Fused-Ring Systems

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Construction of a Hemifullerene Skeleton: A Regioselective Intramolecular Oxidative Cyclization**

Toru Amaya, Takanori Ito, and Toshikazu Hirao**

Abstract: *A two-step synthesis of a strained π bowl, with hemifullerene skeleton from sumanene, was achieved in a high yield. The first step is a base-promoted condensation reaction with a benzophenone compound, bis(3,5-dimethylphenyl)methanone. The second step is the regioselective intramolecular oxidative cyclization, which is a key reaction for the hemifullerene skeleton synthesis. This regioselective cyclization is likely to be under thermodynamic control. This strategy will allow facile synthesis of various highly strained π bowls.*

Exploration leading to the rational synthesis of curved carbon conjugated molecules consisting of distorted benzene rings is still a challenge, even though the field of organic synthesis has significantly matured.[1] Thus, a well-designed and sophisticated strategy is desired to synthesize such compounds.

The compounds focused on herein are bowl-shaped π-conjugated molecules. (The term "π bowls" is used for such compounds in the present paper, whereas they have been also called open geodesic polyarenes[2] or buckybowls.[3]) Such compounds have an inherent distortion because of the benzene rings fused with imbedded five-membered rings. Representative molecules include corannulene, sumanene (**1**), and hemifullerene, whose skeletons are represented by a partial structure of fullerene C_{60} or the end-cap of a carbon nanotube (Figure 1). These molecules are expected to be not only a building block for the synthesis of fullerene and carbon nanotube skeletons but also organic materials, such as organic semiconductors and liquid crystals.[4] A pioneering work is the synthesis of corannulene in 1966.[5] Subsequent development of flash vacuum pyrolysis (FVP) has proven to be an effective tool for forming curved bonds.[6] In fact, highly strained π bowls, such as hemifullerene ($C_{30}H_{12}$; Figure 1),[7] circumtrindene ($C_{36}H_{12}$),[8] and even C_{60},[1a] were synthesized using this methodology. Even triazafullerene was constructed by the related method using a platinum catalyst.[9] However, reaction conditions of FVP are quite harsh and suitable functional groups are limited. In contrast, a nonpyrolytic synthetic strategy is advantageous for scale-up and the allowable range of functional groups. In fact, the practical scale synthesis for corannulene is conducted using a nonpyrolytic method.[10] The utility of cross-coupling reactions with transition-metal catalysts such as palladium has been demonstrated for the construction of highly distorted ring-fused structures.[11] Scott and co-workers achieved the synthesis of the end-cap of a [5,5] carbon nanotube based on a strategy of combined palladium-catalyzed cyclization and FVP.[1c] Cove-region closure, mediated by Al_2O_3, by C–F bond activation is also reported to construct a relatively flat ring system.[12] Meanwhile, we achieved the synthesis of sumanene (**1**) based on a nonpyrolytic approach,[13] and have studied the structure,[14] dynamics,[15] derivatization,[16] complexation,[17] application for organic electrical materials,[4a] and laser-induced carbonization.[18] Thus, development of a synthetic method for π bowls has actively been studied.[19]

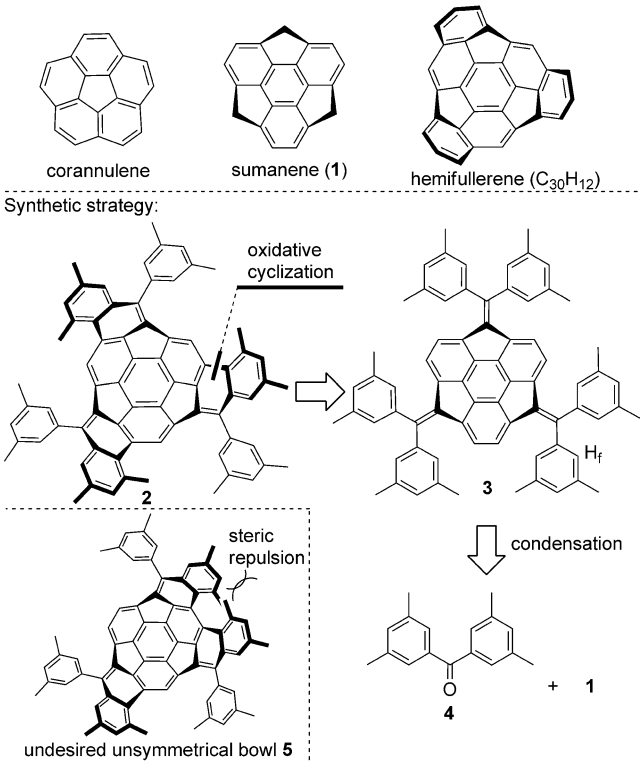

Figure 1. Corannulene, sumanene (**1**), and hemifullerene. Synthetic strategy for **2** having a hemifullerene skeleton.

[*] Dr. T. Amaya, T. Ito, Prof. Dr. T. Hirao
Department of Applied Chemistry
Graduate School of Engineering, Osaka University
Yamada-oka, Suita, Osaka 565-0871 (Japan)
E-mail: amaya@chem.eng.osaka-u.ac.jp
hirao@chem.eng.osaka-u.ac.jp
Prof. Dr. T. Hirao
JST, ACT-C
4-1-8 Honcho, Kawaguchi, Saitama, 332-0012 (Japan)

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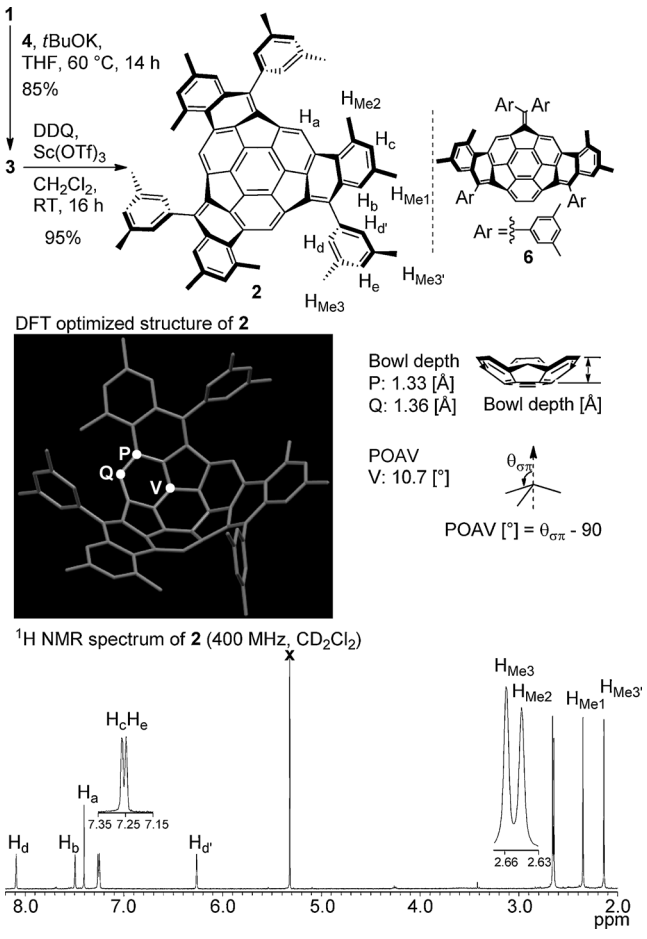
In this context, **1** is regarded as a useful building block in the synthesis of deeper bowls because the three reactive benzylic positions are available for the transformation. We have already demonstrated the construction of the hemifullerene skeleton from **1** by the following three-step protocol: 1) tribromination, 2) cross-coupling with 2-formylboronic acid, and 3) intramolecular condensation by treatment with a base.[16b] The issue in this strategy is the low selectivity of bromination. In this work, we chose the molecule **2**, with a hemifullerene skeleton, as a target. The strategy for **2** includes two steps: 1) condensation with the benzophenone compound **4** to give **3**, and 2) intramolecular oxidative cyclization (Figure 1). Methyl substituents are introduced at both the 3- and 5-position of the two phenyl groups in benzophenone to prevent the formation of the undesired isomer **5**, which results from the steric hindrance. Herein, we report the achievement of the selective synthesis for the C_3-symmetric π bowl **2** in a high yield.

Condensation reaction of **1** with **4** was carried out in the presence of *t*BuOK as a base in THF at 60 °C for 14 hours (Scheme 1). The desired product **3** was isolated in 85 % as a yellow-orange solid. Then, dehydrogenative oxidative cyclization of **3** was investigated. After screening oxidants and either protic or Lewis acids, a combination of DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) and $Sc(OTf)_3$[20] was found to be optimal. After stirring the reaction mixture for 16 hours at room temperature the reaction was quenched. To our surprise, only the peaks attributable to **2** were observed in ^{1}H NMR spectrum of the crude reaction mixture. Specifically, the absence of the side products such as **5** and **6**, as well as the tetra-, penta-, and hexacyclized ones surprised us because **5** and/or **6** must be formed if the regioselectivity of cyclization depends on the statistics. After purification by filtering through a short pad of silica gel, the desired product **2** was isolated as a yellow solid in a high yield (95 %). The solubility of **2** is good in various solvents (CH_2Cl_2, $CHCl_3$, toluene, etc). MALDI-TOF mass spectroscopy clearly showed the parent mass ($M^{\bullet+}$) and the good correlation of the isotope pattern with that of the corresponding simulation. The ^{1}H NMR spectrum in CD_2Cl_2 (Scheme 1) consists of only ten peaks including six peaks for aromatic protons ($\delta = 6.26$, 7.25, 7.27, 7.41, 7.50, and 8.09 ppm) and four peaks for methyl protons ($\delta = 2.14$, 2.35, 2.65, and 2.66 ppm). The peaks in the ^{1}H NMR spectrum were assigned based on two-dimensional (2D) NOESY, HSQC, and HMBC experiments (see the Supporting Information). The protons H_a on the sumanene skeleton are present at $\delta = 7.41$ ppm, which is at a lower magnetic field compared to the corresponding protons in **3** ($\delta = 6.45$ ppm; Figure 2). The protons of the 3,5-dimethylphenyl group (H_{Me3} and $H_{Me3'}$, H_d and $H_{d'}$) are not equivalent. $H_{Me3'}$ and $H_{d'}$ appeared at the upper magnetic field region ($\delta = 2.14$ and 6.26 ppm) because of the shielding effect of the ring current since they are positioned on the concave side of the bowl structure. Conversely, H_{Me3} and H_d appeared at the lower magnetic field range ($\delta = 2.66$ and 8.09 ppm). The crosspeaks for the chemical exchange between these peaks were not observed in the 2D NOESY spectrum, thus suggesting the slow or no rotation of the phenyl group. This observation is in contrast to the those of the corresponding protons H_f in **3** (Figure 1), which are observed as a broad singlet. This broadening indicates that the 3,5-dimethylphenyl groups in **3** rotate more rapidly compared to those in **2**.

To gain information on the mechanism of the reaction, the reaction was monitored using ^{1}H NMR spectroscopy. Figure 2 shows the range from $\delta = 5.95$ to 6.50 ppm, which is the region corresponding to the peripheral CH-CH aromatic protons on the sumanene skeleton ($\delta = 6.00$–6.25 ppm) and the concave protons H* in the 3,5-dimethylphenyl group of **2** and **6**–**8**. The NMR simulations based on GIAO-DFT calculations were carried out for the optimized structures of the mono- and dicyclized products **7**, **6**, and **8**, and the product **2** (GIAO-B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p), see Tables S1 and S2 in the Supporting Information). The peripheral CH–CH aromatic protons on the sumanene skeleton in **7**, **6**, and **8** were predicted to appear at a higher region relative to the other aromatic protons. Comparison of the observed and calculated shifts in the completely assigned compound **2** promises a certain level of validity of the calculation (see Table S1). After stirring the reaction mixture at room temperature for 40 minutes, a singlet ($\delta = 6.45$ ppm) and two sets of doublets ($\delta = 6.02$ and 6.10; $\delta = 6.14$ and 6.20 ppm) appeared, probably derived from the monocyclized compound **7**. About 10 minutes later, very complex peaks were observed. They



Scheme 1. Synthesis, DFT optimized structure, and ^{1}H NMR spectrum of **2**. Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

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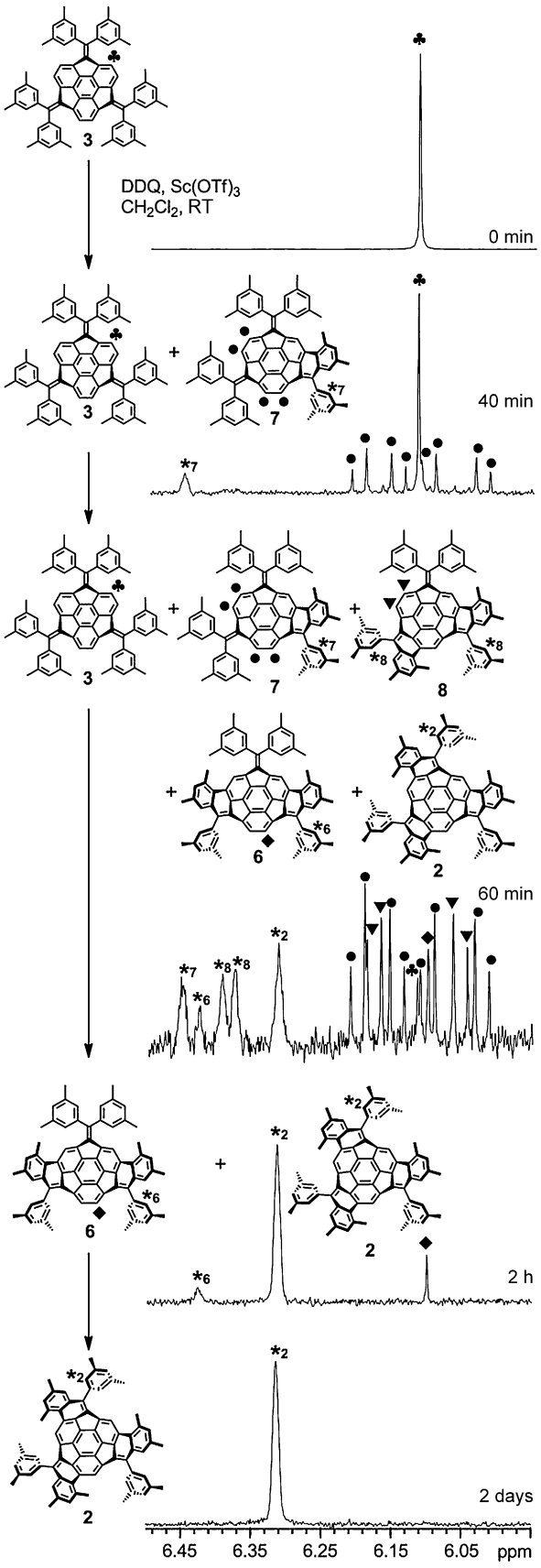
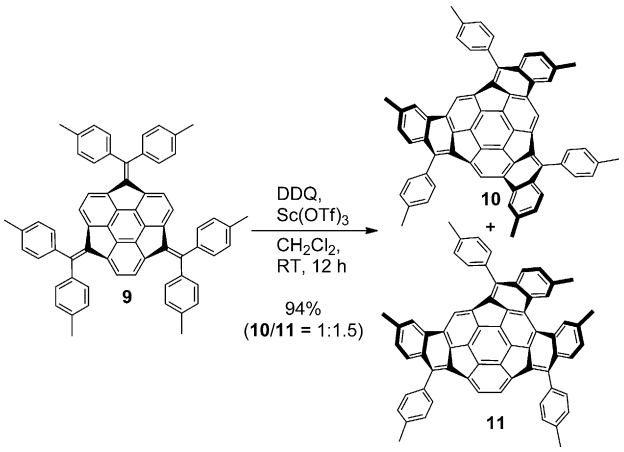


Figure 2. Progress of the oxidative cyclization from **3** to **2** as monitored by ^{1}H NMR spectroscopy.

are likely to include the peaks from the starting substrate **3**, mono- and dicyclized products **7**, **6** and **8**, and the product **2**. After 2 hours, they converged to one singlet derived from **2** and two singlets ($\delta = 6.10$ and 6.43 ppm). Judging from the symmetry, these two singlets are thought to belong to **6**. Finally, the complete conversion of these peaks into those of **2** was observed.

These results suggest that the regioselectivity is controlled thermodynamically. Lewis acid and/or the protic acid derived from the dehydrogenative oxidation may trigger the ring opening and re-cyclization to the isomer, thus resulting in the path for the formation of the most stable C_3-symmetric product **2** (a plausible path from **6** to **2** via **8** is shown in Scheme S1). The related ring opening and re-cyclization mechanism during the oxidative cyclization are less common, but several studies indicate isomerization by ring-opening and re-cyclization when electron-rich starting substrates, such as those having methoxy groups, are used.[21] In our case, the compounds do not have methoxy groups, but ring strain may prompt the facile ring opening.

For comparison, the oxidative cyclization of the π bowl **9**, having methyl groups on the 4-position on each phenyl group, was conducted (Scheme 2). The reaction proceeded in a high



Scheme 2. Oxidative cyclization of **9**.

yield (94%). Concerning the regioselectivity, not only the C_3-symmetric compound **10** but also **11** was formed in the ratio of 1:1.5. These structures were determined by 2D NOESY experiments (see the Supporting Information). It is thought that the [5]helicene-like structure in **11** was formed because of reduced steric hindrance compared to that in **5**.

To see the structural effect of the additional fused rings on the sumanene skeleton, the structural optimization of **2** using DFT calculations was conducted at the B3LYP/6-31G(d,p) level of theory (Scheme 1). The optimized structure is described in terms of the bowl depth (BD) and the π-orbital axis vector (POAV). Here, the BD is defined as the height from the plane of the six-membered ring at the base. The POAV angle is defined as $\theta_{\sigma\pi\text{-}90}$, which indicates the extent of the pyramidalization.[22] The selected BDs and POAVs are shown in Scheme 1. The compound **2** exhibited a more strained structure as compared to **1** (BD: 1.11 Å), where the

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BDs for **2** are 1.36 and 1.33 Å at P and Q, respectively. These values are comparable to hemifullerene.[23] As for the POAVs, the degree of the curvature was found to increase from the carbon rims to the hub benzene ring for **2**. The carbon atoms (V) of the hub benzene ring are the most curved (POAV = 10.7°). This value is still smaller than the corresponding one in fullerene C_{60} (11.6°).[22]

The spectroscopic properties of the π bowls **2** and **3** were investigated using UV/Vis absorption and emission spectroscopy. Figure 3 shows the UV/Vis absorption spectra for **2** and

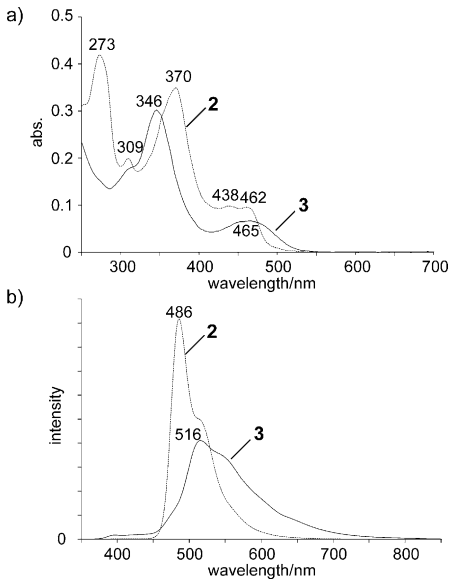

Figure 3. a) UV/Vis absorption and b) emission spectra of **2** and **3** (5.0×10^{-6} M in CH_2Cl_2) under nitrogen. Excitation wavelengths for **2** and **3** are 369 and 350 nm, respectively.

3 in CH_2Cl_2 solution (5.0×10^{-6} M, under nitrogen). The λ_{max} for **2** was observed at 273, 309, 370, 438, and 462 nm and the slope extended out to around 540 nm. The λ_{max} for **3** was observed at 346 and 465 nm and the slope extended out to around 560 nm. The difference was also observed in the emission spectra of **2** and **3**. The λ_{max} for **2** and **3** was observed at 486 and 516 nm, respectively. Thus, the π bowl **2** with a hemifullerene skeleton shows the smaller Stokes shift. It is considered to be due to the rigid skeleton.

In conclusion, the two-step synthesis of the strained π bowl **2** with a hemifullerene skeleton from sumanene (**1**) was achieved in a high yield and based on regioselective intramolecular oxidative cyclization as the key reaction. This regioselective cyclization is likely to be under thermodynamic control. This strategy allows the facile synthesis of various highly strained π bowls.

Keywords: arenes · fullerenes · fused-ring system · regioselectivity

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