

Synthesis and Structural Analysis of a Highly Curved Buckybowl Containing Corannulene and Sumanene Fragments

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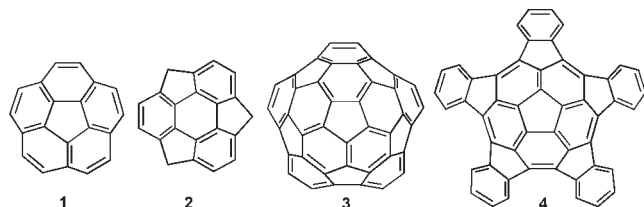
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S Supporting Information

ABSTRACT: Buckybowls **7**, **9**, and **10** were prepared from benzo[*k*]fluoranthene **6** and fluoranthene **8** using straightforward procedures involving key palladium-catalyzed cyclization reactions. The structures of bowl-shaped molecules **7** and **10** were determined by using X-ray crystallographic methods. The observed p-orbital axis vector (POAV) angle of **7** was found to be 12.8°.

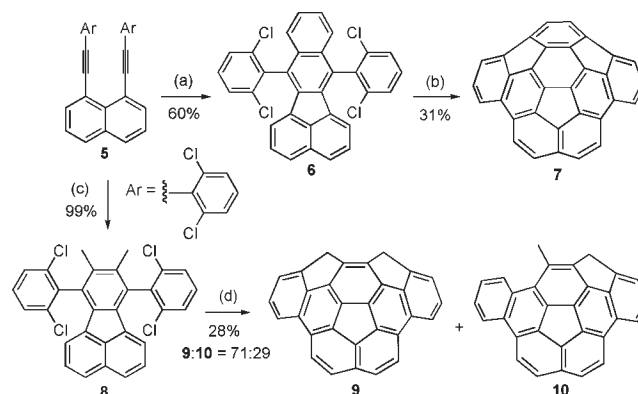
Introducing five-membered rings into sp² hexagonal networks leads to the formation of aromatic bowls. Representative examples of substances in this family include corannulene (**1**)¹ and sumanene (**2**),² both of which are elementary subunits of buckminsterfullerene. However, the structural, chemical, and physical properties of these substances differ markedly. The so-called *mixed* *buckybowls*, molecules that contain both corannulene and sumanene fragments, have relatively high degrees of curvature and deep bowl depths. Indeed, mixed buckybowls, such as circumtrindene (C₃₆H₁₂)³ and hemifullerene (C₃₀H₁₂)⁴ exhibit these expected structural characteristics.⁵ In this regard, compound **3** (C₄₀H₁₀) is also a mixed buckybowl that is predicted to be the simplest capped nanotube.⁶

Chart 1. Representative Examples of Buckybowls



The currently available mixed buckybowls are prepared exclusively by using high-temperature flash vacuum pyrolysis (FVP) methods.^{3–5} The conditions required for FVP have limited functional group tolerance, and they can potentially cause thermal rearrangements of molecular frameworks.⁷ Owing to the fact that metal-catalyzed carbon–carbon bond formation occurs under mild conditions, synthetic protocols employing solution phase processes do not suffer from these drawbacks.^{7,8} Several less strained bowls have been produced in this manner. However, for the construction of highly strained π-bowls, a special strategy is needed that relies on extension of the backbone of a smaller bowl.⁹ Examples of this approach are found in the

Scheme 1. Preparation of Buckybowls **7** and **9**^a



^a Reagents and conditions: (a) C₆H₅I (1.5 equiv), Pd(OAc)₂ (5 mol %), AgOAc (1 equiv), *p*-xylene, 110 °C, 36 h; (b) Pd(PCy₃)₂Cl₂ (40 mol %), DBU, DMF, 160 °C, 36 h; (c) 2-butyne (3 equiv), Rh(PPh₃)₃Cl (2.5 mol %), *p*-xylene, 110 °C, 60 h; (d) Pd(PCy₃)₂Cl₂ (40 mol %), DBU, NMP, 160 °C, 36 h.

synthesis of pentaindenocorannulene **4**^{9a,c} and buckybowl C₄₂H₁₈^{9b} from corannulene and sumanene, respectively. Buckybowl **4** is considered to be a possible precursor to an “arm-chair” [5,5]-nanotube. Unlike the two synthetic strategies presented above, the one employed in our recent studies involves direct generation of highly curved buckybowls from easily accessible planar precursors. Below, we describe the results of this effort that focused on the preparation of the bowl-shaped substances **7** and **9** selected as targets because of their rarity¹⁰ and potential applications to the synthesis of **3**.

The first step of the route devised for the synthesis of **7** employed a recently developed procedure¹¹ involving a Pd-catalyzed [(2 + 2) + 2] cycloaddition reaction of 1,8-bis(aryl-ethynyl)naphthalene **5** with iodobenzene to produce benzo[*k*]fluoranthene **6** (Scheme 1). Cyclization of **6** in the presence of DBU and Pd(PCy₃)₂Cl₂ then generated the desired easily purified product **7** in 31% yield. This synthetic approach is both simpler and more efficient than those that rely on the use of conventional methods devised to date.

The results of our recent studies¹² indicated that crowded environments and the short distances between the haloaryl and the methyl groups enhance the efficiencies of palladium

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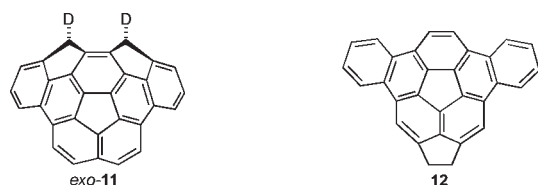
Table 1. Bowl-to-Bowl Inversion Barrier^a

	Exptl	B3LYP/cc-pVDZ	M06-2X/cc-pVDZ
1	ca. 11	9.1	9.9
2	ca. 20	18.2	
9	>40	56.2	59.1
10	>23.5	24.1	26.9

^a kcal mol⁻¹.

promoted benzylic C–H bond activation reactions. In accord with the earlier findings, the bis-methylene bridged buckybowl **9**, which has a backbone that is similar to that of **7**, can be obtained by treatment of the tetrachlorofluoranthene derivative **8** with Pd(PCy₃)₂Cl₂. The starting fluoranthene **8** was prepared by employing a simple Rh-catalyzed cocyclotrimerization reaction of diyne **5** with 2-butyne.^{9d} It should be noted that the Pd-catalyzed cyclization reaction of **8** produced a mixture of **9** and **10** in a 7:3 ratio (28% yield). Although simple chromatographic purification did not lead to complete separation of these substances, both **9** and **10** were obtained in their pure forms. It should be emphasized that the synthetic approach we have developed for the preparation of methylene-bridged buckybowls differs from the one developed earlier by Sakurai et al.^{2a} In the ¹H NMR spectra of **9** and **10**, each pair of methylene protons appears with respective coupling constants of 20.0 and 19.8 Hz, which are typical values for AB systems and also indicate that they are bowls.

With buckybowls **7**, **9**, and **10** in hand, the focus was turned toward determining accurate values for the bowl-to-bowl inversion barriers of the latter two substances using variable-temperature NMR. Based on the results of earlier structure/energy correlation studies by Siegel and co-workers,¹³ the order of the bowl-to-bowl inversion barriers should be **7** > **9** > **10**. We observed that the resonances for protons in the 500 MHz ¹H NMR spectra of **9** and **10** in *o*-dichlorobenzene-*d*₄ at both room temperature and 443 K were essentially the same (see Supporting Information). Moreover, the inversion dynamics of **9** were investigated by carrying out the 2D EXSY NMR experiments with its deuterium substituted derivative *exo*-**11**, which was prepared by using a previously described procedure¹⁴ involving treatment of a solution of **9** in THF-*d*₈ with *t*-BuLi and subsequent quenching with methanol-*d*₄. The 2D EXSY spectrum of a solution of *exo*-**11** in *o*-dichlorobenzene-*d*₄ at 443 K (see Supporting Information) did not reveal that exchange of the methylene protons takes place.



The experimental results demonstrate that buckybowl **9** has a much higher inversion barrier (>40 kcal mol⁻¹) in comparison to those of both corannulene (ca. 11 kcal mol⁻¹)^{13,15} and sumanene (ca. 20 kcal mol⁻¹).^{2a,14} Due to its availability in only limited amounts, buckybowl **10** could not be converted into an analog that is suitable for EXSY studies. However, it is expected that its inversion barrier is slightly higher than that of **12** (ca. 23.5 kcal mol⁻¹) because it has a higher coalescence temperature, bowl depth, and maximum p-orbital axis vector (POAV) angle (see below).^{8b,13}

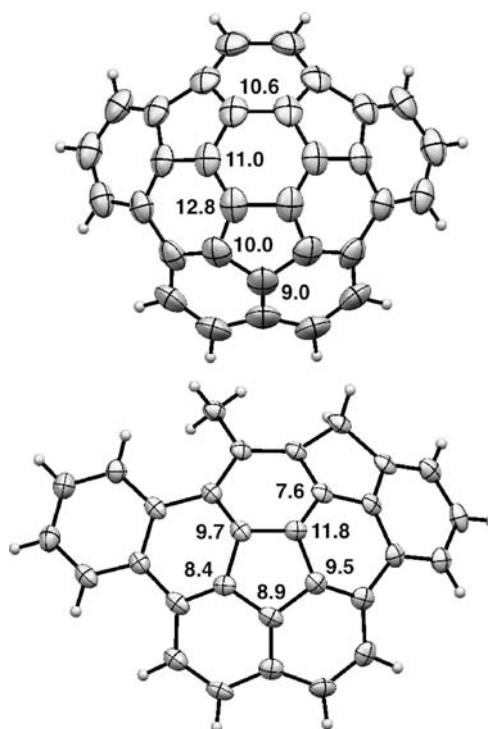


Figure 1. Crystallographic structures and the POAV pyramidalization angles of buckybowls **7** (top) and **10** (bottom). The POAV angles for **10** are average values of those in two nonequivalent molecules.

Density functional theory (DFT) calculations were performed to examine bowl-to-bowl inversions of buckybowls **9** and **10** (Table 1). Optimized geometries and frequencies of these substances were calculated at the B3LYP/cc-pVDZ and M06-2X/cc-pVDZ levels using the Gaussian 09 program. The computed bowl-to-bowl inversion barriers were observed to be close to those found experimentally.

X-ray quality crystals of **7** and **10** were obtained by slow evaporation of CH₂Cl₂/MeOH solutions at ambient temperature.¹⁶ As expected, the X-ray crystallographic structure of **7** shows that it has a deeper bowl depth compared to **10**. The bowl depths of the corannulene and sumanene cores of **7** were determined to be 1.24 and 1.48 Å, respectively. These values are significantly larger than those of the parent corannulene (0.87 Å)¹⁷ and sumanene (1.11 Å).¹⁸ Finally, the bowl depth for **10** was observed to be 1.04 Å, which also exceeds that of corannulene.

The POAV pyramidalization angle is useful for quantifying the curvature that exists in buckybowls. For example, the values of planar benzene and C₆₀ are observed to be 0° and 11.6°, respectively.¹⁹ As shown in Figure 1, the maximum POAV angles of **7** (12.75°) and **10** (11.8°) exceed that of C₆₀. It is interesting to note that bowl-shaped molecules rarely have such high POAV angles.²⁰ The maximum curvatures in **7** and **4** (12.36°–12.99°, avg. 12.69°) are comparable. To the best of our knowledge, **4** and **7** are the most curved π-bowls observed to date. The methylene bridge in **10** actually enhances the curvature as shown by comparisons of the POAV angles of the central Hub ring.

The results of the studies described above demonstrate that a simple solution phase synthetic approach exists for preparing buckybowls **7**, **9**, and **10** and that these substances possess interesting structural properties. Continuing investigations of the physical properties of **7**, **9**, and **10** and potential applications of

the synthetic method to the construction of the capped tubular molecule **3** are currently underway.²¹

ASSOCIATED CONTENT

S Supporting Information. Experimental procedures and characterizations, NMR spectra, crystal data, and computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) For reviews of corannulene-based buckybowl, see: (a) Sygula, A. *Eur. J. Org. Chem.* **2011**, 1611. (b) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868. (c) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843. (d) Sygula, A.; Rabideau, P. W. In *Carbon-Rich Compounds: From Molecules to Materials*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006; p 529.
- (2) (a) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, 1878. Reviews for sumanene-type buckybowl, see: (b) Higashibayashi, S.; Sakurai, H. *Chem. Lett.* **2011**, *40*, 122. (c) Amaya, T.; Hirao, T. *Chem. Commun.* **2011**, 47, 10524.
- (3) (a) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743. (b) Ansems, R. B. M.; Scott, L. T. *J. Am. Chem. Soc.* **2000**, *122*, 2719. (c) Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5766.
- (4) (a) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **1995**, *117*, 6410. (b) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed.* **1997**, *36*, 406.
- (5) The structure of the mixed buckybowl acenaphtho[3,2,1,8-ijklm]-diindenol[4,3,2,1-cdef:1',2',3',4'-pqra]triphenylene has not been analyzed by using X-ray crystallography; see: Marcinow, Z.; Grove, D. I.; Rabideau, P. W. *J. Org. Chem.* **2002**, *67*, 3537.
- (6) Baldrige, K. K.; Siegel, J. S. *Theor. Chem. Acc.* **1997**, *97*, 67.
- (7) Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427.
- (8) Several buckybowl have been synthesized by using palladium-catalyzed intramolecular arylation reactions; see: (a) Wang, L.; Shevlin, P. B. *Org. Lett.* **2000**, *2*, 3703. (b) Marcinow, Z.; Sygula, A.; Ellern, A.; Rabideau, P. W. *Org. Lett.* **2001**, *3*, 3527. (c) Chang, H.-I.; Huang, H.-T.; Huang, C.-H.; Kuo, M.-Y.; Wu, Y.-T. *Chem. Commun.* **2010**, 46, 7241. (d) Whalley, A. C.; Plunkett, K. N.; Gorodetsky, A. A.; Schenck, C. L.; Chiu, C.-Y.; Steigerwald, M. L.; Nuckolls, C. *Chem. Sci.* **2011**, *2*, 132.
- (9) (a) Steinberg, B. D.; Jackson, E. A.; Filatov, A. S.; Wakamiya, A.; Petrukhina, M. A.; Scott, L. T. *J. Am. Chem. Soc.* **2009**, *131*, 10537. (b) Amaya, T.; Nakata, T.; Hirao, T. *J. Am. Chem. Soc.* **2009**, *131*, 10810. (c) Jackson, E. A.; Steinberg, B. D.; Bancu, M.; Wakamiya, A.; Scott, L. T. *J. Am. Chem. Soc.* **2007**, *129*, 484. (d) Wu, Y.-T.; Hayama, T.; Baldrige, K. K.; Linden, A.; Siegel, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 6870.

(10) Buckybowl **7** was first prepared in a 0.14% yield from 7,12-bis(2-bromophenyl)benzo[*k*]fluoranthene by using FVP at 1100 °C, but its structure has not been analyzed by X-ray crystallography; see: Clayton, M. D.; Rabideau, P. W. *Tetrahedron Lett.* **1997**, *38*, 741.

(11) Kung, Y.-H.; Cheng, Y.-S.; Tai, C.-C.; Liu, W.-S.; Shin, C.-C.; Ma, C.-C.; Tsai, Y.-C.; Wu, T.-C.; Kuo, M.-Y.; Wu, Y.-T. *Chem.—Eur. J.* **2010**, *16*, 5909.

(12) Hsiao, C.-C.; Lin, Y.-K.; Liu, C.-J.; Wu, T.-C.; Wu, Y.-T. *Adv. Synth. Catal.* **2010**, 352, 3267.

(13) Seiders, T. J.; Baldrige, K. K.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517.

(14) Amaya, T.; Sakane, H.; Muneishi, T.; Hirao, T. *Chem. Commun.* **2008**, 765.

(15) (a) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920. (b) Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc.* **1996**, *118*, 339.

(16) X-ray crystallographic data for compounds **7** (CCDC-835497) and **10** (CCDC-835496) can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/const/retrieving.html.

(17) Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. *J. Org. Chem.* **2005**, *70*, 5713.

(18) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580.

(19) (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137. (b) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385. (d) Haddon, R. C. *Science* **1993**, *261*, 1545.

(20) For other buckybowl with maximum POAV angles larger than 12°, see: circumtrindene (ref 3c) and indenocorannulene family (ref 9a). The central pentagon of **3** is calculated to have a POAV angle of ca. 12.2° (ref 6).

(21) This Communication is Part XII in the series, Metal-Catalyzed Reactions of Alkynes. For Part XI, see: Wu, T.-C.; Chen, J.-J.; Wu, Y.-T. *Org. Lett.* **2011**, *13*, 4794.