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

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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 (∆G°) 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, as well as due to their application in organic electronics.[1-4] Among them, fullerene C₆₀, C₇₀ has a reduced symmetry of D₃h. Moreover, C₇₀ contains five types of carbon atoms (a-e, blue) and features eight types of C-C bonds (1-8, purple) (Scheme 1). Compared to C₆₀, which is a representative n-type semiconductor 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.[5-7]

Scheme 1. Structure of fragment of C₇₀.

Here, we demonstrate the efficient synthesis of a novel fused dibenzo[a,m]rubicone, dibiphenyldi(2-chlorophenyl)ethynyl(4-tert-butyl)phenyl-4'-di(4-tert-butyl)phenylphenyl(2'-chloro-5'-dicyano-1,1'-diiodobenzene(4) in 85% yield. The synthesis of a buckybow 1 embedding two pentagons is depicted in Scheme 2. First, compound 2-(4-(tert-butyl)phenyl)-4'- (4-(tert-butyl)phenyl)ethynyl(2'-chloro-5'-dicyano-1,1'-diiodobenzene)[4]tetr phenylene[4] (3) was prepared by two-fold Suzuki coupling of 2,5-dibromo-2,2'-dichloro-1,1'-terphenyl (2) with 3,4,5-tri(4-tert-butyl)phenyl)-4'-di(4-tert-butyl)phenylphenyl(2'-chloro-5'-dicyano-1,1'-diiodobenzene(4) in 63% yield. The yield was subsequently improved to 85%. The iodinated cyclization was subsequently performed to provide 6,13-bis(4-(tert-butyl)phenyl)-7,14-bis(2-chlorophenyl)-5,12-diiodobenzene[4]tetr phenylene[4] (4) in 85% yield. Next, the iodine 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 (TFA) in dry dichloromethane (DCM) at 0 °C, affording 5,14-bis(4-(tert-butyl)phenyl)-9,18-di-
chlorodibenzo[a,n]rubene (6) in 45% yield including a highly selective 1,2-shift of aryl groups.\textsuperscript{[20]} Finally, intramolecular cyclization of 6 was performed in the presence of [Pd-(PCy\textsubscript{3})\textsubscript{2}]Cl\textsubscript{2} 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.\textsuperscript{[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.** Reagents and conditions: (a) Pd(PPh\textsubscript{3})\textsubscript{4}, K\textsubscript{2}CO\textsubscript{3}, dioxane/H\textsubscript{2}O, 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/CF\textsubscript{3}SO\textsubscript{2}H, DCM, 0 °C, 1 h, 45%; (e) PdCl\textsubscript{2}(PCy\textsubscript{3})\textsubscript{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).\textsuperscript{[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 6 in the single crystal. b, Top view of 1. c. Side view of 1. d. Bond lengths of 1 from single crystal analysis. e, Harmonic oscillator model of aromaticity (HOMA) values and resonance structure of 1.

**Figure 2.** Variable temperature \(^1\)H NMR spectra of buckybowl 1 (500 MHz, C\textsubscript{6}D\textsubscript{6}Cl\textsubscript{4}).

Compound 1 was further investigated by variable temperature \(^1\)H-NMR spectra. The bowl-to-bowl inversion of 1 was detected at room temperature by using the dynamic NMR analysis (Figure 2). The \(^1\)H NMR spectrum of 1 in 1, 1, 2, 2-tetrachloroethane-d\textsubscript{2} at −40 °C exhibited four doublet peaks for phenyl protons of tert-butyl-phenyl groups at \(\delta=8.24, 7.78, 7.39\) 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 (\(\Delta G^2\)) was calculated by two-dimensional exchange spectroscopy (2D EXSY) experiments. At 333 K, \(\Delta G^2\) was determined to be 16.7 (± 0.2) kcal mol\textsuperscript{-1}.\textsuperscript{[33]} This value is higher than that of the parent corannulene (10.2 ± 0.2 kcal mol\textsuperscript{-1}).\textsuperscript{[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 Gaussian\textsuperscript{[9]} suite of programs)\textsuperscript{[35]} show that compound 1 undergoes a bowl-to-bowl conversion through a flat transition state (Figure 3), with free activation energy of \(\Delta G^2=14.4\) kcal mol\textsuperscript{-1}. The computed inversion barrier is in reasonable agreement with experiment and much higher than that of corannulene (9.1 kcal
mole-1) calculated at the same level of theory. Two different conformations of I were found in the same crystal, that is, conformers M and P coexist in a ratio of 1:1 in the crystal (Figure 3).\textsuperscript{136}

In summary, we have demonstrated an efficient synthetic approach toward an unprecedented fragment of the fullerene C\textsubscript{70} containing two five-membered rings. The geometric and optoelectronic nature of the resulting buckybowls 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 C\textsubscript{70} subunit and determine the activation energy to be 16.7 kcal mol\textsuperscript{-1}. This synthetic investigation can help to provide an in-depth insight into the chemistry of fullerene C\textsubscript{70} and other higher fullerene analogs. 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.

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REFERENCES

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