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Synthesis of Highly Strained π-Bowls from Sumanene

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Bowl-shaped π-conjugated carbon molecules (geodesic polyarenes, buckybowls, or π-bowls) are considered to be another group of key materials in addition to C_{60} and carbon nanotubes in the curved π-conjugated carbon systems. Most of the investigation in π-bowl chemistry has been performed on corannulene ($C_{20}H_{10}$, Figure 1) and its derivatives.[1] Deeper π-bowls are more interesting because they may have properties more similar to those of fullerenes or nanotubes. Therefore, it is important to develop their efficient synthetic routes. Furthermore, highly strained π-bowls are still challenging targets in synthetic organic chemistry.[2] To this end, flash vacuum pyrolysis (FVP) has proven to be an effective tool for forming curved bonds.[3] In fact, highly strained π-bowls, such as hemifullerene ($C_{30}H_{12}$, Figure 1),[4] circumtrindene ($C_{36}H_{12}$),[5] and even C_{60},[6] were synthesized using this methodology. On the other hand, a nonpyrolytic synthetic strategy has been strongly required for the elaborate synthesis of this class of molecules because the reaction conditions of FVP are quite severe and an employable functional group is limited. Recently, Scott and co-workers reported the synthesis of the highly strained bowl $C_{50}H_{20}$ from corannulene using intramolecular Mizoroki−Heck reactions as a key step.[2] Meanwhile, we achieved the synthesis of sumanene (**1**, $C_{21}H_{12}$, Figure 1) based on the nonpyrolytic approach[7] and have studied the structure,[8] dynamics,[9] derivatization,[10] complexation,[11] and application for organic electrical materials.[12] Herein, we report the facile synthesis of highly strained π-bowls **6**, **11a**, **11b**, and trinaphtosumanene **2** ($C_{42}H_{18}$) from **1**.

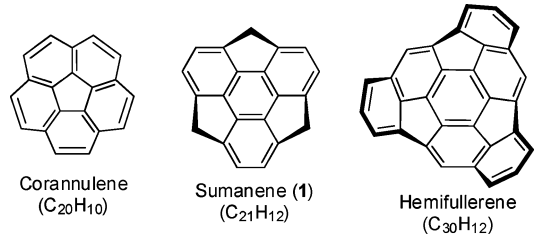
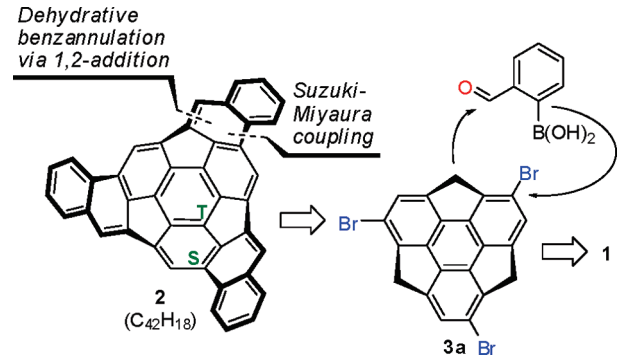


Figure 1. Corannulene, sumanene (**1**), and hemifullerene.

Our synthetic strategy for **2** possessing the hemifullerene skeleton is outlined retrosynthetically in Scheme 1. We envisaged that **2** is constructed via intramolecular dehydrative benzannulation of the trialdehyde via 1,2-addition of the benzylic anions. Such a trialdehyde would arise from the tribromide **3a** through the Suzuki−Miyaura coupling reaction with 2-formylphenylboronic acid. Tribromide **3a** would be prepared from **1** under aromatic bromination conditions.

To investigate the key benzannulation reaction, mononaphtosumanene **6** was chosen as the first target molecule (Scheme 2I). Monoaldehyde **5** was prepared from monobromide **4**[12] in 93% yield via the Pd-catalyzed cross-coupling reaction with *t*-Bu_3P as a ligand. The benzannulation reaction was monitored by ^{1}H NMR. After the treatment of **5** with excess $KN(SiMe_3)_2$ in THF-d_8 at <−80 °C, the

Scheme 1. Synthetic Strategy for **2** ($C_{42}H_{18}$)



reaction mixture was allowed to warm to room temperature, resulting in the disappearance of the aldehyde in the ^{1}H NMR. The usual workup and purification through silica-gel chromatography gave the desired **6** in 98% yield. The structure was confirmed by ^{1}H and ^{13}C NMR, IR, and HRMS. The structural optimization of **6** using molecular orbital calculation (B3LYP/6-31G(d,p)) showed a deeper and more highly strained bowl structure than **1**. The bowl depth at carbon O and Haddon's π-orbital axis vector (POAV)[13] at hub carbon P are 1.33 Å and 10.36°,[14] respectively (Scheme 2I). On the contrary, the corresponding bowl depth and POAV for **1** are 1.11 Å and 8.8°,[15] respectively. Bowl-to-bowl inversion was examined by the conversion to dideuterated **7a**, where the inversion is equivalent to the isomerization between the diastereomers **7a** and **7b** (see ref 16). As the inversion was not observed at room temperature, the equilibration between **7a** and **7b** was monitored in mesitylene-d_{12} at 140 °C by ^{1}H NMR. Growing of the peaks for *exo*-protons (δ 4.42 and 4.54) was observed over a period of hours, as shown in Figure S2a. The observed rate constant (k) and inversion barrier ($\Delta G^{\ddagger}$) of **7** are 8.20×10^{-5} s^{-1} and 32.2 kcal/mol (for details, see Figure S2),[16] which is almost 10 kcal/mol higher than that of **1**. The inversion barrier was approximately reproduced by calculations (31.4 kcal/mol from B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p); see Figure S3).

With the success of the monoannulation reaction, we next aimed toward the synthesis of di- and trinaphtosumanenes. Treatment of **1** with 3.3 equiv of Br_2 gave a mixture of dibromides **8** and tribromides **3** (Scheme 2II), the separation of which being difficult at this stage. The mixture underwent the next Suzuki−Miyaura coupling reaction to give dialdehydes **9a,b** and trialdehydes **10a,b** in two steps in 45 and 41% yields, respectively. The formation of dialdehydes **9c,d** was not observed, which might be attributable to the bromination reaction rather than the cross-coupling reaction. The ratio of **9b** to **9a** was 1.2.[17] In the case of trialdehyde, the desired **10a** was obtained in a lower ratio than that estimated from the statistics (**10a/10b** = 1/5).[17] These ratios of **9a/9b** and **10a/10b** reflect the regioselectivity in the bromination reaction and could

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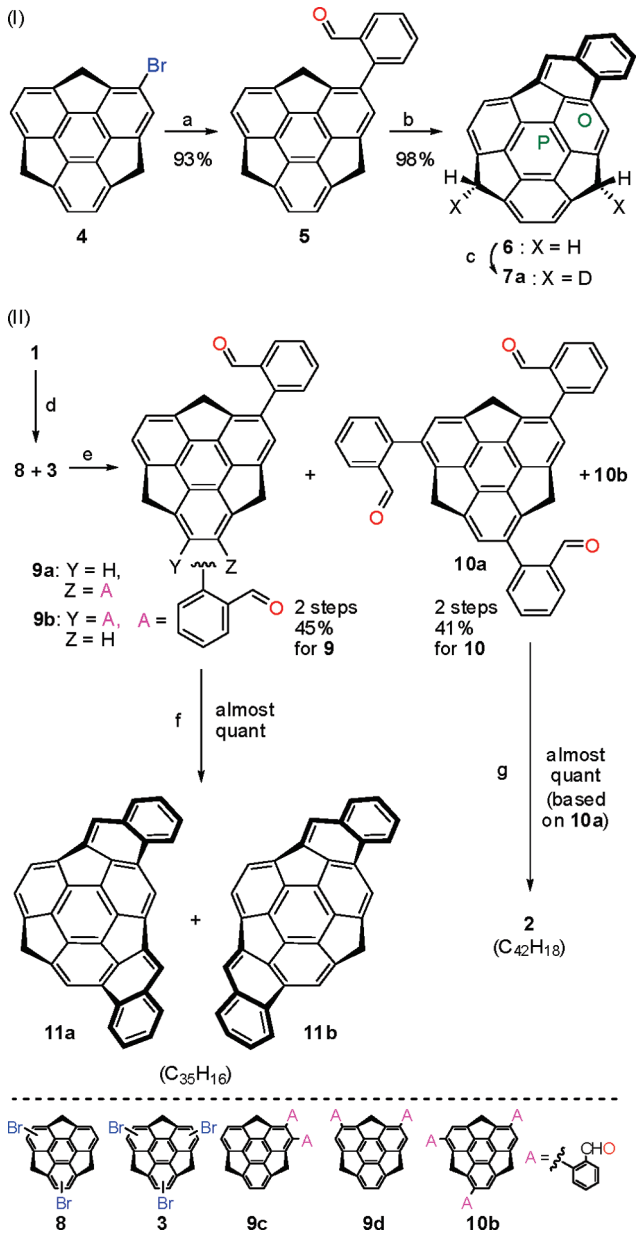
Scheme 2[a]



[a] Reagents and conditions: (I) (a) 2-formylphenylboronic acid, $Pd_2(dba)_3$, *t*-Bu_3P, Cs_2CO_3, dioxane, 80 °C, 24 h; (b) $KN(SiMe_3)_2$, THF-d_8, <−80 °C to rt, 1 h; (c) *t*-BuLi, THF-d_8, <−80 °C to rt, 1 h, then excess CH_3OD, <−80 to −40 °C. (II) (d) Br_2, $CHCl_3/CH_3CN$ = 4/1, 60 °C, 4.5 h; (e) 2-formylphenylboronic acid, $Pd_2(dba)_3$, *t*-Bu_3P, Cs_2CO_3, dioxane, 80 °C, 24 h, **9a/9b** = 1/1.2, **10a/10b** = 1/5. (f) $KN(SiMe_3)_2$, THF-d_8, <−80 °C to rt, 1 h, **11a/11b** = 1/1.2. (g) $KN(SiMe_3)_2$, THF-d_8, <−80 °C to rt, 1 h.

be rationalized from the HOMO density of monobromide **4** and dibromides **8**, as shown in Figure S4a and S4b, respectively.

Annulation reaction of **9a,b** was carried out using $KN(SiMe_3)_2$ to give dinaphtosumanene **11a,b** ($C_{35}H_{16}$) almost quantitatively (**11a/11b** = 1/1.2) (Scheme 2II). For triannulation, the reaction of **10a** proceeded well to afford the desired **2** ($C_{42}H_{18}$) in almost quantitative yield based on C_3 symmetric tribromide **3a**, where the corresponding dibenzannulated monoaldehyde from **10b** was also observed from the EI-MS analysis. Compensating for the strain energy by the aromatization is likely to make the annulation reaction proceed efficiently. The solubility of **2** is low in various solvents, such as $CHCl_3$, CH_2Cl_2, and toluene as well as polar solvents, such as THF, acetone, etc. ^{1}H NMR spectrum consists of only six peaks (δ 8.60, 8.44, 8.04, 7.97, 7.68, 7.56 in CD_2Cl_2/CS_2 = 1/1). The structure of **2** was also supported by 2D NMR (COSY, NOESY, HMQC, and HMBC), IR, and HRMS. The structural optimization of **11a,b** and **2** using molecular orbital calculation (B3LYP/6-31G(d,p)) showed the deeper bowl depth and POAV. The estimated bowl depth and POAV for **2** reach 1.37 Å at carbon S and 10.75° at hub carbon T (Scheme 1),[14] which are comparable to the corresponding values in hemifullerene.[18] Accordingly, bowl inversion is unlikely to occur with **2**.[19]

In conclusion, the short step synthesis (only three steps from **1**) of highly strained naphtosumanenes was successfully achieved through a nonpyrolytic approach. It should be noted that the annulation reaction proceeds in quite high yield. This strategy will allow the facile synthesis of various highly strained π-bowls.

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Supporting Information Available: Experimental details, spectral data for **2**, **3**, and **5**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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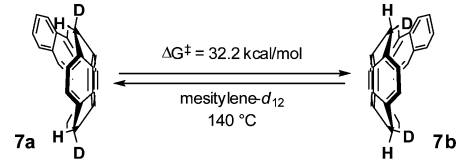
(13) The POAV angle is widely used to gauge the curvature of a given center in bowls: Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676.
(14) The details for the bowl depth and POAV are shown in Figure S1c.
(15) Calculated from the crystal structure of **1**.
(16) Bowl-to-bowl inversion between **7a** and **7b**.



(17) Determined by ^{1}H NMR.
(18) Bowl depth and POAV are 1.39 Å and 10.83°, which are determined from the reported crystal structure. Petrukhina, M. A.; Andreini, K. W.; Peng, L.; Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5477.
(19) Estimated to be 63.8 kcal/mol by the DFT calculation (B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p); see Figure S3).

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