

Fused Dibenzo[*a,m*]rubicene: A New Bowl-shaped Subunit of C₇₀ Containing Two Pentagons

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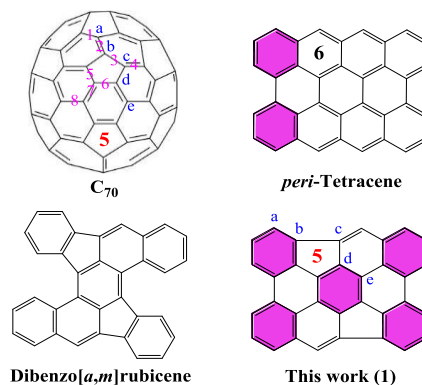
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Supporting Information Placeholder

ABSTRACT: Total synthetic approaches of fullerenes are a holy grail for organic chemistry. So far, the main attempts have been focused on the synthesis of the buckminsterfullerene C₆₀. In contrast, access to subunits of the homologue C₇₀ remains challenging. Here, we demonstrate an efficient bottom-up strategy towards a novel bowl-shaped polycyclic aromatic hydrocarbons (PAH) C₃₄ with two pentagons. This PAH represents a subunit for C₇₀ and also of other higher fullerenes. The bowl-shaped structure was unambiguously determined by X-ray crystallography. Especially, a bowl-to-bowl inversion for a C₇₀ fragment in solution was investigated by dynamic NMR analysis, showing a bowl-to-bowl inversion energy (ΔG^\ddagger) of 16.7 kcal mol⁻¹, which is further corroborated by DFT calculations.



Bowl-shaped polycyclic aromatic hydrocarbons, also named buckybowl, have attracted interest due to their unique chemical and physical properties,^[1-4] such as bowl inversion,^[5,6] supramolecular assembly,^[7,8] electronic conductivity,^[9,10] and chirality.^[11,12] In the past decade, C_{3v}-symmetric sumanene^[13,14] and C_{5v}-symmetric corannulene,^[2,3] as the typical subunits of C₆₀, have been intensively investigated. These molecules can not only serve as precursors for the bottom-up synthesis of fullerene C₆₀ and carbon nanotubes,^[15-17] but also provide insight into the chemical and physical properties of corresponding fullerenes. Based on this groundwork, Scott and coworkers have reported the first rational synthesis of C₆₀ by using the smaller buckybowl molecules.^[15,18] In contrast to C₆₀, C₇₀ has a reduced symmetry of D_{5h}.^[19,20] Moreover, C₇₀ contains five types of carbon atoms (a-e, blue) and features eight types of C-C bonds (1-8, purple) (Scheme 1).^[21-23] Compared to C₆₀, which is a representative n-type semiconducting material, C₇₀ displays stronger light absorption and deeper HOMO and LUMO levels. Thus far, most studies on fullerene chemistry have been focused on the synthesis of bowl-shaped molecules as subunits of fullerene C₆₀, the synthesis of fragments of C₇₀ remains elusive mostly due to the lack of proper synthetic protocols as well as their accessibility in reasonable amounts.^[24,25]

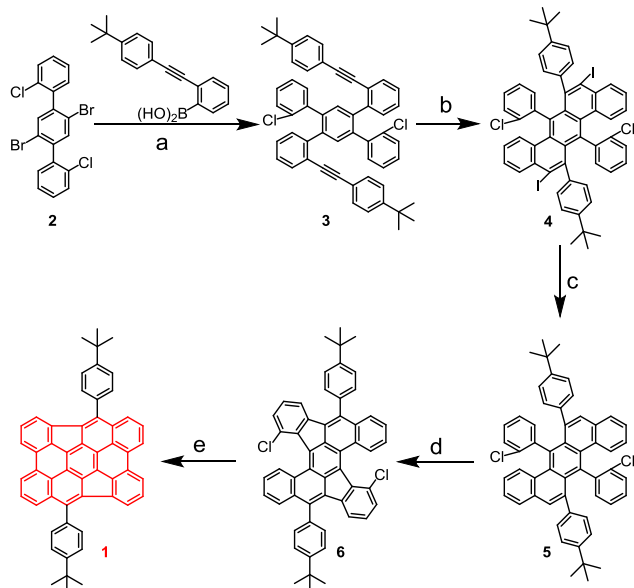
Scheme 1. Structure of fragment of C₇₀.

Here, we demonstrate the efficient synthesis of a novel fused dibenzo[*a,m*]rubicene, dinaphtho[1,2,3,4,5-*ijklm*:1',2',3',4',5'-*uvwxa*]rubicene (**1**), by the palladium-catalyzed intramolecular cyclization of the pre-fused dibenzo[*a,m*]rubicene^[26,27] derivative as the key reaction (Scheme 1). Compound **1**, with 34 carbon atoms, is a fragment for investigating C₇₀, because it contains all the types of carbon atoms present in C₇₀ (Scheme 1). Furthermore, **1** also can serve as a fragment of other higher fullerenes, such as C₇₆, C₇₈ and C₈₄.^[28,29] A number of unique structural and physical properties were disclosed for compound **1**, such as a bowl-to-bowl inversion at the room temperature.

The synthesis of a buckybowl **1** embedding two pentagons is depicted in Scheme 2. First, compound 2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)-2'-chloro-5'-(2-chlorophenyl)-1,1':2',1''-terphenyl (**3**) was prepared by two-fold Suzuki coupling of 2',5'-dibromo-2,2''-dichloro-1,1':4',1''-terphenyl (**2**) with 2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)boronic acid in 63% yield. ICl-induced cyclization was subsequently performed to provide 6,13-bis(4-(*tert*-butyl)phenyl)-7,14-bis(2-chlorophenyl)-5,12-diiodobenzo[*k*]tetraphene (**4**) in 85% yield. Next, the iodo substituents were removed by using *n*-BuLi to afford compound **5** in 58% yield. Then a Scholl reaction of **5** was carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and trifluoromethanesulfonic acid (TfOH) in dry dichloromethane (DCM) at 0 °C, affording 5,14-bis(4-(*tert*-butyl)phenyl)-9,18-di-

chlorodibenzo[*a,m*]rubicene (**6**) in 45% yield including a highly selective 1,2-shift of aryl groups.^[26] Finally, intramolecular cyclization of **6** was performed in the presence of [Pd-(PCy₃)₂Cl₂] and a stoichiometric amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *N,N*-dimethylformamide (DMF) providing compound **1** in 34% yield.^[4] The chemical identity of **1** was firstly confirmed by MALDI-TOF MS analysis, as depicted in Figure S1. There is only one dominant peak in the mass spectra of **1**, revealing its defined molecular composition. The isotopic distribution pattern of the mass peak is in good agreement with the calculated one.

Scheme 2. Synthesis of buckybowl 1. ^aReagents and conditions: (a) Pd(PPh₃)₄, K₂CO₃, dioxane/H₂O, 90 °C, 36 h, 63%; (b) ICl (1 M in DCM), -78 °C, 3 h, 85%; (c) *n*-BuLi, THF, MeOH, 1 h, 58%; (d) DDQ/CF₃SO₃H, DCM, 0 °C, 1 h, 45%; (e) PdCl₂(PCy₃)₂, DBU, DMF, 160 °C, 6 h, microwave, 34%.



Single crystals of **1** were grown by slow evaporation from solutions in hexane/dichloromethane, the bowl-shaped structure of **1** was elucidated by X-ray diffraction (Figure 1). Five-membered rings embedded in a hexagonal lattice impart geodesic curvature, as in fullerenes. The bowl depth, which is defined as the distance between the mean plane that consists of four carbons at the edge and the centroid of the six member ring, is 1.68 Å. This value is higher than that of corannulene (0.86 Å). The X-ray diffraction data also disclose the detailed bonding parameters of **1** (Figure 1e). The C-C bonds at the five-membered rings of **1** (red one in Figure 1e) are obviously longer (1.56 Å) than other bonds, which suggests their single bond character. On the basis of the crystal structures, the local aromaticity of individual rings was analyzed using the harmonic oscillator model of aromaticity (HOMA).^[31,32] As shown in Figure 1f, ring A in **1** has the highest value of HOMA (0.999) followed by rings B and C with HOMA values larger than 0.83 while rings D and E have significantly lower HOMA values (0.409 and 0.406). Thereby, there are five Clar's aromatic sextets in **1** in the ground state, while *peri*-tetracene has only two Clar's aromatic sextets (Scheme 1). According to the Clar sextet rule, the compound with more aromatic sextets is more stable as a result of gaining the aromatic stabilization energies, which suggests that the pentagon-embedding *peri*-tetracene **1** has enhanced stability compared to the conventional *peri*-tetracene that consists solely of six-membered rings.

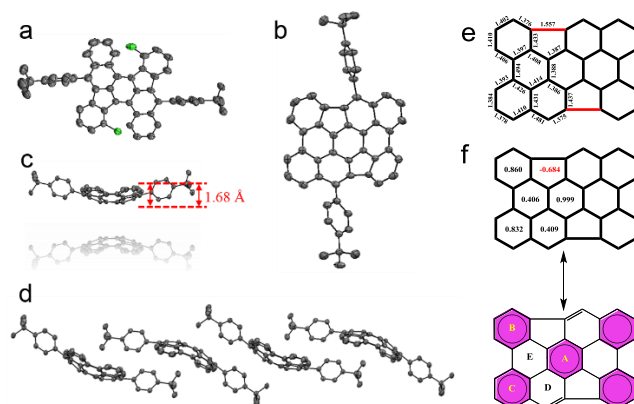


Figure 1. Structural features of the buckybowl **1**. a, Top view of **1** in the single crystal. b, Top view of **1**. c, Side view of **1**. d, Packing mode of **1** in the crystal. e, Bond lengths of **1** from single crystal analysis. f, Harmonic oscillator model of aromaticity (HOMA) values and resonance structure of **1**.

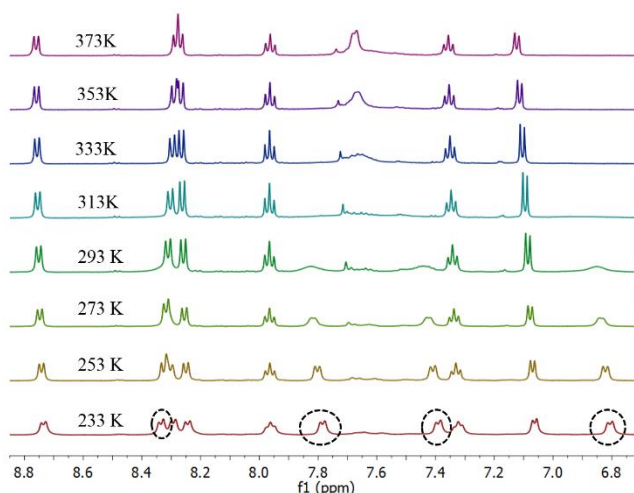


Figure 2. Variable temperature ¹H NMR spectra of buckybowl **1** (500 MHz, C₂D₂Cl₄).

Compound **1** was further investigated by variable temperature ¹H-NMR spectra. The bowl-to-bowl inversion of **1** was detected at room temperature by using the dynamic NMR analysis (Figure 2). The ¹H NMR spectrum of **1** in 1, 1, 2, 2-tetrachloroethane-*d*₂ at -40 °C exhibited four doublet peaks for phenyl protons of *tert*-butyl-phenyl groups at δ =8.24, 7.78, 7.39 and 6.81 ppm. This non-symmetric feature indicates that there is no bowl-to-bowl inversion for compound **1** at such low temperature. However, when the temperature is increased, the phenyl proton signals of *tert*-butyl-phenyl groups gradually broaden (Figure 2) and these signals coalesce at 333 K. Accordingly, the bowl-to-bowl inversion energy (ΔG^\ddagger) was calculated by two-dimensional exchange spectroscopy (2D EXSY) experiments. At 333 K, ΔG^\ddagger was determined to be 16.7 (\pm 0.2) kcal mol⁻¹.^[33] This value is higher than that of the parent corannulene (10.2 \pm 0.2 kcal mol⁻¹).^[34] The experimentally determined bowl-inversion energy of **1** is further corroborated by theoretical calculation. DFT calculations at the B3LYP/cc-pVDZ level of theory (using the Gaussian09 suite of programs^[35]) show that compound **1** undergoes a bowl-to-bowl conversion through a flat transition state (Figure 3), with free activation energy of ΔG^\ddagger =14.4 kcal mol⁻¹. The computed inversion barrier is in reasonable agreement with experiment and much higher than that of corannulene (9.1 kcal

mol⁻¹)^[33] calculated at the same level of theory. Two different conformations of **1** were found in the same crystal, that is, conformers **M** and **P** coexist in a ratio of 1:1 in the crystal (Figure 3).^[36]

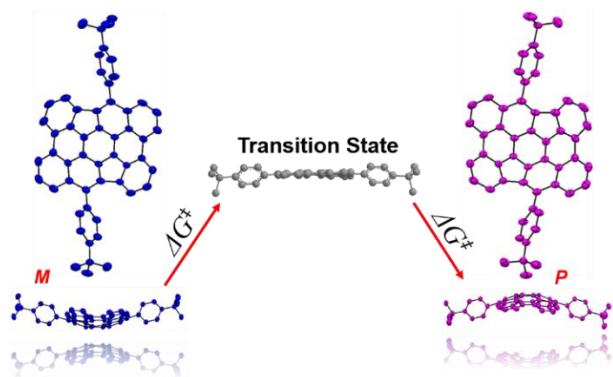


Figure 3. Inversion dynamics of the **M** and **P** conformers of buckybowl **1**.

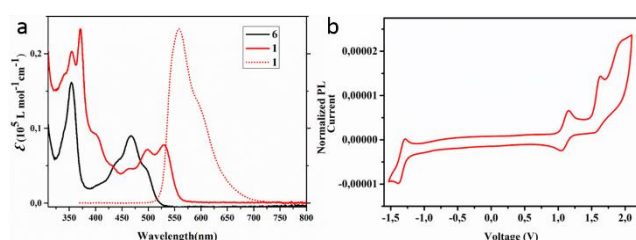


Figure 4. Physical properties of buckybowl **1**. a. UV-Vis absorption spectra (solid) and fluorescence spectra (dot) of **6** and **1**. (for all spectra: 10⁻⁵ M in DCM). b. Cyclic voltammetry of **1** (0.1 M nBu₄NPF₆ in DCM) at scan rate of 50 mVs⁻¹.

Compound **1** has good solubility in common organic solvents such as dichloromethane (DCM), tetrahydrofuran (THF), toluene, and even hexane. The UV-vis absorption spectra of precursor **6** and final product **1** in DCM solutions are compared in Figure 4a. Compound **1** shows a significant absorption maximum red shifted by 36 nm relative to that of **6**, with an absorption maximum at 529 nm and two other shoulder peaks at 499 and 461 nm, respectively. This reflects the extended conjugation in compound **1**. Thus, the optical band gaps of **6** and **1** are determined from the onsets of their UV-vis absorption spectra, which are 2.40 and 2.21 eV, respectively. Compound **1** shows fluorescence in DCM solution with a maximum at 559 nm and a quantum yield of 12% (Fluorescein as the reference, $\Phi_f=90\%$ in 0.1 M NaOH aqueous solution),^[37] as shown in Figure 4a. Time dependent DFT (TD-DFT) calculations on compound **1** yield optical transitions matching well the experimental spectrum, with namely a low-energy HOMO-to-LUMO transition at 526 nm and two higher-energy shoulders at 441 and 403 nm involving deeper occupied molecular orbitals (see SI).

The electrochemical properties of **1** were investigated by cyclic voltammetry (CV) in DCM solutions (Figure 4b). Notably, compound **1** displays one reversible and two irreversible oxidations with first, second and third oxidation potentials of $E_{ox,1} = +1.01$ V, $E_{ox,2} = +1.47$ V and $E_{ox,3} = +1.50$ V versus the ferrocene/ferrocenium couple (Fc/Fc⁺). In the negative potential region, one reversible reduction wave was observed at $E_{red} = -1.17$ V (versus Fc/Fc⁺). Compared to the corannulene or C₆₀, which are reduced easily (up to four- and six-electron reductions, respectively), and are slightly difficult to oxidize, due to electron-accepting ability of the five-membered rings.^[38-41] In contrast, compound **1** can be oxidized easily as well as reduced. The HOMO and LUMO energy levels are

estimated from the onsets of the first reversible oxidation and reduction peaks to be -5.81 eV and -3.63 eV, respectively. Thus, the energy gap of **1** is about 2.18 eV calculated based on the CV measurement, which is consistent with the optical band gap.

In summary, we have demonstrated an efficient synthetic approach toward an unprecedented fragment of the fullerene C₇₀ containing two five-membered rings. The geometric and optoelectronic nature of the resulting buckybowl is comprehensively investigated by single crystal X-ray, dynamic NMR, UV-Vis absorption, and cyclic voltammetry analysis. For the first time, we were able to investigate the bowl-to-bowl inversion behavior of a C₇₀ subunit and determine the activation energy to be 16.7 kcal mol⁻¹. This synthetic investigation can help to provide an in-depth insight into the chemistry of fullerene C₇₀ and other higher fullerene analogues. They also pave the way toward stable *peri*-acene-like molecules, possibly incorporating five-, seven-, and/or eight-membered rings.

ASSOCIATED CONTENT

Supporting Information

Experimental details, synthesis, characterizations, single-crystal data (CIF), computational studies, and NMR spectra. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was financially supported by ERCF grants on NANOGRAPH and 2DMATER, EU Project GENIUS, the EC under Graphene Flagship (No. CNECT-ICT-604391) and Center for Advancing Electronics Dresden (cfaed). D.B. is a FNRS Research Director. The authors sincerely thank Wen Zhang for high-resolution MALDI-TOF MS measurements.

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