

Buckybowls. 2. Toward the Total Synthesis of Buckminsterfullerene (C₆₀): Benz[5,6]-as-indaceno[3,2,1,8,7-mnopqr]indeno[4,3,2,1-cdef]chrysene[†]

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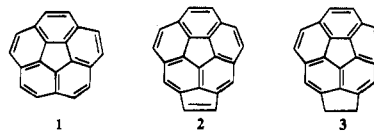
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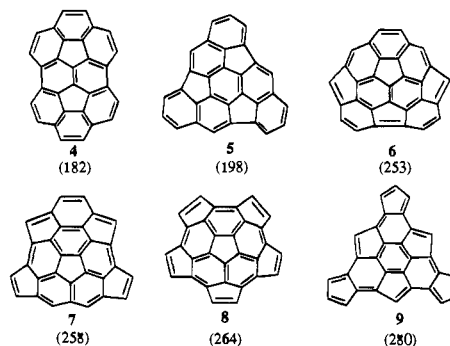
The discovery of buckminsterfullerene (C₆₀) and related carbon cages has generated enormous interest, and the availability of C₆₀ in macroscopic amounts has spawned a considerable amount of research.¹ However, the production of C₆₀ by the vaporization of carbon rods notwithstanding, the total synthesis of C₆₀ provides an exciting but formidable challenge to organic chemists. Clearly, the most critical step in such a synthesis will be the production of intermediates that possess significant degrees of curvature, and one approach, suggested by several groups, is the dimerization of two C₃₀H₁₂ halves.^{2–5} We now report the first synthesis of a C₃₀H₁₂ hydrocarbon (benz[5,6]-as-indaceno[3,2,1,8,7-mnopqr]indeno[4,3,2,1-cdef]chrysene) that represents precisely half of the C₆₀ carbon framework, albeit as enantiomeric pairs.⁶

To date, only a few compounds are known that consist of fused five- and six-membered rings with carbon frameworks represented on the buckminsterfullerene surface. The simplest example is corannulene (**1**), the “polar cap” of buckminsterfullerene recently made accessible by the discovery of new synthetic methods.^{7–9} Although considerably curved, the bowl shape of **1** is rather transitory since several derivatives have been shown to undergo rapid bowl-to-bowl inversion with barriers of ~10–11 kcal/mol.¹⁰ However, further elaboration

on the C₆₀ surface to include a second five-membered ring (**2,3**) “locks” the bowl since **3**¹¹ shows separate signals for each pair of its benzylic protons in solution NMR, even at elevated temperatures.



Recently we reported the first synthesis of a semibuckminsterfullerene, or “buckybowl,” a C₃₀H₁₂ hydrocarbon (**4**) whose carbon framework is represented on the buckminsterfullerene C₆₀ surface.¹² However, **4** does not correspond to a symmetrical half of buckminsterfullerene since “removal” of its carbon framework from the C₆₀ surface leaves behind a different C₃₀ unit that includes two exocyclic carbons. On the other hand, there are a number of C₃₀H₇ hydrocarbons that can result from “halving” buckminsterfullerene to produce two isometric (i.e., identical or enantiomeric) bowl-shaped units, followed by adding hydrogens to the dangling bonds (**5–9**; MM2 calculated heats of formation in parentheses). Among them, the hydrocarbon predicted to be the most stable, and the one most sought after as a synthetic intermediate for C₆₀, is **5**.



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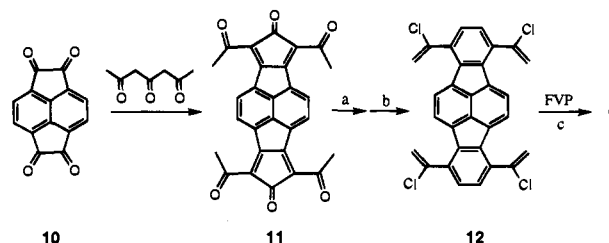
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Our synthesis of bucky bowl **4** (Scheme 1) was accomplished¹² in a manner analogous to the Scott corannulene procedure⁷ except that we began with 1,2,5,6-tetraketopyracene (**10**) rather than acenaphthenequinone (Scheme 1). Knoevenagel condensa-

Scheme 1^a

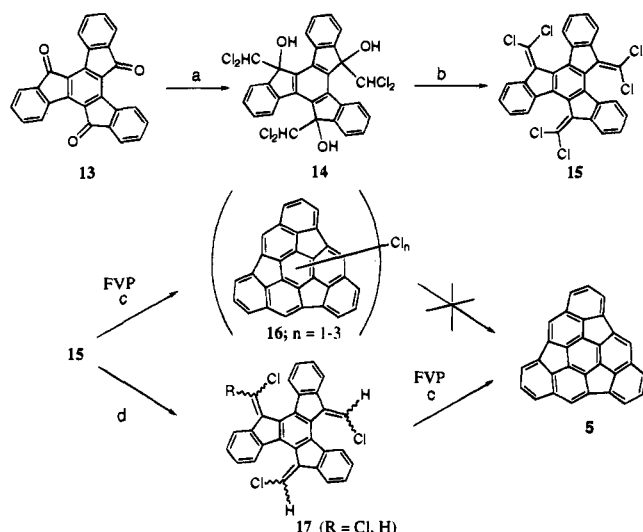


^a Key: (a) norbornadiene; (b) PCl₅; (c) FVP, 1000 °C, N₂ stream, 1.5 Torr.

tion of 2,4,6-heptanetrione with **10** produces hexaketone **11**; subsequent reaction with norbornadiene, followed by PCl₅, affords tetrachlorovinyl derivative **12**, which undergoes flash vacuum pyrolysis (FVP) to produce **4**. Given the success of this route, we decided to explore a similar approach for the synthesis of **5**. In this case, however, the most easily synthesized precursor (**15**) contained dichlorovinyl groups (Scheme 2). In contrast to the synthesis of **4**, where a quadruple ring closure proceeded rather smoothly, producing **4** as the major product of the pyrolysis,¹² FVP of **15** provided a complex mixture of

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Scheme 2^a

^a Key: (a) lithium dicyclohexylamide, DCM, 0 °C, 0.5 h; 80%; (b) *p*-TsOH, benzene, reflux for 20 h, 60%; (c) FVP, 1000 °C, N₂ stream, 1.5 Torr; (d) *n*-BuLi, THF, -78 °C, 1.5 h, 45%.

products. While GC/MS and LC/MS analysis of the pyrolysate suggested that some products with the correct carbon framework containing varying amounts of chlorine were formed (i.e., **16**), no significant amounts of **5** could be produced from the chlorinated mixture utilizing a variety of reagents. Hence we sought to reduce the amount of chlorine prior to pyrolysis so as to avoid having to remove it later. However, while the trichlorovinyl derivative is an obvious choice, treatment of **15** with various amounts of *n*-butyllithium, under a variety of conditions, has yet to be successful in removing precisely three chlorines. However, we did isolate tetrachloro and trichloro derivatives (**17**) as a mixture of isomers, and so we subjected it to pyrolysis. This was indeed successful in producing **5** together with some incomplete ring closure products and a number of lower molecular weight, polynuclear aromatic hydrocarbons. Careful chromatography (silica gel, hexane-DCM 25:1) of the pyrolysate followed by crystallization from petroleum ether allowed the isolation of **5** as an orange solid. High-resolution mass spectroscopy confirmed it to be a C₃₀H₁₂ hydrocarbon, and ¹H NMR showed a singlet, two doublets, and a doublet of doublets for four aromatic protons, as expected for the structure of **5**.¹³ Moreover, ¹³C NMR showed four CH aromatic and six quaternary aromatic carbons,¹³ confirming the structural assignment. However, the yield is quite low since **5** accounts for only ~5–10% of the pyrolysate, and we are continuing to explore methods for the preparation of the trichlorovinyl derivative with the hope of improving this last step.

The poor formation of **5**, as compared to **4**, may also be related to the relative stabilities of the two hydrocarbons. Indeed, **5** is expected to be significantly less stable than the isomeric **4** since it contains more five-membered rings in its carbon framework. Theoretical calculations¹⁴ support this prediction, with **4** more stable than **5** by 16 kcal/mol according to molecular mechanics (MM2/87) and 18 kcal/mol by ab initio methods (HF/6-31G**/3-21G).

(13) Isolated as an orange solid that darkens, softens, and sublimes over 250 °C in a sealed capillary tube, but does not melt below 340 °C. ¹H NMR (CDCl₃, 400.13 MHz): δ 7.39 (dd, 3H), 7.62 (d, *J* = 8.0 Hz, 3H), 7.67 (d, *J* = 6.9 Hz, 3H), 7.85 (s, 3H). ¹³C NMR (CDCl₃, 100.61 MHz): δ 120.7, 125.0, 127.4, 128.3 (all four CH by DEPT-90 experiment), 135.4, 138.2, 138.6, 144.9, 148.3, 153.1. MS (*m/e*, relative intensity): 373 (M + 1, 22), 372 (M, 74), 186 (100), 185 (85), 184 (50), 172 (20), 171 (15). HRMS: calcd for C₃₀H₁₂ 372.0939, found 372.0936.

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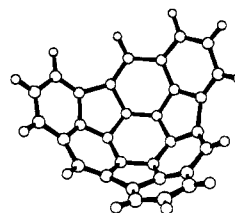


Figure 1. HF/3-21G calculated minimum energy structure of **5**.

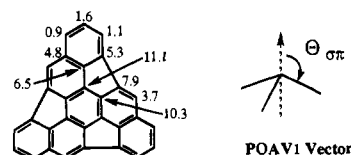


Figure 2. POAV1 pyramidalization angles ($\Theta_{\sigma\pi} - 90^\circ$) of the symmetry-independent carbon atoms of **5** from the HF/3-21G optimized structure.

While we have yet to obtain a crystal of **5** suitable for X-ray analysis, the ab initio HF/3-21G minimum energy structure shown in Figure 1 provides an illustration of the considerable curvature expected for semibuckminsterfullerene **5**. One method for evaluating and comparing curvature in π -electron systems is π -orbital vector analysis (POAV1¹⁵), where pyramidalization angles are defined as $\Theta_{\sigma\pi} - 90^\circ$. Application of this method using the ab initio geometry of **5** gives pyramidalization angles of 11.10 and 10.3° for the two symmetry-independent carbon atoms within the central six-membered ring—the region of greatest curvature—while a value of 5.3° is obtained when the curvature is averaged over all carbon atoms (Figure 2). Thus, the curvature of **5** in the region of maximum curvature is expected to be quite comparable with that of buckminsterfullerene, which has a pyramidalization angle of 11.6°. The predicted curvature of **5** is also very similar to the calculated curvature for **4**, which yields maximum and average pyramidalization angles of 11.4° and 5.2°, respectively.¹² Hence **4** and **5** are expected to be among the most curved π -electron systems ever reported, with only buckminsterfullerene and 9,9',10,10'-tetrahydroanthracene showing more curvature.^{15c}

While the possible dimerization of **5** to C₆₀ will be explored, such experiments will be limited due to the low yields afforded by Scheme 2, and an immediate goal will be to improve this process. In any event, these buckybowls represent an exciting new class of compounds and will likely show some unique chemistry. For example, unlike C₆₀, **4** and **5** possess accessible concave as well as convex surfaces, and a number of theoretical papers have appeared concerning the preference of convex vs concave complexation of **5** with metals.^{3,16,17} In addition, it will be quite interesting to learn how far one must go on the buckminsterfullerene surface to generate hydrocarbons that will have fullerene-like properties.

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Supplementary Material Available: Synthetic details and characterization of intermediates for the preparation of **5** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and some be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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