

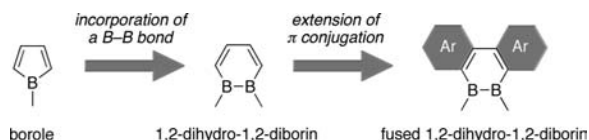
A B–B Bond-Containing Polycyclic π -Electron System: Dithieno-1,2-dihydro-1,2-diborin and Its Dianion

Atsushi Wakamiya,* Kenji Mori, Takafumi Araki, and Shigehiro Yamaguchi*

Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

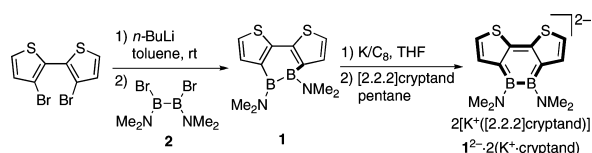
Received June 18, 2009; E-mail: wakamiya@chem.nagoya-u.ac.jp; yamaguchi@chem.nagoya-u.ac.jp

Boracycles have gained continuous attention^{1–3} not only from a fundamental viewpoint but also as potential materials for various applications, such as optoelectronics and sensors.³ Of particular interest is the fact that the incorporation of an electron-deficient boron atom having a vacant p orbital into a π -conjugated cyclic skeleton enables us to produce a π -electron system isoelectronic to its cationic carbon analogue. For instance, borole, a boracyclopentadiene, is isoelectronic to a cyclopentadienyl cation and thus has four- π -electron antiaromatic character.⁴ Consequently, the borole derivatives are unstable but exhibit unusual photophysical properties. In this context, 1,2-dihydro-1,2-diborin (hereafter abbreviated as 1,2-diborin), a six-membered diboracyclohexadiene, is also fascinating as a B–B bond homologue of the borole. Its two-electron reduction would produce a dianionic species isoelectronic to benzene. Although a few dianionic 1,2-diborins have been reported,⁵ little is known about the potential of this ring skeleton as a building unit for extended π -conjugated materials.⁶ We now disclose a dithieno-fused 1,2-diborin, **1**, as an example of a B–B bond-embedded polycyclic π system and discuss how the B–B bond participates in the π conjugation in this skeleton in both its neutral and dianionic states.



The synthesis of **1** was accomplished using diaminodiborane **2** as the B–B source,⁷ as shown in Scheme 1. Thus, the reaction of 3,3'-dilithio-2,2'-bithiophene with **2** in toluene followed by recrystallization from pentane afforded **1** in 32% yield as air- and moisture-sensitive yellow crystals. X-ray structural analysis of **1** revealed that the 1,2-diborin ring has a twisted nonplanar structure with a C1–B1–B2–C4 dihedral angle of 44.5°, whereas the two thiophene rings maintain coplanarity with a dihedral angle of 18.0° (Figure 1a). The twisted geometry of the diborin ring is due to the steric congestion of the two planar B–N moieties. The B–N bond lengths are 1.391(4) and 1.399(3) Å, which are shorter than those in B=N bond-containing heterocycles or borazine (B₃N₃) derivatives (1.40–1.45 Å),^{2a,8} indicative of their B=N double-bond character. Indeed, in the ¹H NMR spectrum, the methyl protons of the NMe₂ groups were observed as two singlet peaks at 2.69 and 2.68 ppm. Variable-temperature NMR measurements showed the

Scheme 1



coalescence of these peaks at ~343 K, from which the rotation barrier (ΔG^\ddagger) of the B–N bond was estimated to be 18.4 kcal/mol.

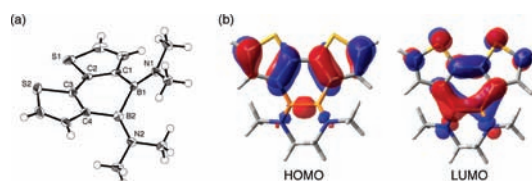


Figure 1. Molecular and electronic structures of **1**: (a) ORTEP drawing (50% probability for thermal ellipsoids); (b) pictorial presentations of the HOMO and LUMO [B3LYP/6-31G(d)].

Notably, in the UV–vis spectra in THF, **1** showed a rather long wavelength absorption band ($\lambda_{\text{max}} = 386$ nm) with a moderate intensity ($\log \epsilon = 3.73$). The λ_{max} is red-shifted more than 80 nm relative to that of 2,2'-bithiophene (302 nm). In the fluorescence spectrum, **1** showed a blue emission at $\lambda_{\text{em}} = 465$ nm with a moderate quantum yield of 0.16.

To elucidate how the B–B bond contributes to the electronic structure in **1**, we conducted DFT calculations at the B3LYP/6-31G(d) level. The optimized structure also has a nonplanar diborin ring (C–B–B–C dihedral angle of 45.8°) with a short B–N bond length (1.412 Å). Despite these structural features, its LUMO is delocalized over the bithiophene and B–B moieties (Figure 1b), demonstrating the significant contribution of the vacant p orbitals of the B–B moiety to the LUMO. In addition to this p– π^* conjugation, the σ – π conjugation between the B–B σ bond and bithiophene skeleton is observed in the HOMO. Notably, the twisted geometry of the diborin ring makes this orbital interaction possible. These orbital interactions decrease the HOMO–LUMO energy gap, leading to the red-shifted absorption in **1**. Moreover, the p– π^* conjugation in the LUMO endows a weak four- π -electron antiaromaticity, despite the B=N bond character. The NICS(0) value calculated for the diborin ring at the HF/6-31+G(d,p)/B3LYP/6-31G(d) level was +8.3 ppm.

The cyclic voltammogram of **1** in THF exhibited two irreversible reduction waves at $E_{\text{pc}} = -2.84$ and -3.02 V (vs Fc/Fc⁺), indicative of the possible reduction to a dianion. The chemical reduction of **1** with excess K/C₈ in THF indeed gave a dark-purple solution of the dianion **1**²⁻ (Scheme 1). Slow diffusion of a pentane solution of [2.2.2]cryptand into this mixture successfully produced dark-purple crystals of the K⁺·cryptand salt of **1**²⁻. X-ray structural analysis revealed that the dithienodiborin skeleton has a nearly planar geometry (C1–B1–B2–C4 dihedral angle = 10.0°) while the nitrogen atoms of the NMe₂ groups are slightly pyramidalized (sum of the angles around N = 347.8, 355.4°), accompanied by elongation of the B–N bond [1.501(6) Å] (Figure 2a). Compared with neutral **1**, **1**²⁻ has rather elongated ring-fusing C1–C2 and C3–C4 bonds [1²⁻, 1.454(5), 1.455(5) Å; **1**, 1.390(3), 1.386(3) Å],

while the B–B bond [1^{2-} , 1.671(8) Å; **1**, 1.721(4) Å], B–C bonds [1^{2-} , 1.524(7), 1.531(6) Å; **1**, 1.570(4), 1.587(4) Å], and C2–C3 bond [1^{2-} , 1.366(5) Å; **1**, 1.458(3) Å] are shortened in 1^{2-} . The long ring-fusing C–C bonds in 1^{2-} are noticeable even in comparison with those in the 1,2-diamino-1,2-diborin dianion 3^{2-} , which has less bond alternation in the butadiene moiety (Figure 2b).^{5a} In addition, the B–B bond in 1^{2-} is longer than those in other diborane dianions, such as [Mes₂B=B(Mes)Ph]²⁻ [1.636(11) Å].⁹

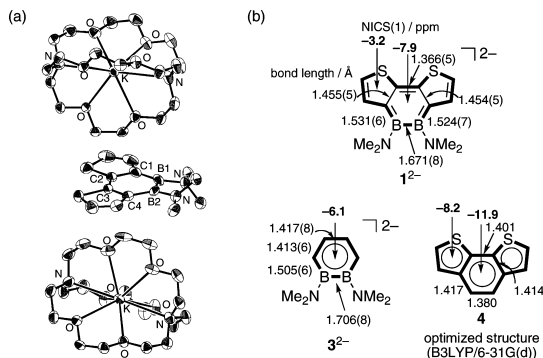


Figure 2. (a) ORTEP drawing (50% probability for thermal ellipsoids) of the structure of $1^{2-} \cdot 2(K^+ \cdot [2.2.2]cryptand)$. (b) Comparison of the structural parameters and NICS(1) values among 1^{2-} , 3^{2-} , and **4**.

These structural features indicate that the reduction of **1** produces neither the B=B double bond nor the six- π -electron aromatic 1,2-diborin ring but instead forms a peripheral π conjugation with 14 π electrons. This is in sharp contrast to the isoelectronic benzodithiophene **4** (Figure 2b), in which each of the three rings has an independent six- π -electron aromatic character. **4** has NICS(1) values [HF/6-31+G(d,p)] of -11.9 and -8.2 ppm for the benzene and thiophene rings, respectively, whereas the diborin and thiophene rings in 1^{2-} have the less negative values of -7.9 and -3.2 ppm, respectively. However, these values are slightly more negative than those for the diborin ring in 3^{2-} (-6.1 ppm) and a thiophene ring in 2,2'-bithiophene dianion (-0.3 ppm) (see the Supporting Information), indicative of a certain aromaticity for the peripheral conjugation.

Finally, we found that the dianion 1^{2-} showed a drastic counteraction effect on the absorption property (Figure 3). The THF solution of $1^{2-} \cdot 2(K^+ \cdot cryptand)$ showed a black color, with the longest λ_{max} at 820 nm. The replacement of the counteraction with K^+ alone or with Li^+ resulted in substantial color changes along with blue shifts in λ_{max} ($1^{2-} \cdot 2K^+$, 561 nm, purple; $1^{2-} \cdot 2Li^+$, 490 nm, orange). The DFT calculations provided a rationale for these changes: In the optimized structures of these salts, the distance between the dithienodiborin plane and the counteraction becomes shorter in the order $1^{2-} \cdot 2(K^+ \cdot cryptand)$ (6.7 Å) > $1^{2-} \cdot 2K^+$ (2.8 Å) > $1^{2-} \cdot 2Li^+$ (1.9 Å), whereas the dithienodiborin geometry itself is not significantly deformed. As the counteraction locates closer to the π framework, the highest π MO is stabilized to a greater extent. This change makes the π - π^* transition energy higher, resulting in the blue shifts in λ_{max} . This finding suggests the possibility of electronic tuning of the fused diborin π systems by the counteractions.

In summary, we have revealed the intriguing orbital interactions and π -conjugation modes in B–B bond-embedded polycyclic π

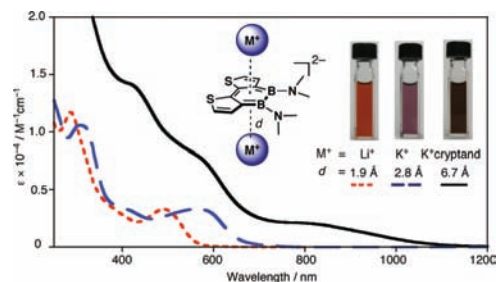


Figure 3. Absorption spectra of 1^{2-} salts (Li^+ , K^+ , and $K^+ \cdot [2.2.2]cryptand$) in THF, with photos of their THF solutions.

systems, indicative of their potential application as building units for extended π -electron systems. The produced dithieno-fused derivative would have an advantage of facile functionalization at the thiophene ring. To explore their potential as optoelectronic materials, the synthesis of a series of derivatives is now in progress in our laboratory.

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Supporting Information Available: Experimental details, crystallographic data (CIF), and theoretical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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