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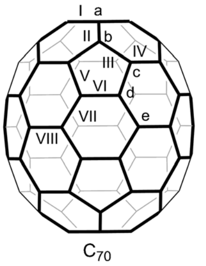
Buckybowls

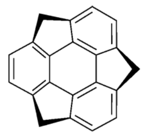
Bowl-Shaped Fragments of C_{70} or Higher Fullerenes: Synthesis, Structural Analysis, and Inversion Dynamics**

Tsun-Cheng Wu, Min-Kuan Chen, Yen-Wei Lee, Ming-Yu Kuo, and Yao-Ting Wu**

Most investigations into fullerene chemistry have focused on C_{60},[1] not only owing to its abundance and low cost, but also because of its simple structure. C_{60} is composed of 60 equivalent carbon atoms with two distinct types of C–C bonds.[2] In contrast, C_{70} contains five types of carbon atoms (a–e) with eight types of C–C bonds (I–VIII).[3] The C_{70} molecule can be regarded as two C_{60}-like hemispheres that are connected by a new set of ten carbon atoms (labeled e). Studies of the bowl-shaped subunits of fullerenes may help give an insight into their chemistry. These buckybowls are important because of their interesting physical properties.[4] A very unusual characteristic of these π bowls is their polarity, which is generated by the non-uniform electronic distribution within the curved surface.[5] As a result, they may form polar crystals that exhibit the pyroelectric effect.[6] The chemistry of corannulene (**1**), sumanene (**2**), and other bowl-shaped fragments of C_{60} has been intensively investigated in the past two decades.[4] In contrast, the bowl-shaped subunits of C_{70} that contain the unique bond type VIII are almost completely unstudied; to the best of our knowledge, only tetraindenopyrene derivative **3** has been reported.[7] Theoretical analysis has revealed that **3** is not a rigid molecule, and its bowl-to-bowl inversion barrier is only 0.33 kcal mol^{-1}. Compounds **9** (Scheme 1) are ideal prototypes for investigation because they contain all the types of carbon atoms that are in C_{70} and are also fragments of many higher fullerenes,[8] including C_{76},[9] C_{78},[9] and C_{84}.[10] This investigation presents the synthesis, structures, and physical properties of new bowl-shaped molecules **9**.



C_{70}



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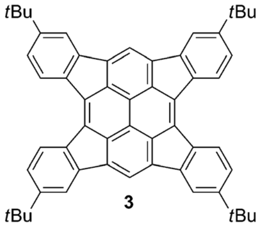

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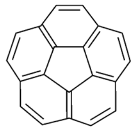

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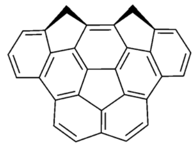

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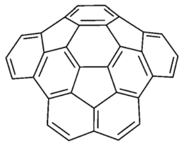

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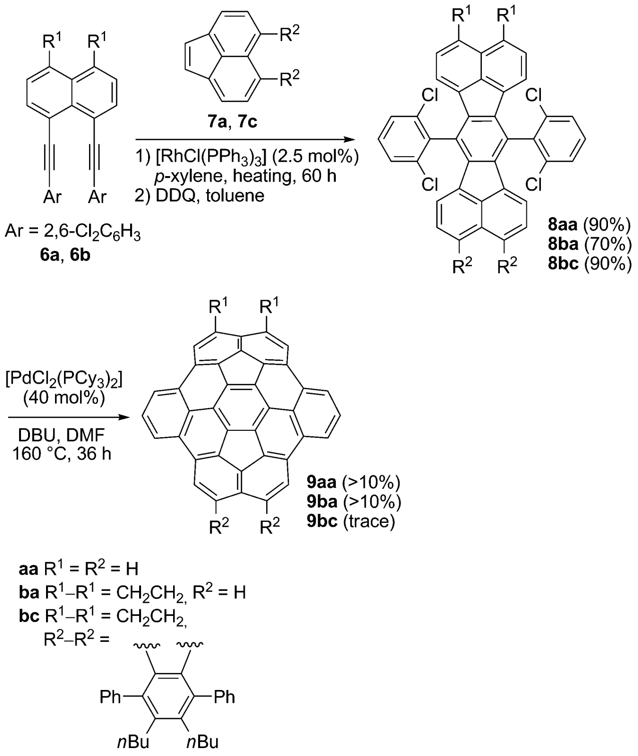

Scheme 1. Preparation of buckybowls **9**. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DMF = *N,N'*-dimethylformamide.

Based on the successful syntheses of **4** and **5**,[11] buckybowls **9** were synthesized using metal-catalyzed C–C bond formation reactions.[12] The synthetic approach is presented in Scheme 1; **8aa** was efficiently prepared by the simple Rh-catalyzed [2+2+2] cycloaddition of diyne **6a** with acenaphthylene (**7a**), and was subsequently aromatized by treatment

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[*] Dr. T.-C. Wu, M.-K. Chen, Prof. Y.-T. Wu
Department of Chemistry, National Cheng Kung University
No. 1 Ta-Hsueh Rd., 70101 Tainan (Taiwan)
E-mail: ytwuchem@mail.ncku.edu.tw

Y.-W. Lee, Prof. M.-Y. Kuo
Department of Applied Chemistry, National Chi Nan University
No. 1 University Rd., 54561 Puli, Nantou (Taiwan)
E-mail: mykuo@ncnu.edu.tw

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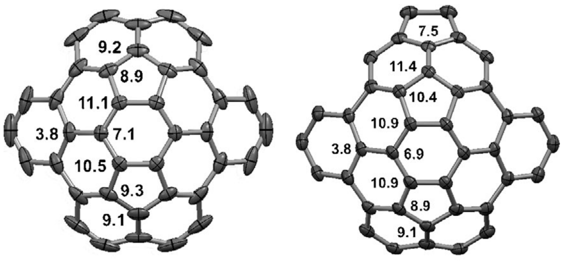
with DDQ. The Pd-catalyzed cyclization of **8aa** gave **9aa** in low yield. This three-step protocol was also adopted for the preparation of new fullerene fragments, such as more-extended buckybowls **9ba** and **9bc**, both of which are also fragments of C_{70},[3] C_{76},[9] C_{84},[10] and other fullerenes. It should be emphasized that the solubility of **9aa** and **9ba** in common organic solvents is low, and some of the product remained on the column after chromatography. An attempt was made to synthesize **9bc** because we believe its two *n*-butyl groups would likely improve the solubility. Unfortunately, only a trace amount of **9bc** was obtained. Presumably, the highly curved structure was the main reason for the inefficient conversion.

The structures of **9aa** and **9ba** were analyzed by X-ray crystallography, and found to be bowl-shaped (Figure 1).[13] The depth of the bowl **9aa** was determined to be 2.28 Å, by measuring the perpendicular distance from the center of the hexagonal base defined by C5, C6, C7, C7′, C6′ and C5′ to the plane composed of the 14 rim carbon atoms (Table 1). Buckybowl **9aa** is less curved than its counterpart in C_{70}, as revealed by comparing the distances between the two carbon atoms C2 and C10 (8.21 Å for **9aa** and 7.90 Å for C_{70}). Similar to corannulene (**1**) and acecorannulene (**10**),[14] the *peri* annelation in **9ba** increases both the bowl depth (2.33 Å) and the curvature ($d(C_2–C_{10}) = 8.03$ Å).



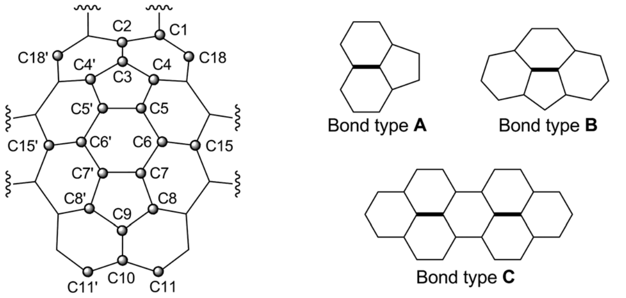
9aa **9ba**

Figure 1. X-ray crystallographic structures and the POAV pyramidalization angles of buckybowls **9aa** and **9ba**. Only the carbon atoms are shown for clarity, and the thermal ellipsoids are set at 30% and 50% probability for **9aa** and **9ba**, respectively.

The point symmetries of buckybowls **9aa** and **9ba** are quasi-C_{2v} and quasi-C_s, respectively. The slight deviation from the ideal geometry may be caused by intermolecular interactions in the solid. Table 1 shows selected structural data for **9** and C_{70}. Most of the C–C bond lengths in **9aa** and **9ba** are smaller than those of their counterparts in C_{70}. Table 1 presents segments of **9** and their representative bond types **A**–**C** (shown in bold); the bond lengths follows the order **C** > **B** > **A**. Importantly, bond type **C**, which is bond VIII on the equator of C_{70} and C6–C15 in buckybowls **9**, is found only in C_{70} or higher fullerenes. Like C_{60},[2] C_{70} and buckybowls **9** generally exhibit alternating C–C distances, such that the 6:6 ring junctions are shorter than the 6:5 ring junctions, but bond type **C** is an exception. For a detailed comparison of the structural data of **9** and C_{70}, see the Supporting Information.

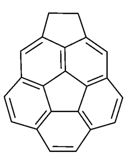
The central six-membered ring in both **9aa** and **9ba** is twisted with a torsion angle (C5-C6-C7′-C6′) of approximately 12°. This twisted conformation is slightly more stable (5.57 kcal mol^{-1} for **9aa**) than a planar conformation, based on density functional theory (DFT) calculations (see the Supporting Information). The twisted six-membered rings were also observed in C_{70} (11.0°). To further examine the conformation of the central six-membered ring, the structures of **2**, **11**, and **12** were analyzed and compared. In the solid state, the central six-membered ring in curved sumanene (**2**)[15] and that in planar coronene (**12**)[16] are planar, whereas that in **11** is found to have a torsion angle of approximately 5°, based on a DFT calculations (Supporting Information). These findings suggest that the arrangement of five- and six-membered rings on the rim affects the conformation of the central six-membered ring in these arenes.

Table 1: Selected distances and the torsion angles for C_{70}, **9aa**, and **9ba** based on X-ray crystallography.[a]



	C_{70}^{b}	**9aa**	**9ba**
Bond length [Å]/bond type			
C2–C3/**A**	1.379(1)	1.377(5)	1.368(3)
C3–C4/**B**	1.456(1)	1.416(2)	1.418(2)
C4–C5/**B**	1.456(1)	1.421(2)	1.430(2)
C5–C5′/**B**	1.440(1)	1.415(3)	1.425(2)
C5–C6/**A**	1.401(1)	1.387(2)	1.397(2)
C6–C15/**C**	1.478(2)	1.443(3)	1.444(2)
Torsion angle [°]			
C5-C6-C7′-C6′	11.0	12.9	12.3
C5′-C5-C7-C7′	0	0	0.3

[a] The values obtained by averaging the symmetry-related bond distances. [b] Taken from $C_{70}\cdot(S_8)_6$ (Ref. [3b]).



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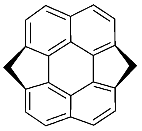

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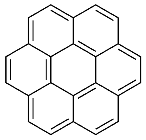

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The POAV (p-orbital axis vector) pyramidalization angle[17] is useful for quantifying the curvature of buckybowls. For example, the values for planar benzene and C_{60} are 0° and 11.6°, respectively. The maximum POAV pyramidalization angle of **9aa** was observed at the C5/C7 position, with a mean value of 10.8° (Figure 1). The additional ethylene bridge in **9ba** strongly increases the POAV pyramidalization angle at the C3 position to 11.4°. The twisted conformation of the central six-membered ring in **9** explains the low POAV

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pyramidalization angle at atom C6. Buckybowls **9** are less curved than **5** (12.8°) or the pole carbon atoms in C_{70} (12.1°),[3b] because they are on the longitudinal part of C_{70}.

The molecular aggregates of **9 aa** and **9 ba** in the solid state differ completely from each other, even though the only structural difference between **9 aa** and **9 ba** is the ethylene bridge. Figure 2 a shows an infinite stack of bowl molecules **9 aa**. The bowl directions of the molecular pairs **A** and **B** up the stack are the same, but the bowls slip from side to side with a slipping angle of 19.5°. The slipping angle is defined as that formed between the stacking axis and the normal to the central six-membered ring of the molecules. Although the separation between two molecules **A** is 8.375 Å, this separation produces very close contacts between two pairs of nonbonded carbons in adjacent bowls (that is, between **A** and **B**). The shortest of these contacts are 3.202 Å between C11/C11′ in a bowl and C7/7′ in the next bowl, and 3.387 Å between C18/C18′ in one bowl and C11/C11′ in the adjacent one. These two values are smaller than the sum of the van der Waals radii of two carbons (3.42 Å).[18] Notably, all of the bowl stacks are aligned in one direction to generate polar crystals of space group $Cmc2_1$. Unlike the polar columnar packing seen for **9 aa**, **9 ba** packs in a centrosymmetric crystal form. Why do these closely related structures pack so differently? One possible explanation considers the nature of concave/convex (cc/cv) orientation of nearest neighbors to the concave/concave (cc/cc) orientation. For a bowl with no perturbation to its rim, cc/cv stacking fills space densely, whereas cc/cc leaves a void; the degree of "penalty" being proportional to the size of the void. For high curvature bowls, the cc/cc polymorph is excluded. In contrast, for a bowl with a tab on its rim, the tab of one bowl can "fill" the cavity of another bowl in a cc/cc dimer, thus allowing this form to pack more densely. The core repeating structure of **9 ba** can be so viewed as a tab-to-cavity cc/cc dimer (Figure 2 b).

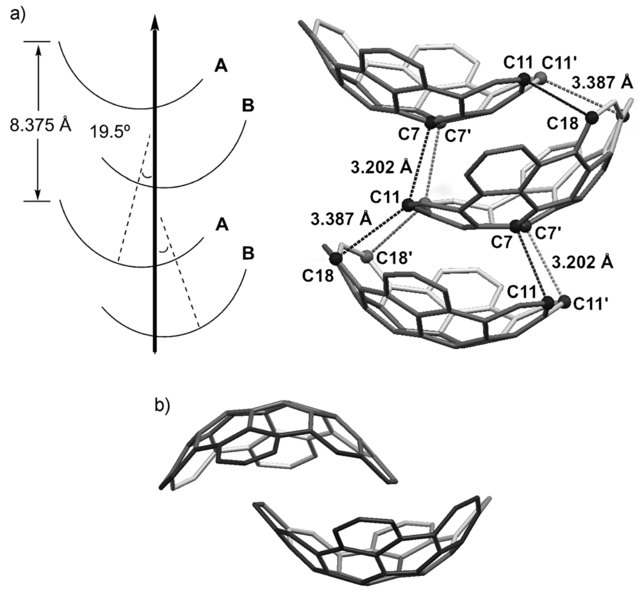
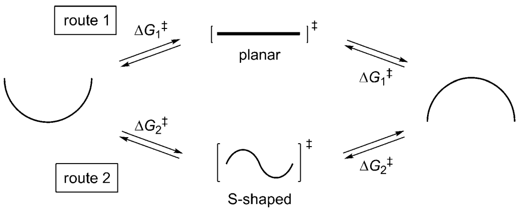


Figure 2. a) Bowl stacks and intermolecular interactions of **9 aa** and b) a concave/concave dimer of **9 ba**.

The inversion of all previously studied buckybowls, such as corannulene (**1**),[14b,19] sumanene (**2**),[20] and even the highly curved **4**,[11] proceeds via a planar transition state (route 1 in Scheme 2), to the best of our knowledge. However, based on DFT calculations at the B3LYP/cc-pVDZ level, **9** should have a different inversion route. As indicated in Scheme 2, the inversion of **9 aa** by route 2 via an S-shaped transition structure is suggested to have a lower inversion barrier ($\Delta G_2^{\ddagger} = 79.8$ kcal mol^{-1}) than route 1 ($\Delta G_1^{\ddagger} = 116.3$ kcal mol^{-1}, Supporting Information). This unusual result is likely due to the unique structure of **9** (see below). The pseudo intrinsic reaction coordinate (pseudo-IRC) verifies the inversion mechanism of **9 aa** (see the Supporting Information). To describe the inversion process, the segments of **9 aa** are classified as two pole regions and a central part along the C2–C10 axis. The inversion process concerns the relative motion of these segments (Figure 3). Pulling down a pole region while simultaneously raising the interior of the central part (C5, C6, C7, C7′, C6′, and C5′) transforms bowl 1 into the S-shaped transition structure, which is converted into bowl 2 by continuously raising the central part and pushing down on the other pole region.



Scheme 2. Inversion dynamics of buckybowls.

As expected, *peri* annelation in **9 ba** and **9 bb** increases their inversion barriers (Table 2). The high inversion barrier of **9** (approximately 80–90 kcal mol^{-1}) reveals that they are static bowls at room temperature, unlike corannulene (approximately 11 kcal mol^{-1})[14b,19] and sumanene (approx-

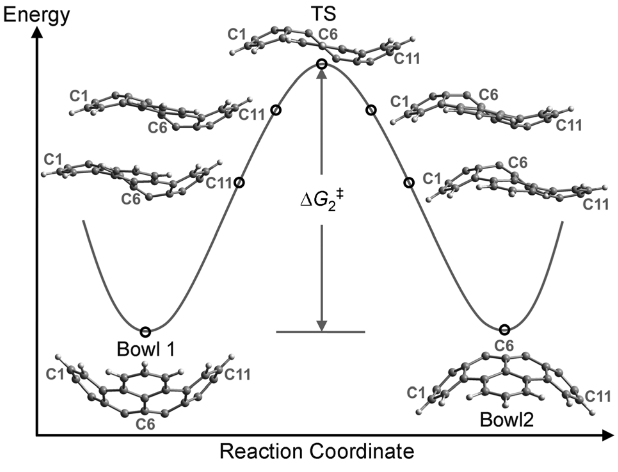


Figure 3. Energy diagram of the inversion process of **9 aa** (side view).

Table 2: Theoretical analysis of bowl-to-bowl inversion barriers.[a]

Compound	$\Delta G_1^{\ddagger}$	$\Delta G_2^{\ddagger}$	$\Delta\Delta G^{\ddagger}$
4	56.2[b]	–	–
5	134.3	124.3	10.0
9aa	116.3	79.8	36.5
9ba	148.4	84.3	64.1
9bb[c]	181.4	87.4	90.4

[a] Calculated in kcal mol^{-1} at B3LYP/cc-pVDZ level. $\Delta\Delta G^{\ddagger} = \Delta G_1^{\ddagger} - \Delta G_2^{\ddagger}$. [b] Ref. [11]. [c] Substituents for **9bb**: R^1–R^1=R^2–R^2=$(CH_2)_2$.

imately 20 kcal mol^{-1}).[20] The inversion barrier of **5** is even higher (124.3 kcal mol^{-1}) and the inversion of **5** most probably also proceeds along route 2 (Scheme 2) via an S-shaped transition structure. An interesting transition in the inversion process was observed from **4** (through route 1) to **5**/**9** (via route 2). In compounds **9**, the preference for route 2 follows the order **9bb** > **9ba** > **9aa** (Table 2). The longitudinal length of these buckybowls critically affects the inversion dynamics: greater distance corresponds to greater preference for route 2. The less-curved structure and the twisted central six-membered ring of **9** cause these molecules to have a lower inversion barrier than **5**.

In conclusion, this investigation demonstrates a simple synthetic approach for preparing buckybowls **9**, which exhibit unique structural properties and inversion dynamics, and help to give an insight into the chemistry of the longitudinal part of C_{70}. Chiral derivatives of **9** should be configurationally stable at room temperature,[21] owing to the high predicated bowl inversion. Preparation of an enantiopure buckybowl **9** is under way.

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[1] a) A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123; b) *Fullerenes: Principles and Applications* (Eds.: F. Langa, J.-F. Nierengarten), RSC, Cambridge, **2007**; c) C. Thilgen, F. Diederich, *Chem. Rev.* **2006**, *106*, 5049; d) A. Hirsch, M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, **2005**; e) "Fullerenes and Related Structures": *Topics in Current Chemistry*, *Vol. 199* (Ed.: A. Hirsch), Springer, Berlin, **1999**.

[2] H. B. Bürgi, E. Blanc, D. Schwarzenbach, S. Liu, Y. Lu, M. M. Kappes, J. A. Ibers, *Angew. Chem.* **1992**, *104*, 667; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 640.

[3] Theoretic studies: a) Z. Slanina, J. M. Rudzinski, M. Togasi, E. Osawa, *J. Mol. Struct.* **1989**, *202*, 169; X-ray diffraction, $[C_{70}\cdot(S_8)_6]$: b) G. Roth, P. Adelmann, *J. Phys. I* **1992**, *2*, 1541; $[C_{70}\cdot Ni]$ complex: c) P. D. Croucher, J. M. E. Marshall, P. J. Nichols, C. L. Raston, *Chem. Commun.* **1999**, 193; $[C_{70}\cdot$azatriquinacene$]$: d) D. Pham, J. Ceron-Bertran, M. M. Olmstead, M. Mascal, A. L. Balch, *Cryst. Growth Des.* **2007**, *7*, 75; electron diffraction: e) K. Hedberg, L. Hedberg, M. Bühl, D. S. Bethune, C. A. Brown, R. D. Johnson, *J. Am. Chem. Soc.* **1997**, *119*, 5314; f) D. R. McKenzie, C. A. Davis, D. J. H. Cockayne, D. A. Muller, A. M. Vassallo, *Nature* **1992**, *355*, 622; neutron diffraction: g) A. V. Nikolaev, T. J. S. Dennis, K. Prassides, A. K. Soper, *Chem. Phys. Lett.* **1994**, *223*, 143.

[4] Reviews for buckybowls, see: a) *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry* (Eds.: M. A. Petrukhina, L. T. Scott), Wiley, Hoboken, **2012**; b) A. Sygula, *Eur. J. Org. Chem.* **2011**, 1611; c) S. Higashibayashi, H. Sakurai, *Chem. Lett.* **2011**, *40*, 122; d) T. Amaya, T. Hirao, *Chem. Commun.* **2011**, *47*, 10524; e) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868; f) Y.-T. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843; g) A. Sygula, P. W. Rabideau in *Carbon-Rich Compounds: From Molecules to Materials* (Eds.: M. M. Haley, R. R. Tykwinski), Willey-VCH, Weinheim, **2006**, pp. 529.

[5] K. K. Baldridge, J. S. Siegel, *Theor. Chem. Acc.* **1997**, *97*, 67.

[6] a) F. C. Krebs, P. S. Larsen, J. Larsen, C. S. Jacobsen, C. Boutton, N. Thorup, *J. Am. Chem. Soc.* **1997**, *119*, 1208; b) G. K. H. Madsen, F. C. Krebs, B. Lebech, F. K. Larsen, *Chem. Eur. J.* **2000**, *6*, 1797; for a review, see: c) D. Y. Curtin, I. C. Paul, *Chem. Rev.* **1981**, *81*, 525.

[7] H. A. Wegner, H. Reisch, K. Rauch, A. Demeter, K. A. Zachariasse, A. de Meijere, L. T. Scott, *J. Org. Chem.* **2006**, *71*, 9080.

[8] For reviews for higher fullerenes, see: a) P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Dover Publications, Mineola, **2006**; b) C. Thilgen, A. Herrmann, F. Diederich, *Angew. Chem.* **1997**, *109*, 2362; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2268; c) R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1993**, 813.

[9] X-ray structures of $[C_{76}(D_2)\cdot Ag]$ and $[C_{78}(C_{2v})\cdot Cu]$: L. Epple, K. Y. Amsharov, M. Jansen, *Fullerenes Nanotubes Carbon Nanostruct.* **2009**, *17*, 67.

[10] X-ray structure of $[C_{84}(C_s)\cdot Ag]$ complex: L. Epple, K. Amsharov, K. Simeonov, I. Dix, M. Jansen, *Chem. Commun.* **2008**, 5610.

[11] T.-C. Wu, H.-J. Hsin, M.-Y. Kuo, C.-H. Li, Y.-T. Wu, *J. Am. Chem. Soc.* **2011**, *133*, 16319.

[12] Several buckybowls have been synthesized by Pd-catalyzed intramolecular arylation. For recent examples, see: a) E. A. Jackson, B. D. Steinberg, M. Bancu, A. Wakamiya, L. T. Scott, *J. Am. Chem. Soc.* **2007**, *129*, 484; b) B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina, L. T. Scott, *J. Am. Chem. Soc.* **2009**, *131*, 10537; c) H.-I. Chang, H.-T. Huang, C.-H. Huang, M.-Y. Kuo, Y.-T. Wu, *Chem. Commun.* **2010**, *46*, 7241; d) A. C. Whalley, K. N. Plunkett, A. A. Gorodetsky, C. L. Schenck, C.-Y. Chiu, M. L. Steigerwald, C. Nuckolls, *Chem. Sci.* **2011**, *2*, 132; for other nonpyrolysis coupling techniques, see: e) Y.-T. Wu, T. Hayama, K. K. Baldridge, A. Linden, J. S. Siegel, *J. Am. Chem. Soc.* **2006**, *128*, 6870; f) K. T. Rim, M. Siaj, S. Xiao, M. Myers, V. D. Carpentier, L. Liu, C. Su, M. L. Steigerwald, M. S. Hybertsen, P. H. McBreen, G. W. Flynn, C. Nuckolls, *Angew. Chem.* **2007**, *119*, 8037; *Angew. Chem. Int. Ed.* **2007**, *46*, 7891; g) O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574; h) K. Y. Amsharov, M. A. Kabdulov, M. Jansen, *Angew. Chem.* **2012**, *124*, 4672; *Angew. Chem. Int. Ed.* **2012**, *51*, 4594.

[13] CCDC 901335 (**9aa**) and 901336 (**9ba**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] a) A. Sygula, H. E. Folsom, R. Sygula, A. H. Abdourazak, Z. Marcinow, F. R. Fronczek, P. W. Rabideau, *J. Chem. Soc. Chem. Commun.* **1994**, 2571; for the structure/energy correlation of corannulene-based buckybowls, see: b) T. J. Seiders, K. K. Baldridge, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **2001**, *123*, 517.

[15] H. Sakurai, T. Daiko, H. Sakane, T. Amaya, T. Hirao, *J. Am. Chem. Soc.* **2005**, *127*, 11580.

[16] T. M. Krygowski, M. Cyranski, A. Ciesielski, B. Swirska, P. Leszczynski, *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 1135.

[17] a) R. C. Haddon, L. T. Scott, *Pure Appl. Chem.* **1986**, *58*, 137; b) R. C. Haddon, *Acc. Chem. Res.* **1988**, *21*, 243; c) R. C. Haddon, *Science* **1993**, *261*, 1545.

[18] a) L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, **1960**. According to the Zefirov's definition, the sum of van der Waals radii of two carbon atoms is 3.42 Å, see: b) Y. V. Zefirov, *Crystallogr. Rep.* **1997**, *42*, 111.

[19] a) T. J. Seiders, K. K. Baldridge, E. L. Elliott, G. H. Grube, J. S. Siegel, *J. Am. Chem. Soc.* **1999**, *121*, 7439; b) A. Sygula, A. H. Abdourazak, P. W. Rabideau, *J. Am. Chem. Soc.* **1996**, *118*, 339; c) L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920.

[20] a) T. Amaya, K. Mori, H. L. Wu, S. Ishida, J. Nakamura, K. Murata, T. Hirao, *Chem. Commun.* **2007**, 1902; b) H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, *301*, 1878.

[21] For selected examples of chiral buckybowls, see: a) S. Higashibayashi, H, Sakurai, *J. Am. Chem. Soc.* **2008**, *130*, 8592; b) Q. Tan, S. Higashibayashi, S. Karanjit, H. Sakurai, *Nat. Commun.* **2012**, *3*, 891.

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