π-electron systems.

Chart 0-2. Structures of triarylborane-based nonlinear optical materials.

The triarylboranes have also been used as the electron-transporting materials for the organic electronics devices. Shirota et al. reported the synthesis of the dimesitylboryl-substituted oligothiophene derivatives (Chart 0-3). They applied these compounds to the amorphous electron-transporting material for the organic light-emitting diodes (OLEDs).[13] This pioneering work has prompted the development of various triarylboranes as the OLED materials.[14]

Chart 0-3. Structures of triarylborane-based electron-transporting materials.

For the practical use of the triarylboranes to these applications, a crucial problem is the inherent high reactivity of the tricoordinate boron atom toward nucleophiles. In the design of new boron-containing materials, how to stabilize the compounds should be always considered. To overcome the issue, at least one or two bulky substituent(s) onto the boron atom are introduced in the conventional tricoordinate boron materials. The bulky substituents kinetically protect the boron center through the prevention of the reaction with nucleophiles. The bulky aryl substituents, such as 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tip), and 2,4,6-tri-*tert*-butylphenyl (Mes*) groups are often employed.[15] However, the bulky groups also hamper the intermolecular contact between the π-conjugated frameworks. This feature sometimes becomes a drawback for the properties in the solid state. The other way for the stabilization is to form a bond with the electron-donating atom, such as nitrogen. Piers et al. clearly demonstrated that the BN-containing pyrenes have a sufficient stability toward air and moisture, despite

their planar structure of the π skeleton (Chart 0-4).[16] The donation of the lone pair electrons from the nitrogen atom to the boron atom results in the decrease in the Lewis acidity.

Chart 0-4. Structure of BN-containing pyrenes.

Planarized Triphenylboranes

As an alternative strategy for the stabilization of the tricoordinate boron compounds, the stabilization by the structural constraint in a planar fashion was recently proposed by our group. Fixation of the three aryl groups in a coplanar fashion to the plane of the boron atom should decrease the reactivity of the tricoordinate boron center with nucleophiles due to the destabilization of the resulting tetracoordinate intermediate. As a model compound to prove the efficacy of this concept, planarized triphenylboranes **1**–**3**, which have methylene tethers on the *ortho* positions of the three phenyl moieties, were designed (Chart 0-5).[17] While a triphenylborane constrained with ethylene tethers was previously reported,[18] a completely planarized derivative was unprecedented at that time. The synthesis of the compounds were achieved by the intramolecular Friedel-Crafts cyclization of a dipropenylphenyl-substituted precursor promoted by $Sc(OTf)_3$ (Scheme 0-1). The planarized products **1**–**3** are sufficiently stable toward air and water, and can be purified by silica gel column chromatography without special precaution. This high stability is in stark contrast to that of Ph_3B, which is easily decomposed on silica gel. These results demonstrate the effectiveness of the planarized constraint for the stabilization of the tricoordinate boron compounds. On the basis of this approach, a series of more π-extended planarized boranes has also been synthesized as a model system of the boron-doped graphene.[19]

Chart 0-5. Planarized triphenylboranes **1**–**3**.

Scheme 0-1. Synthesis of planarized triphenylboranes **1** and **2**

The X-ray crystallographic analysis of the planarized triphenylborane **1** revealed its highly planar structure (Figure 0-4). One notable feature is the shortened B–C bond lengths. The B–C bond lengths in the crystal structure are 1.519(2)–1.520(2) Å, which are much shorter than those of the conventional triarylboranes, such as Ph_3B (1.571(3)–1.589(5) Å)[20] and Mes_3B (1.579(2)–1.580(3) Å).[21] This result suggests that the planarization by the three methylene bridges results in not only fixation of the structural conformation, but also compression of the geometry around the boron atom.

Figure 0-4. ORTEP drawing of planarized triphenylborane (50% probability for thermal ellipsoids).[17]

Notably, the planarized triphenylboranes still possess the Lewis acidity to some extent. While the compounds were inert toward water as well as Lewis basic amines, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,4-diazabicyclo[2.2.2]octane (DABCO), the treatment with a fluoride ion resulted in the formation of the tetracoordinate fluoroborate, which has a bowl-shaped structure.[17] These results suggested that the planarized triphenylborane skeleton is not completely rigid, but still flexible enough to convert into the bowl-shaped structure, despite its structural constraint.

Abstract of This Thesis

As described in the previous sections, the structurally constrained triarylboranes are an attractive class of molecules. In particular, the methylene-bridged triphenylboranes **1** and **2** are of interest not only as a promising building unit for new elaborated organoboron materials, but also as a scaffold to investigate the effects of the structural constraint on the skeletal rigidity/flexibility and reactivity. In this thesis, the author particularly studied the latter issue.

First two chapters are focused on the impacts of the structural constraint on the structural deformation of the planarized triphenylboranes upon the changes in the electronic configuration. The fixation of benzene rings in a coplanar fashion with the three methylene tethers results in the compression of the geometry around the boron atom, particularly shortening the B–C bonds, in the ground state. The author found that this strain is released both in the excited state and reduced state, in which the molecules deform their structures to a bowl shape.

Chapter 1 describes the excited-state dynamics of the planarized triphenylboranes **1** and **2**.[22] The compounds exhibit dual fluorescence in solution. To elucidate this phenomenon, time-resolved spectroscopies, such as the fluorescence lifetime determination and transient absorption spectra, as well as the theoretical calculations in the excited state were conducted. These results demonstrated that the planarized triphenylboranes adopt two local minimum structures, planar and bowl-shaped geometries, in the lowest singlet excited state, each of which emits fluorescence at the different wavelength. The structural relaxation by the elongation of the compressed B–C bonds in the excited state leads to the unusual structural deformation into the bowl-shaped conformation. The π-expanded derivatives also exhibited similar dual fluorescence behavior. The results show the generality of the unique excited-state structural deformation of the methylene-bridged triarylboranes.

Chapter 2 describes the chemical reduction of the planarized triphenylborane **1** to produce the corresponding radical anion.[23] The study of the one-electron-reduced species is relevant to the application of this class of compounds as the electron-transporting materials. The EPR spectrum of the radical anion of **1** revealed that the unpaired electron spin density is highly delocalized over the entire π skeleton. The DFT calculations suggested that the shortening the of the B–C bonds as well as the planarization of the triphenylborane skeleton are responsible for the effective spin delocalization. In addition, two local minimum structures, planar and bowl-shaped one, are calculated for the radical anion in the ground state. In fact, the X-ray crystallographic analysis of the radical anion showed a non-planar structure, indicative of the structural flexibility of this skeleton in the one-electron-reduced state.

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The next two chapters are focused on the reactivity of the planarized triphenylboranes toward bases/nucleophiles. The author employed the planarized triphenylborane **2** with a CH_2 moiety as a substrate for the reactions, since the compound has two reactive sites, namely the benzylic CH_2 group and the boron center. The choice of appropriate bases/nucleophiles enables the control of the reaction modes and produces intriguing derivatives including a borataanthracene and a boracyclophane.

Chapter 3 describes the synthesis of the planarized *B*-phenylborataanthracene anions.[24] Replacement of one carbon atom of aromatic compounds with a main group element is a potent methodology to modify the electronic structure of the parent molecules. From this point of view, borataanthracenes are an attractive boron-containing acene analogue, in which the effects of the boron on their aromaticity as well as electronic properties are of interest. The author synthesized the planarized *B*-phenylborataanthracene anions by the reaction of the planarized triphenylborane **2** with bases, such as potassium hydride or lithium tetramethylpiperidide. The planarized *B*-phenylborataanthracene anions showed no interaction with the counter cation both in solution and in the crystalline state. In addition, this boron congener of anthracene exhibited remarkable photophysical properties, such as an intense orange fluorescence.

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Chapter 4 describes the chemistry of the boracyclophanes.[25] The interaction between an arene and a Lewis acid plays an important role in a wide range of chemistry. The author found that the reaction of the planarized triphenylboranes with *tert*-butyllithium produced not the borataanthracene, but the one-phenyl eliminated product, namely

boracyclophanes. In this compound the boron atom is fixed above the benzene ring in close proximity. Thus, this skeleton is a suitable scaffold to study the interaction between a tricoordinate boron atom and a benzene ring. The theoretical calculations revealed the intrinsic nature of the boron–benzene interaction. In addition, its σ/π character was modulated by changing the electron-donating character of the benzene ring.

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Chapter 1

Dual Fluorescence from Planarized Triphenylboranes: Impact of Structural Constraint on the Excited State Dynamics

Introduction

The development of new π-conjugated skeletons is one of the central subjects to pursue the optical and electronic functions of organic molecules. An important concept in the molecular design is to give a structural constraint to the π skeleton.[1] It limits the structural flexibility and thereby suppresses a nonradiative decay process from the electronically excited state, leading to intense fluorescence. The structural constraint in a planar fashion makes the π conjugation optimal, producing a characteristic electronic structure beneficial to gaining various superb properties, such as stable redox properties and high charge carrier transports. In addition, the structural constraint is a potent method to stabilize an unstable chemical species. A representative example is a triangulenium-type cation, in which the planarization with three methylene tethers or their heteroatom equivalents significantly stabilizes the carbocation.[2] This skeleton is widely used as the key components of fluorescent dyes[3] and DNA intercalators.[4] Our group has recently demonstrated this strategy is also effective for the stabilization of its isosteric triphenylboranes (Figure 1-1a).[5]

Figure 1-1. (a) Structural constraint as an effective strategy for the stabilization of reactive chemical species and (b) chemical structure of planarized triphenylboranes **1**, **2**, and **3**, and trimesitylborane, Mes_3B. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Triarylborane skeletons are useful building units for electron-accepting materials due to the π conjugation through a vacant p orbital of the boron atom.[6] A number of fascinating boron materials have been developed and showed the great potentials as

organic light-emitting diode (OLED) materials,[7] two-photon absorption materials,[8] and sensors.[9] One crucial issue in their molecular design is how to stabilize the highly Lewis acidic boron compounds. The conventional strategy is to exert the kinetic stabilization. Most of the stable boron materials reported to date have at least one or two bulky aryl groups on the boron atom.[7,8,10] However, this strategy sometimes gives a detrimental effect by preventing the effective intermolecular interaction. An alternative strategy for the stabilization our group previously demonstrated is to constrain the triarylborane skeleton in a planar fashion.[5] Thus, three-methylene-bridged triphenylboranes **1** and **2** were synthesized (Figure 1-1b), which were stable not only to moisture and air, but also to amines, and were purified by silica gel column chromatography without any special precaution. On the basis of this approach, we also recently succeeded in synthesizing more expanded π-conjugated systems, which could be regarded as a model system of the boron-doped graphenes.[11]

One notable feature of the planarized triphenylborane skeleton is the significantly compressed B–C bonds.[5] The B–C bond lengths in **1** are 1.519(2)–1.520(2) Å, which are about 3% shorter than the ordinary B–Csp^2 bond lengths (1.57 Å). It is also found that this skeleton is not completely rigid, but still flexible enough to undergo a plane-to-bowl structural change upon the reaction with a Lewis base like a fluoride ion.[5]

In the upsurge of the triarylborane chemistry, a current important issue may be the detailed elucidation of the excited-state behavior. Although a variety of emissive triarylboranes has been synthesized to date,[12] the detailed studies on the excited state dynamics have been limited to a few triarylboranes.[13] The infancy is also for a new series of the planarized triarylboranes. The accumulation of more information on their excited state behaviors is essential for further development of more elaborated triarylborane-based materials. From this point of view, in this chapter, the author focuses attention on our previous unusual observation.[5] Namely, compound **1** showed a significantly red-shifted fluorescence band around 400 nm together with a weak fluorescence band around 340 nm. The author sheds light on the origin of this phenomenon based on the experimental and quantum chemical studies. The elucidation of the dual fluorescence properties provides an important impact of the structural constraint, namely, which is not only the strategy to construct a rigid skeleton, but also a viable mechanism to impart the flexibility to the skeleton.

Results and Discussion

Photophysical Properties of Planarized Triphenylboranes

The author first investigated the absorption and fluorescence properties of the planarized triphenylboranes **1** and **2** at room temperature (Figure 1-2). Their data are summarized in Table 1-1, together with those of trimesitylborane (Mes_3B) for comparison.

In THF, Mes_3B as one of the conventional propeller-type triarylboranes shows an absorption band at 332 nm and a relatively broad fluorescence band at 374 nm and thereby the Stokes shift of the compound is 3470 cm^{-1}. In contrast, the planarized triphenylborane **1** exhibited the longest-absorption band at 320 nm as a shoulder, which was shorter than that of Mes_3B, despite the planar structure. More importantly, **1** showed a more red-shifted fluorescence band at 407 nm compared to that of Mes_3B, together with a weak fluorescence band at 337 nm. Such dual fluorescence behavior was also observed for the CH_2-bridgd compound **2**, which showed a more obvious shorter-wavelength fluorescence band. In nonpolar 3-methylpentane (3MP), both compounds have similar absorption and fluorescence spectra compared to those in THF, whereas the longest-absorption bands became sharper and the shorter-wavelength emission bands decreased in intensity.

Figure 1-2. Absorption and fluorescence spectra of (a) **1** and (b) **2** at room temperature in THF (blue) and 3MP (red). Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Table 1-1. Absorption and Fluorescence Properties of Compounds **1** and **2**, and Mes_3B at Room Temperature

	Solvent	λ_{abs} [nm][b]	log ε [$M^{-1}cm^{-1}$]	λ_f [nm]	ν_{abs}–ν_f [cm^{-1}]	Φ_f[a]
1	3MP	319(sh)	4.18	325(sh)	580	0.08
				397	6160	
	THF	320(sh)	3.97	337(sh)	1580	0.10
				407	6680	
2	3MP	322(sh)	4.05	328	570	0.09
				386	5150	
	THF	325(sh)	3.90	340	1360	0.09
				392	5260	
Mes_3B	3MP	331	4.19	369	3110	0.11
	THF	332	4.17	374	3470	0.08

[a]Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error. [b]sh denotes a shoulder band.

The energy differences between the absorption maxima (ν_{abs}) and the shorter-wavelength fluorescence maxima (ν_f) observed for **1** and **2** were 580 and 570 cm^{-1}, respectively, in 3MP and those values in THF were 1580 and 1360 cm^{-1}. These small values are reasonable for their rigid and planar structures. However, the energy shifts (ν_{abs}–ν_f) from the absorption band to the longer-wavelength fluorescence band in **1** and **2** were 6160 and 5150 cm^{-1}, respectively, in 3MP, and those values in THF were 6680 and 5260 cm^{-1}, which were much larger than those for Mes_3B (3110 cm^{-1} in 3MP and 3470 cm^{-1} in THF). The extraordinarily large energy differences observed for **1** and **2** suggest unusual structural deformation in the excited singlet state, despite their supposedly rigid planar structures. It is worth noting that the fluorescence spectra are independent of the concentration of the compound, ruling out any intermolecular interactions, such as excimer formation, as the origin of the longer-wavelength fluorescence band of **1** or **2**. To elucidate the excited state behavior of the planarized triphenylboranes **1** and **2**, the author investigated the time-resolved spectroscopy and performed theoretical calculations on the excited states.

Fluorescence Lifetimes

The fluorescence lifetimes of **1** and **2** in THF were determined by a picosecond time-correlated single photon-counting (TCSPC) method (Table 1-2). Upon monitoring fluorescence at 400 nm, time profiles at and after a few tens of ps following the excitation were well reproduced by single exponential decay functions and the fluorescence lifetimes (τ_f) for the emission band around 400 nm were determined to be 2.7 and 2.9 ns for **1** and **2**, respectively. On the other hand, the time profiles monitored at 340 nm showed double exponential decay for both compounds. Deconvolution analysis of the decay profile of **1** demonstrated that the short ($\tau_f(s)$) and long fluorescence lifetimes ($\tau_f(l)$) to be 5.7 ps (97.6%) and 2.8 ns, respectively. Similar analysis of the fluorescence decay profile of **2** gave $\tau_f(s)$ = 12 ps (83.8%) and $\tau_f(l)$ = 2.9 ns (Table 1-2). It is worth emphasizing that the $\tau_f(l)$ values determined for **1** and **2** at 340 nm agrees very well with those determined at 400 nm. These results demonstrate that two different excited singlet states contribute to the fluorescence behavior.

Table 1-2. Fluorescence Lifetimes of Compounds **1** and **2** in THF at Room Temperature (λ_{ex} = 315 nm)[a]

	Monitoring wavelength	Lifetime (% ratio of pre-exponential factors)
1	340 nm	5.7 ps (97.6%) 2.80 ns (2.4%)
	400 nm	2.71 ns
2	340 nm	12 ps (83.8%) 2.92 ns (16.2%)
	400 nm	2.89 ns

[a]Determined by a picosecond time-correlated single-photon counting (TCSPC) method.

Transient Absorption Spectra

To elucidate dynamic behavior more precisely, transient absorption spectra of **1** and **2** in THF excited by femtosecond 310 nm laser pulses were measured. Figure 1-3a exhibits time-resolved transient absorption spectra of **1**. The absorption band appeared around 520 nm immediately after laser pulse excitation and time decay of the 520 nm absorption band accompanied evolution of the two bands at 430 and 650 nm in the initial 10 ps time range. The decay time constant of the transient absorption band at 520

nm was 4.5 ps, while the rise times of the absorption bands at 430 and 650 nm were 3.8 and 4.1ps, respectively (Figure 1-4 and Table 1-3). The results indicate that time decay of the band at 520 nm results in formation of the new transient species at 430 and 650 nm. Furthermore, these time constants (3.8–4.5 ps) are almost the same with the fast decay component of the fluorescence monitored at 340 nm ($\tau_f(s)$), demonstrating that the transient absorption band around 520 nm is assigned to the species showing the fluorescence around 340 nm. With an increase in the delay time after excitation, the absorption bands at 430 and 650 nm are gradually replaced by a band at 550 nm. The decay time constant of the absorption band at 430 nm agreed very well with the rise time of the absorption band at 550 nm: ca. 2.8 ns (Figure 1-4 and Table 1-3). These time constants are in agreement with the slow component of the fluorescence decay monitored at 340 nm ($\tau_f(l)$) and the decay component at 400 nm (Table 2). These results demonstrate that the transient absorption showing the maxima around 430 and 650 nm is attributed to the species displaying the longer-wavelength fluorescence around 400 nm. The transient absorption band at 550 nm surviving longer than a few ns may be ascribed to the excited triplet state of **1**, because it appears with the decay of the fluorescent state.

Figure 1-3. Time-resolved transient absorption spectra of (a) **1** and (b) **2** in THF at room temperature, excited by femtosecond 310 nm laser pulses. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Figure 1-4. Time profiles of the transient absorbance of **1** in THF following excitation with a femtosecond 310 nm laser pulse. Solid lines are curves calculated from a triple exponential function. In the analysis, the longest time constant was fixed as 2.8 ns. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Table 1-3. Time Constants Obtained for **1**

Monitoring wavelength	τ_1[a]	τ_2	τ_3 (fixed)
430 nm	200±10 fs	4.5±0.2 ps	2.8 ns
520 nm	50±70 fs	3.8±0.3 ps	2.8 ns
550 nm	200±10 fs	3.2±0.5 ps	2.8 ns
650 nm		4.1±0.6 ps	2.8 ns

[a]The fastest time constant may be due to the relaxation from the excited Franck-Condon state to the S_1 state and/or the contribution from the coherent artifact.

A time evolution of the transient absorption spectrum similar to that for **1** was also observed for **2**, as shown in Figure 1-3b. The decay time constant of the absorption band at 520 nm agreed with the rise time constant of the bands at 430 and 650 nm (11.2

ps), which was almost the same with the fast decay component of the fluorescence monitored at 340 nm. In the longer time region, the absorption bands at 430 and 650 nm were gradually replaced with a band at 550 nm ascribable to the excited triplet state of **2** with the time constant of ca. 2.9 ns (Figure 1-5 and Table 1-4).

By integrating the above results on transient absorption spectroscopy and the fluorescence dynamics, it is deduced that there are two local minima in the excited singlet state, one of which (**A**) is produced immediately after excitation and shows the shorter-wavelength fluorescence around 340 nm. It converts into the other local minimum structure **B**, which shows the longer-wavelength fluorescence around 400 nm with the time constants of 5–10 ps.

Figure 1-5. Time profiles of the transient absorbance of **2** in THF following excitation with a femtosecond 310 nm laser pulse. Solid lines are curves calculated from a triple exponential function. In the analysis, the longest time constant was fixed as 2.9 ns. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Table 1-4. Time Constants Obtained for **2**

Monitoring wavelength	τ_1[a]	τ_2	τ_3 (fixed)
430 nm	80±30 fs	11.0±1.0 ps	2.9 ns
520 nm	81±10 fs	11.3±0.3 ps	2.9 ns
550 nm	80±15 fs		2.9 ns
650 nm		11.6±1.6 ps	2.9 ns

[a]The fastest time constant may be due to the relaxation from the excited Franck-Condon state to the S_1 state and/or the contribution from the coherent artifact.

Quantum Chemical Calculations

To elucidate the two emissive excited-state structures, the quantum chemical calculations on both the ground (S_0) and lowest-energy excited singlet (S_1) state of **1** and **2**, were carried out. Since the results obtained for **1** and **2** were similar to each other, the author focus the discussion on the results obtained for compound **1**. The results of the quantum chemical calculations of compound **2** are given in Experimental Section.

The optimized geometry of **1** in the ground state, calculated at the PBE0/def-SV(P) level of theory, predicts a planar structure, in which the three benzene rings are completely coplanar with the plane of the tricoordinate boron atom (Figure 1-6a). The B–C bond lengths are 1.525 and 1.526 Å, which are in good agreement with those determined by X-ray crystallographic analysis (B–C: 1.519(2) and 1.520(2) Å).[5] Vertical excitation energy calculations estimated the lowest transition energy at 4.17 eV (λ_{calc} 298 nm) with the small oscillator strength (f) of 0.081 (Figure 1-7). The calculated transition energy is consistent with the experimentally observed value (3.88 eV, λ_{max} 320 nm).

Structural optimizations of the S_1 state were conducted at the TD-PBE0/def-SV(P) starting from the planar S_0 optimized geometries, and characterization of the stationary points was performed by employing analytical second geometry derivative calculations at the CIS/def-SV(P) level of theory. A local minimum structure having a planar conformation with deformation around the boron center was predicted (Figure 1-6b). This structure showed a B–C bond elongated to 1.536 Å, while the other two B–C bonds are shortened (1.502 Å). The fluorescence wavelength calculated for this local minimum planar structure was 322 nm (3.85 eV, f = 0.041). This result is consistent with the experimentally observed small Stokes shift for the shorter-wavelength

fluorescence at 340 nm, indicating that this planar S_1 structure corresponds to the transient absorption species **A**.

In addition to the planar S_1 structure, the author also found another local minimum structure in the S_1 state, which has a bowl-shaped conformation (Figures 1-6c and d). In this structure, the B–C distances are 1.531, 1.531, and 1.514 Å, which are more elongated than those in the planar S_1 structure. To accommodate the long B–C bonds, the molecule with the structural constraint may need to take a pyramidal structure. The sum of the C–B–C angles is 351.6°. The bowl-depth, a distance between the boron atom and the plane defined by three *para*-carbon atoms of the benzene rings, is 1.477 Å (Figure 1-6d). Notably, the bowl-shaped S_1 structure is more stable than the planar S_1 structure by 7.32 kcal/mol. The fluorescence wavelength for the bowl-shaped structure was calculated to be 426 nm (2.91 eV, f = 0.023), which well agrees with the experimentally observed longer-wavelength fluorescence at 407 nm. Namely, the significantly red-shifted fluorescence observed for **1** is attributed to structural relaxation to the bowl-shaped conformation in the S_1 state.

Figure 1-6. Optimized structures of **1** calculated at the PBE0/def-SV(P) level of theory. Hydrogen atoms are omitted for clarity. Distances are shown in Å. (a) Planar S_0 structure, (b) planar S_1 structure **A**, and (c) bowl-shaped S_1 structure **B** and (d) its side view. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Figure 1-7. Representation of HOMO and LUMO of **1** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

A plausible excited state dynamics of the planarized triphenylboranes is suggested by the potential energy surfaces shown schematically in Figure 5. The results of the time-resolved spectroscopies and theoretical calculations on the excited state demonstrated that the planarized triphenylboranes **1** and **2** can have two local minimum structures in the S_1 state, a planar structure **A** and a bowl-shaped structure **B**, which are both responsible for the dual fluorescence.

Figure 1-8. A Schematic illustration of the plausible excited state dynamics of the planarized triphenylborane **1**. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Charge distribution calculations in the optimized structures of **1** and **2** also gave insights into the nature of their excited state (Figure 1-9). While the boron atoms showed slight deviation from the neutral charge (**1**: –0.092, **2**: +0.239) in the ground state, those in their planar S_1 structure were negatively charged (**1**: –0.472, **2**: –0.414). These charge changes are rationalized as the charge-transfer (CT) character of the excited state, in which the charge is transferred from the peripheral benzene moieties to the boron center. The nature of the S_1 state is dominated by the HOMO–LUMO transition, where the LUMO is mainly localized on the vacant p orbital of the boron atom, while the doubly-degenerated HOMO and HOMO–1 are delocalized on the benzene moieties (Figure 1-7). By the deformation to the bowl-shaped S_1 structures, the negative charges on the boron atoms are further increased to –0.564 and –0.594 for **1** and **2**, respectively. In the non-constrained ordinary triarylboranes, the charge redistribution by the CT transition may be compensated by elongation of the B–C bond lengths and/or by varying of the torsion angles of the boron and aryl moieties.[14] However, in the case of the planarized triphenylboranes **1** and **2**, the structural constraint by the three methylene bridges results in a structural deformation in a different fashion, namely, a pyramidalization of the boron atom forming the bowl-shaped structure.

Figure. 1-9. Charge distributions on the boron atom of **1** and **2** calculated at the PBE0/def-SV(P) level of theory. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Emission Properties at Low Temperature

Interestingly, the author found that the dual fluorescence behaviors of the planarized triphenylboranes are dependent on temperature (Figure 1-10). The author measured the emission spectra of **1** at varied temperatures using 3-methylpentane (3MP) as a solvent, as it forms a transparent glass at low temperature (glass transition temperature, T_g = 155 K). As mentioned previously, a broad fluorescence band around 400 nm and a weak band around 330 nm were observed at room temperature (Table 1-1). Upon cooling the temperature, whereas little change was observed up to 150 K, the fluorescence intensity of **1** around 400 nm gradually decreased without any appreciable change in the spectral band shape, and finally disappeared around 100 K. Concomitant with this change, the fluorescence intensity around 330 nm dramatically increased (Figure 1-10a). These observations indicated that the structural conversion from the planar structure to the bowl-shaped structure in the S_1 state of **1** was suppressed in the 3MP glass matrix at low temperature. Upon further cooling from 100 to 77 K, a new structured emission band and a broad emission band appeared again around 380 and 460 nm, respectively (Figure 1-10b). Judging from the long lifetime (5.30 ms) of the emission band at 380 nm at 77 K, this new emission is assigned to phosphorescence from **1**. The temperature dependence of the emissions similar to that of **1** was also observed for **2** (Figures 1-10c and d), demonstrating that these properties are general to the structurally constrained triphenylboranes. The total quantum yields of the fluorescence and phosphorescence at 77 K were 0.71 and 0.70 for **1** and **2**, respectively (Table 1-5). It should be noted that, despite the simple triphenylborane luminophore, the compounds **1** and **2** show simultaneously dual fluorescence and phosphorescence at low temperature.

Figure 1-10. Emission spectra of **1** in 3MP at (a) 170–100 K and (b) 100–77 K. Emission spectra of **2** in 3MP at (c) 170–100 K and (d) 100–77 K. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Table 1-5. Emission Properties of **1** and **2** in 3MP at 77 K

	λ_{em} [nm]	$\Phi_{em}{}^{a}$	$\Phi_{f}{}^{a}$	$\Phi_{ph}{}^{a}$
1	322, 378	0.71	0.40	0.31
2	325, 377	0.70	0.45	0.25

[a]Absolute emission quantum yields determined by a calibrated integrating sphere system within ±3% error.

Synthesis and Photophysical Properties of π-Expanded Derivatives

The sysnthesis and photophysical properties of the planarized 9,10-diphenyl-9,10-dihydro-9,10-diboraanthracene **3** was reported as a π-expanded analogue of the planarized triphenylboranes (Figure 1-1b). In contrast to compounds **1** and **2**, the diboron-analogue **3** only showed a fluorescence with the small Stokes shift of

484 cm^{-1} in THF.[5] These distinct fluorescence properties led to a question whether the dual fluorescence is unique to the triphenylborane skeleton or has a generality in more expanded π-conjugated systems. In order to investigate this issue, the author synthesized trigonally π-expanded planarized triphenylboranes and investigated their fluorescence properties. The author selected the CH_2-bridged triphenylborane **2** as a core skeleton, because **2** showed the more apparent dual fluorescence than **1**. The author synthesized two derivatives, phenyl-substituted **5** and *p*-hexyloxyphenyl-substituted **6**. These compounds were synthesized from **2** in two steps via the direct borylation[17] promoted by an iridium catalyst to produce a triborylated intermediate **4**, followed by Suzuki-Miyaura cross-coupling reaction (Scheme 1-1). Both compounds **5** and **6** are stable enough to isolate by silica gel column chromatography without any precaution.

Scheme 1-1. Synthesis of π-expanded planarized triphenylborane derivatives **5** and **6**. *Reagents and conditions*: a) $(pinB)_2$ (3.3 equiv), $[Ir(OMe)cod]_2$ (2 mol%), 4,4′-di-*t*-butyl-2,2′-bipyridine (4 mol%), cyclohexane, 80 °C, 5 h; b) *p*-BrC_6H_4R (3.3 equiv), $[Pd_2(dba)_3]\cdot CHCl_3$ (15 mol%), XPhos (60 mol%), CsF (10 equiv), toluene, 80 °C, 13 h. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

The absorption and fluorescence properties of **5** and **6** were then studied at room temperature (Figure 1-11) and low temperature in 3MP (Figure 1-12). The data are summarized in Table 1-6.

At room temperature, the absorption maxima of **5** (λ_{max} 333 nm) and **6** (λ_{max} 344 nm) were red-shifted compared to that of **2**, while compounds **5** and **6** exhibited broad and single fluorescence band with the maximum wavelengths of 406 and 416 nm, respectively. Thus, these compounds seem not to show the dual fluorescence behavior at room temperature. The Stokes shift observed for **5** and **6** were 5400 and 5030 cm^{-1},

respectively. The fluorescence quantum yields of **5** and **6** were 0.70 and 0.84, respectively, which were much higher than that of **2** (0.09).

Figure 1-11. Absorption (red) and fluorescence (blue) spectra of (a) **5** and (b) **6** in 3MP at room temperature. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

However, These compounds also exhibited the temperature dependent fluorescence properties (Figures 1-12). Upon cooling to 150 K, the fluorescence intensities of **5** and **6** around 400 nm increased, probably due to suppression of non-radiative decay at low temperature. Further cooling resulted in the gradual decrease in the fluorescence intensity around 400 nm and the concomitant increase in the fluorescence intensity around 350–400 nm. At 77K, compound **5** exhibited the fluorescence maximum at 345 nm, while that of **6** was 388 nm. The fluorescence quantum yields of **5** and **6** at 77 K were 0.87. Thus, the trigonally π-expanded derivatives **5** and **6** exhibited the dual fluorescence behavior at low temperature similar to those of **1** and **2**, although these compounds did not show phosphorescence at low temperature unlike **1** and **2**.

The difference in the maximum wavelength between the shorter and longer-wavelength fluorescence bands is smaller for the electron-donating hexyloxyphenyl-substituted **6** (28 nm, 1730 cm^{-1}) compared to that (61 nm, 4360 cm^{-1}) for the phenyl-substituted **5**. This difference should reflect the different character of the excited state structures. To gain insights into this issue, the author also carried out theoretical calculations of **5** and a model compound **6′**, in which the three hexyloxy groups are replaced with methoxy groups.

Figure 1-12. Fluorescence spectra of (a) **5** and (b) **6** in 3MP upon cooling from 290 to 77 K. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Table 1-6. Absorption and Fluorescence Properties of **5** and **6** in 3MP

	Temp.	λ_{abs} [nm]	log ε [$M^{-1}cm^{-1}$]	λ_f [nm]	ν_{abs}–ν_f [cm^{-1}]	Φ_f^a
5	290 K	333	4.92	406	5400	0.70
	77 K	–[b]	–[b]	345	1040[c]	0.87
6	290 K	344	4.94	416	5030	0.84
	77 K	–[b]	–[b]	388	3300[c]	0.87

[a]Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error. [b]Not measured. [c]Energy difference between the absorption maximum energy at 290 K and the fluorescence maximum energy at 77 K.

Theoretical Insight into the Ground and Excited Singlet States of the π-Expanded Derivatives

The DFT and TD-DFT calculations for compounds **5** and **6′** followed closely the methodology described for compounds **1** and **2**. It was found that the phenyl-substituted **5** has a planar structure in the ground state and two minimum structures in the S_1 state, namely a planar-like and bowl-shaped structures, respectively (Figure 1-13). Excitation energies computed at the ground and excited state optimized geometries reproduced the absorption and fluorescence properties experimentally observed for **5**. While the absorption transition energy for the S_0 optimized geometry was estimated to be 327 nm (3.80 eV, f = 0.715), the fluorescence wavelengths from the planar-like and bowl-shaped S_1 structures were predicted to be 360 nm (3.45 eV, f = 0.820) and 419 nm (2.96 eV, f = 0.402), respectively (Figure 1-14). These results confirm that the dual

fluorescence behavior of the π-expanded planarized borane **5** is also originated by the structural relaxation in the S_1 state into the two minimum geometries, *i.e.*, the planar-like and bowl-shaped structures.

Figure 1-13. Optimized structures of **5** calculated at the PBE0/def-SV(P) level of theory. Hydrogen atoms are omitted for clarity. Distances are shown in Å. (a) Planar S_0 structure, (b) planar S_1 structure, and (c) bowl-shaped S_1 structure and (d) its side view. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Figure 1-14. Representation of HOMO and LUMO of **5** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

The geometry optimization of **6′** also predicted a planar-like and bowl-shaped structure in the S_1 state (Figure 1-15). The computed excitation energies at these geometries well reproduced the experimental results. The calculated fluorescence wavelengths for the planar-like and bowl-shaped structures were 385 nm (3.22 eV, f = 0.848) and 433 nm (2.86 eV, f = 0.546), respectively (Figure 1-16). It is worth noting that the calculated oscillator strengths for **5** and **6′**, which represent the transition probability between the S_0 and S_1 states, were much higher than those calculated for **1** and **2**. The results rationalize the higher fluorescence quantum yields observed for **5** and **6** compared to those of **1** and **2**, which are resulted from the increase in the radiative decay rate constants.

The planar-like S_1 structure of **6′** has one elongated B–C bond (1.530 Å) and two shortened B–C bonds (1.506 and 1.509 Å) compared to those of the optimized geometry in the S_0 state. This deformation mode is similar to that in **1**, while in the structure of **6′**, the carbon atom of the CH_2 moiety deviates from the triphenylborane plane by 0.453 Å (Figures 1-15b). On the other hand, in the bowl-shaped S_1 structure of **6′** as shown in Figures 1-15c and d, one B–C bond is significantly elongated to 1.546 Å, while the other two B–C bonds are also slightly elongated compared to those in the planar-like S_1 structure. The bowl depth defined by the distance between the boron atom and the plane consists of the *para*-carbon atoms of the three phenyl moieties in the triphenylborane is 1.248 Å, which is slightly smaller than the one observed for **1**.

Figure 1-15. Optimized structures of **6′** calculated at the PBE0/def-SV(P) level of theory. Hydrogen atoms are omitted for clarity. Distances are shown in Å. (a) Planar S_0 structure, (b) planar S_1 structure, and (c) bowl-shaped S_1 structure and (d) its side view. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Figure 1-16. Representation of HOMO and LUMO of **6′** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

The major difference in the potential energy surfaces in the S_1 state between **5** and **6′** is that the alkoxyphenyl-substituted **6′** has closer energies between the planar-like and bowl-shaped S_1 structures. Their difference is only 2.56 kcal/mol, while that in **5** is 4.34 kcal/mol. The closer energy in **6′** may be rationalized by the consideration that its planar-like structure already has a more enhanced CT character compared to that in **5**, due to the electron-donating effect of the terminal alkoxy groups in **6′**. The calculated charge distribution of the boron atom in the planar-like S_1 structure in **6′** is –0.447, which is slightly more negative than that (–0.415) in **5**. The enhanced CT character in **6′** significantly alters the character of the planar-like S_1 structure, since this structure inherently has a π–π* transition character with less CT character, while the bowl-shaped S_1 structure is less affected by this substituent effect. As a result, the fluorescence from the planar-like S_1 structure is largely red-shifted and thereby the energy difference between the dual fluorescence bands in **6** becomes smaller than that in **5**.

Figure. 1-17. Charge distributions on the boron atom of **5** and **6′** calculated at the PBE0/def-SV(P) level of theory. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Conclusion

The author has demonstrated that the planarized triphenylboranes show dual fluorescence despite the structural constraint and revealed its origin based on the experimental study on their excited state dynamics as well as the quantum chemical calculation in the excited state. The constrained planar structure with the three methylene bridges is still flexible enough to undergo the plane-to-bowl structural relaxation in the excited state. As a consequence, the planarized triphenylboranes can have two local minimum structures in the S_1 state, *i.e.*, the planar and bowl-shaped structures, whose fluorescence are the origin of the dual fluorescence. The dual fluorescence behavior was temperature-dependent and the dramatic fluorescence thermochromism was observed upon cooling. Moreover, below 90 K, the boron compounds also showed phosphorescence. The dual fluorescence behavior was also observed for the trigonally π-expanded derivatives, demonstrating the generality of the excited state behavior of the planarized triarylboranes.

The planarization by the structural constraint is generally recognized as an effective strategy to form a rigid structure. In contrast to this established idea, the present results give an important implication. Namely, by embedding a compressed bond within the planarized framework, the structural constraint becomes a mechanism to induce a flexible motion. In the present case, the B–C bond is significantly compressed in the planarized triphenylborane framework in the ground state. Upon excitation, the intramolecular charge transfer character in the excited state elongates the B–C bonds and thereby led to the pyramidalization of the boron atom. As a consequence, the planarized triphenylboranes can show the extraordinary red-shifted fluorescence as a simple triphenylborane luminophore. These results clearly demonstrated another worthy of the concept of the structural constraint as a methodology of the structural modification and may thus provide an interesting design principle for new triarylborane-based materials with intriguing properties

Experimental Section

General. Melting points (mp) were determined with a Yanaco MP-S3 instrument. ^{1}H, ^{13}C, and ^{11}B NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 128 MHz for ^{11}B) in $CDCl_3$ or acetone-d_6. Chemical shifts are reported in δ ppm. ^{1}H NMR spectra are referenced to residual protons in the deuterated solvent as an internal standard. ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent as an internal standard. ^{11}B NMR spectra are referenced to $BF_3{\cdot}OEt_2$ as an external standard. Mass spectrometry was performed with a Bruker Daltonics micrOTOF Focus with the APCI ionization method. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel 60 F_{254} (Merck). Column chromatography was performed using silica gel PSQ 100B (Fuji Silysia Chemical). Recycling preparative gel permeation chromatography (GPC) was performed using LC-918 equipped with polystylene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) using chloroform as an eluent. Commercially available solvents and reagents were used as received. Dry toluene was purchased from Kanto Chemical, and degassed by bubbling of nitrogen for 30 minutes before use. Cyclohexane was dried over Na, and distilled before use. $BF_3{\cdot}OEt_2$ was distilled from CaH_2. CsF was dried by heating in vacuum at 80 °C for 2 h before use. The planarized triphenylboranes **1** and **2**,[5] $[Ir(OMe)cod]_2$,[16] and $[Pd_2(dba)_3]{\cdot}CHCl_3$[17] were prepared as described in the literature. All reactions were carried out under an argon or nitrogen atmosphere.

Synthesis of 4. To a solution of **2** (402 mg, 1.20 mmol) in cyclohexane (6 mL) was added bis(pinacolato)diboron (1.01 g, 3.99 mmol), $[Ir(OMe)cod]_2$ (16.1 mg, 0.024 mmol), and 4,4′-di-*t*-butyl-2,2′-bipyridine (13.1 mg, 0.049 mmol). The mixture was allowed to warm to 80 °C, and stirred for 5 h. After the addition of a saturated aqueous solution of NH_4Cl, the mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After filtration, volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel using EtOAc as an eluent, followed by GPC to give 691 mg (0.971 mmol) of **4** in 81% yield as pale yellow solids: mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 36H), 1.88 (s, 12H), 4.62 (s, 2H), 7.88 (s, 2H), 8.12 (s, 2H), 8.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.11 (q), 34.56 (q), 37.27 (t), 43.09 (s), 84.02 (s), 84.10 (s), 130.09 (d), 130.31 (d), 131.36 (d), 145.43

(s), 155.62 (s), 155.87 (s), four signals for the carbon atoms bound to the boron atoms were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0, 46.0; HRMS (APCI, pos) *m*/*z* calcd for $C_{43}H_{57}{}^{11}B_4O_6$ $[M+H]^+$ 713.4548, found: 713.4546.

Synthesis of 5. To a solution of **4** (70.9 mg, 0.100 mmol) in toluene (1 mL) was added bromobenzene (51.7 mg, 0.329 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15.6 mg, 0.015 mmol), XPhos (28.6 mg, 0.060 mmol), and CsF (168.0 mg, 1.11 mmol). The mixture was allowed to warm to 80 °C, and stirred for 13 h. After the addition of $BF_3\cdot OEt_2$ (0.12 mL) and H_2O (6 mL), the mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After filtration, volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel using $CHCl_3$ as an eluent, followed by GPC to give 10.7 mg (0.0190 mmol) of **5** in 19% yield as pale yellow solids: mp >300 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.97 (s, 12H), 4.79 (s, 2H), 7.43–7.47 (m, 3H), 7.53–7.58 (m, 6H), 7.80 (s, 2H), 7.86–7.90 (m, 6H), 8.07 (s, 4H); ^{13}C NMR (100 MHz, acetone-d_6) δ 34.83 (q), 38.17 (t), 44.17 (s), 123.99 (d), 124.24 (d), 125.02 (d), 128.39 (d), 128.53 (d), 128.61 (d), 128.63 (d), 129.83 (d), 129.88 (d), 142.63 (s), 142.97 (s), 146.09 (s), 146.61 (s), 147.82 (s), 157.88 (s), 157.97 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 45.4; HRMS (APCI, pos) *m*/*z* calcd for $C_{43}H_{35}{}^{11}B$ 562.2832, found: 562.2824.

Synthesis of 6. To a solution of **4** (142 mg, 0.199 mmol) in toluene (3 mL) was added 1-bromo-4-(hexyloxy)benzene (170 mg, 0.661 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (31.2 mg, 0.030 mmol), XPhos (57.1 mg, 0.120 mmol), and CsF (317 mg, 2.09 mmol). The mixture was allowed to warm to 80 °C, and stirred for 13 h. After the addition of $BF_3\cdot OEt_2$ (0.24 mL) and H_2O (10 mL), the mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After filtration, volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel using $CHCl_3$ as an eluent, followed by GPC to give 106 mg (0.123 mmol) of **6** in 61% yield as pale yellow solids: mp 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92–0.95 (m, 9H), 1.36–1.40 (m, 12H), 1.49–1.53 (m, 6H), 1.80–1.88 (m, 6H), 1.91 (s, 12H), 4.03–4.07 (m, 6H), 4.70 (s, 2H), 7.03–7.07 (m, 6H), 7.63 (s, 2H), 7.67–7.69 (m, 6H), 7.84–7.85 (m,

4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.20 (q), 22.78 (t), 25.93 (t), 29.46 (t), 31.78 (t), 34.74 (q), 37.87 (t), 43.41 (s), 68.32 (t), 115.05 (d), 122.95 (d), 123.14 (d), 123.89 (d), 128.15 (s), 128.76 (d), 128.85 (d), 129.87 (s), 134.48 (s), 134.95 (s), 144.85 (s), 145.29 (s), 146.64 (s), 156.74 (s), 156.89 (s), 159.25 (d), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 43.6; HRMS (APCI, pos) *m*/*z* calcd for $C_{61}H_{72}{}^{11}BO_3$ $[M+H]^+$ 863.5579, found: 863.5588.

Photophysical Measurements at the Steady State. UV-visible absorption spectra were recorded on a Shimadzu UV-3510 spectrometer. The concentrations of sample solutions were set ~10^{-5} M for room temperature measurements. Fluorescence spectra were recorded on a Hitachi F-4500 spectrometer for both room temperature and temperature-controlled measurements. 3-Methylpentane was purified by passing through a $AgNO_3$–Al_2O_3 column.[18] The sample solutions were degassed by a least three freeze-pump-thaw cycles before measurements. For temperature-controlled experiments, the solution in a 1 cm square quartz cell equipped with a Teflon stopcock was cooled by an Oxford Optistat DN cryostat. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system.

Transient Absorption Measurements. For observations of dynamic behaviors in a femtosecond–nanosecond time region, a dual NOPA/OPA laser system was used for transient absorption measurements. The details of the system were described elsewhere.[19] Briefly, the output from a femtosecond Ti:Sapphire laser (Tsunami, Spectra-Physics) pumped by the second harmonics of a cw Nd^{3+}:YVO_4 laser (Millennia Pro, Spectra-Physics) was regeneratively amplified with a 1 kHz repetition rate (Spitfire, Spectra-Physics). The amplified laser pulses (802 nm, 0.9mJ/pulse energy, 85 fs fwhm, 1 kHz) were divided into two beams at the same energy (50%). One of these beams was guided into a NOPA (non-collinear optical parametric amplifier) system (TOPAS-white, Light-Conversion). The NOPA output can cover the wavelength region between 500 and 1000 nm with 1–40 mW output energy with ca. 20 fs fwhm. In the present work, the output wavelength was set at 620 nm and second harmonic pulses at 310 nm were used as excitation light. White light continuum was generated by focusing the fundamental light beam (802 nm) into a 1 mm CaF_2 window, which covers the

wavelength region from 350 to 720 nm. Polarization of the two laser beams was set at a magic angle for all the measurements. The signal and the reference pulses were respectively detected with multichannel photodiode array systems (PMA-10, Hamamatsu) and the detected signals were sent to a personal computer for further analysis. In order to correct the transient absorption spectrum for the dispersion of probe light, we measured the optical Kerr effect of CCl_4 and determined the wavelength-dependent arrival times of femtosecond white light at the sample position. From the cross correlation trace between the NOPA output and the super-continuum at the sample position, the response pulse duration was estimated to be ca. 80 fs. A rotating sample cell with an optical pathlength of 2 mm was used and the absorbance of the sample at the excitation wavelength was set ~1.0.

Fluorescence Lifetime Measurements. For fluorescence lifetime measurements, a time-correlated single-photon counting (TCSPC) method using a home-built cavity-dumped Cr:forsterite laser[20] with a 0.1 MHz repetition rate was employed. The fourth harmonic light at 315 nm was used for excitation. A photomultiplier tube (Hamamatsu Photonics, R3809U-50) equipped with an amplifier (Hamamatsu Photonics C5594) and a photon counting module (PicoQuanta, PicoHarp 300) was used for signal detection. A monochromator was placed in front of the photomultiplier tube. The instrumental response function was estimated by the fwhm of scattered light from a colloidal solution for the excitation light pulse. In the present measurements, the instrumental response time was 32 ps. The time profiles of fluorescence were analyzed by the deconvolution procedures with linear and nonlinear least-square methods.

Phosphorescence Lifetime Measurement at 77 K. Phosphorescence lifetime of **1** in 3MP at 77 K was determined with a Hamamatsu picosecond fluorescence measurement system C4780. The solution in a 1 cm square quartz cell was cooled by an Oxford Optistat DN cryostat.

Computational Details. We have adopted the all-electron Gaussian-type double-ζ-quality polarized basis set def-SV(P) of Schäfer *et al.*[21] for this work. After screening several choices for density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations, we selected the PBE0

exchange-correlation functional[22] as it is in good agreement with the observed experimental excitation energies. Ground state calculations employed a Lebedev integral grid comprising 96 radial points and 590 angular points, while excited states calculations employed a Lebedev integral grid comprising 48 radial points and 110 angular points. Geometry optimizations as well as energy calculations in the ground and excited states were carried out with the GAMESS computational chemistry package.[23] Atomic charges in the ground and excited states were computed at the previously optimized geometries by means of a fit of point charges due to an electrostatic potential approach as implemented in TURBOMOLE[24] at the PBE0/def-SV(P) and TD-PBE0/def-SV(P) level. The results of the quantum chemical calculations of compound **2** are shown in Figures 1-18 and 1-19. The Cartesian coordinates are shown in Tables 1-7–1-18.

Figure 1-18. Optimized structures of **2** calculated at the PBE0/def-SV(P) level of theory. Hydrogen atoms are omitted for clarity. Distances are shown in Å. (a) Planar S_0 structure, (b) planar S_1 structure, and (c) bowl-shaped S_1 structure and (d) its side view. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Figure 1-19 Representation of HOMO and LUMO of **2** in the ground state at each optimized geometry, together with the transition energies calculated at the TD-PBE0/def-SV(P)//PBE0/def-SV(P) level of theory. Reproduced from *Chem. Sci.* DOI: 10.1039/C3CS52751D with permission of the Royal Society of Chemistry.

Table 1-7. Coordinates of the Optimized Structure of **1** in the Ground S_0 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*		*x*	*y*	*z*
B	0.0003186421	-0.0000368524	0.0000060109	C	0.1898362498	-2.9842097311	0.0000024481
C	0.0478262792	-0.7614053551	1.3212895307	C	-0.0943497069	1.4920164572	2.5895821018
C	0.0018020416	-0.0398708089	2.5343781126	C	-0.0943528807	1.4920219066	-2.5895660223
C	0.1365150265	-2.1706792165	1.3016909230	C	-1.0114905768	-3.9568176976	0.0000016233
C	0.0460132530	-0.7561906867	3.7350558133	H	-1.9623483464	-3.3970414713	0.0000069519
C	0.1787436103	-2.8502440670	2.5236510539	H	-0.9989005753	-4.6079241044	-0.8898445477
C	0.1335586218	-2.1456464091	3.7236413212	H	-0.9988950173	-4.6079319329	0.8898419461
H	0.0130722250	-0.2422275421	4.6997788251	C	1.5097148642	-3.7888845151	0.0000036266
H	0.2478091010	-3.9410386847	2.5603793281	H	1.5840414049	-4.4358858991	0.8899058115
H	0.1674105664	-2.6920094475	4.6718180021	H	1.5840473821	-4.4358796863	-0.8899026229
C	0.0478271160	-0.7614025614	-1.3212792108	H	2.3776511818	-3.1075627231	0.0000089694
C	0.0018032395	-0.0398652257	-2.5343660173	C	1.1386077108	2.0156851918	3.3608386388
C	0.1365169191	-2.1706764193	-1.3016836959	H	2.0677575085	1.7629079950	2.8220634577
C	0.0460166697	-0.7561819406	-3.7350453614	H	1.1004608724	3.1113366974	3.4796235042
C	0.1787479348	-2.8502381084	-2.5236456483	H	1.1977781155	1.5728573088	4.3690544674
C	0.1335638421	-2.1456375319	-3.7236342064	C	-1.3831205356	1.8571825618	3.3610477686
H	0.0130755972	-0.2422164472	-4.6997670669	H	-1.3853675026	1.4115918116	4.3696958921
H	0.2478144499	-3.9410326327	-2.5603765373	H	-1.4834174036	2.9490103229	3.4788606677
H	0.1674176570	-2.6919977511	-4.6718123987	H	-2.2732782239	1.4888269896	2.8230745313
C	-0.0958993766	1.5226342708	0.0000078697	C	-1.3831271657	1.8571843734	-3.3610274559
C	-0.1395665800	2.2102781710	1.2327216762	H	-1.4834332782	2.9490125156	-3.4788296819
C	-0.1395681632	2.2102809630	-1.2327043314	H	-1.3853704036	1.4116033188	-4.3696799706

C	-0.2277191095	3.6061538156	1.2114586270
C	-0.2277204109	3.6061561604	-1.2114386563
C	-0.2708812632	4.2909859338	0.0000106709
H	-0.2642615940	4.1831932020	2.1396984366
H	-0.2642648846	4.1831984270	-2.1396768602
H	-0.3398226594	5.3836615474	0.0000104907
H	-2.2732818774	1.4888161630	-2.8230579439
C	1.1386000237	2.0156959998	-3.3608268087
H	1.1004509976	3.1113478773	-3.4796067266
H	2.0677527388	1.7629176465	-2.8220571609
H	1.1977660283	1.5728725648	-4.3690447238

Table 1-8. Coordinates of the Planar Optimized Structure of **1** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	-0.0006796648	0.0218780242	-0.0379987342
C	0.0468645360	-0.7448384911	1.2924509109
C	0.0020839276	-0.0421453154	2.5088205915
C	0.1348638246	-2.1474659901	1.2908992303
C	0.0478923527	-0.7818017566	3.7492974923
C	0.1787542369	-2.8496295954	2.5531357518
C	0.1352335133	-2.1701715490	3.7664472903
H	0.0138082475	-0.2449668166	4.7000489512
H	0.2481292786	-3.9397557198	2.5629500919
H	0.1693006159	-2.7151958813	4.7123783892
C	0.0470214343	-0.7495264985	-1.3259565498
C	0.0017472978	-0.0384670592	-2.5543019158
C	0.1357767675	-2.1665441108	-1.3090908050
C	0.0465833686	-0.7657369194	-3.7435896654
C	0.1784220371	-2.8547225977	-2.5213522603
C	0.1342367751	-2.1619440848	-3.7339555768
H	0.0141235658	-0.2554403488	-4.7115173461
H	0.2474899575	-3.9474536555	-2.5510862764
H	0.1684377087	-2.7132836684	-4.6782252901
C	-0.0958574158	1.5206565736	-0.0126566460
C	-0.1402064158	2.2145572930	1.2253895465
C	-0.1406924834	2.2267993712	-1.2438660187
C	-0.2284228068	3.6063387696	1.2164823678
C	-0.2287546828	3.6183036420	-1.2073696179
C	-0.2725656403	4.3080389322	0.0090332015
H	-0.2649394472	4.1783440567	2.1498595962
H	-0.2655408977	4.2000730314	-2.1339486277
H	-0.3416638828	5.3998094687	0.0153433671
C	0.1883427888	-2.9669530066	0.0088481293
C	-0.0933228125	1.4756957738	2.5789394337
C	-0.0946612830	1.5019245406	-2.6067212004
C	-1.0137851340	-3.9473353226	0.0419692686
H	-1.9648288335	-3.3895149564	0.0201291360
H	-0.9844404676	-4.6015441617	-0.8439855356
H	-1.0087108874	-4.5980085354	0.9339906730
C	1.5108483826	-3.7781791374	0.0420405933
H	1.5932723132	-4.4236576661	0.9341315265
H	1.5692027709	-4.4304440042	-0.8440067134
H	2.3786415705	-3.0980414331	0.0199610853
C	1.1432587333	1.9745343900	3.3725003443
H	2.0710508534	1.7407748858	2.8241438610
H	1.0893071345	3.0680597132	3.4956838370
H	1.2103943607	1.5308802412	4.3814191519
C	-1.3819008300	1.8155623227	3.3738714111
H	-1.3908177718	1.3679219834	4.3831678449
H	-1.4664533701	2.9072264574	3.4963381758
H	-2.2735806597	1.4659876095	2.8272010412
C	-1.3811166093	1.8677266622	-3.3792523354
H	-1.4826800050	2.9604965549	-3.4950933889
H	-1.3833813600	1.4215698800	-4.3885668310
H	-2.2707623090	1.4981386752	-2.8411084936
C	1.1368307135	2.0255391996	-3.3779288432
H	1.1003248835	3.1223120511	-3.4947401019
H	2.0650387917	1.7711431987	-2.8381219372
H	1.1968845045	1.5821390644	-4.3867636639

Table 1-9. Coordinates of the Bowl-Shaped Optimized Structure of **1** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	-0.4303529778	-0.0299558129	0.0303495138
C	-0.1582927673	-0.7687910186	1.3234075284
C	0.0473779534	-0.0229175154	2.5128388702
C	0.1011704488	-2.1630364314	1.2786726653
C	0.5183161536	-0.6866049588	3.6453991266
C	0.5709768643	-2.7932158824	2.4307092352
C	0.7766334046	-2.0598387450	3.6029462141
H	0.7042212841	-0.1515154565	4.5795826864
H	0.7963452191	-3.8621983488	2.4402270027
H	1.1521941124	-2.5663274616	4.4975918415
C	-0.1504811165	-0.7382944602	-1.2977639723
C	0.0784001625	0.0603423949	-2.4685872105
C	0.1955845030	-2.1127563199	-1.2608009495
C	0.8658766253	-0.4676093737	-3.5060262550
C	0.9345102030	-2.6098318283	-2.3288735148
C	1.2674050074	-1.7930423549	-3.4368584998
H	1.0994726605	0.1194912806	-4.3962911628
H	1.3116147795	-3.6352806818	-2.3175165248
H	1.8225348814	-2.2321600112	-4.2716628340
C	-0.2080727171	1.4838543557	-0.0164609070
C	0.0850291431	2.1530182460	1.1987020596
C	0.0242798821	2.1063115296	-1.2890200223
C	0.7781447810	3.3553338180	1.1097291244
C	0.7651717692	3.2996720768	-1.3348140053
C	1.1155254224	3.9191448553	-0.1447674455
H	1.1154073739	3.8733870268	2.0106783010
H	1.0004010665	3.7856293861	-2.2836405325
H	1.6327126119	4.8833542025	-0.1711628975
C	-0.2044458140	-2.9311757409	-0.0250705027
C	-0.3161092097	1.4772901894	2.5176443854
C	-0.5766815098	1.4417365670	-2.5295822779
C	-1.7381044817	-3.1336994438	-0.0950787811
H	-2.2615781415	-2.1626876556	-0.0917323047
H	-2.0185546495	-3.6788330619	-1.0146256395
H	-2.0840400683	-3.7125470761	0.7791957795
C	0.4448471405	-4.3158399907	-0.0397065689
H	0.0729767648	-4.9287420444	0.7968666221
H	0.1858931987	-4.8595970466	-0.9640423746
H	1.5443663129	-4.2605392237	0.0385136255
C	0.2803848176	2.2080230229	3.7216264002
H	1.3827320805	2.1555195057	3.7359085920
H	-0.0204095645	3.2694178059	3.7230344267
H	-0.0946135913	1.7769311647	4.6636337121
C	-1.8574249883	1.5799018982	2.6263595908
H	-2.2042118214	1.0985684144	3.5575897226
H	-2.1791557610	2.6371859474	2.6330048133
H	-2.3445488577	1.0722032894	1.7767187681
C	-2.1068523191	1.3341511745	-2.4141378493
H	-2.5550702996	2.3431597389	-2.3894860089
H	-2.5128598593	0.7894594735	-3.2848095642
H	-2.4060625180	0.7984344472	-1.4991289993
C	-0.2479017496	2.1923530260	-3.8159315135
H	-0.7051005203	3.1958592393	-3.7975453395
H	0.8362174845	2.3127525877	-3.9749563945
H	-0.6642256474	1.6565640634	-4.6854399457

Table 1-10. Coordinates of the Optimized Structure of **2** in the Ground S_0 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	0.0603513745	0.0018508948	-0.0208573163
C	0.0006528703	-0.7553544971	1.3001075126
C	-0.1062088475	-0.0258136126	2.5051546070
C	0.0531050049	-2.1670126999	1.2849329732
C	-0.1605480419	-0.7402678769	3.7066291856
H	-0.2296545078	4.2150414821	2.0673977935
H	0.0555296626	4.1505711330	-2.2191229419
H	-0.1300668315	5.3947875849	-0.0789716958
C	0.1701203748	-2.9881813310	-0.0112032704
C	-0.1648255791	1.5111026123	2.5528741021

C	-0.0044850698	-2.8426911882	2.5085228217
C	-0.1100168559	-2.1319728890	3.7015170107
H	-0.2434509774	-0.2238758422	4.6671274702
H	0.0319652504	-3.9348540077	2.5528084846
H	-0.1539181570	-2.6760943932	4.6505922418
C	0.1764991862	-0.7690776605	-1.3332923372
C	0.2308820793	-0.0485658797	-2.5445200501
C	0.2287296346	-2.1780587004	-1.3151070725
C	0.3389918235	-0.7456366580	-3.7492652179
C	0.3372210088	-2.8484709050	-2.5391300566
C	0.3913972951	-2.1375097317	-3.7382037018
H	0.3826538066	-0.2038526205	-4.7004572986
H	0.3814415087	-3.9406402970	-2.5802460869
H	0.4763009013	-2.6844197603	-4.6829045826
C	0.0048785313	1.5273646668	-0.0246601223
C	-0.1006129947	2.2268898912	1.1950762901
C	0.0617153224	2.2084343970	-1.2583843626
C	-0.1477685870	3.6251580050	1.1498974251
C	0.0126616370	3.6035768922	-1.2708866262
C	-0.0915118240	4.3006217087	-0.0694347903
C	0.1736294258	1.4609020580	-2.5664162171
C	-1.0574533238	-3.9235079496	-0.0922318142
H	-1.9886484129	-3.3352382907	-0.1576284462
H	-1.0031514365	-4.5761888767	-0.9795245656
H	-1.1258070481	-4.5731406254	0.7962850970
C	1.4609111870	-3.8332085501	0.0785413962
H	1.4550809114	-4.4791341245	0.9722985527
H	1.5731427245	-4.4853469506	-0.8037110624
H	2.3482296422	-3.1798265561	0.1352489503
C	1.0272850293	2.0045542047	3.4035194726
H	1.9834888135	1.7239053299	2.9298445690
H	1.0106801062	3.1016429616	3.5146670789
H	1.0060396702	1.5663897112	4.4152895436
C	-1.4912521567	1.9137271124	3.2360522436
H	-1.5733742008	1.4727005354	4.2435113851
H	-1.5679992831	3.0085994810	3.3438440548
H	-2.3537288965	1.5681677902	2.6409060764
H	1.0692864743	1.8330606829	-3.1013972527
H	-0.6749633010	1.7644132643	-3.2105691363

Table 1-11. Coordinates of the Planar Optimized Structure of **2** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	0.0591541196	-0.0119401992	0.0033211522
C	0.0005601286	-0.7556994888	1.3007197076
C	-0.1070112641	-0.0290983016	2.5189782610
C	0.0528904689	-2.1772801915	1.2947877955
C	-0.1608552071	-0.7428636940	3.7144809784
C	-0.0045070219	-2.8481658122	2.5147363352
C	-0.1105563723	-2.1412417453	3.7176847350
H	-0.2437740155	-0.2256622997	4.6761847412
H	0.0320749875	-3.9417735725	2.5589642708
H	-0.1543187406	-2.6849421720	4.6660296339
C	0.1752379138	-0.7702743894	-1.3118578346
C	0.2303373610	-0.0544156852	-2.5304756175
C	0.2283511513	-2.1739569349	-1.3125156833
C	0.3393968096	-0.7468246456	-3.7570841401
C	0.3383566955	-2.8427381721	-2.5625589442
C	0.3934233365	-2.1416259978	-3.7699805013
H	-0.2295127163	4.2265609851	2.0543034467
H	0.0567330039	4.1408118776	-2.2321150056
H	-0.1301717324	5.4225032674	-0.0957062250
C	0.1704998321	-2.9919689691	-0.0148321104
C	-0.1651816934	1.5161632860	2.5543277726
C	0.1729276352	1.4447976844	-2.5382873406
C	-1.0554047733	-3.9302216817	-0.1133869124
H	-1.9871532188	-3.3419303126	-0.1661334812
H	-1.0061883639	-4.5811812965	-1.0038793637
H	-1.1162466000	-4.5830025170	0.7733733675
C	1.4620666719	-3.8401537031	0.0572377984
H	1.4492687556	-4.4897228558	0.9482813682
H	1.5794250899	-4.4902135463	-0.8275247151
H	2.3483559304	-3.1869149078	0.1264475489
C	1.0261626000	2.0263639566	3.3987706249
H	1.9821243755	1.7350903864	2.9315307955

H	0.3816119522	-0.1877850325	-4.6986692173
H	0.3819989697	-3.9352291083	-2.5967016941
H	0.4779830341	-2.6841674875	-4.7152075651
C	0.0048362615	1.5095324472	-0.0127228056
C	-0.1003579921	2.2226595971	1.1928941471
C	0.0614902368	2.1993401196	-1.2462522578
C	-0.1474314661	3.6424889982	1.1330352675
C	0.0126223597	3.6108922635	-1.2739221134
C	-0.0918224396	4.3301192353	-0.0821200616
H	1.0146562598	3.1251119740	3.5072758763
H	0.9974475561	1.5914926874	4.4118001921
C	-1.4914489486	1.9353735811	3.2311055579
H	-1.5666590493	1.4981477108	4.2407638902
H	-1.5731980393	3.0315399399	3.3355440774
H	-2.3536075909	1.5790282504	2.6422582934
H	1.0600769579	1.8287382564	-3.0953094189
H	-0.6657391045	1.7608062601	-3.2031058146

Table 1-12. Coordinates of the Bowl-Shaped Optimized Structure of **2** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	-0.4351732551	-0.0349408035	-0.0251599336
C	-0.1404585293	-0.7526513113	1.2988158226
C	0.1027076213	0.0480910947	2.4677322405
C	0.2117378627	-2.1248357361	1.2492387893
C	0.9270313960	-0.4710004085	3.4810000995
C	0.9867935246	-2.6122961795	2.2962615429
C	1.3404228274	-1.7917787305	3.3970031998
H	1.1755088368	0.1161903827	4.3671524273
H	1.3783050747	-3.6322276256	2.2726175534
H	1.9191548571	-2.2279695331	4.2172137583
C	-0.1734104531	-0.7812109037	-1.3167683793
C	0.0343047521	-0.0359403982	-2.5017353386
C	0.0697897086	-2.1783090832	-1.2879525242
C	0.4598516853	-0.6878998255	-3.6559092054
C	0.5008212284	-2.8040102839	-2.4583640751
C	0.6869374489	-2.0671996089	-3.6342799112
H	0.6316706209	-0.1223060013	-4.5787815254
H	0.7097077709	-3.8763930392	-2.4814484663
H	1.0276167124	-2.5769434289	-4.5409087796
C	-0.2239573612	1.4762156646	0.0333303445
C	-0.0109533619	2.1086931365	1.3035245285
C	0.0627526041	2.1567253986	-1.1734929331
C	0.6636831485	3.3426117731	1.3435629486
C	0.6768754614	3.4005224299	-1.0974126014
C	0.9749406010	3.9885576785	0.1548863160
H	0.8797690334	3.8375969316	2.2924928787
H	0.9771302609	3.9196119415	-2.0144519572
H	1.4382876481	4.9795063789	0.1852491616
C	-0.2105885068	-2.9461779557	0.0214181974
C	-0.5751115681	1.4168260607	2.5490036411
C	-0.2309316410	1.4600614160	-2.4841910084
C	-1.7420783435	-3.1502702038	0.1217931127
H	-2.2666293141	-2.1797015469	0.1257803531
H	-2.1038774261	-3.7313715409	-0.7444523055
H	-2.0048055482	-3.6936376420	1.0476749877
C	0.4430100719	-4.3288081517	0.0246529874
H	0.2098741217	-4.8708332062	0.9569688101
H	0.0518563269	-4.9449848704	-0.8006714775
H	1.5398944082	-4.2701917675	-0.0830007196
C	-0.2406521935	2.1618291802	3.8371397531
H	0.8428728343	2.3134924826	3.9727196342
H	-0.7276432865	3.1512556039	3.8407192883
H	-0.6217743354	1.6047023060	4.7094386935
C	-2.1045481926	1.2784356177	2.4553359209
H	-2.4874837733	0.7185624117	3.3269740848
H	-2.5726452679	2.2785761897	2.4455083516
H	-2.4057984440	0.7456925771	1.5391455759
H	0.3181958840	1.9532064896	-3.3044958268
H	-1.3089295113	1.6161850785	-2.7066825334

Table 1-13. Coordinates of the Optimized Structure of **5** in the Ground S_0 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*		*x*	*y*	*z*
B	-0.0007581224	-0.2018110269	0.0112296110	H	-8.4065315335	-5.0771815308	-0.1367560593
C	-1.3245964616	-0.9550412955	-0.0026696103	C	0.0175613847	5.5958251629	0.0538389770
C	-3.7391290466	-2.3726508357	-0.0408772489	C	0.0264050630	8.4144442511	0.0742570467
C	-1.3101458954	-2.3641169568	-0.0103675688	C	-0.9148441746	6.3155478350	0.8176658514
C	-2.5390614223	-0.2409205800	-0.0126951533	C	0.9544958106	6.3207000536	-0.6995173941
C	-3.7313334440	-0.9686818453	-0.0330613665	C	0.9585481977	7.7137701453	-0.6911162189
C	-2.5174155729	-3.0598555737	-0.0272963398	C	-0.9101544136	7.7085923490	0.8294242994
H	-4.6956432603	-0.4534045742	-0.0167080309	H	-1.6385387900	5.7730251151	1.4333955695
H	-2.5163785959	-4.1545856735	-0.0598467436	H	1.6748115710	5.7826200442	-1.3230615814
C	0.0040445766	1.3186644785	0.0209963967	H	1.6922303490	8.2569640885	-1.2948201894
C	0.0128540379	4.1136497021	0.0427865458	H	-1.6404243621	8.2475634250	1.4409953292
C	-1.2257244539	2.0115373609	0.0239570801	H	0.0298384901	9.5086382456	0.0822087672
C	1.2381589321	2.0037412332	0.0281596375	C	5.0020408209	-3.1469802106	-0.0097263226
C	1.2188730097	3.3997734287	0.0371192787	C	7.4320160676	-4.5755684178	-0.0315817103
C	-1.1976435141	3.4073838896	0.0373931874	C	6.0986845089	-2.6958990544	-0.7613353090
H	2.1515679391	3.9693901625	0.0690045002	C	5.1508655385	-4.3306561836	0.7303330058
H	-2.1267296511	3.9833383215	0.0157203509	C	6.3518597457	-5.0364239595	0.7211089899
C	1.3183134078	-0.9634939062	0.0111850770	C	7.2994580159	-3.4019379357	-0.7736339406
C	3.7240199959	-2.3964898541	0.0003218942	H	5.9990833999	-1.7907231463	-1.3678394845
C	2.5373552778	-0.2571314217	0.0153174726	H	4.3188319773	-4.6892938483	1.3436308631
C	1.2949482135	-2.3724422263	0.0032700137	H	6.4470346894	-5.9513323985	1.3141480392
C	2.4978700982	-3.0758709666	-0.0004829822	H	8.1369478149	-3.0357895189	-1.3755839100
C	3.7251091442	-0.9924798824	0.0088619193	H	8.3752695993	-5.1301276109	-0.0400039732
H	2.4901293744	-4.1705677077	-0.0333003500	C	-3.3695736309	1.7298204473	1.2661241668
H	4.6924116561	-0.4834248366	0.0382080560	H	-2.8397846673	1.4076800409	2.1788032179
C	-2.5899354118	1.2959928919	0.0046147221	H	-4.3794389399	1.2870481876	1.2836911811
C	2.5977528915	1.2793542734	0.0397556198	H	-3.4852951867	2.8258506136	1.3068071861
C	-0.0100006194	-3.1367878911	-0.0131099687	C	-3.3497309149	1.7570514667	-1.2593778014
H	-0.0166977607	-3.8280516313	0.8521240964	H	-4.3594535959	1.3151659685	-1.3001862989
H	-0.0075621659	-3.8042827678	-0.8968511856	H	-2.8064377171	1.4530248760	-2.1703328038
C	-5.0216999600	-3.1150150709	-0.0659410591	H	-3.4647754618	2.8535312009	-1.2806726560
C	-7.4600393358	-4.5284631623	-0.1169428328	C	3.3467869800	1.7007319708	1.3241545972
C	-5.1869075812	-4.2973386164	0.6727804331	H	2.7909606473	1.3762694185	2.2203236631
C	-6.1062422038	-2.6574627701	-0.8310799965	H	3.4679773679	2.7956588768	1.3757977904
C	-7.3111424099	-3.3560318540	-0.8577984931	H	4.3525943573	1.2501042994	1.3650270649
C	-6.3920799860	-4.9956315370	0.6491411274	C	3.3934695378	1.7426244903	-1.2007849142
H	-4.3646460827	-4.6608663372	1.2962968962	H	3.5164284024	2.8384531000	-1.2112575616

H	-5.9936175033	-1.7532579399	-1.4367481802
H	-8.1388842238	-2.9850085430	-1.4701542835
H	-6.5001624684	-5.9096469105	1.2413427029
H	2.8726686174	1.4478414805	-2.1278317078
H	4.4014922978	1.2955931248	-1.2180485413

Table 1-14. Coordinates of the Planar-Like Optimized Structure of **5** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	-0.0011227731	-0.2137317280	0.0140813935
C	-1.3212740296	-0.9472082372	0.0076419650
C	-3.7530431373	-2.3778664168	-0.0239455257
C	-1.3164782324	-2.3674863955	0.0055164943
C	-2.5483270430	-0.2403685180	-0.0057850513
C	-3.7347119258	-0.9667382710	-0.0255529598
C	-2.5183763937	-3.0585326015	-0.0050996760
H	-4.6964444197	-0.4463267768	-0.0080903755
H	-2.5096641306	-4.1533024436	-0.0354775814
C	0.0042709784	1.3101054466	0.0166383267
C	0.0130568035	4.1302115895	0.0301835201
C	-1.2407009616	2.0191419063	0.0250009125
C	1.2535286256	2.0113406636	0.0137561958
C	1.2309060507	3.3922201840	0.0095788863
C	-1.2094218119	3.3997115494	0.0429437426
H	2.1705493102	3.9466879425	0.0352674272
H	-2.1455734731	3.9603750747	0.0247206615
C	1.3147791128	-0.9551894312	0.0095655102
C	3.7377427047	-2.4016026877	-0.0110781537
C	2.5467228017	-0.2560278691	0.0026333542
C	1.3009237668	-2.3759487188	0.0083158113
C	2.4982067527	-3.0743985686	0.0026194846
C	3.7281982616	-0.9898923711	-0.0119700805
H	2.4823039604	-4.1690390743	-0.0276127022
H	4.6929058748	-0.4754670553	0.0130020731
C	-2.6067770007	1.3008558620	0.0090399109
C	2.6151437817	1.2846365468	0.0277605382
C	-0.0102470107	-3.1381383315	0.0011911050
H	-0.0129247815	-3.8257161328	0.8701757346
H	-0.0112969659	-3.8123029963	-0.8783152075
C	-5.0275131059	-3.1148699209	-0.0417874822
C	-7.4762088186	-4.5341673056	-0.0768130157
C	-5.1519783037	-4.3758271125	0.5749202635
H	-8.4226829729	-5.0829640315	-0.0904600819
C	0.0177993143	5.5806259608	0.0390983066
C	0.0270170827	8.4166087293	0.0558041977
C	-1.1203323549	6.3268406201	0.4549459425
C	1.1608302352	6.3243063705	-0.3677973628
C	1.1603771814	7.7090652144	-0.3638659381
C	-1.1109078538	7.7115246563	0.4671956241
H	-2.0106283848	5.8032510093	0.8090841972
H	2.0477918639	5.7991795435	-0.7279652521
H	2.0503499650	8.2508846680	-0.6973087647
H	-1.9973382554	8.2551447133	0.8070771927
H	0.0305617279	9.5105185425	0.0622766301
C	5.0071237998	-3.1461095736	-0.0223837851
C	7.4474175066	-4.5806176456	-0.0459276821
C	6.1592558333	-2.6227234521	-0.6435420856
C	5.1183911387	-4.4128236231	0.5859015174
C	6.3177721692	-5.1172417117	0.5751018580
C	7.3582418944	-3.3278398145	-0.6558305611
H	6.1030479863	-1.6583458535	-1.1562936873
H	4.2542636016	-4.8378604837	1.1040235715
H	6.3746386601	-6.0938992138	1.0660999406
H	8.2318532410	-2.8991251047	-1.1570711904
H	8.3905326259	-5.1352418713	-0.0551181336
C	-3.3828864871	1.7382041096	1.2711933870
H	-2.8498653684	1.4188157974	2.1829109913
H	-4.3889710065	1.2873414086	1.2922527123
H	-3.5086706470	2.8341926717	1.3124784067
C	-3.3671961227	1.7624195720	-1.2539370512
H	-4.3729804312	1.3120015869	-1.2944638811
H	-2.8235526404	1.4594782399	-2.1650119834
H	-3.4928569571	2.8588338022	-1.2771946084
C	3.3601098187	1.7077330495	1.3134824760
H	2.8009444789	1.3846763141	2.2080820267

C	-6.1701122114	-2.5890608288	-0.6774639420
C	-7.3735914316	-3.2867499849	-0.6952788837
C	-6.3557297589	-5.0730288474	0.5584619100
H	-4.2949854596	-4.8021156862	1.1038722787
H	-6.1029221400	-1.6288424923	-1.1967624970
H	-8.2398520853	-2.8563543512	-1.2077419004
H	-6.4230929009	-6.0455539787	1.0563188512
H	3.4905999094	2.8026895730	1.3667854049
H	4.3621048703	1.2490661958	1.3573674194
C	3.4121768259	1.7500902727	-1.2107713711
H	3.5461578725	2.8456410923	-1.2220366407
H	2.8915353242	1.4577522381	-2.1386040198
H	4.4163781875	1.2950259755	-1.2280990349

Table 1-15. Coordinates of the Bowl-Shaped Optimized Structure of **5** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	-0.3168481368	-0.1520255679	0.2777639541
C	-0.7200504789	-0.7473644317	1.6445074478
C	-0.4651388825	0.0197215213	2.8257583009
C	-1.0375373716	-2.1434361335	1.7150542751
C	-0.3312252071	-0.6609752453	4.0199438631
C	-0.8741356432	-2.7869692960	2.9269790594
C	-0.5139299691	-2.0712210818	4.1003280587
H	-0.0376799354	-0.1257675307	4.9233481952
H	-1.0719003586	-3.8560973115	3.0090194197
C	-0.1415518676	-1.1380533667	-0.8614243046
C	0.6524877584	-0.7531152049	-1.9713007413
C	-0.5564238817	-2.4924036012	-0.7175661303
C	1.0445012127	-1.7088585972	-2.8947857227
C	-0.1257505156	-3.4323139664	-1.6477000609
C	0.6689622005	-3.0653923536	-2.7525093659
H	1.7000872935	-1.4208876202	-3.7230603344
H	-0.4374916342	-4.4750727315	-1.5648697612
C	0.4728042197	1.1413861919	0.3024061927
C	0.6204475161	1.8749838338	1.5107362358
C	1.2480163859	1.4828740131	-0.8331058583
C	1.5584415586	2.9003615698	1.5667163802
C	2.1607827450	2.5238583599	-0.7525845871
C	2.3381119451	3.2498392598	0.4454168678
H	1.6847005001	3.4862745483	2.4791528965
H	2.7919454616	2.7562540679	-1.6167098132
C	-1.5192602408	-2.8362190444	0.4347886014
C	-0.3227990614	1.5399870422	2.6827280189
C	1.0490720777	0.7017045504	-2.1164963541
C	-2.9133526811	-2.2636711272	0.0880302375
C	-1.7247252106	2.0982878679	2.3387181875
H	-2.4415868736	1.8805130168	3.1511072075
H	-1.6700759051	3.1921824755	2.1984615377
H	-2.1088172792	1.6547165127	1.4047367532
H	1.9427942561	0.7893356530	-2.7580756748
H	0.2310181988	1.2043462768	-2.6779843112
C	1.0937895973	-4.0720561852	-3.7405859647
C	1.2774690080	-3.7331927614	-5.0952841699
C	1.3345086096	-5.4087297853	-3.3670314980
C	1.6793604279	-4.6829755132	-6.0295194699
H	1.0720758645	-2.7112589415	-5.4261820021
C	1.7373022218	-6.3584688745	-4.3005579004
H	1.2340958411	-5.6997514730	-2.3175208120
C	1.9120740092	-6.0026437775	-5.6391307962
H	1.8040516380	-4.3913386973	-7.0771218062
H	1.9276241238	-7.3869314089	-3.9777610628
H	2.2291405500	-6.7493534632	-6.3733823442
C	3.3193814253	4.3480626113	0.5238120075
C	3.6000267340	5.1566058256	-0.5937745613
C	4.0137691776	4.6248405884	1.7166993161
C	4.5280004724	6.1916394935	-0.5220844735
H	3.0581685615	4.9869595112	-1.5286284059
C	4.9417917583	5.6595025989	1.7892663487
H	3.8443097039	3.9954973470	2.5951664405
C	5.2054749427	6.4508085970	0.6701567116
H	4.7178328069	6.8092258639	-1.4057054435
H	5.4737486954	5.8434753892	2.7281263694
H	5.9355091109	7.2639194966	0.7266591636
C	-0.3869022549	-2.7658410756	5.3772751233

H	-2.8687298725	-1.1711721971	-0.0556139937
H	-3.2838729093	-2.7160050116	-0.8486959833
H	-3.6347127917	-2.4822144477	0.8961081067
C	-1.6724466534	-4.3438511582	0.6291834780
H	-2.3793125489	-4.5623603865	1.4475368556
H	-2.0896558902	-4.8093507156	-0.2783308318
H	-0.7107769565	-4.8356011449	0.8553729366
C	0.1264353051	2.1904091159	3.9905872692
H	1.1358235324	1.8633156703	4.2938621090
H	0.1373336267	3.2878743096	3.8931825282
H	-0.5785576621	1.9561692751	4.8063719865
C	-0.5516732102	-2.0889476125	6.6102698431
C	-0.0835448217	-4.1485713223	5.4314909825
C	-0.4236676423	-2.7550150019	7.8206149189
H	-0.8185003773	-1.0296222208	6.6148135693
C	0.0544846281	-4.8092763965	6.6436699499
H	0.0866479575	-4.7012336436	4.5045881571
C	-0.1175019396	-4.1191834848	7.8472821658
H	-0.5694952824	-2.2083114603	8.7569561951
H	0.3073210875	-5.8736213793	6.6537865682
H	-0.0120885482	-4.6418208855	8.8025675641

Table 1-16. Coordinates of the Optimized Structure of **6′** in the Ground S_0 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	-0.0002450358	-0.1689846173	0.0390483700
C	1.3223484786	-0.9235458589	0.0432569601
C	3.7379893718	-2.3454247187	0.0357708029
C	1.3072522894	-2.3324999101	0.0271041606
C	2.5381158713	-0.2116790915	0.0572597640
C	3.7294494637	-0.9408159261	0.0542050374
C	2.5137024450	-3.0294764813	0.0238557861
H	4.6932622700	-0.4257846711	0.0938862333
H	2.5101234899	-4.1239366694	-0.0182383903
C	-1.3195839485	-0.9287396481	0.0114531830
C	-3.7287565022	-2.3601296384	-0.0549189410
C	-2.5381455503	-0.2217240724	-0.0029273848
C	-1.2985011308	-2.3376399547	-0.0052350880
C	-2.5017372287	-3.0392290904	-0.0392233211
C	-3.7262475107	-0.9555083391	-0.0350098859
H	-2.4929619727	-4.1335658805	-0.0836858368
H	-4.6925747971	-0.4439954232	-0.0172550411
C	-0.0034544063	1.3509540157	0.0562622817
C	-0.0094011000	4.1487319875	0.0923044352
C	1.2264030669	2.0430607920	0.0835951854
C	-1.2362920045	2.0383038704	0.0463441848
C	-1.2154571825	3.4339838738	0.0652801527
C	1.1996813199	3.4386919513	0.1020071795
H	-2.1486326466	4.0032940324	0.0889244258
H	2.1305970422	4.0121258120	0.0958796068
H	1.6658963686	5.8161174212	1.4663744073
H	-1.6840961460	5.8395287920	-1.2412766687
H	-1.7068620262	8.2879449183	-1.2168570016
H	1.6592514884	8.2990964433	1.4743620546
C	5.0179468564	-3.0889609975	0.0258071198
C	7.4655802924	-4.5149788961	0.0007703806
C	5.1674905869	-4.2988260059	0.7285198635
C	6.1288898098	-2.6208082836	-0.6860487867
C	7.3387661515	-3.3146563769	-0.7073982903
C	6.3636860766	-4.9988978881	0.7210263102
H	4.3308276036	-4.6864260958	1.3173097449
H	6.0453473840	-1.6983256845	-1.2684432753
H	8.1709099822	-2.9127895619	-1.2890123593
H	6.4785645305	-5.9318686185	1.2789827909
C	-3.3663982873	1.7283176179	1.3058250338
H	-4.3732977668	1.2786912513	1.3269083402
H	-3.4866333548	2.8230929937	1.3637289494
H	-2.8255641290	1.3963371890	2.2083992427
C	-3.3718045800	1.7879381781	-1.2189101626
H	-4.3796040679	1.3415061656	-1.2564715471
H	-2.8356467045	1.4995289328	-2.1391998087
H	-3.4936315528	2.8839957649	-1.2233564049
C	3.3472407410	1.7514116904	1.3620982268
H	3.4627169420	2.8471800497	1.4112705702
H	4.3562101543	1.3073624102	1.3957219486

C	0.0060323249	-3.1035738499	0.0000622682
H	0.0183649241	-3.7705562235	-0.8839467131
H	-0.0033217181	-3.7952160215	0.8650636958
C	-2.5969214635	1.3150511472	0.0310061098
C	2.5901280640	1.3254568709	0.0843913912
C	-5.0058214487	-3.1077126621	-0.0931320672
C	-7.4491556689	-4.5394304905	-0.1675626125
C	-6.1082414133	-2.6368472421	-0.8300141739
C	-5.1677456477	-4.3126825989	0.6010667320
C	-6.3662461761	-5.0258042069	0.5734598322
C	-7.3050271168	-3.3347107504	-0.8710637951
H	-6.0146149122	-1.7128976392	-1.4083797743
H	-4.3429538389	-4.6996642429	1.2068843497
H	-6.4446321774	-5.9542626282	1.1427290531
H	-8.1541345230	-2.9711057857	-1.4556514152
C	-0.0118400381	5.6290453923	0.1089374269
C	-0.0146910259	8.4616492271	0.1374915682
C	0.9313671775	6.3544272120	0.8599646720
C	-0.9506266000	6.3658329794	-0.6230148263
C	-0.9611394738	7.7607532032	-0.6183532898
C	0.9325720461	7.7403679546	0.8787863267
H	2.8004974124	1.4245025782	2.2630092514
C	3.3732946887	1.7925680910	-1.1628713328
H	3.4901976221	2.8890154768	-1.1761671681
H	2.8459636493	1.4942541186	-2.0850512588
H	4.3828546416	1.3490285762	-1.1878814229
O	-8.6480349856	-5.1488545027	-0.2631192011
O	0.0627639149	9.8055905145	0.2133215219
O	8.5869269057	-5.2620633713	0.0484465785
C	-8.8495052450	-6.3594841557	0.4080597487
H	-8.1530640485	-7.1451823585	0.0562557329
H	-9.8809929527	-6.6717219035	0.1853944255
H	-8.7383745073	-6.2456055547	1.5038665194
C	-0.8610699110	10.5798576392	-0.4963867645
H	-0.7885888183	10.4087114338	-1.5879790785
H	-0.6155854306	11.6313198465	-0.2837784738
H	-1.9004011523	10.3812115380	-0.1700759885
C	9.7212118187	-4.8288832735	-0.6460886612
H	9.5356230172	-4.7624507103	-1.7357063301
H	10.5045498095	-5.5799456773	-0.4635184185
H	10.0757024762	-3.8451593113	-0.2817052139

Table 1-17. Coordinates of the Planar-Like Optimized Structure of **6′** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	0.0067188282	-0.1258403753	-0.3166721425
C	1.3069761863	-0.8933293952	-0.3064290607
C	3.7061606867	-2.3622230469	-0.0873210822
C	1.2935337048	-2.3093517505	-0.4083788314
C	2.5316785704	-0.2037253769	-0.1200620188
C	3.7019318385	-0.9495301376	-0.0267219192
C	2.4729498457	-3.0233557146	-0.2761947361
H	4.6570543585	-0.4442288049	0.1406625718
H	2.4569538147	-4.1142638867	-0.3727962768
C	-1.3180327166	-0.8896979703	-0.3403045612
C	-3.7177612259	-2.3556638684	-0.1457620659
C	-2.5460995958	-0.1911685527	-0.1831023189
C	-1.2968839987	-2.3126824327	-0.4391699755
C	-2.4732111899	-3.0227357638	-0.3081489522
C	-3.7149152930	-0.9337063622	-0.1050659582
H	1.7901224116	5.8010303276	1.3361118991
H	-1.7959235538	5.9237692869	-1.0526535988
H	-1.8198881617	8.3628382096	-0.9163352674
H	1.7860777898	8.2750221681	1.4419238166
C	4.9594933247	-3.1195736477	0.0304245891
C	7.3834326385	-4.5878352386	0.2602955048
C	4.9863227852	-4.4301436074	0.5583210936
C	6.1939204354	-2.5807727333	-0.3761746171
C	7.3868902984	-3.2907091856	-0.2686384153
C	6.1638126022	-5.1479372127	0.6732015935
H	4.0582424588	-4.8834666765	0.9171943399
H	6.2241229252	-1.5828799136	-0.8221131029
H	8.3132053540	-2.8254037741	-0.6122326164
H	6.1744286592	-6.1558348802	1.0966839062
C	-3.3560267826	1.7358852001	1.1878087207

H	-2.4470751178	-4.1132979881	-0.3913186461
H	-4.6673703989	-0.4202048037	0.0423119090
C	-0.0069370718	1.3698094802	-0.1472161499
C	-0.0068094248	4.1795070840	0.0521213665
C	1.2263409103	2.0663176446	-0.0460974230
C	-1.2394543201	2.0707625604	-0.0952428405
C	-1.2149449971	3.4588666792	-0.0093657895
C	1.2009438347	3.4534046565	0.0475653609
H	-2.1496749086	4.0243745954	0.0489932825
H	2.1371678610	4.0175272478	0.0866633030
C	0.0021109031	-3.0227925466	-0.7590809548
H	0.0088408352	-3.1954638696	-1.8578600124
H	-0.0068317818	-4.0329690598	-0.3114462047
C	-2.6067417611	1.3480581472	-0.1058109622
C	2.5893022021	1.3359231957	-0.0356612368
C	-4.9585688545	-3.1017575804	-0.0380226712
C	-7.3833971739	-4.5744827442	0.1819353030
C	-6.2246952575	-2.5045503919	-0.3009591042
C	-4.9748004365	-4.4718856218	0.3380392051
C	-6.1482617918	-5.1955306440	0.4514900789
C	-7.3991117737	-3.2147294157	-0.1983217953
H	-6.2727464924	-1.4631673964	-0.6250445510
H	-4.0352283895	-4.9721680083	0.5809227348
H	-6.1022700451	-6.2416437410	0.7602357251
H	-8.3649221010	-2.7517232304	-0.4153694013
C	-0.0066339946	5.6508000929	0.1303111449
C	-0.0073610404	8.4892635127	0.2782868321
C	1.0023530196	6.3564815961	0.8192861418
C	-1.0096760966	6.4223276219	-0.4783834091
C	-1.0208030126	7.8149610252	-0.4122386566
C	1.0057027256	7.7397177155	0.8943231666
H	-4.3738984029	1.3096951272	1.2167030745
H	-3.4551453327	2.8303225134	1.2747373312
H	-2.8069476831	1.3754446259	2.0743615764
C	-3.4068351068	1.8369523078	-1.3331628192
H	-4.4167799856	1.3902892523	-1.3603473083
H	-2.8862020870	1.5649139720	-2.2672189719
H	-3.5244487338	2.9337455390	-1.3174070633
C	3.3157510971	1.7223988089	1.2709996599
H	3.4254784658	2.8164367814	1.3583842600
H	4.3264861230	1.2827976849	1.3177986717
H	2.7477580911	1.3663310485	2.1474035740
C	3.4081114766	1.8298914748	-1.2487984005
H	3.5342925682	2.9260565979	-1.2280160519
H	2.8995793053	1.5629585950	-2.1909664414
H	4.4127091983	1.3721570698	-1.2615734648
O	-8.5687368221	-5.1789379216	0.2577699942
O	0.0771053358	9.8318595675	0.4029500415
O	8.4789314605	-5.3594630349	0.4093053374
C	-8.6467144448	-6.5338908372	0.6257585202
H	-8.1043179640	-7.1767783546	-0.0916979370
H	-9.7144535877	-6.7949390574	0.6106772043
H	-8.2464131129	-6.6975307663	1.6432361847
C	-0.9089953350	10.6279343805	-0.1852385342
H	-0.9398532502	10.5008731938	-1.2851690570
H	-0.6472471038	11.6720469933	0.0448698629
H	-1.9139656330	10.4112088347	0.2271806886
C	9.7245371047	-4.8522730323	0.0251795052
H	9.7565457634	-4.6172609987	-1.0564387847
H	10.4623476243	-5.6398436810	0.2408593703
H	9.9918122393	-3.9430174060	0.5978277314

Table 1-18. Coordinates of the Bowl-Shaped Optimized Structure of **6′** in the Excited S_1 State Calculated at the PBE0/def-SV(P) Level of Theory

	x	*y*	*z*
B	-2.0510991391	0.4142060439	-0.0802774337
C	-1.9838189301	1.3556222052	-1.3042332841
C	-1.4616106382	2.6739288304	-1.1283191392
C	-2.6937707974	0.9947666622	-2.4895147259
C	-1.8123083570	3.6472467079	-2.0461536876
C	-3.0085476676	1.9934768097	-3.3927244694
C	-6.3131263565	-3.5118296207	-0.2289786487
C	-7.2038717038	-3.6164018118	0.8511995557
C	-6.5603626844	-4.3505542728	-1.3359082088
C	-8.2834307315	-4.4981777408	0.8424133610
H	-7.0718015231	-2.9663832265	1.7207319144
C	-7.6282369663	-5.2329413639	-1.3600782845

C	-2.6015870116	3.3404233310	-3.1871008817
H	-1.4502222283	4.6679848943	-1.9207751664
H	-3.6236101847	1.7628515066	-4.2629875481
C	-3.0255236430	-0.7459664843	-0.1659391790
C	-3.4832934044	-1.3379967899	1.0377288929
C	-3.6435850495	-1.0844834214	-1.3995986512
C	-4.5422626820	-2.2324771882	1.0064537841
C	-4.7091034713	-1.9786591642	-1.3975993980
C	-5.1791982725	-2.5707344919	-0.2068534852
H	-4.8811364121	-2.6978434126	1.9381781711
H	-5.2317455338	-2.2178931896	-2.3259437098
C	-1.7149564067	1.0280816111	1.2667115048
C	-1.1272838689	2.3202412556	1.3487609487
C	-2.2043643830	0.3997686625	2.4397820532
C	-1.0711778440	2.9585323846	2.5830680372
C	-2.1266229834	1.0584370170	3.6569662020
C	-1.5602366172	2.3486615953	3.7569591585
H	-0.6688575163	3.9702810267	2.6642850130
H	-2.4950737162	0.5626372754	4.5613110626
C	-3.0608305859	-0.4823972616	-2.6925509208
C	-0.5304896176	2.9283509967	0.0658156421
C	-2.7727924907	-1.0000665435	2.3323603086
C	-1.7422634681	-1.2332124846	-3.0017394042
H	-1.0228155546	-1.1218563355	-2.1732176327
H	-1.9437080828	-2.3108122382	-3.1355895171
H	-1.2769360611	-0.8418372288	-3.9248231219
C	-3.9913129413	-0.6759234448	-3.8899246600
H	-3.5309404458	-0.2830408071	-4.8125101780
H	-4.1755302499	-1.7475893876	-4.0676483120
H	-4.9667371259	-0.1805619785	-3.7442574315
C	-0.2067492139	4.4134242908	0.2274650730
H	-1.1041619718	5.0133926964	0.4573795163
H	0.5216021596	4.5635887586	1.0405767640
H	0.2608533961	4.8151823338	-0.6874650177
C	0.7991406049	2.1921887523	-0.2283907266
H	1.2693879975	2.5887688932	-1.1466705104
H	1.4999369128	2.3256606514	0.6147317861
H	0.6290329036	1.1107104566	-0.3615627410
H	-3.4293870977	-1.2117815035	3.1939862375
H	-1.9188554533	-1.7062116195	2.4298214253

H	-5.8763031596	-4.3305169346	-2.1890763788
C	-8.5060960925	-5.3185028351	-0.2695192203
H	-8.9507709132	-4.5268695973	1.7064080342
H	-7.8026350854	-5.8879449363	-2.2179443604
C	-1.4822970015	3.0407376073	5.0547227965
C	-2.4498292624	2.8351675414	6.0611905135
C	-0.4435665520	3.9373957420	5.3535917693
C	-2.3845725533	3.4878587558	7.2809474533
H	-3.2934007077	2.1668617718	5.8671607752
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C	-1.3379183119	4.3807985159	7.5561625733
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C	-2.9406673316	5.7558554175	-3.7895790220
C	-3.3207652685	4.0751468450	-5.4789368441
C	-3.2835833052	6.7415088110	-4.6882383875
H	-2.6937097082	6.0471069802	-2.7665920845
C	-3.6597141846	5.0561706843	-6.3956451427
H	-3.3137522766	3.0367376371	-5.8165092346
C	-3.6478071272	6.4093324788	-6.0097764449
H	-3.2936449545	7.7954968405	-4.3997051860
H	-3.9252427402	4.7651988787	-7.4137533787
O	-9.5181393908	-6.2056427865	-0.3802150795
O	-1.3542236105	4.9695799464	8.7706452591
O	-3.9615543919	7.4292979916	-6.8100361178
C	-0.3383775706	5.8716452002	9.0994958104
H	-0.3203016225	6.7398809977	8.4121023174
H	-0.5542804305	6.2281044781	10.1181928266
H	0.6586202179	5.3893775987	9.0927402888
C	-10.4164751346	-6.3421322535	0.6818348154
H	-10.9611250725	-5.3992821729	0.8845923758
H	-11.1413410570	-7.1140432493	0.3813998692
H	-9.9093896333	-6.6686963589	1.6107341282
C	-4.3457121987	7.1857943056	-8.1401021388
H	-5.2564289345	6.5607195285	-8.1879461281
H	-4.5583982328	8.1691501172	-8.5833075035
H	-3.5339783403	6.6980870319	-8.7108439153

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14. Our preliminary calculations of Mes_3B at the TD-B3LYP/def2-SV(P)//B3LYP/def2-SV(P) level of theory showed that one B–C bond is elongated (1.590 Å in the S_0 state and 1.611 Å in the S_1 state) and torsion angles between the benzene moieties and the boron plane are changed by ~10° in the excited S_1 state. The calculation of the fluorescence wavelength for the S_1 optimized structure (λ_{em} = 396 nm, f = 0.0270) sufficiently reproduced the experimental observation (λ_{em} = 374 nm in THF).
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Chapter 2

A Radical Anion of Planarized Triphenylborane: Spin-Delocalization and Deformation to Non-planar Structure

Introduction

Triarylboranes with an extended π-conjugation have emerged as a promising class of electronic materials because of their characteristic electron-accepting ability due to conjugation through a vacant p orbital of the boron atom.[1] Their application as electron-transporting materials for organic light-emitting diodes (OLEDs) has attracted increasing attention.[2] For such use, the investigation of the one-electron-reduced species should provide crucial information, because they are assumed to be the real species for the electron transportation in the devices. Furthermore, triarylborane radical anions are also of interest as the isoelectronic congener of the triarylmethyl radicals, which represent one of the stable organic radicals.[3] Based on these characteristics, the reduction of the triarylboranes with alkali metals to form the corresponding radical anions has been studied for a long time.[4] The electrochemical reduction of triarylboranes has also been investigated.[5] The electron paramagnetic resonance (EPR) studies of the one-electron-reduced triarylboranes revealed the distribution of the unpaired electron spin density, which is mainly localized on the boron center.[6–9] However, the structural information about the radical anions is still quite limited. X-ray crystallographic analysis of the triarylborane radical anion has been achieved only for trimesitylborane, namely $[Li(12\text{-crown-}4)_2]^+[Mes_3B]^{\bullet-}$ (Mes = 2,4,6-trimethylphenyl).[10] Therefore, the accumulation of more information about the structure–properties relationship for the radical anions of the triarylboranes is required for advancing the applied chemistry of the triarylborane-based materials.

Our group has recently reported the synthesis of a planarized triphenylborane **1**, in which three benzene rings are fixed in a coplanar fashion with the three methylene bridges.[11] Thanks to the structural constraint, the compound and its derivatives exhibit an outstanding stability not only to water and oxygen, but also to silica gel and amines, despite the absence of the steric protection of the boron atom. Based on this finding, a series of more π-extended planarized boranes has also been synthesized as a model system of the boron-doped graphene.[12] The planarized triphenylborane was also a useful precursor to produce a borataanthracene, which showed an intense fluorescence (Chapter 3).[13] In addition, compound **1** itself showed intriguing fluorescence properties with a significantly red-shifted emission despite its constrained structure (Chapter 1).[11] These results suggest the significant potential of this skeleton as a building unit for more elaborated triarylborane-based materials, including electron-transporting materials.

Based on this consideration, the author becomes interested in the reduced state of the planarized triphenylborane. In this chapter, the author reports the chemical reduction of the planarized triphenylborane **1** to produce its radical anion. The structure of the product was successfully determined by an X-ray crystallographic analysis. The author also investigated the electronic structure, especially the distribution of the unpaired electron spin density, of the radical anion by an EPR analysis as well as quantum chemical calculations. The author revealed that the structural constraint in a planar fashion not only effectively delocalizes the spin density over the molecule, but also allows the structural deformation into a non-planar bowl-shaped conformation upon the one-electron reduction.

Results and Discussion

Reduction of Planarized Triphenylborane 1

In our previous study, it was reported that the cyclic voltammetry analysis of the planarized triphenylborane **1** showed a reversible redox wave at the half-wave potential of –2.59 V (vs Fc/Fc^+) in THF with n-$Bu_4N^+PF_6^-$ as the supporting electrolyte.[11] The reversibility indicates the formation of a stable radical anion under the measurement conditions. Therefore, the author conducted the chemical reduction of **1** to isolate the radical anion species. The reaction of **1** with potassium metal in THF resulted in the immediate color change of the solution from colorless to deep blue. Recrystallization from the reaction mixture by slow diffusion of a hexane solution of [2.2.2]cryptand gave deep blue crystals of a potassium salt of the radical anion **1·K** in 62% yield (Scheme 2-1). The compound **1·K** was thermally stable in the solid state. It did not decompose up to 200 °C, at which the deep blue color of the crystals first turned to reddish purple then black.

Scheme 2-1. Chemical reduction of planarized triphenylborane **1**. Reproduced from *Organometallics* **2013**, *32*, 6654 with permission of the American Chemical Society.

EPR Analysis

The EPR spectrum of the radical anion **1·K** was measured in THF at 195 K (Figure 2-1a), which showed hyperfine splitting, and the *g* value was 2.0039. The simulation analysis successfully reproduced the spectrum. The hyperfine coupling constants for the boron atom and the peripheral hydrogen atoms were estimated as shown in Figure 2-1b. The most notable feature is the hyperfine coupling constant for the boron $a(^{11}B)$ of 6.2 G, which is lower than those of the radical anions of the conventional triarylboranes, such as $[Ph_3B]^{\bullet-}$ (7.84 G)[7] and $[Mes_3B]^{\bullet-}$ (9.87 G).[8] This result suggested a lower localized character of the spin density on the boron center in the planarized radical anion **1·K**. Furthermore, the hyperfine coupling constant for the peripheral hydrogen atoms ($a(p\text{-}^1H)$ = 3.1 G and $a(m\text{-}^1H)$ = 0.8 G) were greater than those of $[Ph_3B]^{\bullet-}$, in which $a(p\text{-}^1H)$ and $a(m\text{-}^1H)$ are 2.73 G and 0.670 G, respectively.[7] These comparisons clearly indicated that the unpaired electron spin is more delocalized over the three benzene rings in the planarized skeleton. A comparison with the isoelectronic triphenylmethyl radicals is also worthy of note. The hyperfine coupling constants for the peripheral hydrogen atoms of **1·K** were comparable to those of a neutral carbon congener **2**, in which the $a(p\text{-}^1H)$ and $a(m\text{-}^1H)$ were reported to be 3.13 G and 0.95 G, respectively (Figure 1-1c).[3c] These results demonstrate that the unpaired electron spin is similarly distributed on these methylene-bridged planarized structures regardless of the central atoms. In other words, the planarized framework in **1·K** is beneficial for the effective delocalization of the unpaired electron spin density over the entire molecule.

Figure 2-1. (a) EPR spectrum of **1·K** in THF at 195 K together with its simulated spectrum and hyperfine coupling constants of (b) the planarized triphenylborane radical anion **1·K**, and (c) the planarized triphenylmethyl radical **2**. Reproduced from *Organometallics* **2013**, *32*, 6654 with permission of the American Chemical Society.

Theoretical Studies of the Effect of the Structural Constraint

The author conducted theoretical calculations at the UB3PW91/6-31+G(d) level of theory[14] to clarify the origin of the greater extent of spin delocalization in the structurally constrained system **1·K**. The structural optimization gave a planar conformation **p-1**$^{\bullet-}$ as a local minimum structure. The author first compared the spin density on the boron atom between the optimized structures of **p-1**$^{\bullet-}$ and $[Ph_3B]^{\bullet-}$. The calculated spin density on the boron center in **p-1**$^{\bullet-}$ (0.502) was lower than that of $[Ph_3B]^{\bullet-}$ (0.574) (Figures 2-2a and b). Since the spin density ρ is correlated to the hyperfine coupling constants a in the EPR spectrum with McConnell's equation $a = Q \cdot \rho$, where Q is the proportional constant,[15] the calculated spin distributions are in good agreement with the experimental results that **1·K** has the lower $a(^{11}B)$ value than that of $[Ph_3B]^{\bullet-}$.

There are two structural differences between the planarized radical anion **p-1**$^{\bullet-}$ and $[Ph_3B]^{\bullet-}$. One is the dihedral angles of the phenyl groups to the plane of the central boron moiety, which are 0° in **p-1**$^{\bullet-}$, while those in $[Ph_3B]^{\bullet-}$ are twisted by 29.4°. The other difference is the B–C bond lengths. The previous report of the neutral **1** demonstrated the constrained **1** has the shorter B–C bond lengths (1.519(2)–1.520(2) Å)[11] by about 0.05–0.07 Å compared to those in Ph_3B (1.571(3)–1.589(5) Å).[16] In the radical anion species, the B–C bond length of the optimized structure of **p-1**$^{\bullet-}$ (1.516 Å) is 0.056 Å shorter than that (1.572 Å) in $[Ph_3B]^{\bullet-}$.

To elucidate the impacts of these structural differences on the spin delocalization, the author constructed several structurally constrained model geometries for $[Ph_3B]^{\bullet-}$ and assessed their spin distribution based on single-point calculations. When the dihedral angles of the phenyl groups to the boron plane were fixed to 0° while maintaining the B–C bond lengths of 1.572 Å, the spin density on the boron atom decreased to 0.538 (Figure 2-2c). On the other hand, when the B–C bond lengths were shortened to 1.520 Å while maintaining the propeller structure with the dihedral angle of 29.4°, this deformation also decreased the spin density to 0.536 (Figure 2-2d). Namely, these two different structural deformations result in the comparable degree of decrease in the spin density on the boron center to each other. This result suggests that both the coplanarization of the triphenylborane skeleton and the shortening of the B–C bond lengths almost equally contribute to the effective spin delocalization in **1**$^{\bullet-}$.

Figure 2-2. The calculated unpaired electron spin densities on the boron atom ρ(B) in (a) the optimized geometry of **p-1**$^{\bullet-}$, (b) the optimized geometry of $[Ph_3B]^{\bullet-}$, and model geometries of $[Ph_3B]^{\bullet-}$ with (c) the fixed dihedral angles, and (d) the shortened B–C bonds (UB3PW91/6-31+G(d)). Reproduced from *Organometallics* **2013**, *32*, 6654 with permission of the American Chemical Society.

Notably, the structural optimization of the radical anion **1**$^{\bullet-}$ at the UB3PW91/6-31+G(d) level also gave another local minimum structure in addition to the planar **p-1**$^{\bullet-}$ geometry, which has a bowl-shaped conformation **b-1**$^{\bullet-}$ (Figure 2-3). The **b-1**$^{\bullet-}$ conformation was estimated to be energetically less stable than the planar conformation **p-1**$^{\bullet-}$ only by +0.70 kcal/mol. This rather low ΔE_0 implies that **p-1**$^{\bullet-}$ and **b-1**$^{\bullet-}$ likely convert into each other at ambient temperature. Although the author also investigated the viability of the pyramidalized conformation for the non-constrained $[Ph_3B]^{\bullet-}$, the author could not find such a geometry as a local minimum in the geometry optimization. Thus, the bowl-shaped conformation is unique to the structurally constrained triphenylborane framework. The B–C bond length in **b-1**$^{\bullet-}$ is 1.531 Å, which is slightly more elongated than that (1.516 Å) in the **p-1**$^{\bullet-}$ conformation. To accommodate the elongated B–C bonds within the structurally constrained triphenylborane framework with the three methylene bridges, the molecule may be forced to take the bowl-shaped conformation. In the **b-1**$^{\bullet-}$ conformation, the sum of the C–B–C angles is 352.9°.

Figure 2-3. Optimized structures of the radical anions **p-1**$^{\bullet-}$ and **b-1**$^{\bullet-}$, and the energy difference, ΔE_0, calculated at the UB3PW91/6-31+G(d) level of theory. Reproduced from *Organometallics* **2013**, *32*, 6654 with permission of the American Chemical Society.

X-ray Crystallographic Analysis

The viability of the bowl-shaped conformation **b-1**$^{\bullet-}$ has been demonstrated by the X-ray crystal structure analysis of the **1·K** with [2.2.2]cryptand. As shown in Figure 2-4, it was revealed that the radical anion **1**$^{\bullet-}$ does not have a planar, but a shallow bowl-shaped structure. This is in contrast to a planar geometry around the boron center reported for $[Li(12\text{-crown-}4)_2]^+[Mes_3B]^{\bullet-}$.[10] Whereas the pyramidalized geometries were reported for the amine- or phosphine-coordinated boryl radicals,[17] the non-planar structure is rare for the triarylborane radical anions. The structure is not a symmetrical bowl-shape, where one benzene ring is significantly deviated from the central boron moiety (Figure 2-4b). The dihedral angle between the deviated benzene ring and the plane that consists of the boron atom and the three *ipso* carbon atoms (C1, C10, and C16) is 23.7°, while those for the other two benzene rings are 14.6° and 10.5°, respectively. As for the geometry around the boron atom, the B–C bond lengths are 1.517(4), 1.523(4), and 1.521(4) Å for the B1–C1, B1–C10, and B1–C16 bonds, respectively, which are slightly shorter than the calculated values (1.531 Å) and comparable to those in the crystal structure of the neutral **1** (1.519(2)–1.520(2) Å).[11] The boron atom is slightly pyramidalized. The sum of the three C–B–C angles is 354.3°. These structural parameters imply that the triphenylborane framework constrained with the three methylene bridges is still flexible enough to form the bowl-shaped structure upon the one-electron reduction.

Figure 2-4. (a) ORTEP drawing of **1·K** (50% probability for thermal ellipsoids). THF molecule and hydrogen atoms are omitted for clarity. (b) Side view of the anion part of **1·K**. Selected bond lengths (Å) and angles (deg): B(1)–C(1), 1.517(4); B(1)–C(10), 1.523(4); B(1)–C(16), 1.521(4); C(1)–B(1)–C(10), 118.8(3); C(1)–B(1)–C(16), 117.5(3); C(10)–B(1)–C(16), 118.0(3). Reproduced from *Organometallics* **2013**, *32*, 6654 with permission of the American Chemical Society.

The impact of the Structural Constraint in the Radical Anion $1^{\bullet-}$

According to the structural optimization at the B3PW91/6-31+G(d) level, the neutral **1** has a planar conformation, which is consistent with its X-ray crystal structure.[11] The bowl-shaped structure is not a local minimum on the potential energy surface in the ground state, and therefore, the plane-to-bowl structural change unlikely occurs in the ground state of the neutral **1**. In contrast, the increase in the electron density on the boron center by the one-electron reduction renders the bowl-shaped structure being a local minimum on the energy surface. This result is interesting, because it is opposite to the general idea of the structural constraint in a planar fashion, which is an effective strategy for making the skeleton rigid. A key for producing this discrepancy is the compressed B–C bonds in the neutral **1**. The structural constraint with the three methylene bridges in the triphenylborane framework forces the B–C bonds to be shortened to a significant extent. The change in the electronic configuration of the boron atom in such a confined situation results in inducing the significant structural deformation through the elongation of the B–C bonds. This structural change is also relevant to the structural deformation of **1** in the excited state, as described in Chapter 1.

Conclusion

The author has succeeded in the synthesis and characterization of the planarized triphenylborane radical anion **1·K**. The EPR analysis of **1·K** demonstrated that the unpaired electron spin is more delocalized over the three benzene rings compared to the non-constrained $[Ph_3B]^{\bullet-}$. The theoretical calculations predicted that the bowl-shaped geometry is a viable conformation for $\mathbf{1}^{\bullet-}$ in addition to the planar conformation. The small energy difference between the planar and bowl-shaped conformations suggested that the plane-to-bowl conversion likely takes place at room temperature. Actually, the X-ray crystal structure analysis revealed that **1·K** adopts a non-planar bowl-shaped conformation. These structural features are unique for the structurally constrained triphenylborane skeleton. These findings clearly demonstrated the impacts of the structural modifications on the intrinsic characteristics of the boron-centered radical species, and should provide important information for the application of the planarized triphenylborane skeleton as a building unit for more extended π-conjugated materials.

Experimental Section

General. Melting points (mp) were determined with a Yanaco MP-S3 instrument. Electron paramagnetic resonance (EPR) spectrum was measured with a JEOL JES-FA 200 ESR Spectrometer in sealed tube in THF, which was dried over sodium-potassium (NaK) alloy and degassed by freeze-pump-thaw cycles before measurement. The EPR spectrum was simulated with the Bruker WIN-EPR Sim Fonia program using Gaussian line function. Planarized triphenylborane **1** was prepared as described in the literature.[11] THF and hexane were distilled over sodium-benzophenone ketyl or calcium hydride and degassed by freeze-pump-thaw cycles. The reactions were carried out under an argon atmosphere. Due to the instability of the product **1·K** toward air and moisture, elemental analysis could not be performed.

Radical anion 1·K. To a solution of planarized triphenylborane **1** (29.3 mg, 80.9 mmol) in THF (1 mL) was added potassium metal (3.2 mg, 82 mmol) at room temperature. The reaction mixture was stirred for 1 h, while the color turned to deep blue. Recrystallization from THF with slow diffusion of a hexane solution of [2.2.2]cryptand (30.3 mg, 80.5 mmol) gave 42.2 mg (49.6 mmol) of **1·K** in 62% yield as deep blue crystals: mp >200 °C (dec.).

X-Ray Crystallographic Analysis of 1·K. The intensity data were collected on a Rigaku Saturn CCD diffractometer with graphite monochromator MoKa radiation (l = 0.71070 Å) at 123 K. A total of 59509 reflections were measured at the maximum 2θ angle of 50°, of which 8149 were independent reflections (R_{int} = 0.0509). The structure was solved by direct methods (SHELXS-97)[18] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[18] While all hydrogen atoms were placed using AFIX instructions, all the other atoms were refined anisotropically. The crystal data are as follows: $C_{49}H_{71}BKN_2O_7$; FW = 849.99, Orthorhombic, *Pbca*, a = 19.628(10) Å, b = 21.691(13) Å, c = 21.830(12) Å, V = 9294(9) Å^3, Z = 8, D_{calcd} = 1.215 g cm^{-3}. The refinement converged to R_1 = 0.0666 (I>2s(I)), wR_2 = 0.1733 (all data), GOF = 1.096.

Theoretical Calculations

Geometry optimization and frequency calculations of **p-1**$^{\bullet-}$, **b-1**$^{\bullet-}$, and $[Ph_3B]^{\bullet-}$ were performed using the Gaussian 09 program[14] at the UB3PW91/6-31+G(d) level of theory. The model geometries of $[Ph_3B]^{\bullet-}$ with the fixed dihedral angles and the shortened B–C bond lengths were derived from the optimized geometry of $[Ph_3B]^{\bullet-}$, and calculated at single-point at the UB3PW91/6-31+G(d) level of theory. The Cartesian coordinates are shown in Tables 2-1–2-5.

Table 2-1. Coordinates of the Optimized Geometry of **p-1**$^{\bullet-}$ at the UB3PW91/6-31+G(d) Level

atom	*x*	*y*	*z*
B	-0.00011386	0.00000105	-0.00000000
C	-0.75822883	1.31329045	-0.00000000
C	-2.16225529	3.74443773	0.00000000
C	-0.04683431	2.54365439	-0.00000000
C	-2.17966330	1.31227780	0.00000000
C	-2.85945067	2.53176419	0.00000000
C	-0.76347101	3.74171245	0.00000000
H	-3.94861647	2.56247772	0.00000000
H	-0.24517254	4.70006202	0.00000000
H	-2.70679949	4.68774168	0.00000000
C	-0.75814175	-1.31333829	-0.00000000
C	-2.16198994	-3.74458854	0.00000000
C	-2.17957585	-1.31242638	-0.00000000
C	-0.04666035	-2.54365206	-0.00000000
C	-0.76320687	-3.74176244	0.00000000
C	-2.85927338	-2.53196435	0.00000000
H	-0.24483607	-4.70007396	0.00000000
H	-3.94843608	-2.56275997	0.00000000
H	-2.70646518	-4.68793230	0.00000000
C	1.51643080	0.00005078	-0.00000000
C	4.32418252	0.00015474	0.00000000
C	2.22644252	-1.23117007	0.00000000
C	2.22635518	1.23132242	0.00000000
C	3.62224779	1.21008226	0.00000000
C	3.62233530	-1.20982481	0.00000000
H	4.19261558	2.13841289	0.00000000
H	4.19277300	-2.13811124	0.00000000
H	5.41336731	0.00019531	0.00000000
C	-2.99843510	-0.00009789	-0.00000000
C	1.49977180	-2.59695428	-0.00000000
C	1.49960190	2.59705369	-0.00000000
C	-3.89787787	-0.00011390	1.26206593
H	-4.54260561	0.88653693	1.29309678
H	-3.27851952	-0.00012361	2.16617118
H	-4.54260506	-0.88676461	1.29307719
C	-3.89787787	-0.00011390	-1.26206593
H	-3.27851952	-0.00012361	-2.16617118
H	-4.54260561	0.88653694	-1.29309678
H	-4.54260506	-0.88676461	-1.29307719
C	1.94904891	3.37631803	1.26189372
H	3.03910632	3.49386244	1.29197684
H	1.64159721	2.83906352	2.16627921
H	1.50104196	4.37697075	1.29355585
C	1.94904891	3.37631803	-1.26189372
H	1.64159721	2.83906352	-2.16627921
H	3.03910632	3.49386244	-1.29197684
H	1.50104196	4.37697075	-1.29355585
C	1.94923879	-3.37620745	1.26189340
H	1.50118440	-4.37683903	1.29359924
H	1.64185138	-2.83891655	2.16627903
H	3.03929038	-3.49380402	1.29193290
C	1.94923879	-3.37620745	-1.26189340
H	1.64185138	-2.83891655	-2.16627903
H	1.50118440	-4.37683903	-1.29359924
H	3.03929038	-3.49380402	-1.29193290

Table 2-2. Coordinates of the Optimized Geometry of **b-1**$^{\bullet-}$ at the UB3PW91/6-31+G(d) Level

atom	*x*	*y*	*z*
C	-0.07129881	-1.51064573	0.08752979
C	-0.19659645	-4.14497947	-0.85648648
C	-1.33354310	-2.12797605	-0.12751152
C	1.12692140	-2.24457594	-0.12765540
C	1.04663125	-3.55349676	-0.60643382
C	-1.37831599	-3.43888670	-0.60581442
H	1.94275603	-4.13642835	-0.80539236
H	-2.32595392	-3.93407840	-0.80351854
H	-0.24463962	-5.16286157	-1.24196466
C	-1.27244893	0.81751464	0.08733505
C	-3.48914156	2.24214934	-0.86368881
C	-2.50680904	0.14700766	-0.12954180
C	-1.17562694	2.21913353	-0.12868646
C	-2.28723971	2.91262240	-0.61085016
C	-3.59954083	0.87017017	-0.61140963
H	-2.24122998	3.98053996	-0.81041927
H	-4.55189130	0.38489655	-0.81119553
H	-4.34512541	2.79220813	-1.25320076
C	1.34401081	0.69349512	0.08748167
C	3.68541814	1.90221556	-0.86314795
C	2.50956723	-0.09098739	-0.12912569
C	1.38014208	2.09809289	-0.12836291
C	2.55232179	2.68338191	-0.61064880
C	3.66569408	0.52608080	-0.61059016
H	2.60766287	3.75073952	-0.81070922
H	4.56813978	-0.04645953	-0.81022917
H	4.58975070	2.36880493	-1.25235381
C	-2.60481616	-1.34322751	0.25770506
C	0.13862413	2.92732319	0.25930211
C	2.46685562	-1.58401641	0.25777969
C	3.66789239	-2.35567064	-0.30636599
H	3.67513103	-2.36126372	-1.40329621
H	3.66165845	-3.39408983	0.04358465
H	4.60996629	-1.91789276	0.04239020
C	2.57559637	-1.65349084	1.80714346
H	1.74123304	-1.11832124	2.27116167
H	3.51440202	-1.19414859	2.14553452
H	2.54925819	-2.69847821	2.14502029
C	-3.87349955	-1.99817257	-0.30597104
H	-4.76972677	-1.47334681	0.04345319
H	-3.96504312	-3.03264435	0.04362150
H	-3.88171240	-2.00274877	-1.40290575
C	-2.71987453	-1.40137924	1.80710668
H	-3.61338778	-0.85860089	2.14475183
H	-1.84075715	-0.94389278	2.27159437
H	-2.78860733	-2.44407331	2.14613846
C	0.20595220	4.35519166	-0.30035288
H	-0.64412041	4.95040836	0.05163817
H	0.20576242	4.36867826	-1.39732148
H	1.10876972	4.86759333	0.05057083
C	0.14421080	3.05389657	1.80913663
H	-0.72415464	3.63528661	2.14812749
H	1.06101649	3.55556053	2.14797837
H	0.09981356	2.06378664	2.27352383
B	-0.00005748	0.00005609	0.32492344

Table 2-3. Coordinates of the Optimized Geometry of $[Ph_3B]^{\bullet-}$ at the UB3PW91/6-31+G(d) Level

atom	*x*	*y*	*z*
B	-0.00000275	0.00000002	0.99833637
C	-0.00000136	0.00000164	-0.57358914
C	0.00000109	0.00000455	-3.45055747
C	-0.58710419	1.04312124	-1.34005686
C	0.58710278	-1.04311639	-1.34005796
C	0.59130667	-1.04724084	-2.73252792
C	-0.59374089	-3.75328900	1.96211644
H	-1.07640005	-2.50219811	0.29471833
H	1.07331487	-0.63537010	3.51778805
H	1.07321736	-2.75616282	4.75054273
H	-1.07104200	-4.62783721	1.51836215
H	0.00238491	-4.79395833	3.77143298

C	-0.59130572	1.04724849	-2.73252681	C	0.00033590	1.36090975	1.78522219
H	-1.06964831	1.86546828	-0.81412262	C	-0.00162546	3.85120099	3.22620288
H	1.06964599	-1.86546451	-0.81412457	C	-0.58984190	1.50249640	3.07049465
H	1.06610827	-1.87093170	-3.26698982	C	0.59050944	2.54599896	1.26816530
H	-1.06610640	1.87094041	-3.26698787	C	0.59374185	3.75328611	1.96212392
H	0.00000202	0.00000565	-4.53963295	C	-0.59551686	2.70574119	3.77137288
C	-0.00033858	-1.36091142	1.78521930	H	-1.07331716	0.63536636	3.51779034
C	0.00162765	-3.85120568	3.22619470	H	1.07639778	2.50219807	0.29472274
C	-0.59051082	-2.54600039	1.26816038	H	1.07104385	4.62783455	1.51837104
C	0.58984054	-1.50249992	3.07049094	H	-1.07321547	2.75615646	4.75054950
C	0.59551785	-2.70574619	3.77136662	H	-0.00238090	4.79395247	3.77144317

Table 2-4. Coordinates of the Model Geometry of $[Ph_3B]^{\bullet-}$ with Fixed Dihedral Angles (0°)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
B	-0.00000275	0.00000002	0.99833645	C	-0.00318398	-3.80672376	1.93504441
C	0.00586007	-0.04461440	-0.57294499	H	-0.01419790	-2.67281273	0.12051144
C	0.01659019	-0.12626858	-3.44873454	H	0.00543864	-0.41264998	3.77916982
C	0.00843712	1.13014047	-1.37307353	H	-0.00106427	-2.49787369	5.07116309
C	0.00900035	-1.26287709	-1.30512491	H	-0.01084835	-4.76101964	1.40700125
C	0.01583391	-1.30805220	-2.69685767	H	-0.00663564	-4.71246444	3.90776019
C	0.01199044	1.09627334	-2.76513960	C	-0.00325352	1.38269575	1.74627160
H	-0.01091436	2.09799253	-0.87447711	C	-0.01099400	3.91233441	3.11698285
H	0.02442870	-2.20087503	-0.75228468	C	-0.00837541	1.48654458	3.16382987
H	0.02781027	-2.27352337	-3.20408036	C	-0.00111610	2.62677440	1.05899208
H	0.00400080	2.03140632	-3.32640190	C	-0.00318161	3.85374103	1.71753608
H	0.02065207	-0.15717874	-4.53736379	C	-0.01427316	2.70806984	3.83233721
C	-0.00261745	-1.33802906	1.82352522	H	-0.02574415	0.56976941	3.75116116
C	-0.00562547	-3.78581569	3.33558088	H	0.02096559	2.61870256	-0.02960510
C	-0.00008219	-2.61910060	1.20794527	H	0.00847185	4.77654024	1.13626611
C	-0.00789476	-1.36127620	3.24469161	H	-0.02842634	2.72494378	4.92276817
C	-0.00723572	-2.54290094	3.98145709	H	-0.01405114	4.86995624	3.63565343

Table 2-5. Coordinates of the Model Geometry of $[Ph_3B]^{\bullet-}$ with Shortened B–C Bonds (1.520 Å)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
B	-0.00000268	0.00000001	0.99841537	C	-0.59372976	-3.70825036	1.93615388
C	-0.00000133	0.00000158	-0.52158474	H	-1.07638895	-2.45715938	0.26875564
C	0.00000112	0.00000448	-3.39855329	H	1.07332614	-0.59033123	3.49182560
C	-0.58710421	1.04312126	-1.28805252	H	1.07322863	-2.71112411	4.72458038
C	0.58710284	-1.04311654	-1.28805362	H	-1.07103090	-4.58279863	1.49239954

C	0.59130674	-1.04724098	-2.68052368
C	-0.59130573	1.04724851	-2.68052257
H	-1.06964837	1.86546836	-0.76211824
H	1.06964609	-1.86546472	-0.76212018
H	1.06610837	-1.87093190	-3.21498562
H	-1.06610646	1.87094049	-3.21498367
H	0.00000205	0.00000559	-4.48762885
C	-0.00032739	-1.31587259	1.75925671
C	0.00163883	-3.80616705	3.20023222
C	-0.59049967	-2.50096166	1.24219777
C	0.58985178	-1.45746110	3.04452845
C	0.59552908	-2.66070747	3.74540419

H	0.00239610	-4.74891977	3.74547055
C	0.00032476	1.31587099	1.75925952
C	-0.00163660	3.80616241	3.20024032
C	-0.58985308	1.45745764	3.04453208
C	0.59049835	2.50096029	1.24220260
C	0.59373076	3.70824752	1.93616127
C	-0.59552804	2.66070253	3.74541037
H	-1.07332838	0.59032754	3.49182779
H	1.07638672	2.45715939	0.26875996
H	1.07103279	4.58279603	1.49240835
H	-1.07322669	2.71111780	4.72458706
H	-0.00239204	4.74891397	3.74548066

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Chapter 3

Planarized *B*-Phenylborataanthracene Anions: Structural and Electronic Impacts of Coplanar Constraint

Introduction

Boracyclic π-conjugated compounds are attractive not only from fundamental curiosity, including the degree of π-conjugation in the ring affecting their aromaticity, but also from their potentials as materials for organic electronics.[1] Boroles **I** exhibit 4π antiaromaticity, which gives rise to a small HOMO–LUMO gap.[2] In contrast, ring-fused borepins **II** are regarded as the acene analogues due to the 6π aromatic character of the 7-membered ring.[3] Bora- and borataacene derivatives **III** and **IV** are also isoelectronic with acenes. While the shortest homologues, the bora- and boratabenzenes, have been extensively investigated,[4] the studies of higher acene homologues, espetially the bora- and borataanthracenes, are still limited.[5] Only a few strctural characterizations have been reported to date.[6,7]

Figure 3-1. Structures of boracyclic π-conjugated systems **I–IV**. Reproduced from *Chem. Commun.* **2012**, *48*, 10715 with permission of the Royal Society of Chemistry.

Our group has recently synthesized a series of stable planarized triphenylborane derivatives that have three methylene bridges to fix the three benzene rings in a coplanar fashion.[8] In this study, it has been demonstrated that the structural constraint is a powerful strategy for the stabilization of tricoordinate boron compounds, an alternative to the conventional concept of the kinetic stabilization with bulky groups. The author has now come up with the idea that compound **1**, one of the planarized triphenylboranes with a CH_2 bridge, should be a suitable precursor for producing a new borataanthracene anion, the study of which should enable to elucidate the structural and electronic impacts of the structural constraint. In this chapter, the author reports the synthesis and characterization of a new *B*-phenylborataanthracene anion **2**, whose phenyl group on the boron atom is completely fixed in a coplanar fashion with the borataanthracene skeleton. The coplanarization produces attractive properties, such as a more intense and red-shifted fluorescence compared to the parent anthracene as well as the hitherto-known borataanthracenes.

Results and Discussion

Synthesis

The phenyl-planarized borataanthracene anions **2** were successfully prepared by treatment of **1** with appropriate bases (Scheme 3-1). When KH was used, the deprotonation slowly proceeded at room temperature and required 24 h for completion. The slow diffusion of a hexane solution of [2.2.2]cryptand to the mixture produced red crystals of **2·K** in 66% yield. In contrast, the reaction with lithium tetramethylpiperidide (LiTMP) was completed within 1 h at 0 °C. The slow diffusion of hexane into the mixture gave the product **2·Li** in 66% yield as a salt of $Li^{+}(thf)_4$. Both of the products, **2·K** and **2·Li**, were stable in an inert atmosphere, but sensitive toward moisture, leading to reproduction of **1** by protonation

Scheme 3-1. Synthesis of planarized *B*-phenylborataanthracene anions **2·K** and **2·Li**. Reproduced from *Chem. Commun.* **2012**, *48*, 10715 with permission of the Royal Society of Chemistry.

Investigations of the Structures of 2·K and 2·Li

Structural characterization of the phenyl-planarized borataanthracenes was carried out by X-ray crystallographic analysis. In the structure of **2·K**, the potassium ion is completely included by the [2.2.2]cryptand. No interaction is observed between the borataanthracene moiety and the cation (Figure 3-2a). The crystal structure of the cation-separated borataanthracene is unprecedented in the literature. Even in **2·Li**, the lithium ion is coordinated by four THF molecules and there is no interaction with the borataanthracene plane (Figure 3-2b). This result is in stark contrast to the crystal structure of a Li^{+}(tmeda) salt of *B*-phenylborataanthracene **3·Li** reported by Bazan and co-workers, in which the lithium ion is coordinated in an η^6 fashion by the central 6-membered ring of the borataanthracene skeleton.[6] These results demonstrate that the low coordination ability of the borataanthracene moiety is a characteristic feature of the phenyl-planarized borataanthracene anion. This is likely due to the delocalization of the

anion charge of the borataanthracene over the planarized phenyl moiety. Based on the natural population analysis (NPA) by the DFT calculations at the B3LYP/6-31+G(d) level,[9] the sum of the partial charges on the central boratabenzene ring in **2** is –0.30, which is smaller than that (–0.37) of the non-planarized analogue **3**.

Figure 3-2. ORTEP drawings of (a) **2·K** and (b) **2·Li** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity. The distances between the boron atom and the nearest metal ion are 6.138 and 5.361 Å for **2·K** and **2·Li**, respectively. Reproduced from *Chem. Commun.* **2012**, *48*, 10715 with permission of the Royal Society of Chemistry.

Table 3-1. Selected Bond Lengths and Angles for **1**, **2·K**, and **3·Li**[a]

	1	**2·K**	**3·Li**[b]
B(1)–C(1) [Å]	1.519(3)	1.492(7)	1.532(3)
B(1)–C(5) [Å]		1.495(7)	1.549(3)
C(1)–C(2) [Å]	1.414(3)	1.435(7)	1.444(3)
C(4)–C(5) [Å]		1.430(7)	1.448(3)
C(2)–C(3) [Å]	1.513(3)	1.419(7)	1.409(3)
C(3)–C(4) [Å]		1.420(7)	1.409(3)
B(1)–C(14) [Å]	1.525(4)	1.534(7)	1.582(3)
C(1)–B(1)–C(5) [°]	120.7(2)	119.7(4)	115.9(2)

[a]Structure of **3·Li** is shown below. [b]Data from ref 6.

3·Li

The solvent-separated ion pair structure seems retained even in solution according to the NMR spectra. The ^{11}B NMR chemical shifts (+30.0 ppm for **2·K** and +30.4 ppm for **2·Li** in THF-d_8) are upfield-shifted compared to that of the non-planarized **3·Li** (+39.8 ppm in C_6D_6).[6] The absence of any interaction between the borataanthracene anion and the metal ions should increase the electron density of the borataanthracene moiety, resulting in the upfield shifts. The fact that the ^{7}Li NMR chemical shift of +0.51 ppm for **2·Li** in THF-d_8 is close to that (0 ppm) of the solvated LiCl also supports the solvent-separated ion pair structure for **2·Li** in THF.

Selected bond lengths and angles for **1**, **2·K**, and **3·Li**[6] are summarized in Table 3-1. The crystal structure of **2·K** consists of two crystallographically independent structures, whose structural parameters are almost comparable to each other. Therefore, the data for one of those structures are listed in Table 1. The lithium salt **2·Li** also contains six crystallographically independent structures. Their structural parameters for the borataanthracene moiety are all comparable to those of **2·K**. The most notable feature is that **2·K** has a more regular hexagon geometry for the central boratabenzene ring compared to **3·Li**. From the triphenylborane precursor **1** to the borataanthracene salt **2·K**, the B(1)-C(1)/B(1)–C(5) bond lengths as well as the C(2)-C(3)/C(3)-C(4) bond lengths are shortened. Notably, the B(1)-C(1)/B(1)-C(5) bond lengths of **2·K** are significantly shorter than those of **3·Li**. This is due to the structural constraint in **2·K**. This trend is already observed in the comparison between the planarized triphenylborane **1** and non-constrained congeners, such as Ph_3B and Mes_3B.[10] The C(1)-B(1)-C(5) angle of **2·K** is also wider than that of **3·Li**. As a consequence, the geometry of the borataanthracene in **2·K** more resembles to that of the parent anthracene than **3·Li**.

Photophysical Properties of 2·K

The impacts of the structural features in the phenyl-planarized borataanthracene on the photophysical properties were next investigated. In THF, **2·K** exhibited absorption bands with the maxima (λ_{abs}) of 568, 531, and 500 nm (Figure 3-3). According to the literature, the absorption spectrum of an in-situ generated *B*-mesitylborataanthracene showed a broad absorption band with the λ_{abs} at 435 nm.[5b] The comparison of these spectra exhibits two significant differences. First, whereas *B*-mesitylborataanthracene did not show any vibronic structure, **2·K** exhibited a well-separated spectrum. It is

likely due to the more rigid borataanthracene skeleton in **2**. Secondly, the fixation of the *B*-phenyl group in a coplanar fashion gives rise to the significant red shift of the λ_{abs} of nearly 100 nm. The planarization results in the extension of the π conjugation, which should be responsible for the red shift (*vide infra*). In the florescence spectrum, **2·K** exhibited an intense orange emission at 584 nm with a fine vibronic structure. Its quantum yield was 0.45. To the best of our knowledge, the fluorescence of the borataanthracene anions has not been reported, except for the NHC-stabilized neutral boraanthracene.[7] The planarization by the structural constraint endows the borataanthracene skeleton with the intense and red-shifted fluorescence.

Figure 3-3. UV-vis absorption (solid line) and fluorescence spectra (dashed line) of **2·K** in THF. Reproduced from *Chem. Commun.* **2012**, *48*, 10715 with permission of the Royal Society of Chemistry.

Theoretical Insights on the Effect of the Planarization

To gain a deeper insight into the electronic structure, the theoretical calculations of **2** and **3** were conducted. First, the author estimated the aromaticity of the boratabenzene moiety in **2** and **3** by the nucleus independent chemical shift (NICS).[11] The $NICS(1)_{zz}$ values of the boratabenzene moiety, calculated at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) level,[9] are –22.6 ppm for **2** and –28.1 ppm for **3**, indicative of the lower aromaticity in **2** (Figure 3-4). This result seems to be not consistent with the structural features, as the more regular hexagon geometry in **2** suggests a higher aromaticity in **2** compared to **3**. Actually, the harmonic oscillator model of aromaticity (HOMA) index[12] of the central ring in **2·K** (0.63), calculated from the bond lengths of the crystal structure, is significantly higher than that of the distorted

boratabenzene ring in **3·Li** (0.26). For rationalization of this discrepancy, the author evaluated the NICS(1)$_{zz}$ values of the boratabenzenes HBC_5H_5 **2′** and **3′**, whose geometries are directly derived from the optimized structures of **2** and **3**, to preclude the effects of the peripheral annulated rings and the phenyl group on the boron atom. The calculated values for **2′** (–24.8 ppm) and **3′** (–24.6 ppm) are comparable to each other (Figure 3-4). This result suggests that the structural deformation of the boratabenzene moiety has little influence on the aromaticity in terms of the ring current effect. The difference in the NICS values between **2** and **3** may be attributed to the difference in the localized charge on the central boratabenzene moiety. As previously mentioned, the negative charge in **2** is more delocalized over the entire molecule including the *B*-phenyl group compared to **3**. The decreased electron density on the central ring in **2** results in the less negative NICS value due to the reduced ring current effect.[13] This is one of the impacts of the planarization of the *B*-bound phenyl group.

Figure 3-4. The NICS(1)$_{zz}$ values for the boratabenzene ring of the optimized structures of **2** and **3**, and their substructures **2′**$_{//}$, **2′**$_{\perp}$, **2′**, **3**$_{//}$, **3′**$_{//}$, **3′**$_{\perp}$, and **3′**, whose geometries are derived from the optimized structures of **2** and **3**, respectively. The selected bond lengths (Å) for the boratabenzene ring are given. Reproduced from *Chem. Commun.* **2012**, *48*, 10715 with permission of the Royal Society of Chemistry.

Secondly, the author looked into the effects of the structural constraint on the frontier orbitals (Figure 3-5). In the non-constrained **3**, the change in the orientation of the

B-phenyl group from a perpendicular geometry (**3**$_{\perp}$) to a coplanar geometry (**3**$_{//}$) significantly decreases the LUMO energy level, while the HOMO level remained unchanged. The comparison between **3**$_{//}$ with **2** demonstrates that the introduction of the methylene bridges slightly increases both the HOMO and LUMO levels due to the inductive effect of the alkyl substituents.

Figure 3-5. Comparison of HOMO and LUMO energy levels among **2**, **3**$_{\perp}$, and **3**$_{//}$ based on the calculations at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) level of theory. Reproduced from *Chem. Commun.* **2012**, *48*, 10715 with permission of the Royal Society of Chemistry.

To rationalize the significant red shift in the absorption spectrum for **2·K**, the TD-DFT calculations were conducted on **2** and **3** using $Li^{+}(OMe_2)_3$ as the counter cation (Figure 3-6).[9] While the excitation energy of **3** bearing $Li^{+}(OMe_2)_3$ at 1.9 Å above the borataanthracene core is estimated to be 482 nm (2.57 eV, f = 0.0551), that of the separated ion pair of **2** and $Li^{+}(OMe_2)_3$ (the distance is fixed at 7.0 Å) is 514 nm (2.41 eV, f = 0.0968). Although the experimentally observed difference was not fully reproduced by these calculations, it is clear that the planarization of the phenyl group plays a significant role in lowering the π–π* excitation energy.

Figure 3-6. Comparison of the π and π* orbital energy levels, and the excitation energies among **2**, $\mathbf{3}_{\perp}$, and $\mathbf{3}_{//}$ with $Li(OMe_2)_3$ as the counter cation, based on the TD-DFT calculations at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) level. Reproduced from *Chem. Commun.* **2012**, *48*, 10715 with permission of the Royal Society of Chemistry.

Conclusion

The author succeeded in the synthesis of the planarized *B*-phenylborataanthracene anions with methylene bridges. The fixation of the *B*-phenyl group in a coplanar fashion with the borataanthracene skeleton affects the electronic structure by reducing the anionic charges through the effective extension of the π conjugation. Consequently, **2** exhibited the solvent-separated ion pair structures and showed intriguing photophysical properties, such as the red-shifted absorption and intense fluorescence, totally different from the known borataanthracenes. These results should provide an important guideline for further molecular designs of new boracycle-based π-conjugated systems.

Experimental Section

General. Melting points (mp) were determined with a Yanaco MP-S3 instrument. ^{1}H, ^{13}C, ^{7}Li, and ^{11}B NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 155 MHz for ^{7}Li, and 128 MHz for ^{11}B) in sealed tube in THF-d_8 that was dried over sodium-potassium (NaK) alloy and degassed by freeze-pump-thaw cycles. Chemical shifts are reported in δ ppm. ^{1}H NMR spectra are referenced to residual protons in the deuterated solvent as an internal standard. ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent as an internal standard. ^{7}Li NMR spectrum is referenced to LiCl as an external standard. ^{11}B NMR spectra are referenced to $BF_3 \cdot OEt_2$ as an external standard. THF and hexane were distilled over sodium-benzophenone ketyl or calcium hydride and degassed by freeze-pump-thaw cycles. UV-visible absorption spectrum was recorded on a Shimadzu UV-3510 spectrometer. A sample solution (2.9×10^{-4} M) in a 1 mm quartz cell in degassed THF that were dried over NaK alloy was used for the measurement. Fluorescence spectrum was recorded on a Hitachi F-4500 spectrometer. Absolute fluorescence quantum yield was determined with a Hamamatsu C9920-02 calibrated integrating sphere system. THF solvent was dried over NaK alloy and degassed by three freeze-pump-thaw cycles, then transferred into the sample in vacuo. A 1 cm square quartz cell including the sample solution was sealed before the measurement. Due to the higher sensitivity of **2·Li** to moisture, photophysical measurement of **2·Li** could not be performed. Presumably the photophysical properties of **2·Li** should be essentially similar to that of **2·K**. Planarized triphenylborane **1** was prepared as described in the literature.[8] All reactions were carried out under an argon or a nitrogen atmosphere. Due to the instability of the product **2·K** and **2·Li** toward air and moisture, elemental analysis could not be performed.

Potassium salt of planarized *B*-phenylborataanthracene 2·K. To a solution of planarized triphenylborane **1** (50.5 mg, 0.15 mmol) in THF (5 mL) was added potassium hydride (6.6 mg, 0.16 mmol) at room temperature. After stirring for 24 h, the resulting red solution was filtered off and concentrated under reduced pressure. Recrystallization from THF with slow diffusion of a hexane solution of [2.2.2]cryptand (57.0 mg, 0.15 mmol) gave 73.7 mg (0.098 mmol) of **2·K** in 66% yield as red crystals: mp 172-180 °C (dec.); ^{1}H NMR (400 MHz, THF-d_8) δ 1.65 (s, 12H), 2.01 (t, ^{3}J = 4.8 Hz,

12H), 3.00 (t, ^3J = 4.8 Hz, 12H), 3.08 (s, 12H), 6.64 (d, ^3J = 6.8 Hz, 2H), 6.77 (s, 1H), 7.01–7.07 (m, 3H), 7.21 (d, ^3J = 8.4 Hz, 2H), 7.29 (d, ^3J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8) δ 36.1 (q), 42.7 (s), 54.2 (t), 67.9 (t), 70.7 (t), 102.5 (d), 109.5 (d), 122.4 (d), 122.9 (d), 125.7 (d), 126.2 (d), 141.1 (s), 152.7 (s), 154.7 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, THF-d_8) δ 30.0.

Lithium salt of planarized *B*-phenylborataanthracene 2·Li. To a solution of tetramethylpiperidine (20 mL, 0.12 mmol) in THF (1 mL) was added a hexane solution of *n*-BuLi (1.6 M, 75 mL, 0.12 mmol) at 0 °C. After stirring for 1 h at 0 °C, the solution was added to a solution of planarized triphenylborane **1** (39.8 mg, 0.12 mmol) in THF (3 mL), then stirred for 1 h at 0 °C. The volatile materials were removed in vacuo at room temperature. Recrystallization from THF with slow diffusion of hexane under an argon atmosphere gave 49.3 mg (0.078 mmol) of **2·Li** in 66% yield as red crystals: mp 135-144 °C; ^{1}H NMR (400 MHz, THF-d_8) δ 1.63 (s, 12H), 1.78 (m, 16H), 3.62 (m, 16H), 6.63 (d, ^3J = 6.8 Hz, 2H), 6.71 (s, 1H), 7.02–7.08 (m, 3H), 7.19 (d, ^3J = 8.0 Hz, 2H), 7.28 (d, ^3J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8) δ 26.2 (t), 36.1 (q), 42.6 (s), 68.0 (t), 102.1 (d), 109.5 (d), 122.1 (d), 123.1 (d), 125.8 (d), 126.3 (d), 141.0 (s), 152.6 (s), 154.7 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{7}Li NMR (155 MHz, THF-d_8) δ 0.51; ^{11}B NMR (128 MHz, THF-d_8) δ 30.4.

X-Ray Crystallographic Analysis of 1. The intensity data were collected on a Rigaku Saturn CCD diffractometer with graphite monochromator MoKa radiation (l = 0.71070 Å) to $2\theta_{max}$ = 50° at 123 K. The structure was solved by direct methods (SHELXS-97)[14] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[14] While all hydrogen atoms were placed using AFIX instructions, all the other atoms were refined anisotropically. The crystal data are summarized in Table 3-2.

X-Ray Crystallographic Analysis of 2·K. The intensity data were collected on a Rigaku Saturn CCD diffractometer with graphite monochromator MoKa radiation (l = 0.71070 Å) to $2\theta_{max}$ = 50° at 123 K. The structure was solved by direct methods (SHELXS-97)[14] and refined by full-matrix least-squares procedures on F^2 for all

reflections (SHELXL-97).[14] While all hydrogen atoms were placed using AFIX instructions, all the other atoms were refined anisotropically. The crystal data are summarized in Table 3-2.

X-Ray Crystallographic Analysis of 2·Li. The intensity data were collected on a Rigaku Saturn CCD diffractometer with graphite monochromator MoKa radiation (l = 0.71070 Å) to $2\theta_{max}$ = 48° at 123 K. The structure was solved by direct methods (SHELXS-97)[14] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[14] While all hydrogen atoms were placed using AFIX instructions, all the other atoms were refined anisotropically. The crystal data are summarized in Table 3-2.

Theoretical Calculations

The NPA calculations of **2** and **3** were carried out using the Gaussian 03 program[9] at the B3LYP/6-31+G(d) level for the optimized structures obtained at the B3LYP/6-31+G(d) level. The calculated NPA natural charges of **2** and **3** at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) are summarized in Table 3-3.

Nucleus independent chemical shift (NICS) calculations of **2** and **3** were carried out using the Gaussian 03 program[9] at the B3LYP/6-31+G(d) level for the optimized structures obtained at the B3LYP/6-31+G(d) level. The NICS values of $\mathbf{2'}_{//}$, $\mathbf{2'}_{\perp}$, $\mathbf{2'}$, $\mathbf{3}_{//}$, $\mathbf{3'}_{//}$, $\mathbf{3'}_{\perp}$, and $\mathbf{3'}$ were calculated using the corresponding geometries directly derived from the optimized structures of **2** and **3**.

Time-dependent density functional theory (TD-DFT) calculations of **2**, $\mathbf{3}_{\perp}$, and $\mathbf{3}_{//}$ with a cation were carried out using the Gaussian 03 program[9] at the B3LYP /6-31+G(d) level. The Structures of the anion parts were optimized at B3LYP/6-31+G(d) level, and then $Li(OMe_2)_3$ as the counter cation was fixed at 1.9 or 7.0 Å above the borataanthracene core.

The Cartesian coordinates are shown in Tables 3-4–3-6.

Table 3-2. Crystal Data for **1**, **2·K**, and **2·Li**

	1	**2·K**	**2·Li**
CCDC ID code	895473	895474	895475
Empirical formula	$C_{25}H_{23}B$	$C_{43}H_{58}BKN_2O_6$	$C_{41}H_{54}BLiO_4$
Formula weight	334.24	748.82	628.59
Color	colorless	red	red
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$C222_1$ (#20)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	10.150(15)	23.898(8)	10.938(16)
b (Å)	17.72(3)	18.387(4)	34.75(3)
c (Å)	10.24(3)	18.78(2)	57.15(6)
β (deg)	90	104.083(17)	97.81(3)
V (Å^3)	1842(7)	8004(9)	21521(43)
Z	4	8	24
D_{calcd} (g cm^{-3})	1.205	1.243	1.164
F(000)	712	3216	8160
μ (mm^{-1})	0.067	0.182	0.072
Index ranges	$-12 \le h \le 12$	$-25 \le h \le 28$	$-11 \le h \le 12$
	$-20 \le k \le 20$	$-21 \le k \le 21$	$-37 \le k \le 39$
	$-12 \le l \le 11$	$-22 \le l \le 22$	$-65 \le l \le 65$
Reflections collected	6113	52851	97827
Independent reflections	1605 [R_{int} = 0.0500]	14066 [R_{int} = 0.0803]	31987 [R_{int} = 0.1087]
Goodness-of-fit on F^2	0.969	1.151	1.085
R_1, wR_2 (I>2σ(I))	0.0405, 0.0968	0.1028, 0.2467	0.1098, 0.2654
R_1, wR_2 (all data)	0.0466, 0.0994	0.1357, 0.2771	0.1963, 0.3531

Table 3-3. The Natural Charges of **2** and **3** Based on the NPA Calculations at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) Level of Theory

2

3

2			**3**		
atom	No.	charge	atom	No.	charge
H	1	0.21764	H	1	0.21677
C	2	–0.25125	C	2	–0.26266
H	3	0.21642	H	3	0.21566
C	4	–0.25385	C	4	–0.24232
C	5	0.03080	C	5	–0.18269
C	6	–0.02874	C	6	–0.03317
C	7	–0.30939	C	7	–0.32097
C	8	–0.34659	C	8	–0.38972
C	9	–0.29994	C	9	–0.30806
H	10	0.21281	H	10	0.21748
C	11	–0.02874	C	11	–0.04311
H	12	0.20649	H	12	0.20466
C	13	–0.25385	C	13	–0.22119
C	14	–0.34659	C	14	–0.38979
B	15	0.53930	B	15	0.58546
C	16	–0.25125	C	16	–0.27382
H	17	0.21642	H	17	0.21597
H	18	0.21764	H	18	0.21676
C	19	–0.30939	C	19	–0.32087
H	20	0.21281	H	20	0.21744
C	21	0.03080	C	21	–0.18289
C	22	–0.27664	C	22	–0.26802
C	23	–0.26008	C	23	–0.27579
C	24	0.01409	C	24	–0.22864
C	25	0.01409	C	25	–0.22864
C	26	–0.25047	C	26	–0.25684
C	27	–0.25047	C	27	–0.25684
H	28	0.21981	H	28	0.22437
H	29	0.21981	H	29	0.22437
H	30	0.22245	H	30	0.22276
C	31	–0.11422	H	31	0.22770
C	32	–0.11422	H	32	0.23447
C	33	–0.65261	H	33	0.22771
H	34	0.22657	H	34	0.23447
H	35	0.24484	Total		–0.99999
H	36	0.21978			
C	37	–0.65261			
H	38	0.24484			
H	39	0.22657			
H	40	0.21978			
C	41	–0.65261			
H	42	0.24484			
H	43	0.21978			
H	44	0.22657			
C	45	–0.65261			
H	46	0.22657			
H	47	0.21978			
H	48	0.24484			
Total		–0.99999			

Table 3-4. Coordinates of the Optimized Geometry of **2** at the B3LYP/6-31+G(d) Level

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H	0.00000000	4.62641473	-3.14000757	C	0.00000000	-1.23290757	1.85905432
C	0.00000000	3.68575103	-2.58860307	C	0.00000000	-1.21318775	3.26125093
H	0.00000000	2.48712230	-4.36876407	C	0.00000000	1.21318775	3.26125093
C	0.00000000	2.49106862	-3.27829054	H	0.00000000	-2.13854229	3.83369416
C	0.00000000	2.53981951	-0.43500036	H	0.00000000	2.13854229	3.83369416
C	0.00000000	1.24771972	-2.57152944	H	0.00000000	0.00000000	5.04455376
C	0.00000000	3.72495870	-1.17002365	C	0.00000000	2.59929039	1.11859308
C	0.00000000	1.29924652	-1.12503816	C	0.00000000	-2.59929039	1.11859308
C	0.00000000	0.00000000	-3.23974407	C	1.26666954	3.38320535	1.56713767
H	0.00000000	4.69721353	-0.68162058	H	1.29540569	4.37757731	1.10760930
C	0.00000000	-1.24771972	-2.57152944	H	2.17231983	2.84553117	1.26400841
H	0.00000000	0.00000000	-4.33117297	H	1.29575971	3.51174167	2.65593632
C	0.00000000	-2.49106862	-3.27829054	C	-1.26666954	3.38320535	1.56713767
C	0.00000000	-1.29924652	-1.12503816	H	-2.17231983	2.84553117	1.26400841
B	0.00000000	0.00000000	-0.37000923	H	-1.29540569	4.37757731	1.10760930
C	0.00000000	-3.68575103	-2.58860307	H	-1.29575971	3.51174167	2.65593632
H	0.00000000	-2.48712230	-4.36876407	C	-1.26666954	-3.38320535	1.56713767
H	0.00000000	-4.62641473	-3.14000757	H	-2.17231983	-2.84553117	1.26400841
C	0.00000000	-3.72495870	-1.17002365	H	-1.29575971	-3.51174167	2.65593632
H	0.00000000	-4.69721353	-0.68162058	H	-1.29540569	-4.37757731	1.10760930
C	0.00000000	-2.53981951	-0.43500036	C	1.26666954	-3.38320535	1.56713767
C	0.00000000	0.00000000	1.16497798	H	1.29540569	-4.37757731	1.10760930
C	0.00000000	0.00000000	3.95536342	H	1.29575971	-3.51174167	2.65593632
C	0.00000000	1.23290757	1.85905432	H	2.17231983	-2.84553117	1.26400841

Table 3-5. Coordinates of the Optimized Geometry of **3**ı at the B3LYP/6-31+G(d) Level

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H	0.00000000	4.60970379	-2.78113272	H	0.00000000	-4.60970379	-2.78113272
C	0.00000000	3.69292727	-2.19106479	C	0.00000000	-3.76737140	-0.77102913
H	0.00000000	2.41994917	-3.91285383	H	0.00000000	-4.73670484	-0.27451975
C	0.00000000	2.46954468	-2.82321283	C	0.00000000	-2.59519274	-0.03568113
C	0.00000000	2.59519274	-0.03568113	C	0.00000000	0.00000000	1.76381046
C	0.00000000	1.23842756	-2.08501029	C	0.00000000	0.00000000	4.61913195
C	0.00000000	3.76737140	-0.77102913	C	-1.19726033	0.00000000	2.50974728
C	0.00000000	1.30272807	-0.63420810	C	1.19726033	0.00000000	2.50974728
C	0.00000000	0.00000000	-2.75695517	C	1.20515488	0.00000000	3.90917911
H	0.00000000	4.73670484	-0.27451975	C	-1.20515488	0.00000000	3.90917911

C	0.00000000	-1.23842756	-2.08501029	H	2.15298095	0.00000000	4.44638177
H	0.00000000	0.00000000	-3.84831423	H	-2.15298095	0.00000000	4.44638177
C	0.00000000	-2.46954468	-2.82321283	H	0.00000000	0.00000000	5.70799818
C	0.00000000	-1.30272807	-0.63420810	H	0.00000000	-2.65408799	1.05230885
B	0.00000000	0.00000000	0.16460716	H	2.14794458	0.00000000	1.97817331
C	0.00000000	-3.69292727	-2.19106479	H	0.00000000	2.65408799	1.05230885
H	0.00000000	-2.41994917	-3.91285383	H	-2.14794458	0.00000000	1.97817331

Table 3-6. Coordinates of the Optimized Geometry of **3**$_{//}$ at the B3LYP/6-31+G(d) Level

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H	0.00000000	4.61000036	-2.78102277	H	0.00000000	-4.61000036	-2.78102277
C	0.00000000	3.69300028	-2.19102272	C	0.00000000	-3.76700029	-0.77102261
H	0.00000000	2.42000018	-3.91302286	H	0.00000000	-4.73700037	-0.27502258
C	0.00000000	2.47000019	-2.82302277	C	0.00000000	-2.59500020	-0.03602256
C	0.00000000	2.59500020	-0.03602256	C	0.00000000	0.00000000	1.76397758
C	0.00000000	1.23800009	-2.08502271	C	0.00000000	0.00000000	4.61897780
C	0.00000000	3.76700029	-0.77102261	C	0.00000000	-1.19700009	2.50997764
C	0.00000000	1.30300010	-0.63402260	C	0.00000000	1.19700009	2.50997764
C	0.00000000	0.00000000	-2.75702277	C	0.00000000	1.20500009	3.90897774
H	0.00000000	4.73700037	-0.27502258	C	0.00000000	-1.20500009	3.90897774
C	0.00000000	-1.23800009	-2.08502271	H	0.00000000	2.15300017	4.44597779
H	0.00000000	0.00000000	-3.84802285	H	0.00000000	-2.15300017	4.44597779
C	0.00000000	-2.47000019	-2.82302277	H	0.00000000	0.00000000	5.70797786
C	0.00000000	-1.30300010	-0.63402260	H	0.00000000	-2.65400020	1.05197753
B	0.00000000	0.00000000	0.16497746	H	0.00000000	2.14800017	1.97797760
C	0.00000000	-3.69300028	-2.19102272	H	0.00000000	2.65400020	1.05197753
H	0.00000000	-2.42000018	-3.91302286	H	0.00000000	-2.14800017	1.97797760

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Chapter 4

Boracyclophanes:
Modulation of the σ/π Character in Boron–Benzene Interactions

Introduction

Friedel-Crafts alkylation is a powerful methodology in organic synthesis for the modification of aromatic compounds. The reaction is categorized as an electrophilic aromatic substitution, in which a carbocation–arene σ complex, namely the arenium ion, has been assumed to be an intermediate. Characterizations of the arenium ions have long been investigated both theoretically and experimentally.[1,2] It is also known that silylium ions (silyl cations) interact with an arene to form a silylarenium species. However, this intermediate exhibits a greater π-complex character rather than the σ-complex character.[3] The characters of the arenium intermediates generated with p-block element electrophiles vary from a η^1 π complex to a σ complex, as shown in Figure 4-1.

Figure 4-1. Structural variation of the interaction between the p-block electrophiles (e.g. $E^+ = C^+$, Si^+) and benzene. T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Tricoordinate group 13 element species ER_3 (E = B, Al, Ga, or In), which are isoelectronic to the carbocation, are also potent Lewis acids and would interact with arenes to form zwitterionic arenium complexes.[4] The interaction of BX_3 (X = H, F, or Cl) with benzene has been investigated by an *ab initio* study, in which the binding energy for the η^1 π complexes are estimated to be 3–6 kcal/mol.[5] In contrast, experimental characterizations of the boron–arene complexes are still limited to only a few examples, including those with triarylboranes[6] or borenium cations.[7] In these examples, constrained arrangements between the boron and arene moieties in close proximity assist in forming the boron–benzene interactions, which are relatively weak and tend to have a η^1 π-complex character rather than a σ-complex character.

Recently, our group reported the synthesis of planarized triphenylboranes **1** (Scheme 4-1, R = H or Me) with three methylene bridges and demonstrated their high stability

toward air and moisture. This result suggested that the structural constraint is an effective strategy for the stabilization of the reactive triarylboranes.[8] However, it was also demonstrated that the planarized triphenylboranes still possess a sufficient Lewis acidity to react with anionic Lewis bases, such as a fluoride ion, resulting in the formation of a bowl-shaped tetracoordinate borate species. These results prompted to study the reactivity of the planarized triphenylboranes with Lewis bases in more detail. The author now employed a stronger carbon nucleophile, *t*BuLi, as the Lewis base. The author found that the reaction produced a boracyclophane, in which a tricoordinate boron moiety was fixed above an eliminated benzene ring in close proximity. Notably, this molecular structure provides an ideal scaffold to study the intrinsic character of the interaction between a tricoordinate boron and a benzene ring. In addition, the author succeeded in modulating the character of the boron–benzene interaction from π- to σ-complex characters by changing the electron-donating character of the benzene ring.

Results and Discussion

Synthesis and Formation Mechanism of Boracyclophane 2

In the previous study (Chapter 3), when the planarized triphenylborane **1** (R = H) was treated with bases, such as potassium hydride and lithium tetramethylpiperidide, a highly fluorescent borataanthracene anion was cleanly obtained.[9] In contrast, the author now found that the reaction of **1** with 3 equivalent of *t*-BuLi followed by quenching with water gave a one benzene ring-eliminated product, namely boracyclophane **2**, as a single product (Scheme 4-1). This compound was isolated by preparative-scale gel permeation chromatography (GPC) in 73% yield as colorless solids. The structure of **2** was unambiguously characterized by NMR spectroscopies, mass spectrometry, and X-ray crystallography.

Scheme 4-1. Synthesis of boracyclophane **2** via borate intermediate **3·Li**. T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

The reaction of **1** with *t*-BuLi cleanly proceeded, and any product produced by the elimination of the other benzene moieties was not observed in the crude mixture, indicating that the boron–benzene bond was selectively cleaved. The yield of **2** was highly dependent on the amount of *t*-BuLi. When 1 equivalent of *t*-BuLi was employed, **2** was obtained only in 18% yield. In contrast, the use of 5 equivalent of *t*-BuLi gave **2** in 71%, which is comparable to that with 3 equivalent of *t*-BuLi (Scheme 4-1). These results can be rationalized by considering the equilibrium between the tricoordinate borane **1** and tetracoordinate *t*-butylborate **3·Li**. The use of excess *t*-BuLi shifts the equilibrium to the borate side, from which the protonation of the most electron-rich benzene ring selectively produces the boracyclophane **2**.

The clean formation of the intermediate **3·Li** was confirmed by monitoring the reaction mixture by NMR spectroscopies (see the Experimental Section). In the ^{11}B NMR spectrum of a 1:1 mixture of **1** and *t*-BuLi in C_6D_6, only two signals were observed. One is a broad signal of **1** at 45.9 ppm. The other one is a sharp signal at –20.1 ppm, which is assignable to the borate intermediate **3·Li** (Figure 4-9). The ^{1}H NMR spectrum also showed the signals of **1** and a new set of signals corresponding to **3·Li** (Figure 4-8). Upon the addition of water to the solution, the signals of the boracyclophane **2** appeared in the ^{1}H NMR spectrum, in addition to those of the unreacted **1**. Based on the integration ratio of the ^{1}H NMR signals, the binding constant of **1** with *t*BuLi was estimated to be $4.0 \times 10\ M^{-1}$, which is rather lower compared to

that with a fluoride ion (7.0×10^5 M^{-1}).[8] Therefore, an excess amount of *t*BuLi was necessary to completely shift the equilibrium to the product side.

X-ray Crystallographic Analysis of 2

The X-ray crystallographic analysis of the boracyclophane **2** revealed the characteristic structural features (Figure 4-2). The tricoordinate boron atom is slightly pyramidalized. The sum of the three C–B–C angles is 349.1°. The most notable feature is that the boron atom is fixed above the eliminated benzene moiety in close proximity. The B1···C1 distance of 2.23 Å is rather shorter than the sum of the van der Waals radii of the boron and carbon atoms (3.62 Å).[10] This structure indicates that an interaction occurs between the boron atom and the benzene ring to some extent. In addition, the ^{11}B NMR spectrum of **2** in $CDCl_3$ showed a signal at 51.1 ppm, which is upfield-shifted compared to that of the alkyldiphenylboranes, such as Ph_2BMe (70.6 ppm),[11] indicative of the electronic perturbation from the eliminated benzene ring to the boron atom. To gain detailed insights into the electronic structure of the boracyclophane **2**, the author conducted theoretical calculations.

Figure 4-2. ORTEP drawing of **2** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C7 1.595(2), B1–C14 1.596(2), B1–C20 1.627(2), C1–C2 1.411(2), C1–C6 1.402(2), C2–C3 1.393(2), C3–C4 1.380(3), C4–C5 1.388(3), C5–C6 1.395(2); C7–B1–C14 110.42(13), C7–B1–C20 118.95(13), C14–B1–C20 119.87(14). T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Theoretical Insights on the structure of 2

The optimized structure of **2** at the B3LYP/6-31G(d) level of theory[12] showed a good agreement with the X-ray structure, expect that the B1···C1 distance was slightly overestimated to be 2.35 Å. While the HOMO is mainly localized on the two benzene rings connected to the boron atom, the LUMO essentially consists of a vertical orbital interaction between the vacant p orbital of the boron atom and the π* orbital of the eliminated benzene ring (Figure 4-3a). This interaction is in stark contrast to an ordinary p–π* orbital interaction in conventional arylboranes.[13] On the other hand, the HOMO–5 indicated a bonding interaction between the boron moiety and the π orbital of the benzene ring (Figure 4-3b).

Figure 4-3. The Kohn-Sham plots of the a) LUMO and b) HOMO–5 of the boracyclophane **2** (B3LYP/6-31G(d) level, isovalue 0.04). T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Therefore, the author conducted the atoms in molecules (AIM) analysis[14,15] of **2** using its crystal structure to evaluate the bonding interaction between the B1 atom and the closest C1 atom in the benzene ring. The author found a bond path between the B1 and C1 atoms with a bond critical point, in which the electron density $\rho(\mathbf{r})$ was 0.037. The small positive value of the $\nabla^2\rho(\mathbf{r})$ (0.046) suggested that the bonding interaction is slightly ionic. These results demonstrated that the vertical p–π orbital overlapping between the boron atom and the benzene ring results in the attractive interaction. However, this interaction should be inherently weak due to low Lewis acidity of the boron moiety and low nucleophilicity of the benzene ring. The author envisioned that the introduction of an electron-donating group onto the eliminated benzene ring would enhance the orbital interaction. Based on this idea, the author synthesized a boracyclophane **4** with a dimethylamino group at the *para*-position of the benzene ring.

Synthesis of Dimethylamino-Substituted Boracyclophane 4

The compound **4** was synthesized in 4 steps from a monobrominated precursor **5** (Scheme 4-2). The planarized triphenylborane **6** with a diphenylimino moiety was prepared via the palladium-catalyzed coupling of **5** with benzophenone imine.[16] Hydrolysis of **6** under acidic conditions gave an amino derivative **7**. The subsequent reductive methylation with aqueous formaldehyde and $NaBH_4$ in the presence of H_2SO_4 successfully produced a dimethylamino-substituted planarized triphenylborane **8** in good yield. Finally, the treatment of **8** with *t*-BuLi followed by quenching with aqueous HCl produced the boracyclophane **4** in 77% yield.

Scheme 4-2. Synthesis of dimethylamino-substituted boracyclophane **4**. *Reagents and conditions*: a) $HN{=}CPh_2$ (1.2 equiv), $[Pd(dba)_2]$ (5 mol%), dppf (10 mol%), *t*-BuONa (1.3 equiv), toluene, reflux, 12 h; b) 4N aq. HCl, THF, RT, 18 h; c) 37% aq. HCHO, $NaBH_4$, 3 M aq. H_2SO_4, THF, 0 °C then RT, 15 h; d) *t*-BuLi (3 equiv), benzene, RT, 1 h, then 1N aq. HCl, RT. T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

X-ray Crystallographic Analysis of 4

The structure of the dimethylamino-substituted **4** was successfully determined by X-ray crystallography. The crystal structure consists of two crystallographically independent molecules, whose structural parameters are almost comparable to each other. Therefore, the structural data for one of these molecules are considered in this discussion, in which the H1 atom was located on the difference Fourier maps and

isotropically refined (Figure 4-4). There are several notable features. First, the structure of **4** has a short contact between the boron atom and the benzene ring. The B1–C1 distance is 1.842(3) Å, which is quite shorter than that in **2** (2.23 Å). The boron atom is more pyramidalized compared to **2**, where the sum of the three angles, C5–B1–C5*, C5–B1–C12, and C5*–B1–C12, is 338.7°. In addition, the C1 atom adopts a tetrahedral-like geometry. The H1–C1–C4 angle is 141.7°. These structural features indicated the strong coordination of the benzene ring to the boron. The AIM analysis[14,15] using the crystal structure of **4** showed a bond path between the B1 and C1 atoms. At the bond critical point, the $\rho(\mathbf{r})$ value was 0.085, which is larger than that of **2**, indicative of the bonding interaction enhancement.

The second notable feature is that **4** has a significant bond alternation in the eliminated benzene ring. Compound **2** only has the small bond alternation in the eliminated benzene ring (1.380(3)–1.411(2) Å). In contrast, the C1–C2 and C3–C4 bond lengths in **4** are elongated to 1.4338(18) and 1.4202(19) Å, respectively, while the C2–C3 bond is shortened to 1.371(2) Å. The C4–N1 bond length is also shortened to 1.353(3) Å, indicative of a double bond character. These data suggest that the benzene ring is significantly deformed to a quinoidal structure like $\mathbf{4_q}$ in Figure 4-4.

Figure 4-4. ORTEP drawing of **4** (50% probability for thermal ellipsoids) and a postulated canonical structure $\mathbf{4_q}$. Hydrogen atoms except H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C1 1.842(3), B1–C5 1.610(2), B1–C12 1.663(3), C1–C2 1.4338(18), C2–C3 1.371(2), C3–C4 1.4202(19), C4–N1 1.353(3); C5–B1–C5* 108.96(17), C5–B1–C12 114.88(10), C2–C1–H1 114.1(5), C2–C1–C2* 119.56(18). T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Structure of 4 in Solution

To confirm the zwitterionic and quinoidal characters in **4**, the author investigated the solvent effect on the structure of **4** by NMR analysis. In $CDCl_3$, the ^{11}B NMR spectrum of **4** showed a signal at 23.0 ppm with the full width at half maximum (FWHM) of 280 Hz. The chemical shift is highly upfield-shifted and the signal is sharpened compared to those of **2** (δ 51.1 ppm; FWHM, 660 Hz). This observation was consistent with the shortened B1–C1 distance in the crystal structure of **4**. Furthermore, the ^{11}B NMR chemical shift of **4** was downfield-shifted to 24.5 ppm in C_6D_6, and upfield-shifted to 17.7 ppm in acetone-d_6, indicating that the interaction between the boron atom and the benzene ring is strengthened as the solvent becomes more polar. In conjunction with these changes, the chemical shift of the H1 atom was also shifted upfield as the solvent polarity increased from C_6D_6 (6.38 ppm) to $CDCl_3$ (6.19 ppm) to acetonce-d_6 (5.85 ppm). Importantly, these results imply that the degree of the boron–benzene interaction can be modulated by the environment around the molecule. The structural optimization calculations (B3LYP/6-31G(d)) taking the solvent polarity into consideration using the polarizable continuum model (PCM) also supported this consideration (Table 4-1).[12] While the optimized structure of **4** in benzene showed the B1–C1 distance of 2.07 Å, it was shortened to 1.94 Å in acetone. On the other hand, the optimized structures of **2** exhibited little solvent-dependence.

Table 4-1. The B1–C1 Bond Lengths [Å] in the Optimized Structures of **2** and **4** in Various Solvents[a]

	Gas phase	Benzene	Chloroform	Acetone	Water
2	2.350	2.341	2.334	2.327	2.325
4	2.144	2.067	2.005	1.944	1.930

[a]Solvents were included using the polarizable continuum model (PCM).

Natural Bond Orbital Analysis

The natural bond orbital (NBO) analysis at the B3LYP/6-31G(d) level of theory[12,17] provided insights into the bonding interaction between the boron atom and the eliminated benzene ring (see the Experimental Section). In the boracyclophane **2**, the author found six σ-bonding NBOs and three π-bonding NBOs in the benzene ring, indicating that the benzene ring remains as a "benzene". No bonding NBO was found between the B1 and C1 atoms. However, the electronic perturbation from the C1–C2 π-bonding orbital to the p orbital on the boron atom was suggested. The charge-transfer stabilization energy was estimated to be 33.86 kcal/mol. The occupancy (1.58) of the C1–C2 π-bonding NBO was less than 2.0, while that of the boron p orbital was 0.25. The Wiberg bond index[18] was calculated to be 0.18 for the B1···C1 of **2**. These results demonstrated that the boracyclophane **2** can be regarded as a π complex between the Lewis acidic boron atom and the benzene ring with electron donation from the π orbital of the benzene to the boron.

In contrast, in the dimethylamino-substituted **4**, while the eliminated benzene ring has six σ-bonding NBOs, only two π-bonding NBOs (C2–C3 and C2*–C3*) were found. These NBOs also support the quinoidal structure of the benzene ring as previously mentioned. Most importantly, the analysis showed a σ-bonding NBO between the B1 and C1 atoms, which consists of the hybrid orbitals of the boron and carbon atoms with a high p character (B: $sp^{4.77}$, C: $sp^{5.08}$). This σ-bonding NBO clearly demonstrated that the boracyclophane **4** has a high σ-complex character, in which the boron atom and the benzene ring are strongly bound to each other. The natural localized molecular orbital (NLMO) also suggested the σ-bonding character (Figure 4-5).[19] The Wiberg bond index for the B1–C1 bond of **4** was 0.49, which was much higher than that for **2**. In addition, the deformation of the benzene ring in **4** was supported by the nucleus independent chemical shift (NICS).[20] While the NICS(0) value of the benzene ring in **2** was calculated to be –6.66 ppm at the B3LYP/6-31+G(d) level of theory, that of **4** was –3.12 ppm, indicative of the reduced aromaticity in **4**.

Figure 4-5. The NLMO isosurface for the B1–C1 bond in **4** calculated at the B3LYP/6-31G(d) level of theory (plotted at an isovalue of 0.08). T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Reduction of Boracyclophane 2

Finally, the author investigated the reduction of the boracyclophane **2** to generate a radical anion species. As previously mentioned, its LUMO consists of the vertical orbital interaction between the vacant p orbital of the boron atom and the π* orbital of the benzene ring. The author envisioned that the one-electron reduction would produce a radical anion with a one-electron B–C bond.[21–23] The treatment of **2** with potassium metal in THF, followed by recrystallization in the presence of [2.2.2]cryptand produced colorless crystals (Scheme 4-3). The NMR spectroscopies and X-ray crystallographic analysis revealed that the product was not the expected radical anion species, but a potassium salt of the *t*-butylborate **3·K**. Although the mechanism of the generation of **3·K** is unclear at this stage, one possibility is the formation of the radical anion followed by elimination of a hydrogen radical. This result was consistent with the cyclic voltammogram of **2**, which showed an irreversible reduction wave with the cathodic peak potential E_{pc} of –2.38 V vs. Fc/Fc^+ (Figure 4-6).

Scheme 4-3. Reduction of boracyclophane **2**. T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Figure 4-6. Cyclic voltammogram of **2** (1 mM) in THF with n-$Bu_4N^+PF_6^-$ (0.1 M), scan rate 0.1 Vs^{-1}. T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

X-ray Crystallographic Analysis of 3·K

In the X-ray crystal structure of **3·K** (Figure 4-7), similar to the previously reported corresponding fluoroborate,[8] the borate $\mathbf{3}^-$ has a bowl-shaped structure. The bowl depth, defined by the distance between the B1 atom and the plane that consists of three carbon atoms (C4, C10, and C17) on the *para*-position of the benzene rings, is 1.36 Å. Thus, the bowl structure of the *t*-butylborate **3·K** is shallower than that of the corresponding fluoroborate, whose bowl depth is 1.65 Å in the crystal structure.[8] Interestingly, the B1–C20 bond adopts an eclipsed conformation, which likely results from avoiding the steric repulsion with the peripheral methyl groups. Consequently, the B1–C20 bond of 1.737(5) Å is rather long. In addition, although the boracyclohexadiene ring with the CH_2 moiety adopts a boat conformation, the two CMe_2 moieties are not significantly deviated from the planes of the remaining four carbon atoms in the boracyclohexadiene. This feature is also likely due to steric repulsion with the *t*-butyl group and the methyl groups on the benzyl position.

Figure 4-7. ORTEP drawing of **3·K** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C1 1.608(5), B1–C7 1.608(5), B1–C14 1.610(5), B1–C20 1.737(5); C1–B1–C7 108.4(3), C1–B1–C14 108.1(3), C7–B1–C14 107.5(3). T. Kushida and S. Yamaguchi: Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene interactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 8054. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Conclusion

The author has investigated the reaction of the planarized triphenylboranes **1** and **8** with *t*-BuLi and obtained the boracyclophanes **2** and **4**, respectively. Despite the structural constraint in the planarized triphenylboranes, they underwent the formal nucleophilic substitution reaction on the boron center through a tetracoordinate borate intermediate. The structural elucidation of the boracyclophanes **2** and **4** provided insights into the interaction between the boron atom and the eliminated benzene ring. Notably, the interaction mode, *i.e.*, the degree of the σ- and π-complex character, is dependent on the electron-donating character of the benzene ring. Thus, the introduction of the dimethylamino group to the benzene ring strongly alters the interaction from a π-complex character to a σ-complex character. These structures can be regarded as the snapshots for the activation of an aromatic benzene ring with a Lewis acid. These findings should be important for the coordination chemistry of the main group compounds.

Experimental Section

General. Melting points (mp) were determined with a Yanaco MP-S3 instrument. ^{1}H, ^{13}C, and ^{11}B NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 128 MHz for ^{11}B) in $CDCl_3$, C_6D_6, or acetone-d_6. Chemical shifts are reported in δ ppm. ^{1}H NMR spectra are referenced to residual protons in the deuterated solvent as an internal standard. ^{13}C NMR spectra are referenced to carbon-13 in the deuterated solvent as an internal standard. ^{11}B NMR spectra are referenced to $BF_3{\cdot}OEt_2$ as an external standard. Mass spectrometry was measured with a Bruker Daltonics micrOTOF Focus with the APCI ionization method. Cyclic voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ reference electrode. The measurements were carried out under an argon atmosphere using a THF solution of sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate (n-$Bu_4N^+PF_6^-$) as a supporting electrolyte with a scan rate of 0.1 V/s. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel 60 F_{254} (Merck). Column chromatography was performed using silica gel PSQ 100B (Fuji Silysia Chemical). Recycling preparative gel permeation chromatography (GPC) was performed using LC-918 equipped with polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) using chloroform as an eluent. Dry benzene, THF, ether, and toluene were purchased from Kanto Chemical. Commercially available solvents and reagents were used as received. Planarized triphenylborane **1** was prepared as described in the literature.[8] All reactions were carried out under an argon or a nitrogen atmosphere unless otherwise mentioned.

Boracyclophane 2. To a solution of planarized triphenylborane **1** (40.4 mg, 0.12 mmol) in benzene (4 mL) was added a n-pentane solution of t-BuLi (1.59 M, 225 μL, 0.36 mmol) at room temperature. The mixture was stirred for 2 h. After addition of 10 mL of distilled water, the mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure. The crude product was purified by GPC to give 34.4 mg (0.0877 mmol) of **2** in 73% yield as colorless solids: mp 158.5-161.0 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 9H),

1.45 (s, 6H), 2.04 (s, 6H), 3.79 (d, ^2J = 19 Hz, 1H), 4.37 (d, ^2J = 19 Hz, 1H), 7.16 (d, ^3J = 7.2 Hz, 2H), 7.26–7.29 (m, 2H), 7.49 (d, ^3J = 8.0 Hz, 2H), 7.57 (s, 1H), 7.66–7.68 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9 (q), 30.0 (q), 38.1 (q), 42.8 (t), 44.5 (s), 117.3 (d), 124.9 (d), 125.1 (d), 125.3 (d), 126.8 (d), 134.2 (d), 138.2 (s), 151.7 (s), 157.0 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 51.1; HRMS (APCI) *m*/*z* calcd for $C_{29}H_{34}{}^{11}B$ $[M+H]^+$ 393.2748, found: 393.2744.

Effect of the amount of *t*-BuLi on the yield of boracyclophane 2. To a solution of planarized triphenylborane **1** in benzene was added a *n*-pentane solution of *t*-BuLi (1.0 equivalent or 5.0 equivalent) at room temperature. The mixture was stirred for 1 h. After addition of 10 mL of 1N aqueous solution of HCl, the mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure. The crude product was purified by GPC to give **2** as colorless solids. The isolated yields are summarized in Table 4-2.

Table 4-2. Effect of the Amount of *t*-BuLi on the Yields of Boracyclophane **2**

t-BuLi	isolated yield of **2**
1.0 equiv	18%
3.0 equiv	73%
5.0 equiv	71%

NMR observation of *in-situ* generated intermediate 3·Li. To a solution of planarized triphenylborane **1** (27.2 mg, 0.081 mmol) in C_6D_6 (1.6 mL) was added a *n*-pentane solution of *t*-BuLi (1.59 M, 50 μL, 0.080 mmol) at room temperature. A portion (0.5 mL) of the mixture was transfered into a NMR tube equipped with J. Young stopcock, which was filled by N_2, then ^{1}H and ^{11}B NMR were measured (Figures 4-8 and 4-9). **3·Li**: ^{1}H NMR (400 MHz, C_6D_6) δ 0.69 (s, 9H), 1.64 (s, 6H), 1.97 (s, 6H), 3.65 (d, ^2J = 18 Hz, 1H), 4.38 (d, ^2J = 18 Hz, 1H), 7.06 (d, ^3J = 7.2 Hz, 2H), 7.20–7.22 (m, 2H), 7.32 (t, ^3J = 7.6 Hz, 1H), 7.38–7.43 (m, 4H); ^{11}B NMR (128 MHz, C_6D_6) δ –20.1.

Figure 4-8. ^{1}H NMR spectrum of a mixture of **1** and *in-situ* generated **3·Li** in C_6D_6.

Figure 4-9. ^{11}B NMR spectrum of a mixture of **1** and *in-situ* generated **3·Li** in C_6D_6.

Determination of the binding constant of 1 with *t*-BuLi. The binding constant K was determined based on the relative integration of the ^{1}H NMR signals (Figure 4-8, 1.74 ppm for **1** and 1.64 ppm for **3·Li**), as described in the literature.[24]

$$K = \frac{[3\cdot Li]}{[1]\cdot[t\text{-BuLi}]} = \frac{x}{(C_0 - x)^2} \qquad C_0 = [1]_0 = [t\text{-BuLi}]_0 = 0.05\ \text{M}$$

The integration values for the two signals (11.83 for 1.74 ppm of **1** and 5.95 for 1.64 ppm of **3·Li**) gave x = 0.025 M, then C_0 – x = 0.025 M. The binding constant K was determined to be 4.0 × 10 M^{-1}.

Potassium salt of borate 3·K. To a solution of boracyclophane **2** (30.8 mg, 0.078 mmol) in THF (1 mL) was added potassium metal (3.5 mg, 0.090 mmol) at room temperature. The reaction mixture was stirred for 49 h. Recrystallization from THF with slow diffusion of a hexane solution of [2.2.2]cryptand (30.1 mg, 0.080 mmol) gave 41.7 mg (0.0517 mmol) of **3·K** in 66% yield as colorless crystals: mp 217.0-225.0 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.30 (s, 9H), 1.52 (s, 6H), 1.96 (s, 6H), 2.29 (t, ^3J = 4.8 Hz, 12H), 3.27 (t, ^3J = 4.8 Hz, 12H), 3.32 (s, 12H), 3.75 (d, ^2J = 18 Hz, 1H), 4.44 (d, ^2J = 18 Hz, 1H), 6.92–6.95 (m, 4H), 7.02 (t, ^3J = 7.6 Hz, 1H), 7.25 (d, ^3J = 6.8 Hz, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 34.4, 34.5, 35.0, 37.3, 42,1, 53.6, 67.3, 70.3, 120.9, 121.0, 121.4, 121.9, 122.4, 141.5, 149.1, 149.2, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ –18.7.

Diphenylimino-substituted planarized triphenylborane 6. To a mixture of Br-substituted planarized triphenylborane **5**[25] (166 mg, 0.402 mmol), [Pd(dba)$_2$] (12.2mg, 0.021 mmol), 1,1′-bis(diphenylphosphino)ferrocene (23.3 mg, 0.042 mmol), and *t*-BuONa (50.4 mg, 0.524 mmol) in toluene (10 mL) was added benzophenone imine (86.8 mg, 0.479 mmol). After the reaction mixture was refluxed for 12 h, 10 mL

of distilled water was added. The mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 7/3, R_f = 0.30) and recrystallization from hexane/CH_2Cl_2 to give 108 mg (0.210 mmol) of **6** in 52% yield as yellow solids: mp 254.5-258.5 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 12H), 4.55 (s, 2H), 7.00 (s, 2H), 7.14–7.18 (m, 5H), 7.38 (d, ^3J = 6.4 Hz, 2H), 7.44–7.62 (m, 7H), 7.85 (d, ^3J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.1 (q), 37.3 (t), 42.7 (s), 117.5 (d), 123.8 (d), 125.0 (d), 127.9 (d), 128.3 (d), 128.5 (d), 129.5 (d), 130.9 (d), 132.0 (d), 136.4 (s), 139.5 (s), 145.8 (s), 155.6 (s), 156.2 (s), 157.0 (s), 168.8 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation, one doublet signal were overlapped with the other signal; ^{11}B NMR (128 MHz, $CDCl_3$) δ 44.2; HRMS (APCI) *m*/*z* calcd for $C_{38}H_{33}{}^{11}BN$ $[M+H]^+$ 514.2701, found: 514.2707.

Amino-substituted planarized triphenylborane 7. Under an ambient atmosphere, 1 mL of 4N aqueous solution of HCl was added to a solution of **6** (51.8 mg, 0.101 mmol) in THF (5 mL). After the mixture was stirred for 18 h at room temperature, distilled water was added. The organic layer was extracted with ether and washed with a saturated aqueous solution of $NaHCO_3$, then dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 3/2, R_f = 0.20) to give 28.3 mg (0.0810 mmol) of **7** in 80% yield as colorless solids: mp 240 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, 12H), 4.07 (s, 2H), 4.56 (s, 2H), 6.94 (s, 2H), 7.38 (d, ^3J = 6.4 Hz, 2H), 7.57–7.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.6 (q), 37.5 (t), 42.9 (s), 111.1 (d), 123.9 (d), 125.1 (d), 131.8 (d), 145.6 (s), 151.0 (s), 156.2 (s), 158.8 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 43.5; HRMS (APCI) *m*/*z* calcd for $C_{25}H_{25}{}^{11}BN$ $[M+H]^+$ 350.2075, found: 350.2059.

Dimethylamino-substituted planarized triphenylborane 8. A mixture of **7** (135 mg, 0.387 mmol) and $NaBH_4$ (233 mg, 6.16 mmol) in THF (10 mL) was added to a mixture of an aqueous solution of HCHO (37wt%, 0.46 mL, 5.5 mmol) and an aqueous solution of H_2SO_4 (3 M, 0.63 mL, 1.9 mmol) at 0 °C. The mixture was allowed to warm to room

temperature, and stirred for 15 h. After the mixture was neutralized with an aqueous solution of NaOH, 20 mL of distilled water was added. The organic layer was extracted with ether and washed with brine, then dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 4/1, R_f = 0.20) to give 118 mg (0.313 mmol) of **8** in 80% yield as colorless solids: mp 266.0-270.0 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 12H), 3.18 (s, 6H), 4.57 (s, 2H), 6.98 (s, 2H), 7.38 (d, ^3J = 6.4 Hz, 2H), 7.57–7.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.9 (q), 37.5 (t), 40.6 (q), 43.2 (s), 108.2 (d), 123.9 (d), 125.1 (d), 131.6 (d), 145.4 (s), 153.9 (s), 156.4 (s), 158.1 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 43.0; HRMS (APCI) *m*/*z* calcd for $C_{27}H_{29}{}^{11}BN$ $[M+H]^+$ 378.2388, found: 378.2380.

Dimethylamino-substituted boracyclophane 4. To a solution of **8** (30.3 mg, 0.080 mmol) in benzene (3 mL) was added a *n*-pentane solution of *t*-BuLi (1.59 M, 150 μL, 0.24 mmol) at room temperature. The mixture was stirred for 1 h. After addition of 10 mL of 1N aqueous solution of HCl, the mixture was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure. The crude product was purified by GPC to give 26.9 mg (0.0618 mmol) of **4** in 77% yield as pale yellow solids: mp 257.0-261.0 °C (dec.); ^{1}H NMR (400 MHz, C_6D_6) δ 0.69 (s, 9H), 1.34 (s, 6H), 2.00 (s, 6H), 2.39 (s, 6H), 3.94 (d, ^2J = 19 Hz, 1H), 4.79 (d, ^2J = 19 Hz, 1H), 6.38 (s, 1H), 6.68 (s, 2H), 7.29 (d, ^3J = 6.8 Hz, 2H), 7.40 (t, ^3J = 7.6 Hz, 2H), 7.48 (d, ^3J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 28.6 (q), 31.8 (q), 38.1 (q), 39.5 (q), 43.6 (t), 45.0 (s), 87.7 (d), 107.9 (d), 124.7 (d), 125.5 (d), 126.4 (d), 140.6 (s), 150.6 (s), 158.3 (s), 170.9 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, C_6D_6) δ 24.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 1.39 (s, 6H), 2.01 (s, 6H), 3.28 (s, 6H), 3.76 (d, ^2J = 19 Hz, 1H), 4.50 (d, ^2J = 19 Hz, 1H), 6.19 (s, 1H), 6.88 (s, 2H), 7.11 (d, ^3J = 7.2 Hz, 2H), 7.21 (t, ^3J = 7.2 Hz, 2H), 7.38 (d, ^3J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4 (q), 31.2 (q), 38.0 (q), 40.4 (q), 43.0 (t), 44.7 (s), 86.2 (d), 107.7 (d), 124.1 (d), 124.7 (d), 125.6 (d), 139.9 (s), 150.2 (s), 158.4 (s), 171.1 (s), two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 23.0; ^{1}H NMR (400

MHz, acetone-d_6) δ 0.28 (s, 9H), 1.38 (s, 6H), 2.01 (s, 6H), 3.37 (s, 6H), 3.71 (d, ^2J = 19 Hz, 1H), 4.44 (d, ^2J = 19 Hz, 1H), 5.85 (s, 1H), 7.03–7.05 (m, 4H), 7.12 (t, ^3J = 7.6 Hz, 2H), 7.39 (d, ^3J = 7.6 Hz, 2H); ^{11}B NMR (128 MHz, acetone-d_6) δ 17.7; ^{13}C NMR spectrum in acetone-d_6 could not be measured due to poor solubility of the compound; HRMS (APCI) *m*/*z* calcd for $C_{31}H_{39}{}^{11}BN$ $[M+H]^+$ 436.3170, found: 436.3157.

X-Ray Crystallographic Analysis of 2, **4**, and **3·K.** The intensity data were collected on a Rigaku Saturn CCD diffractometer with graphite monochromator MoKα radiation (λ = 0.71070 Å) to $2\theta_{max}$ = 50° at 123 K. The structure was solved by direct methods (SHELXS-97)[26] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[26] While all hydrogen atoms, except the H1 and H23 atoms of **4**, were placed using AFIX instructions, all the other atoms were refined anisotropically. The H1 and H23 atoms of **4** were located on the difference Fourier maps and refined isotropically. The crystal data are summarized in Table 4-3.

Theoretical Calculations

Natural bond orbital (NBO) calculations. NBO calculations were carried out using the Gaussian 09 program[12,17] based on the crystal structures of **2** and **4** at the B3LYP/6-31G(d) level of theory. The selected NBOs are summarized in Tables 4-4 and 4-6. The selected total charge-transfer stabilization energies are summarized in Tables 4-5 and 4-7.

Atoms in molecules (AIM) calculations. AIM functions were calculated with the Gaussian 09 program[12] based on the crystal structures of **2** and **4** at the B3LYP/6-31G(d) level of theory, and analyzed employing the AIM2000 program.[15]

Table 4-3. Crystal Data for **2**, **4**, and **3·K**

	2	**4**	**3·K**
CCDC ID code	936367	936368	936369
Empirical formula	$C_{29}H_{33}B$	$C_{31}H_{38}BN$	$C_{47}H_{68}BKN_2O_6$
Formula weight	392.36	435.43	806.94
Color	colorless	pale yellow	colorless
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$ (#14)	*Pnma* (#62)	$P2_1cn$ (#33)
a (Å)	9.2043(16)	32.67(4)	10.442(12)
b (Å)	25.620(4)	16.623(13)	15.763(17)
c (Å)	10.2042(19)	8.764(7)	26.76(5)
β (deg)	113.4661(7)	90	90
V (Å^3)	2207.2(7)	4759(8)	4405(10)
Z	4	8	4
D_{calcd} (g cm^{-3})	1.181	1.215	1.217
F(000)	848	1888	1744
μ (mm^{-1})	0.065	0.068	0.170
Index ranges	$-9 \le h \le 10$	$-38 \le h \le 38$	$-11 \le h \le 12$
	$-30 \le k \le 30$	$-19 \le k \le 13$	$-18 \le k \le 18$
	$-10 \le l \le 12$	$-10 \le l \le 10$	$-31 \le l \le 31$
Reflections collected	14633	29393	28720
Independent reflections	3787 [R_{int} = 0.0516]	4305 [R_{int} = 0.0355]	7676 [R_{int} = 0.0559]
Goodness-of-fit on F^2	1.086	1.100	1.095
R_1, wR_2 (I>2σ(I))	0.0509, 0.1209	0.0478, 0.1161	0.0573, 0.1047
R_1, wR_2 (all data)	0.0578, 0.1261	0.0511, 0.1181	0.0689, 0.1120

Table 4-4. Summary of the Selected NBOs of **2** Calculated at the B3LYP/6-31G(d) Level of Theory

	NBO type	Occupancy	Polarization	Hybridization
B1–C1	BD (bonding)		Not found	
B1–C5	BD (σ bonding)	1.94514	B1(31.03%), C5(68.97%)	B1($sp^{2.15}$), C5($sp^{1.73}$)
B1–C6	BD (σ bonding)	1.94712	B1(32.00%), C6(68.00%)	B1($sp^{1.82}$), C6($sp^{2.17}$)
B1	LP* (vacant p)	0.24835	–	B1($sp^{75.70}$)
C1–H1	BD (σ bonding)	1.95649	C1(61.87%), H1(38.13%)	C1($sp^{2.06}$), H1(s)
C1–C2	BD (σ bonding)	1.96963	C1(50.38%), C2(49.62%)	C1($sp^{2.01}$), C2($sp^{2.03}$)
C1–C2	BD (π bonding)	1.57738	C1(54.63%), C2(45.37%)	C1($sp^{99.99}$), C2($sp^{99.99}$)
C2–C3	BD (σ bonding)	1.97626	C2(50.75%), C3(49.25%)	C2($sp^{1.92}$), C3($sp^{1.98}$)
C3–C4	BD (σ bonding)	1.97809	C3(50.36%), C4(49.64%)	C3($sp^{1.95}$), C4($sp^{1.94}$)
C3–C4	BD (π bonding)	1.65794	C3(52.05%), C4(47.95%)	C3(p), C4(p)
C4–C9	BD (σ bonding)	1.97806	C4(49.68%), C9(50.32%)	C4($sp^{1.97}$), C9($sp^{1.98}$)
C8–C9	BD (σ bonding)	1.97627	C8(50.83%), C9(49.17%)	C8($sp^{1.93}$), C9($sp^{1.97}$)
C8–C9	BD (π bonding)	1.63057	C8(46.34%), C9(53.66%)	C8(p), C9($sp^{99.99}$)
C1–C8	BD (σ bonding)	1.96934	C1(50.36%), C8(49.64%)	C1($sp^{1.96}$), C8($sp^{2.00}$)

Table 4-5. Selected Total Charge-Transfer Stabilization Energy in **2** Estimated by NBO Calculation at the B3LYP/6-31G(d)[a]

Donor NBO	Accepter NBO	ΔE_{CT} [kcal/mol]
π(C1–C2)	LP*(B1)	33.86

[a]Stabilization energy by intramolecular charge-transfer interaction based on the second order perturbation theory analysis of Fock matrix in NBO basis.

Table 4-6. Summary of the Selected NBOs of **4** Calculated at the B3LYP/6-31G(d) Level of Theory

	NBO type	Occupancy	Polarization	Hybridization
B1–C1	BD (σ bonding)	1.60287	B1(25.56%), C1(74.44%)	B1($sp^{4.77}$), C1($sp^{5.08}$)
B1–C5	BD (σ bonding)	1.93592	B1(31.90%), C5(68.10%)	B1($sp^{2.79}$), C5($sp^{1.68}$)
B1–C6	BD (σ bonding)	1.93189	B1(32.91%), C6(67.09%)	B1($sp^{2.33}$), C6($sp^{2.22}$)
C1–H1	BD (σ bonding)	1.91888	C1(64.07%), H1(35.93%)	C1($sp^{3.30}$), H1(s)
C1–C2	BD (σ bonding)	1.96694	C1(50.36%), C2(49.64%)	C1($sp^{2.32}$), C2($sp^{2.01}$)
C1–C8	BD (σ bonding)	1.96694	C1(50.36%), C8(49.64%)	C1($sp^{2.32}$), C8($sp^{2.01}$)
C2–C3	BD (σ bonding)	1.97274	C2(49.93%), C3(50.07%)	C2($sp^{1.90}$), C3($sp^{1.83}$)
C2–C3	BD (π bonding)	1.73081	C2(40.49%), C3(59.51%)	C2($sp^{99.99}$), C3($sp^{99.99}$)
C8–C9	BD (σ bonding)	1.97274	C8(49.93%), C9(50.07%)	C8($sp^{1.90}$), C9($sp^{1.83}$)
C8–C9	BD (π bonding)	1.73084	C8(40.49%), C9(59.51%)	C8($sp^{99.99}$), C9($sp^{99.99}$)
C3–C4	BD (σ bonding)	1.97067	C3(49.04%), C4(50.96%)	C3($sp^{2.14}$), C4($sp^{1.84}$)
C4–C9	BD (σ bonding)	1.97067	C4(50.96%), C9(49.04%)	C4($sp^{1.84}$), C9($sp^{2.14}$)
C4–N1	BD (σ bonding)	1.98798	C4(38.68%), N1(61.32%)	C4($sp^{2.39}$), N1($sp^{1.63}$)
N1	LP (lone pair)	1.66690	–	N1($sp^{99.99}$)
C4	LP* (vacant p)	0.89360	–	C4($sp^{99.99}$)

Table 4-7. Selected Total Charge-Transfer Stabilization Energies in **4** Estimated by NBO Calculation at the B3LYP/6-31G(d)[a]

Donor NBO	Accepter NBO	ΔE_{CT} [kcal/mol]
π(C2–C3)	LP*(C4)	60.01
π(C8–C9)	LP*(C4)	60.01
LP(N1)	LP*(C4)	124.90

[a]Stabilization energies by intramolecular charge-transfer interaction based on the second order perturbation theory analysis of Fock matrix in NBO basis.

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Conclusion

In this thesis, the author has elucidated the effects of the structural constraint of the planarized triphenylboranes on their excited state and one-electron-reduced state. In addition, the author has achieved the synthesis of the borataanthracenes and the boracyclophanes from the planarized triphenylboranes in the course of the studies of their reactivity. Throughout the studies, several important findings can be extracted, which are summarized as follows:

1. The structural constraint of the triphenylborane skeleton with the three methylene tethers in a planar fashion results in the compression of the geometry around the boron atom. Embedding the compressed B–C bonds in the planarized framework is a mechanism to induce a dynamic motion. The stress in the ground state is released upon the increase in the electron density on the boron center in the excited state or in the one-electron-reduced state, exhibiting the large structural deformation.
2. The trigonally π-expanded planarized triphenylboranes showed a characteristic fluorescence property with the large Stokes shift. The results demonstrated that the planarized triphenylboranes would be a promising building unit for new emissive materials.
3. The planarization of the triphenylborane skeleton is an effective methodology to produce a spin-delocalized radical species. The results should provide an important insight on the triarylborane-based electron-transporting materials.
4. The reaction modes of the planarized triphenylborane **2** with a CH_2 moiety can be controlled by choosing appropriate bases/nucleophiles. Potassium hydride and lithium tetramethylpiperidide acted as a base to produce the borataanthracene anion. Notably, the planarized triphenylboranes still have the Lewis acidity. The reaction with a strong nucleophile, *tert*-butyllithium, resulted in formation of the tetracoordinate borate intermediate followed by generation of the boracyclophanes.
5. Introduction of a boron atom into a π-extended acenes is an effective approach to modify their properties. Planarized *B*-phenylborataanthracene showed a red-shifted absorption and an intense fluorescence. In this case, planarization of the π skeleton affects the enhancement of the π conjugation and the delocalization of the anionic charge over the entire molecule.
6. The boracyclophanes, in which the boron atom is fixed above the benzene ring in close proximity, are a suitable scaffold to study the boron–benzene interaction. Its

σ/π character can be modulated by changing the electron-donating ability of the benzene ring. These structures can be regarded as the snapshots for the activation of an aromatic benzene ring with a Lewis acidic borane.

These findings would not only demonstrate the potential of the planarized triphenylboranes as a building unit for the sophisticated π-conjugated materials, but also provide an important insight into the structurally constrained π-electron systems. The author believes that these results serve as an important guideline for the development of unprecedented and ultimate molecular functional materials.