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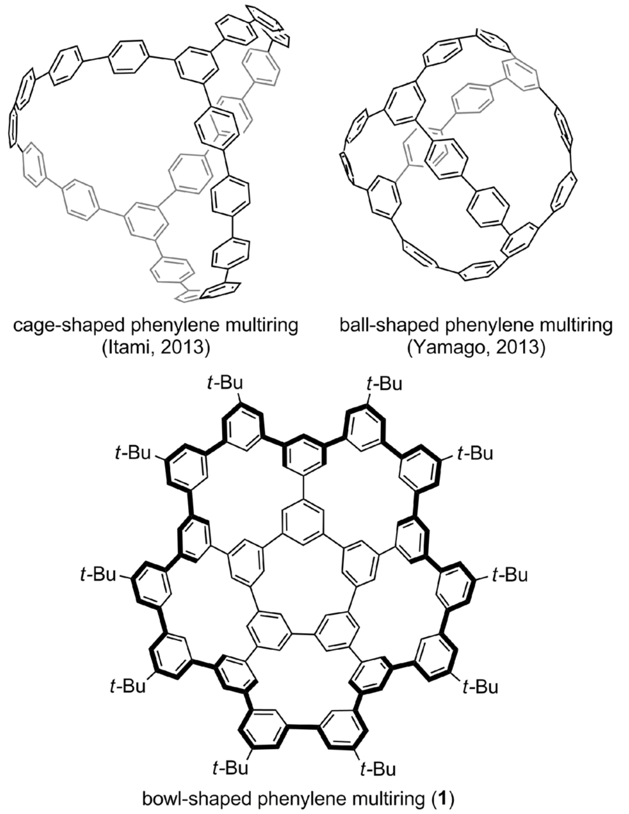
Synthesis and Bowl-in-Bowl Assembly of a Geodesic Phenylene Bowl

*Koki Ikemoto, Ryo Kobayashi, Sota Sato, and Hiroyuki Isobe**

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 90th birthday

Abstract: *A phenylene multiring with a corannulenoidal skeleton was synthesized. Geodesic constraints over 20 phenylene panels resulted in its nanometer-sized, bowl-shaped molecular structure, which was unequivocally revealed by crystallographic analysis. The crystal structure also showed the presence of a bowl-in-bowl dimeric assembly, which was driven by entropic factors in solution.*

The chemistry of cycloarylenes is flourishing, with various molecular structures having been synthesized. Currently, multiring systems constructed with phenylene panels are being exploited to design nanometer-sized carbon-rich molecules with unique three-dimensional shapes. For example, cage- or ball-shaped phenylene multirings have been synthesized through a combination of *para*- and *meta*-linked phenylene panels (Figure 1).[1,2] The three-dimensional molecular shapes were constructed by connecting multiple *para*-phenylene hoops with *meta*-phenylene hubs. Geometry constraints for the three-dimensional shapes thus originated from the curved hoops that were forcibly connected by the hubs. We herein introduce a geodesic design with phenylene multirings for the construction of unique three-dimensional shapes. The geodesic architecture with trigonal planarity allows for the construction of rigid, curved three-dimensional shapes without structural stresses.[3] By using sp^2-hybridized carbon atoms as the basic trigonal planar units, chemists have successfully synthesized a series of geodesic polyarenes such as corannulene.[4] Herein, we used solely *meta*-linked phenylenes as the trigonal planar basis and synthesized bowl-shaped molecule **1** by using geodesic constraints analogous to corannulene. The nanometer-sized, bowl shape of **1** was unequivocally revealed by crystallographic analysis. The crystallographic analysis further revealed bowl-in-bowl assembly in the crystalline state. The dimerization in solution was driven by entropic gains, which might be instructive for understanding the assembly of bowl-shaped nanocarbons.



cage-shaped phenylene multiring (Itami, 2013)

ball-shaped phenylene multiring (Yamago, 2013)

bowl-shaped phenylene multiring (**1**)

Figure 1. Structures of phenylene multirings possessing unique three-dimensional molecular shapes.

We synthesized the bowl-shaped multiring **1** by expanding [5]cyclo-*meta*-phenylene ([5]CMP) with multiple *meta*-linked phenylene units.[5] Thus, terphenylene **5** was synthesized as the outer-rim units from *tert*-butylchlorobenzene **2**[6] through a three-step transformation involving direct C–H borylation,[7] Suzuki coupling,[8] and halogenation[9] reactions (Scheme 1). Five rim units **5** were then coupled with borylated [5]CMP **6**[10] to afford chlorinated precursor **7** in 56% yield. The final cyclization to complete the geodesic skeleton was performed by using a Ni-mediated Yamamoto-type coupling,[11] with fivefold intramolecular homocoupling reactions affording the target **1** in 32% yield.

A single crystal of **1** was obtained from a toluene solution by gradual diffusion of methanol vapor, and was subjected to synchrotron X-ray diffraction experiments (BL17A beam line of KEK Photon Factory). The crystallographic analysis revealed that two molecules with slightly different conformations were stacked to form a dimer ($\mathbf{1}_{\text{out}}\supset\mathbf{1}_{\text{in}}$) assembled in a bowl-in-bowl fashion (Figure 2).[12] These two molecules dimerized in a staggered orientation (see Figure 3c), which

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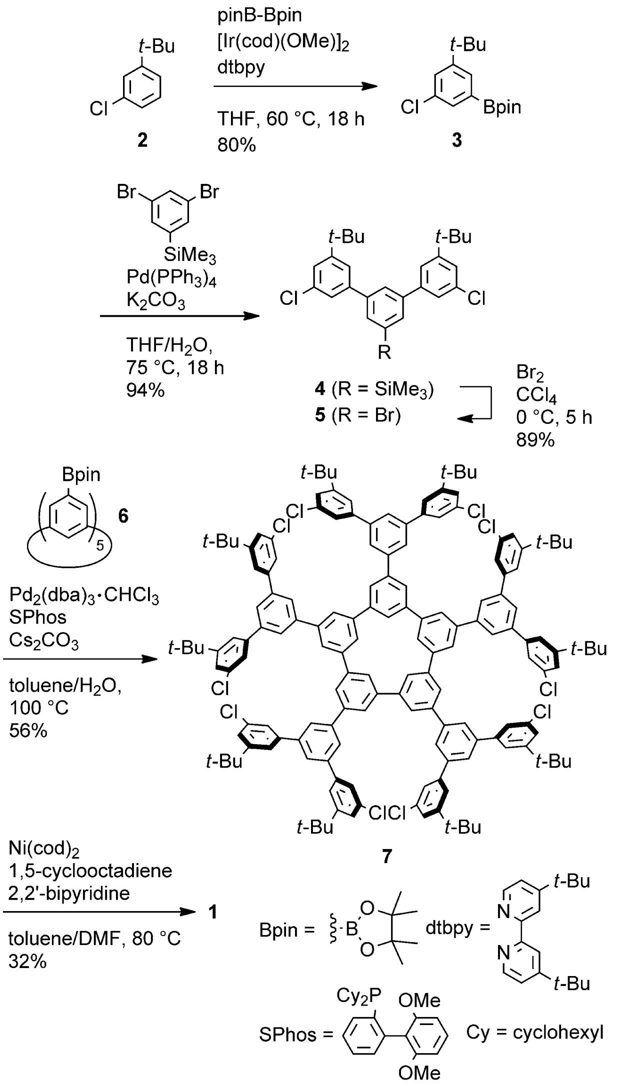
[*] Dr. K. Ikemoto, Dr. S. Sato, Prof. Dr. H. Isobe
Department of Chemistry, The University of Tokyo
JST, ERATO, Isobe Degenerate π-Integration Project
Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-0033 (Japan)
E-mail: isobe@chem.s.u-tokyo.ac.jp

R. Kobayashi, Prof. Dr. H. Isobe
Advanced Institute for Materials Research, Tohoku University
Aoba-ku, Sendai 980-8577 (Japan)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201702063.



Scheme 1. Synthesis of **1**. cod = 1,5-cyclooctadiene, dba = dibenzylideneacetone.

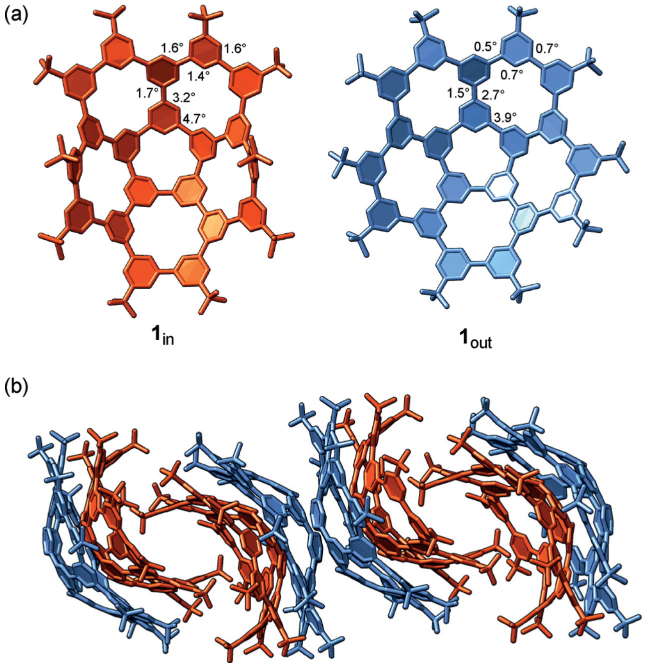


Figure 2. Crystal structures of **1**. a) Two molecular structures found in the bowl-in-bowl assembly. The numbers show the average POAV values of the hub. b) Packing structure. See also Figure 3c for details of the dimer structure.

was most likely due to steric hindrance between the *tert*-butyl substituents. As a result, the bowl-in-bowl assembly did not result in infinite columnar stacks of bowls,[13] and the dimers were packed in a face-to-face orientation. Similar bowl-in-bowl dimerization motifs have been observed with smaller bowl-shaped polyarenes.[12,13] Structural deviations of the phenylene panels from trigonal planar were evaluated by using the π-orbital axis vectors at the sp^2-hybridized carbon atoms of the hub (POAV; Figure 2).[14] The POAV values decreased from 4.7° in the central region to negligible values below 1° toward the periphery of the molecule. The small POAV values imply that the strain energy in these bowl-shaped structures is not high. In contrast, the POAV values for the smaller geodesic polyarenes corannulene and sumanene have been reported to be 8.2° and 9.0°, respectively.[15,16] The geometry constraints from the geodesic skeleton also affected the biaryl torsions. The biaryl linkages of the original [5]CMP molecule were mostly synclinal (sc; 60%),[5,17] whereas those of **1** were mostly synperiplanar (sp; $\mathbf{1}_{\mathrm{in}}$ = 72%, $\mathbf{1}_{\mathrm{out}}$ = 76%; Figure S1). The onset of the UV/Vis absorption of **1** was at $\lambda = 330$ nm, thus red-shifted from that of [5]CMP ($\lambda = 311$ nm; Figure S3). The structural expansion with the *meta*-linked phenylenes, therefore, resulted in planar but curved conjugated systems. Bowl-inversion processes involving conformational changes of 20 phenylene panels connected through 25 biaryl bonds are of interest and will be investigated, for example, through careful designs of periphery structures.[18,19]

Analyses of **1** in [D]chloroform (10 mM) by ^{1}H NMR spectroscopy revealed the formation of bowl-in-bowl dimers ($\mathbf{1}_{\mathrm{out}} \supset \mathbf{1}_{\mathrm{in}}$) in solution. The spectrum recorded at 243 K showed seven singlet resonances (Figure 3a; with intensities of 1:2:2:2:1:2:2 from the downfield to upfield regions), which were ascribed to the highly symmetric monomeric species ($\mathbf{1}_{\mathrm{mono}}$). Interestingly, additional resonances from new species appeared when the temperature was elevated. For example, at 313 K, 13 additional singlet resonances appeared with intensities of 1:4:2:2:2:2:1:2:2:2:2:1:1 together with the original resonances of $\mathbf{1}_{\mathrm{mono}}$. From the bowl-in-bowl dimeric structure observed in the crystal, 14 singlet resonances were expected: 4 resonances of intensity 1, and 10 resonances of intensity 2. The observed resonances of the new species thus matched well with this structure under the assumption that two resonances of intensity 2 were overlapped. From the agreement of the diffusion-ordered spectroscopy (DOSY) with a bowl-in-bowl dimeric structure (see below), we concluded that the new species observed at elevated temperatures was the bowl-in-bowl dimer. The observation of two sets of resonances for two equilibriating species showed that the activation energy was considerably high to slow the exchange processes on the NMR time scale.

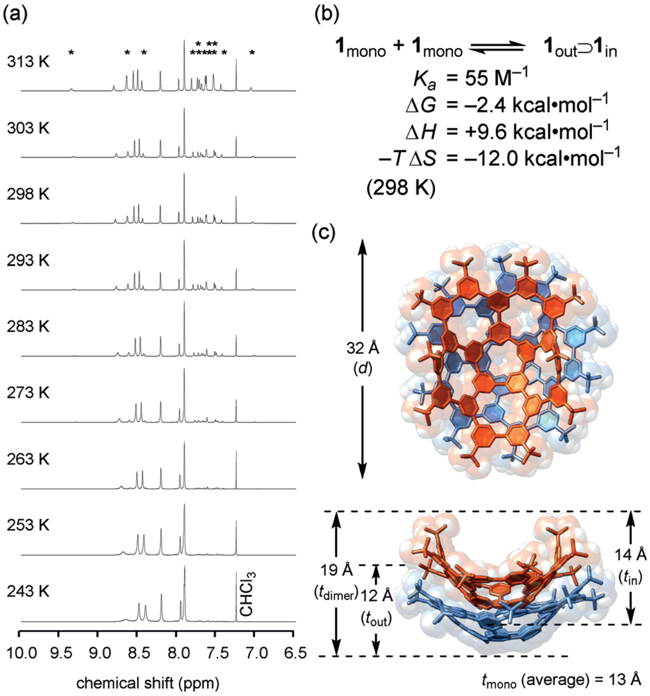


Figure 3. Bowl-in-bowl assembly of **1**. a) VT ^{1}H NMR spectra of **1** in CDCl$_3$ (10 mM). New resonances appearing at 313 K are marked with asterisks. b) Thermodynamics of bowl-in-bowl assembly from the van't Hoff analysis. c) Molecular size of the bowl-in-bowl dimer in the crystal.

We then investigated the association thermodynamics of the dimer formation through variable-temperature (VT) NMR spectroscopy. The concentrations of $\mathbf{1}_{mono}$ and $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$ were determined from the spectra at each temperatures and were converted into association constants through the equation $K_a = [\mathbf{1}_{out}{\supset}\mathbf{1}_{in}]/[\mathbf{1}_{mono}]^2$ (e.g. $K_a = 55\,\text{M}^{-1}$, 298 K; Table S2). The temperature-dependent K_a values were further analyzed by a $1/T-\ln K_a$ plot (Figure S4),[20] which revealed an association enthalpy (ΔH) of $+9.6\,\text{kcal}\,\text{mol}^{-1}$ and an association entropy (ΔS) of $+40.2\,\text{kcal}\,\text{mol}^{-1}\,\text{K}^{-1}$ through a van't Hoff analysis (Figure 3b). The entropy contribution for the association energy ($-T\Delta S$) was thus $-12.0\,\text{kcal}\,\text{mol}^{-1}$, which showed the entropy-driven assembly of $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$. We believe that this entropy-driven assembly originated from desolvation of the curved carbon-rich planes, which has also been observed with other curved π-systems.[21] Similar entropy gains from the desolvation may be crucial for the assembly of gigantic bowl-shaped nanocarbons such as carbon nanocones.[22]

Finally, we analyzed the diffusion constants (D) of $\mathbf{1}_{mono}$ and $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$ at 298 K by DOSY. The D values were $(2.8\pm0.1)\times10^{-10}$ and $(2.4\pm0.1)\times10^{-10}\,\text{m}^2\,\text{s}^{-1}$ for $\mathbf{1}_{mono}$ and $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$, respectively (Figure S5), which were consistent with the monomer/dimer structures of different molecular weights.[23] By applying these values in the Stokes–Einstein relationship,[24] we determined apparent hydrodynamic radii (R_h) of (14.4 ± 0.6) Å for $\mathbf{1}_{mono}$ and (16.5 ± 0.7) Å for $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$. The apparent hydrodynamic radius is an equivalent radius of spherical objects and matches well with the expected hydrodynamic radii calculated from the nonspherical crystal structures. Thus, the diameter (d) was 32 Å for both $\mathbf{1}_{mono}$ and $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$, and the thicknesses ($t$) were 13 and 19 Å for $\mathbf{1}_{mono}$ and $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$, respectively (Figure 3c and Figure S2). These structural parameters can be converted into the expected hydrodynamic radius through Equation (1) to afford the expected values of 15 Å for $\mathbf{1}_{mono}$ and 16 Å for $\mathbf{1}_{out}{\supset}\mathbf{1}_{in}$. This result also confirmed the formation of the bowl-in-bowl dimer in solution.[25]

$$R_h = \frac{3}{4} d \left[\sqrt{1+\left(\frac{t}{d}\right)^2} + \frac{d}{t} \ln\left(\frac{t}{d} + \sqrt{1+\left(\frac{t}{d}\right)^2} \right) - \frac{t}{d} \right]^{-1} \quad (1)$$

In summary, we have synthesized a nanometer-sized, carbon-rich multiring by assembling 20 phenylene panels with 25 biaryl bonds under geodesic constraints. The geodesic design was applied for the first time to phenylene multirings and resulted in the bowl-shaped molecular structure. The large, anomalous molecular shape facilitated concave–convex recognition for formation of the bowl-in-bowl dimer in the crystalline state. The dimerization as well as its thermodynamics were investigated spectroscopically to reveal an entropy-driven assembly in solution. Geodesic arylene multirings may be of interest for exploring carbon-rich materials with unique three-dimensional molecular shapes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: macrocycles · *meta*-phenylene · molecular recognition · nanostructures · self-assembly

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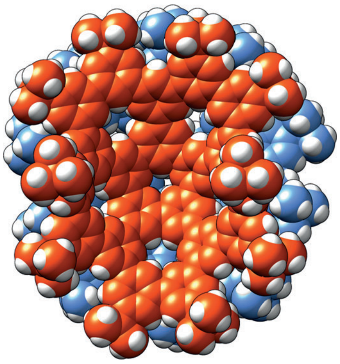
Communications

Molecular Recognition

K. Ikemoto, R. Kobayashi, S. Sato, H. Isobe* ——— ■■■■–■■■■

Synthesis and Bowl-in-Bowl Assembly of a Geodesic Phenylene Bowl



Shape sorting: Geodesic constraints arising from the coupling of trigonal planar phenylenes into a pentagon surrounded by five hexagons resulted in a nanometer-sized bowl-shaped molecule. Concave–convex molecular recognition resulted in the molecules assembling in a bowl-in-bowl fashion. The shape recognition was driven by an entropy gain for the assembly of the large 120 π-systems.