Conference paper

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Synthetic and structural considerations on highly curved bowl-shaped fragments of fullerenes

Abstract: Numerous highly curved fragments of C_{60} and unique subunits of C_{70} were synthesized under mild conditions using metal-catalyzed protocols. According to X-ray crystallographic analyses, highly curved fragments of C_{60} have a maximum π-orbital axis vector (POAV) pyramidalization angle of up to 12.9 °, whereas distinctive fragments of C_{70}, analogous to the tube portion of the rugby-shaped buckyball, are less curved. Among the eight buckybowls studied herein, five form polar crystals. Depending on the molecular geometry, the inversion dynamics of buckybowls involves either a planar or an S-shaped (non-planar) transition structure.

Keywords: alkynes; buckybowls; fluoranthene; fullerenes; ISNA-15; palladium; rhodium.

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Introduction

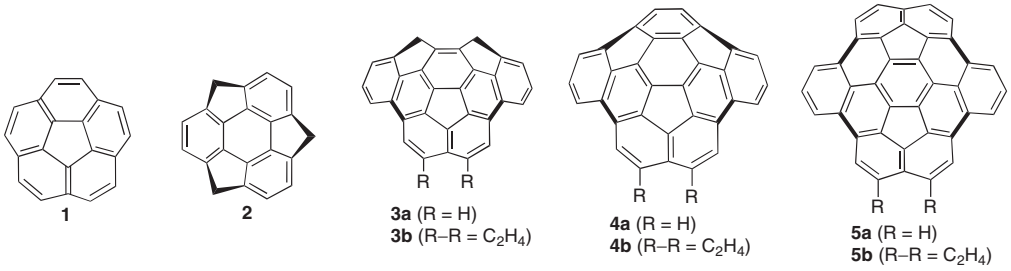
Corannulene (**1**) [1] and sumanene (**2**) [2] are elemental bowl-shaped subunits of C_{60}. The curvature is caused by incorporation of five-membered rings into a sheet of benzenoids, consistent with Euler's rule [3]. These bowl-shaped compounds, so-called buckybowls or π-bowls, can be extended to form fullerenes [4] or carbon nanotubes (CNTs) [5]. Buckybowls have interesting physical properties, and have (potential) applications as electro-optical organic materials such as liquid crystals and organic semiconductors [6]. Another potential application of buckybowls in organic synthesis is that they are suitable precursors of "customized" CNTs [7]. Some CNTs exhibit greater electronic conductivity than copper wire [8], but to date their pure form cannot be acquired in needed amounts [5b,c].

Recently, we have successfully prepared numerous buckybowls **3**–**5** [9–11]. Bowls **3** and **4** are highly curved fragments of C_{60}, and they likely are suitable starting materials for constructing the smallest corannulene-based CNT ($C_{40}H_{10}$) [12]. In contrast, **5** can map on the tube portion of C_{70}. Additionally, **5a** is also a fragment of numerous higher fullerenes, including C_{76}, C_{78} [13], and C_{84} [14]. Herein, a short review on the synthesis, structural analysis, and physical properties of these highly curved buckybowls is reported.

Synthesis

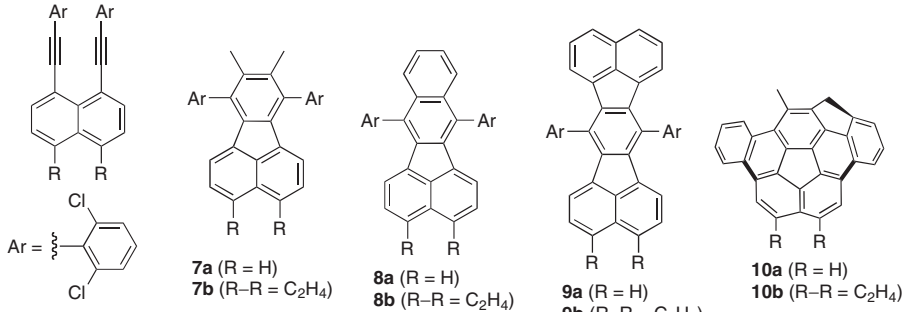
High inherent strain makes synthesis of highly curved buckybowls challenging. Most are prepared using a strategy that involves extension of the backbone of a smaller bowl and/or the use of high-temperature flash vacuum pyrolysis (FVP) as a synthetic tool [1d]. Successively increasing the curvature may facilitate the formation of highly curved buckybowls from a small bowl under mild synthetic conditions. Examples of such approaches include preparations of pentaindenocorannulene [15] and trinaphthosumanene [16] from corannulene and sumanene,

respectively; however, many steps are required to prepare the latter two small π-bowls. Circumtrindene is directly obtained from decacyclene under FVP conditions [17]. High-temperature conditions markedly limit the range of functional groups and potentially cause thermal rearrangement of their molecular framework [18]. In contrast to these conventional methods, attempts were made to prepare highly curved buckybowls from planar precursors through the palladium-catalyzed intramolecular arylation (cyclization) under mild reaction conditions. Similar synthetic approaches have been applied for preparations of less curved buckybowls such as *as*-indaceno[3,2,1,8,7,6-*pqrstuv*]picenes [19], dibenzocorannulenes [18, 20] and others [21]. Taking advantage of the palladium-catalyzed protocol and carefully studying reaction conditions made the desired compounds obtainable.



1 **2** **3a** (R = H) **3b** (R–R = C_2H_4) **4a** (R = H) **4b** (R–R = C_2H_4) **5a** (R = H) **5b** (R–R = C_2H_4)

Methylene-bridged buckybowl **3a** was prepared straightforwardly by rhodium-catalyzed [(2+2)+2] cycloaddition of 1,8-bis(2,6-dichlorophenylethynyl)naphthalene **6a** with 2-butyne to yield fluoranthene **7a** [22], which was subjected to palladium-catalyzed cyclization to give a mixture of **3a** and **10a** (ratio 71:29) in 28 % yield [23]. Cyclopenta-annulated buckybowl **3b** was obtained similarly using 1,2-dihydro-5,6-bis(2,6-dichlorophenylethynyl)naphthalene (**6b**) as the starting material. Presumably because of the increased curvature, the cyclization of **7b** was inefficient (**3b**:**10b** = 39:61; 18 % yield).



6a (R = H) **6b** (R–R = C_2H_4) **7a** (R = H) **7b** (R–R = C_2H_4) **8a** (R = H) **8b** (R–R = C_2H_4) **9a** (R = H) **9b** (R–R = C_2H_4) **10a** (R = H) **10b** (R–R = C_2H_4)

Buckybowl **4a** was first prepared in 0.14 % yield from 7,12-bis(2-bromophenyl)benzo[*k*]fluoranthene using FVP at 1100 °C [24]. Conversely, our protocol allowed **4** to be generated under mild conditions. The palladium-catalyzed annulation of 1,8-bis(2,6-dichlorophenylethynyl)naphthalene **6a** with iodobenzene gave benzo[*k*]fluoranthene **8a** [25], which was converted into **4a** in 31 % yield by palladium-catalyzed cyclization. Cyclopenta-annulated buckybowl **4b** was obtained similarly, but the yield for the palladium-catalyzed cyclization of **8b** was only 5 %. This unsatisfactory result was likely caused by the increased curvature of **4b**.

Buckybowls **5a** and **5b** were prepared by palladium-catalyzed cyclization of naphtho[1,2-*k*]cyclopenta[*cd*]fluoranthene derivatives **9**, which were obtained by rhodium-catalyzed [(2+2)+2] cycloaddition of diynes **6** with acenaphthylene [11], followed by aromatization using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Both buckybowls **5a** and **5b** were obtained in low yields (ca. 10 %), mainly because of their low solubility in common organic solvents. Some product was irreversibly lost during chromatography.

Structural analysis

The structures of buckybowls **3**, **4**, **5**, and **10** have been characterized by X-ray crystallography, and their curvature was determined by analyzing the bowl depth of the corannulene fragment (Table 1). The bowl depths followed

Table 1 X-ray structural data and inversion dynamics of selected buckybowls.

	X-ray structural data[a]		Inversion dynamics[d]		References
	Bowl depth (Å)	POAV (deg)	Path	Barrier (kcal/mol)	
1	0.87	8.2	**I**	ca. 10	[26, 32]
3a	1.19	12.8, 10.0, 8.9	**I**	56.2	[9, 11]
3b	1.32	12.9, 10.9, 10.9	**I**	84.4	[11]
4a	1.24 [1.48]	12.8, 10.0, 9.0	**II**	124.3	[9, 10]
4b	1.34 [1.50]	12.8, 10.8, 10.6	**II**	135.1	[11]
5a	1.07	10.8, 9.2, 9.1	**II**	79.8	[10]
5b	1.21	11.4, 10.9, 10.4	**II**	84.3	[10]
	1.07	10.9, 9.1, 8.9			
10a[b]	1.03	11.9, 9.4, 9.0, 8.3, 9.6	–	24.1	[9]
	1.04	11.7, 9.8, 9.5, 8.9, 8.5			
10b	1.19	12.0, 10.4, 10.9, 10.3, 7.2	–	–	[11]
2	1.11	9.0[c]	**I**	ca. 20	[27, 33]

[a]The values were obtained by averaging symmetry-related data. Bowl depth and the POAV pyramidalization angles were determined from a corannulene core and its hub carbon atoms, respectively. The bowl depth for the sumanene segment is shown in the square bracket. [b]There are two molecules in the asymmetric unit. [c]The POAV pyramidalization angle was determined from the hub six carbons. d. Theoretical studies were calculated at B3LYP/cc-pVDZ level.

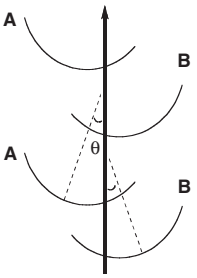
the order **4** > **3** > **5** > **10**, and all exceeded significantly that of corannulene (0.87 Å) [26]. Bowls **5**, which map on the tube portion of C_{70}, are less curved than bowls **3** and **4** due to the lower density of the five-member rings. Cyclopenta-annulated buckybowls **3b**, **4b**, and **5b** have 0.10–0.14 Å deeper bowl depths than their corresponding parent compounds **3a**, **4a**, and **5a**, respectively. Compound **4b** is the deepest bowl with a depth of 1.34 Å. Additionally, the bowl depths of the sumanene segment in **4a** (1.48 Å) and **4b** (1.50 Å) markedly exceed that of sumanene (1.11 Å) [27]. The geometric calculations at the B3LYP/cc-pVDZ level are highly consistent with X-ray structural data.

The curvature of these buckybowls was also analyzed by the POAV (π-orbital axis vector) pyramidalization angle [28]. The POAV pyramidalization angle is highest at the hub carbon atoms of the corannulene core. Buckybowls **3** and **4** have a maximum POAV pyramidalization angle of approximately 12.8 °, exceeding that of C_{60} (11.6 °). To the best of our knowledge, **3**, **4** and pentaindenocorannulene (12.7 °) are the most curved bowl-shaped fragments of fullerenes. Unlike in previous reports, the cyclopenta-annulation in buckybowls **3** or **4** does not increase the maximum POAV pyramidalization angle. This finding may suggest that the maximum POAV pyramidalization angle reaches its highest value, and the increase in curvature reflects only on an increase in bowl depth. This conclusion can be confirmed by analyzing carbon nanotube $C_{50}H_{10}$, whose corannulenyl end cap has a very deep bowl depth (1.54 Å), but with a slightly smaller POAV angle (12.3 °) than **3** or **4** [7]. In contrast to **3** and **4**, the shallower bowls **5** have lower bowl depths and smaller POAV angles.

Molecular packing

The curvature of buckybowls causes their solid-state packing to become highly interesting and complex. The most notable packing characteristic of π-bowls is that they can form bowl-in-bowl stacks and all columns are oriented in the same direction. The resulting polar crystals benefit potential applications as organic materials with high electron mobility (organic semiconductors) [6c], for piezoelectricity or pyroelectricity [29], or for generating second harmonics (nonlinear optoelectronics) [30]. The factors that are required to produce polar crystals are not yet well understood [1e, 31]. Among the eight buckybowls investigated, **3a**, **4a**, **4b**, **5a**, and **10a** form polar crystals; however, these molecules slip from side to side within each stack (Table 2). The non-perfect bowl-in-bowl stacks are likely the result of compromise between the intrastack and interstack interactions guided by π/π stacking and CH···π hydrogen bonding. A slipping angle is defined as that between the stacking axis and the axis normal to the molecule, and a large value should be caused by interstack interactions. Interestingly, **4a**, **4b**, and **5a** crystallize with the orthorhombic space group $Cmc2_1$, and they have

Table 2 The stacking order parameters of the columnar structures [11].

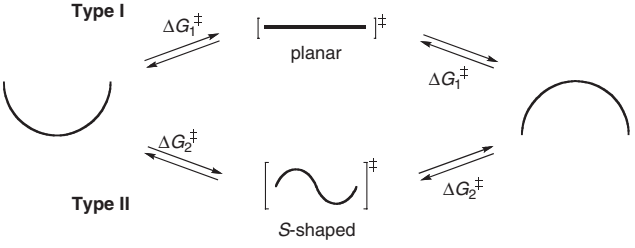


	Slipping angle θ (°)[a]	A···A (Å)
3a	5.0	8.50
4a	31.8	8.14
4b	32.1	8.18
5a	20.0	8.38
10a	17.5	7.76

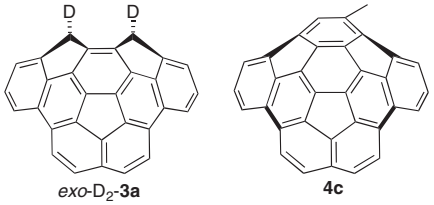
similar packing patterns. Buckybowl **5a** is less curved and has a larger π-surface than **4a** and **4b**, resulting in larger π/π surface overlaps and a smaller slipping angle. The structures of methylene-bridged bowls **3a** and **10a** have the monoclinic space group *C*1*c*1 and the orthorhombic space group $Pna2_1$, respectively. Their methylene protons take part in strong intermolecular CH···π interactions within a columnar stack.

Inversion dynamics

Unlike corannulene (ca. 10 kcal/mol) [32] and sumanene (around 20 kcal/mol) [33], buckybowls **3**–**5** have very high inversion barriers, which cannot be measured using common NMR techniques. Although attempts have been made to conduct a variable-temperature NMR study of **3a** or a 2D EXSY experiment of the dideutero-substituted compound D_2-**3a**, they have been unsuccessful due to instrumental limitations. This suggests that the bowl-to-bowl inversion barrier of **3a** should exceed 35 kcal/mol [9]. Accordingly, the inversion mechanisms and barriers of buckybowls **3**–**5** were analyzed theoretically using DFT calculations at the B3LYP/cc-pVDZ level and the pseudo intrinsic reaction coordinate (pseudo-IRC). Like corannulene (**1**) [1e, 32] and sumanene (**2**) [2], the bowl-to-bowl inversion of the class **3** proceeds via a planar transition state (route I in Scheme 1), whereas the inversion dynamics of buckybowls **4** and **5** involve an S-shaped (non-planar) transition structure (route II in Scheme 1). In contrast to **3**, the buckybowls **4** and **5** are longitudinally long, and they have a greater preference for route II with a lower inversion barrier than that through route I. Among the eight buckybowls studied, **4b** (135.1 kcal/mol) and **3a** (56.2 kcal/mol) have the highest and lowest inversion barriers, respectively. Within a compound class, *peri*-annelation increases the height of the inversion barrier. Finally, buckybowls **3**, **4**, and **5** can be regarded as static bowls at room temperature.



Scheme 1 Inversion dynamics of buckybowls.



Photophysical properties

Bowls **3**/**4** and **5** have absorptions less than and greater than 450 nm, respectively. An absorption band in the region of 450–500 nm plays a critical role in distinguishing between C_{70} and C_{60} [34]. Although buckybowls **3**, **4**, and **5** can map onto C_{70}, theoretical studies indicated that bowls **5** have more π-conjugation and a smaller HOMO/LUMO band gap than **3**/**4**. The photoluminescence of C_{60} and C_{70} is very weak because of the highly efficient intersystem crossing [35]. The photoluminescence of **4** is also very weak, whereas **3** and **5** both have strong fluorescence at approximately 416/436 and 528 nm, respectively.

Chiral resolution

Mono-substituted buckybowl **4c**, which was prepared similar to **4a**, exhibits "bowl chirality" due to its three-dimensional geometry [36]. The chiral resolution of racemic **4c** was performed by HPLC using a chiral column and an eluent system composed of methanol and 2-propanol. Although two well-resolved peaks were observed, chiral resolution in useful amounts is impractical due to the very low solubility of **4c** in the eluent system.

Conclusion

Simple synthetic approaches for preparations of highly curved buckybowls from easily obtained planar precursors under mild reaction conditions have been developed. Depending on molecular geometry, the inversion dynamics of buckybowls involves either a planar or an S-shaped (non-planar) transition structure. Buckybowls are suitable starting materials for the smallest corannulene-based CNT ($C_{40}H_{10}$), and "customized" CNTs. The electron mobility of polar buckybowl crystals, and the surface chemistry of buckybowls on metal surfaces are currently under examination.

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