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Synthesis of Bowl-Shaped Polycyclic Aromatic Hydrocarbons via Palladium-Catalyzed Intramolecular Arylation Reactions

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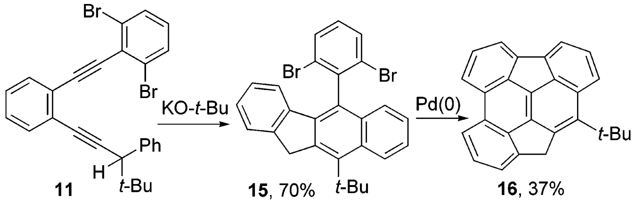
ABSTRACT



Treatment of the benzannulated enediyne 11 with potassium *tert*-butoxide in refluxing toluene for 12 h produced 15 via a cascade sequence of cyclization reactions. Two subsequent palladium-catalyzed intramolecular arylation reactions then afforded the bowl-shaped polycyclic aromatic hydrocarbon 16. The X-ray structures of 16 and two closely related molecules show the presence of significant curvatures.

Bowl-shaped polycyclic aromatic hydrocarbons (buckybowls) have received considerable attention in recent years.[1] This is due in part to the possibility of using these curved hydrocarbons as building blocks for the construction of fullerenes.[2] In addition, the chemical reactivities of the more accessible concave side of the interior carbon atoms of buckybowls could mimic the endohedral chemistry of fullerenes.[3] Furthermore, buckybowls are of interest themselves for a variety of reasons. They provide a platform for the study of the effect of pyramidalization of sp^2-hybridized carbons on aromaticity.[4] On exposure to lithium metal, corannulene (**1**), a $C_{20}H_{10}$ buckybowl, was found to form a fascinating tetraanion.[5] Reports of complexation of buckybowls with transition metals have also begun to emerge.[6]

The first synthesis of corannulene was achieved via a multistep synthetic sequence.[7] The use of flash vacuum pyrolysis to connect distantly separated carbon atoms in

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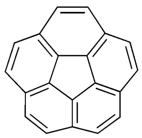

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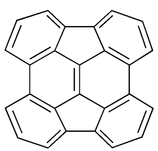

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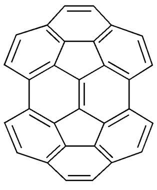

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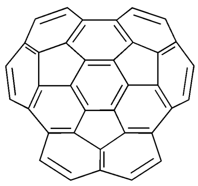

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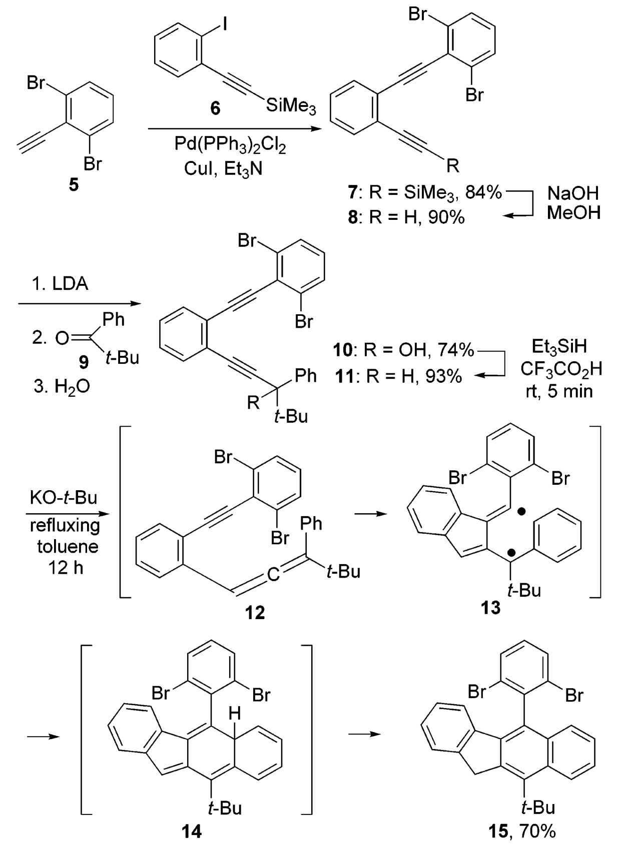
planar polycyclic aromatic precursors provided a more direct route to a host of buckybowls,[1] including corannulene,[8] diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**2**),[9] semibuckminsterfullerene **3**,[10] and circumtrindene (**4**),[11] culminating in the successful synthesis of C_{60} from a $C_{60}H_{27}Cl_3$ molecule.[12] Several efficient nonpyrolytic methods for buckybowls were also reported,[13] including the titanium-, vanadium-, and nickel-mediated intramolecular reductive coupling of benzylic and benzylidene bromides,[13a−d,j] the intramolecular carbenoid coupling of dibromomethyl groups,[13g−i] and the palladium-catalyzed intramolecular arylation of aryl halides.[13e,f] We recently reported an efficient route to 5-phenyl-11*H*-benzo[*b*]fluorenes involving condensation between benzannulated enediynes and aryl ketones to produce benzannulated enediynyl propargylic alcohols followed by reduction and a sequence of cascade cyclization reactions.[14] We have successfully adopted this synthetic method to prepare the corresponding 5-(2,6-dibromophenyl)-11*H*-benzo[*b*]fluorenes for the subsequent palladium-catalyzed intramolecular arylation reactions leading to buckybowls.

The requisite (2,6-dibromophenyl)ethyne (**5**) was prepared by the Sonogashira reaction between 1,3-dibromo-2-iodobenzene and (trimethylsilyl)ethyne followed by desilylation as reported previously.[15] A second Sonogashira reaction between **5** and [(2-iodophenyl)ethynyl]trimethylsilane (**6**)[16] then led to **7**, which was readily desilyated to afford the benzannulated enediyne **8** (Scheme 1). Condensation between **8** and pivalophenone (**9**) then produced enediynyl propargylic alcohol **10**. Treatment of **10** with triethylsilane in the presence of trifluoroacetic acid then afforded **11**. On exposure to potassium *tert*-butoxide in refluxing toluene for 12 h, **11** was converted to 5-(2,6-dibromophenyl)-10-(1,1-dimethylethyl)-11*H*-benzo[*b*]fluorene (**15**) in a single operation. The transformation from **11** to **15** presumably proceeded through an initial 1,3-protropic rearrangement to form the corresponding benzannulated enyne-allene **12**. A Schmittel cyclization reaction[17] to generate biradical **13** for an intramolecular radical−radical coupling to afford, in situ, **14** followed by a

Scheme 1



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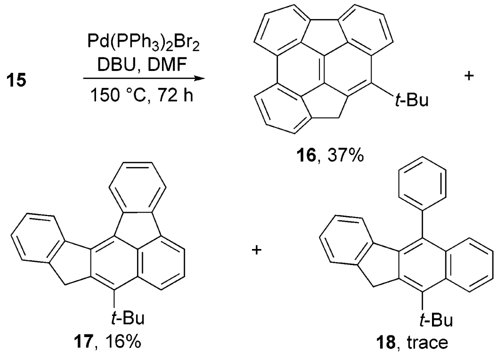
second prototropic rearrangement to regain aromaticity then furnished **15** as proposed previously.[14]

It was gratifying to observe that treatment of **15** with 10 mol % of $Pd(PPh_3)_2Br_2$ in the presence of DBU under the conditions reported by Scott et al.[13e] produced buckybowl **16** (Scheme 2). The structure of **16** was confirmed by X-ray structure analysis (Figure 1). Similar to what was observed previously,[13e] reductive debromination either on one side or on both sides also occurred, giving rise to the monoclosed hydrocarbon **17** as a minor product and a small amount of **18**, respectively. The structure of **17** was tentatively assigned based on the assumption that the first cyclopalladation reaction of **15** occurred preferentially with the naphthyl moiety of **15** producing a five-membered ring as reported previously.[18] The resulting brominated fluoranthene intermediate could undergo either a second cyclopalladation reaction to produce **16** or a reductive debromination reaction to give **17**. Analysis of the crude reaction mixture by GC/MS before purification by silica gel chromatography also suggests the presence of a small amount of **18**.

Scheme 2



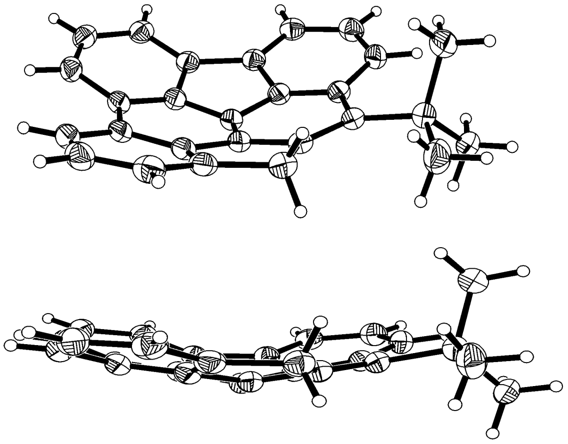


Figure 1. X-ray crystal structure of **16**.

The X-ray structure of **16** indicates the presence of a significant curvature. Compared to **2**, the structure of **16** appears to be less strained with one less ring due to the absence of three sp^2-carbons in the southeastern corner. The pyramidalization angle, defined as $\Theta_{\sigma\pi} - 90$ using the π-orbital axis vector analysis (POAV1),[19] of the central ethylene carbon atoms of **2** was reported to be 9.0°, whereas the pyramidalization angle of the four carbon atoms attached to the central double bond was determined to be 6.7° (Figure 2).[9b] The POAV1 angles of these carbon atoms are clearly larger than those of the corresponding carbon atoms of **16** based on the geometry obtained from the X-ray analysis.

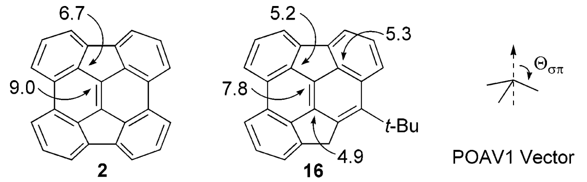


Figure 2. POAV1 pyramidalization angles ($\Theta_{\sigma\pi} - 90$) of **2** and **16**.

The ^1H NMR signal of the diastereotopic methylene hydrogens of **16** occurs as a singlet at δ 4.75 ppm. Barring accidental isochrony, this observation suggests a rapid bowl-to-bowl inversion on the NMR time scale at room temperature, reminiscent of what was observed previously in substituted corannulene derivatives.[13a,20]

Similarly, by using aryl ketones **19a**[14] and **19b**[14] for condensation with the lithium acetylide of **8**, benzannulated enediynyl propargylic alcohols **20a** and **20b** were obtained, respectively. Reduction with triethylsilane in the presence of trifluoroacetic acid then gave benzannulated enediynes **21a** and **21b**. Treatment of **21a** and **21b** with potassium *tert*-butoxide in refluxing toluene for 12 h then furnished **22a** and **22b**, respectively. The palladium-catalyzed intramolecular arylation reactions of **22a** produced buckybowl **23a** and the monocyclized hydrocarbon **24a**. The X-ray structure of **23a** also indicates the presence of a significant curvature. Similarly, buckybowl **23b** along with the monocyclized hydrocarbon **24b** were likewise produced from **22b**. The structure of **23b** was also confirmed by X-ray structure analysis (Figure 3). The presence of an additional five-

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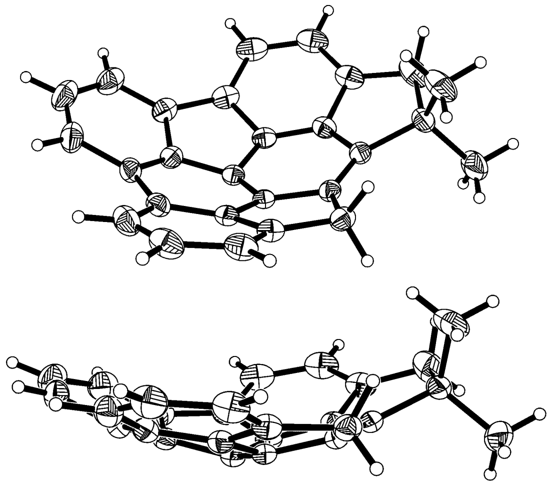
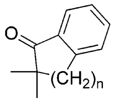
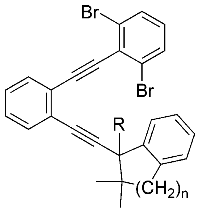


Figure 3. X-ray crystal structure of **23b**.

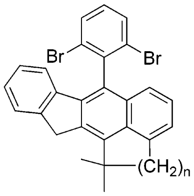
membered ring in **23b** appears to cause its structure to be more strained than those of **16** and **23a**. As a result, the transformation from **22b** to **23b** is less efficient.



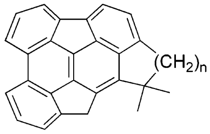
19a: n = 2
19b: n = 1



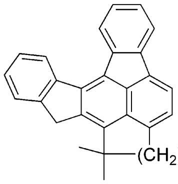
20a: n = 2, R = OH, 69%
20b: n = 1, R = OH, 65%
21a: n = 2, R = H, 89%
21b: n = 1, R = H, 89%



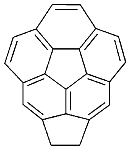
22a: n = 2, 66%
22b: n = 1, 62%



23a: n = 2, 42%
23b: n = 1, 11%



24a: n = 2, 21%
24b: n = 1, 23%



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Based on the geometry obtained from the X-ray analysis, one of the central carbon atoms of **23b** has a POAV1 angle of 10.3° (Figure 4), which is larger than those of **2** and corresponds to 88% of that found for C_{60} with all carbon atoms having a POAV1 angle of 11.64°. In addition, one of the four carbon atoms attached to the central double bond of **23b** has a POAV1 angle of 9.2°, which is also larger than those of the corresponding carbon atoms of **2**.

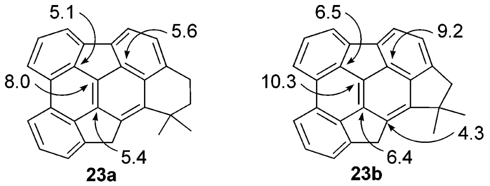

Figure 4. POAV1 pyramidalization angles of **23a** and **23b**.

It was reported that, unlike corannulene, dihydrocyclopentacorannulene (**25**) with an additional five-membered ring "locked" the bowl configuration, preventing a rapid bowl-to-bowl inversion process.[21] However, no such effect was observed for **23b** with the two sets of the methylene hydrogens appeared as two sharp singlets at δ 4.41 and 3.29 ppm and the two groups of methyl hydrogens appeared as a sharp singlet at δ 1.63 ppm at 25 °C. At −33 °C, the methylene signals, recorded on a 600-MHz NMR spectrometer, became two broad humps ranging from ca. δ 4.6 to 4.2 ppm and from ca. δ 3.4 to 3.1 ppm, and the methyl signal also appeared as a broad peak ranging from ca. δ 1.8 to 1.5 ppm. Further broadening but without the appearance of distinct signals for the diastereotopic hydrogens was observed at −40 °C, suggesting relatively fast bowl-to-bowl inversion on the NMR time scale even at −40 °C.

A new synthetic route to buckybowls was developed. The convergent assembly of the benzannulated enediynyl propargylic alcohols and the efficient cascade cyclizations of the resulting enyne-allenes leading to polycyclic aromatic dibromides for subsequent palladium-catalyzed intramolecular arylation reactions are the key features of this synthetic pathway. The use of benzannulated enediynyl propargylic alcohols to form the corresponding aromatic dibromides represents a new approach to the preparation of buckybowl precursors. Three new buckybowls with their structures confirmed by X-ray structure analyses were thus synthesized.

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Supporting Information Available: Experimental procedures, spectroscopic data, and ^{1}H and/or ^{13}C NMR spectra of **7**, **8**, **10**, **11**, **15**−**17**, and **20a**,**b**−**24a**,**b**; ORTEP drawings for **16**, **23a**, and **23b**; and X-ray crystallographic data of **16**, **23a**, and **23b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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