

A Pentacoordinate Boron-Containing π -Electron System with Cl–B–Cl Three-Center Four-Electron Bonds

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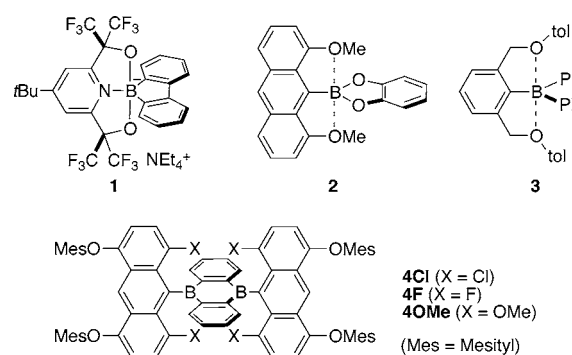
S Supporting Information

ABSTRACT: Tricoordinate boron-containing π -electron systems are an attractive class of compounds with intense fluorescence and strong electron-accepting properties. However, the impact of pentacoordination of the boron atoms on their properties has not been determined. We now disclose a *B,B'*-bis(1,8-dichloro-9-anthryl)-substituted 9,10-dihydro-9,10-diboraanthracene as a new pentacoordinate organoboron compound. In this skeleton, with the aid of the orthogonal arrangement of the anthryl substituent, the B and Cl atoms can form a three-center four-electron (3c–4e) Cl–B–Cl bond. The pentacoordination of the boron atom significantly perturbs the electronic structure and thereby the photophysical and electrochemical properties.

Much attention has been paid to organic compounds possessing extracoordination from both theoretical and experimental points of view.¹ For example, pentacoordinate carbon compounds with trigonal-bipyramidal (TBP) structures have been investigated as models of the transition state in the S_N2 reaction.² Higher-coordinate silicon compounds have drawn continuous attention because of their characteristic reactivity and properties,³ as exemplified by the recent success in the synthesis of pentacoordinate disilanes.⁴ Extracoordination of other elements such as phosphorus, sulfur, and iodine has also been the subject of extensive research.⁵ In contrast, organoboron compounds with pentacoordination are still limited to only a few examples, as the second-row boron atom with its small size preferentially forms tetracoordinate species upon interaction with inter- or intramolecular coordinating groups.⁶

In 1984, Martin's group succeeded in the synthesis of **1** as the first example of a pentacoordinate organoboron compound.⁷ The vacant p orbital of its boron atom interacts with two sets of alkoxylate lone-pair electrons at the axial positions of the TBP geometry. This axial interaction forms a three-center four-electron (3c–4e) bond. Later, compounds **2** and **3** were synthesized by the Akiba and Yamamoto groups as a new family of pentacoordinate boranes (Chart 1).⁸ Accurate X-ray electron density distribution analysis as well as detailed theoretical calculations revealed the character of their 3c–4e bonds. Notably, these examples employed oxygen atoms at the axial positions.⁸ In particular, **2** has an anthryl group that forces the two methoxy groups at the 1- and 8-positions to coordinate to the boron center. The B···O distances are 2.38–2.44 Å, which is ~1.7 times the length of the B–O_{catechol} bonds at the equatorial

Chart 1. Pentacoordinate Organoboron Compounds 1–3 and Dianthryl-Substituted Dihydrodiboraanthracenes 4



positions (1.40 Å). Besides these examples, a pentacoordinate boron compound with a N–B–N bond was also recently reported.⁶

We now disclose the new pentacoordinate borane **4Cl**. This compound consists of a planar dihydrodiboraanthracene π skeleton with a 1,8-dichloro-9-anthryl substituent on each B atom. The attractive electronic and photophysical properties of diboraanthracene π -electron systems with tri- or tetracoordinate boron atoms have been intensively investigated.⁹ In compound **4Cl**, the orthogonal arrangement of each anthryl group forces the two chlorine atoms to be located in close proximity to the boron atom at the TBP axial positions. This compound provides us a suitable molecular scaffold to study (1) the intrinsic character of the Cl···B···Cl axial interaction and (2) the impact of the Cl···B···Cl interaction on the electronic structure of the boron-containing π -electron system. Tri- and tetracoordinate boron-containing π -systems have been proven to have high potential for use in various applications, such as emissive organic solid materials, electron-transporting materials, and chemosensors for anions.¹⁰ However, the impact of pentacoordination of the boron atoms on their electronic properties has not yet been determined.^{8d}

Compound **4Cl** was unexpectedly obtained from orthogonally twisted dianthryl-substituted 9,10-dihydro-9,10-diboraanthracene **5**. Compounds similar to **5** were recently reported by Wagner and co-workers.^{9c} The difference between **5** and those other compounds is that **5** has mesityloxy (OMes) groups at the 4- and 5-positions of the anthryl groups. Our intention was to

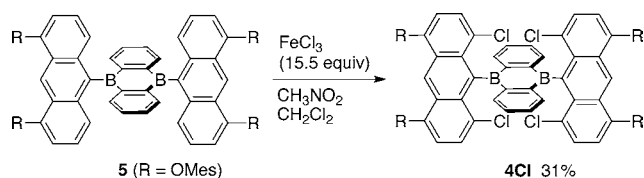
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conduct oxidative annulation of **5** to synthesize a boron-doped teranthrene skeleton, and we envisioned that the electron-donating OMe groups would facilitate the annulation reaction.¹¹ Indeed, using this approach we recently synthesized a boron-doped nanographene-type compound from a diborapentacene precursor, **6** [see the Supporting Information (SI)].¹²

Compound **5** was treated with an excess amount of FeCl₃ (15.5 equiv) in a CH₃NO₂/CH₂Cl₂ mixed solvent (Scheme 1).

Scheme 1. Synthesis of Pentacoordinate Dihydrodiboraanthracene **4Cl**



However, instead of the annulation, the unexpected fourfold chlorination proceeded at the 1- and 8-positions of both of the anthryl groups to give **4Cl** in 31% yield. Although chlorination sometimes takes place as a side reaction when FeCl₃ is employed as an oxidant,¹³ the rather high yield of the tetrachlorinated product was unexpected and is likely due to an enhancement of the reactivity at the 1- and 8-positions by the OMe groups. In addition, this result is in contrast to the fact that **6** smoothly underwent the annulation reaction. This difference may be due to the significant passivation of the diborylated benzene rings in **5** toward the electrophilic substitution reaction.

Notably, the product **4Cl** was stable enough to handle with water and isolate by silica gel column chromatography without any precautions. Although the precursor **5** could be also purified by silica gel column chromatography, a subtle degradation was observed under the high-dilution conditions (10⁻⁵ M) during the photophysical measurements (see the SI). A similar observation was also reported by Wagner's group.^{9c} In contrast, we did not observe any spectral change in **4Cl** even under high-dilution conditions during repeated photophysical measurements.

A single crystal of **4Cl** suitable for X-ray crystallographic analysis was obtained by the vapor diffusion of MeOH into a CHCl₃ solution of the compound.¹⁴ The structural analysis confirmed that the geometry of **4Cl** has C_i symmetry and has an orthogonally twisted conformation in which the terminal anthryl groups and the central diboraanthracene skeleton form the dihedral angles of 87.1° (Figure 1a). Both of the B atoms take a TBP geometry with the sum of the equatorial C–B–C angles equal to 360.0°. More importantly, the B atoms are sandwiched by two Cl atoms in close proximity. The B⋯Cl distances are 2.707(4) and 2.727(4) Å, which are much shorter than the sum of the B and Cl van der Waals radii (3.67 Å)¹⁵ but still ~1.5 times longer than ordinary B–Cl covalent bonds (1.84 Å). The anthryl C–B bond length of 1.609(5) Å in **4Cl** is also elongated compared to those in **5** [1.560(4) and 1.581(4) Å]. This may result from the interaction between the B atom and the two Cl atoms.

To elucidate the intrinsic character of the B⋯Cl interaction in **4Cl**, we conducted quantum-chemical calculations. Our particular interest was whether the B⋯Cl contacts result from attractive 3c–4e Cl–B–Cl bonding or simply from steric enforcement due to the spatial proximity.⁸ We performed full geometry optimizations with tight convergence criteria at several

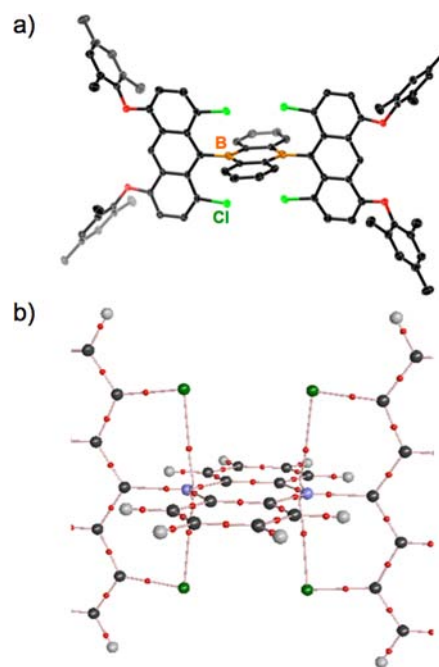


Figure 1. (a) Crystal structure of **4Cl** (50% probability for the thermal ellipsoids). (b) Atoms-in-molecules (AIM) analysis of **4Cl**, showing B (blue), Cl (green), C (black), and H (white) atoms as well as the bond paths (pink wires) and bond critical points (red dots). The peripheral groups have been omitted for clarity.

levels of theory, including B3PW91/6-311+G(2d,p), B3LYP/6-311+G(2d,p), and M06HF/6-311+G(2d,p) (see the SI), among which the B3PW91 calculation reproduced well the structural parameters observed in the crystal structure.¹⁶ In the optimized structure with C_i symmetry, the two B⋯Cl distances become identical to each other at 2.727 Å, which is comparable to the experimental distances. The calculated Cl⋯B⋯Cl angle is 173.1°. Atoms-in-molecules (AIM) analysis of the optimized structure demonstrated that there are bond paths between each central B atom and its two Cl atoms, indicative of their attractive interaction (Figure 1b).¹⁷ The values of the electron density (ρ) and its Laplacian ($\nabla^2\rho$) at the bond critical points (BCPs) were computed to be 0.020 e/a₀³ (where a₀ is the Bohr radius) and 0.048 e/a₀⁵, respectively. These values are comparable to those for the reported pentacoordinate organoboron compounds⁸ and indicate the weak and ionic character of the B⋯Cl interaction. In addition, careful inspection of the molecular orbitals (MOs) showed that **4Cl** has bonding, nonbonding, and antibonding MOs typical for the 3c–4e bond (HOMO–31, HOMO–28, and LUMO+2, respectively; Figure 2). All of these results led to the conclusion that the two B atoms in **4Cl** have pentacoordinate character.

NMR spectroscopy provided insight into the structure of **4Cl** in solution. The ¹¹B NMR spectrum of **4Cl** in CDCl₃ showed a broad signal at 49 ppm, which was shifted slightly upfield from that of **5** (60 ppm) (see the SI). This trend is consistent with those for the reported pentacoordinate boron compounds⁸ and implies that **4Cl** has a pentacoordinate structure even in solution. The shielding effect of the pentacoordination was also supported by the theoretical NMR calculations at the B3PW91/6-311+G(2d,p) level. The calculated chemical shift of the ¹¹B atom in **4Cl** was upfield shifted by 16 ppm relative to that in **5** (see the SI).

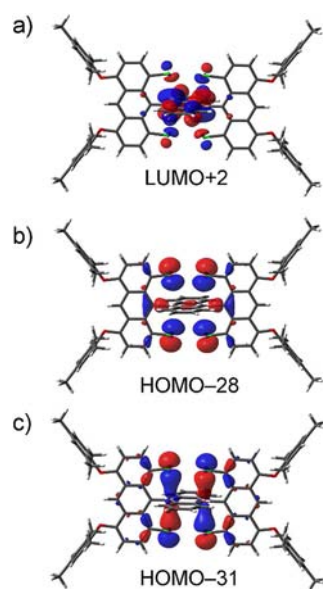


Figure 2. (a) Antibonding, (b) nonbonding, and (c) bonding MOs for the 3c–4e Cl–B–Cl bonds in **4Cl**. The DFT calculation was performed at the B3PW91/6-311+G(2d,p) level.

Importantly, the pentacoordination of the central B atoms via axial coordination of the Cl atoms had a significant impact on the photophysical properties of the π system. While a solution of tricoordinate **5** in common organic solvents showed a pink color, a solution of the pentacoordinate **4Cl** was yellow. The absorption spectrum of **5** in toluene (Figure 3) showed a characteristic

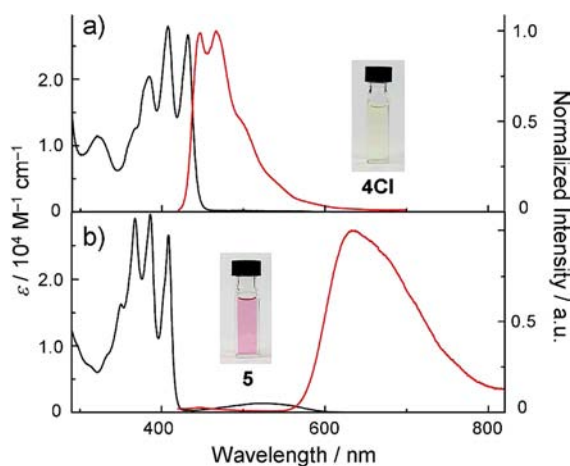


Figure 3. UV/vis absorption (black) and fluorescence (red) spectra for (a) **4Cl** and (b) **5** in toluene. The insets show photographs of **4Cl** and **5** in toluene.

broad, weak band at $\lambda_{\text{max}}^{\text{abs}} = 522$ nm in addition to an intense band at $\lambda_{\text{max}}^{\text{abs}} = 409$ nm with vibronic structure. In contrast, the absorption spectrum of **4Cl** showed only a structured absorption band with a longest $\lambda_{\text{max}}^{\text{abs}}$ of 432 nm. In the fluorescence spectra, while **5** showed a broad band at $\lambda_{\text{max}}^{\text{em}} = 632$ nm with a low quantum yield of $\Phi = 0.06$, **4Cl** showed blue fluorescence at $\lambda_{\text{max}}^{\text{em}} = 447$ nm ($\Phi_{\text{F}} = 0.03$). While the fluorescence spectrum of **5** showed a large solvent effect (solvent, $\lambda_{\text{max}}^{\text{em}}/\text{nm}$: toluene, 632; THF, 693; CHCl_3 , 698; CH_2Cl_2 , 743), the emission band of **4Cl** was less sensitive to the solvent polarity (toluene, 467; THF, 467; CHCl_3 , 473), except for CH_2Cl_2 (512 nm).¹⁸

To elucidate the significant difference in the photophysical properties of **4Cl** and **5**, we compared their electronic structures (Figure 4). Density functional theory (DFT) calculations at the

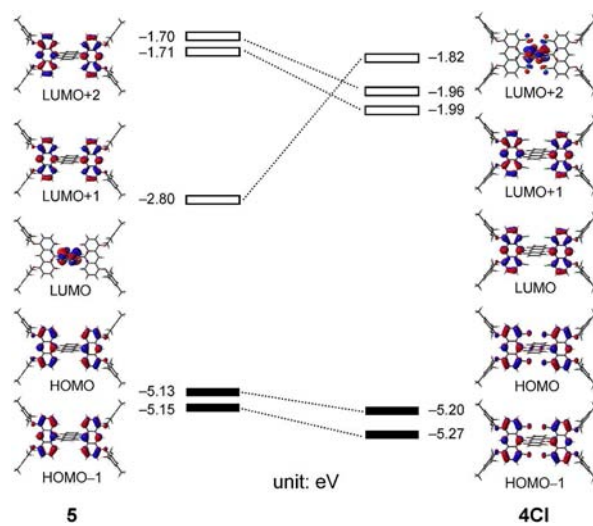


Figure 4. Kohn–Sham MOs of **4Cl** and **5** calculated at the B3PW91/6-311+G(2d,p) level.

B3PW91/6-311+G(2d,p) level demonstrated that the dichlorination of both anthryl groups decreased the energy levels of the π and π^* orbitals localized on the anthryl moieties by ~ 0.1 and ~ 0.3 eV, respectively. These shifts are due to the inductive effect of the electron-withdrawing Cl atoms. In contrast, the LUMO of **5**, which reflects the p– π^* conjugation in the dihydrodiboraanthracene skeleton, is significantly elevated in energy and becomes the LUMO+2 in **4Cl** as a result of the antibonding interaction with the orbitals of the two Cl atoms. The extent of the shift amounts to 1 eV. This is the impact of the pentacoordination on the electronic structure. As a result, the pentacoordinate **4Cl** has a slightly lower HOMO level and a much higher LUMO level compared with **5**. On the basis of time-dependent DFT calculations, the broad absorption band observed for **5** ($\lambda_{\text{max}}^{\text{abs}} = 522$ nm) is assigned to the intramolecular charge transfer (ICT) transition from the electron-donating anthryl moieties to the dihydrodiboraanthracene moiety (see the SI). This assignment was already discussed in the reported 9,10-dianthryl-9,10-diboraanthracene systems.^{9c,d} In contrast, the structured absorption band observed for **4Cl** is the π – π^* transition centered on the terminal anthracene moieties.

Consistent with the calculation results, the pentacoordination significantly perturbs the electrochemical properties as well. In cyclic voltammetry (see the SI), **5** showed two-step reversible redox processes with first and second reduction potentials of $E_{1/2} = -1.68$ and -2.48 V vs Fc/Fc^+ in THF and a quasi-reversible redox wave with the first oxidation potential of $E_{1/2} = +0.61$ V vs Fc/Fc^+ in CH_2Cl_2 .^{9c,d} In contrast, the pentacoordinate **4Cl** showed two-step reversible redox waves with more positive oxidation potentials of $E_{1/2} = +0.70$ and $+0.79$ V vs Fc/Fc^+ (as confirmed by differential pulse voltammetry measurements) and irreversible reduction processes with much more negative cathodic peak potentials ($E_{\text{pc}} = -2.23$, -2.43 , and -2.64 V vs Fc/Fc^+) than **5**.

Finally, to clarify the features of the 3c–4e Cl–B–Cl bond compared with other X–B–X interactions, we conducted DFT calculations on the model compounds **4F** and **4OMe** (Chart 1), which have F and MeO substituents, respectively, in place of the

Cl atoms (see the SI). Similar to **4Cl**, their optimized structures have the anthryl moieties arranged orthogonally to the dihydrodiboraanthracene skeleton with dihedral angles of 90.0°. In **4F**, the B...F distance (2.51 Å) is shorter than the sum of the van der Waals radii of the B and F atoms (3.39 Å). Nevertheless, the AIM analysis of **4F** did not show any bond path between the B and F atoms. The absence of an attractive B...F interaction is likely due to the small size and weak donating ability of the F atom. In contrast, the AIM analysis of **4OMe** showed a bond path between the B and O atoms with $\rho = 0.021 \text{ e/a}_0^3$ and $\nabla^2\rho = 0.059 \text{ e/a}_0^5$ at the BCP. These values are comparable to those of **4Cl**, indicating that the B...Cl interaction in the 3c–4e bond is as strong as the B...O interaction. It is also noteworthy that the B...O antibonding interaction in **4OMe** significantly increases the energy level of the $p-\pi^*$ MO localized on the dihydrodiboraanthracene skeleton, but at the same time, the electron-donating effect of the OMe groups also elevates the π^* orbitals centered on the anthryl moieties. Consequently, the $p-\pi^*$ MO localized on the dihydrodiboraanthracene skeleton remains as the LUMO (see the SI). Thus, the switching of the electronic structure in going from tricoordinate **5** to pentacoordinate **4Cl** is not general but instead is unique to the 3c–4e Cl–B–Cl bond.

In summary, we obtained the bis(dichloroanthryl)-substituted dihydrodiboraanthracene **4Cl** as a new pentacoordinate organoborane. The coordination state of the boron compounds is highly dependent on the substituent on the boron atom and the donating ability of the ligand. This study has demonstrated that the Cl atoms have a sufficient donating ability to form the pentacoordinate structure in the boron-containing π -electron system. The Cl–B–Cl 3c–4e bond thus formed is as strong as the O–B–O congener and enhances the stability of the π skeleton. The antibonding interaction in the 3c–4e Cl–B–Cl bond significantly elevates the $p-\pi^*$ MO localized on the dihydrodiboraanthracene skeleton and thereby perturbs the photophysical properties as well as the electrochemical properties. These findings provide an important basis for the design of new boron-containing π -electron materials.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, crystallographic data (CIF) for **4Cl** and **5**, photophysical properties, theoretical calculations, and complete ref 16 (as ref S4). This material is available free of charge via the Internet at <http://pubs.acs.org>. The supplementary crystallographic data for **4Cl** (CCDC-924601) and **5** (CCDC-924602) have also been deposited with the Cambridge Crystallographic Data Centre.

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Notes

The authors declare no competing financial interest.

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