Five-fold-symmetric Pentabromo- and Pentaiodo-corannulenes: Useful Precursors of Heteroatom-substituted Corannulenes

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Abstract: Five-fold-symmetric pentabromo- and pentaiodocorannulenes were synthesized in sub-gram scale in high yields under aerial conditions and were purified without any chromatographic separations. The obtained pentahalocorannulenes were fully characterized by NMR, MS, and X-ray crystallography. The pentahalocorannulenes are useful precursors of five-fold symmetric heteroatom-substituted corannulenes that are difficult-to-address from known corannulene derivatives. As a representative example, pentaphosphinylated corannulene was prepared for the first time and was comprehensively characterized.

Aryl halides are highly versatile substrates for functionalized aromatics since they undergo various types of organic reactions such as nucleophilic aromatic substitution (S_NAr), free-radical reaction, and transition-metal-catalyzed cross-coupling reactions. Especially, for palladium-catalyzed reactions, aryl bromides and aryl iodides are valuable substrates for formation of carbon-carbon or carbon-heteroatom bonds.^[1]



Scheme 1. Pentahalo- and pentaboryl-corannulenes as pivotal building blocks for five-fold symmetric corannulene derivatives.

Corannulene ($C_{20}H_{10}$) is one of polyaromatic hydrocarbons (PAHs) consisting of a central five-membered ring and surrounding five benzene rings.^[2] It takes a bowl-shaped structure, representing a fragment of Buckminster fullerene C₆₀. Since the first synthesis of corannulene by Lawton and Barth in 1966,^[2a] it has been intensively studied for decades in the field of organic

field effect transistors (OFETs),^[3] organic light emitters,^[4] metalorganic frameworks.^[5] and self-assemblies.^[6] In addition to the distinct bowl-shaped structure, corannulene is also attractive in that it serves as a C_5 -symmetric building block, which is rare in organic molecules (Scheme 1). In 2001, pentachlorocorannulene 1^[7a] was reported as the first example of sym-penta-substituted corannulene derivatives for versatile transformations. Another milestone was reported in 2012 featuring pentakis(pinacolatoboryl)corannulene 2[7h] by regioselective iridium-catalyzed borylation reaction. Various kinds of sym-pentasubstituted corannulene derivatives can be prepared from these pentaaryl-,^[7b,i] materials.^[7] including pentaalkynyl-,^[7b,d,e] pentaoxy-,[7b,f] pentafluoro-,[7l] pentathio-,[7a-c,j,k,n] pentaselenylcorannulenes.^[7m,n] Yet, other kinds of quintuply substituted corannulenes such as pentaphosphinyl-, pentaphosphoryl-, and pentaamino-corannulenes have not been explored. It is partly because of the absence of useful five-fold symmetric precursors such as the corresponding bromo- and iodo-corannuelnes. In other words, pentabromo- and pentaiodo-corannulenes are missing pieces of sym-pentahalogenated corannulenes.



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Scheme 2. Synthesis of pentahalocorannulenes and their derivatization to pentaphosphinylcorannulene. Ar = 4-*tert*-butylphenyl.

Herein, we report the synthesis of pentaiodocorannulene **3** and pentabromocorannulene **4** in good yields in sub-gram scale. The method can be operated under aerial conditions without any tedious chromatographic purifications. To demonstrate their usefulness, we also synthesized *sym*-pentaphosphinylated corannulene **5** from **3** or **4**.

Copper-mediated transformation of arene boronic acid into haloarene has emerged as an efficient method, especially for obtaining electron deficient haloarenes.^[8] This was indeed utilized to access β -halogenated porphyrins and 2,5,8,11-halogenated perylenediimides, which were difficult to obtain via direct SEAr reactions due to the selectivity issue.[8e,f] We then decided to employ the same method with pentaborylcorannulene 2 that was available in a gram scale. First, the synthesis of sym-3 pentaiodocorannulene was examined from pentaborylcorannulene 2 in the presence of copper reagent (Scheme 2). After reflux heating of 2, N-iodosuccinimide, and copper(I) iodide in DMF/toluene (v/v = 2/1) under aerial conditions for 11 h, gray solids containing the target pentaiodocorannulene 3 formed. However, the target material was guite insoluble in common organic solvents even at elevated temperature. Therefore, the normal purification by column chromatography or recrystallization was difficult. We then examined a facile purification procedure, namely repetitive washing. The reaction mixture containing insoluble materials were directly filtrated. The solids were dispersed with acetonitrile and the suspension was sonicated for 10 minutes.^[9] Then the solids were again collected by suction filtration. This sonication-filtration procedure was repeated several times to remove excessive copper iodide. under reduced Finally. after drvina pressure. pentaiodocorannulene 3 was obtained in 80% yield as pale green solids. The ¹H NMR spectrum in 1,1,2,2-tetrachloroethane-d₂ at 80 °C showed a singlet signal at 8.31 ppm, reflecting five-fold symmetric structure of the product (Figure 1a). Molecular ion peak was observed at m/z = 879.5608, calcd. for C₂₀H₅I₅ = 879.5620 [M]⁻ by HR-APCI-TOF mass spectrometry (Figure 1b).

Similarly, *sym*-pentabromocorannulene **4** was synthesized from pentaborylcorannulene **2**, *N*-bromosuccinimide, and copper(I) bromide. The reaction progress was slower than that of the iodination reaction and it took prolonged reaction time of 42 h. The product **4** was almost insoluble in organic solvents. Thus, the precipitated solids were purified by sonication-filtration procedure using aqueous hydrochloric acid, affording pure **4** in 77% yield as off-white solids. Five-fold symmetric ¹H NMR spectrum and HR-APCI-TOF mass spectrum are consistent with the molecular structure of **4** (Figure 1c and 1d).



Figure 1. (a) ¹H NMR spectrum of pentaiodide **3** in 1,1,2,2-tetrachloroethane- d_2 at 80 °C; (b) HR-APCI-TOF mass spectrum of **3**; (c) ¹H NMR spectrum of pentabromide **4** in CDCI₃ at room temperature; (d) HR-APCI-TOF mass spectrum of **4**.



Figure 2. X-Ray crystal structure of **4**. (a) Top view, (b) side view, (c) packing structure (view along *c*-axis), and (d) packing structure (view along *b*-axis).

Fortunately, thin needles suitable for X-ray diffraction analysis were obtained by slow cooling of a hot solution of **4** in 1,1,2,2-tetrachloroethane, and the structure of **4** was unambiguously determined. The bromine atoms were symmetrically installed, and the molecules were vertically stacked in a columnar fashion in the crystal. The intermolecular distance was 3.78 Å, indicating weak π - π interaction between the corannulenes. The void space between the corannulene columns were packed with disordered

solvent molecules (1,1,2,2-tetrachloroethane). The bowl-depth was calculated to be 0.87 Å.

Τo demonstrate the usefulness of svm-pentahalocorannulenes 3 and 4 for symmetrical derivatization, we examined the synthesis of sym-pentaphosphinylated corannulene. In an initial trial, we attempted to introduce five diphenylphosphinyl units, but the product seemed to be poorly soluble and its purification was unsuccessful. Then, we used bis(4-tert-butylphenyl)phosphine oxide^[10] as a coupling partner. sym-Pentahalocorannulenes and bis(4-tertbutylphenyl)phosphine oxide was heated in DMF in the presence of palladium(II) acetate, bis(diphenylphosphino)butane, and triethylamine to afford sym-pentaphosphinylated product 5. The yield was 31% from iodide 3 and 82% from bromide 4. In the ¹H NMR spectrum at 80 °C, phosphinylated corannulene 5 showed a doublet peak for the corannulene-proton at 8.24 ppm with J =15.6 Hz due to the coupling with the phosphorus atoms (See SI). In the ³¹P NMR spectrum of **5** in THF-*d*⁸ at room temperature, a doublet was observed at 20.7 ppm with J = 13.1 Hz, confirming the introduction of phosphorus atoms (See SI). In optical spectra in CH₂Cl₂, 5 exhibits red-shifted absorption and fluorescence (*P*_F = 0.016) compared with the pristine corannulene 6 (Figure 3a).[11] The MO energy calculation revealed that the LUMO of 5 is largely stabilized by ca. 0.5 eV (See SI). This is also consistent with the quasi-reversible two-step reduction waves at -1.66 V and -2.17 V in cyclic voltammogram recorded in benzonitrile (Figure 3b, See SI).



Figure 3. (a) UV/vis absorption (solid) and fluorescence (dashed) spectra of 5 (red) and pristine corannulene 6 (black) in CH_2Cl_2 . (b) Cyclic voltammogram of 5. (Conditions) solvent: benzonitrile, electrolyte: "Bu4NPF6, working electrode; glassy carbon, counter electrode: Pt wire, reference electrode; Ag/AgClO4 in acetonitrile containing 0.1 M "Bu4N(ClO4) and 0.01 M AgNO3, scan rate; 0.05 V/s.

In summary, *sym*-pentaiodocorannulene **3** and *sym*-pentabromocorannulene **4** were synthesized from *sym*-pentakis(pinacolatoboryl)corannulene **2** by copper-mediated reactions under aerial conditions in a sub-gram scale. The obtained *sym*-pentahalocorannulenes were derivatized to *sym*-pentaphosphinylated corannulene **5** in up to 82% yield under palladium catalysis. As demonstrated, pentahalocorannulenes **2** and **3** are good synthons for five-fold symmetric functionalization of corannulene, which is actively studied in our laboratory.

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Keywords: corannulene • halogenation • phosphinylation • X-ray crystallography

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