Buckybowls: Synthesis and ab Initio Calculated Structure of the First Semibuckminsterfullerene

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Received May 5, 1994

The discovery of the spherical, C_{60} molecule known as buckminsterfullerene (**1**) has led to one of the most exciting areas of investigation in recent decades.[1] The attention that **1** has drawn has generated a renewed interest in aromatic hydrocarbons with curved surfaces, but unfortunately, these latter structures have provided a considerable synthetic challenge to organic chemists. Corannulene (**2**), which represents the polar cap of buckminsterfullerene, has been known for some time,[2,3] but it has only recently been accessible for study due to the discovery of a new synthetic method.[4,5] Recently we synthesized cyclopentacorannulene **3** which, in contrast to **2**,[6] is "locked" in the bowl conformation and does not undergo fast (NMR time scale) bowl-to-bowl inversion in solution.[7] This report describes the first synthesis and characterization of a C_{30} hydrocarbon (**4**) whose carbon framework represents half of the buckminsterfullerene C_{60} surface.

1

2

3

4

Such C_{30} structures represent a new class of compounds referred to as semibuckminsterfullerenes.[8] These hydrocarbons share common characteristics: (a) 30 sp^2 carbon frameworks, consisting of multiple fused five- and six-membered rings, that may be identified on the buckminsterfullerene surface, and (b) bowl-shaped geometries. Semibuckminsterfullerenes have been regarded as attractive synthetic targets as potential intermediates in a "classical" total synthesis of C_{60}.[9] However, despite these efforts,[8–10] the semibuckminsterfullerenes have heretofore remained elusive.

Our synthesis of **4** was accomplished in a manner analogous to the Scott procedure for the preparation of corannulene **2**[4,11] except that the recently synthesized 1,2,5,6-tetraoxopyracene[12] served as the starting material (Scheme 1). A remarkable quadruple ring closure was required during the flash vacuum pyrolysis step. Surprisingly, the latter pyrolysis proceeded rather smoothly, yielding essentially a single product by GC–MS; **4** was purified by chromatography and was characterized spectroscopically.[13] ^1H NMR showed the expected AB multiplet plus a singlet in the ratio 2:1, and ^{13}C NMR exhibited three methine carbons and five quaternary carbons.

Semibuckminsterfullerene **4** is expected to adopt a bowl-shaped conformation in its lowest energy arrangement as demonstrated by ab initio[14] 3-21G calculations (**4a**; see Figure 1). The depth of the bowl in **4a**, as measured by the distance of the plane defined by the four carbon atoms in the periphery from the parallel plane passing through the central C–C bond, is 2.70 Å, significantly greater than the 0.89 Å value found in **2**.[3] An alternative, partially inverted structure for **4** of C_{2h} symmetry (i.e., **4b**; see Figure 1) is also found by ab initio calculations. Both **4a** and **4b** exhibit no imaginary vibrational frequencies at the HF/3-21G level of theory, and therefore they represent real minima on the potential energy surface of **4**. However, **4b** is 51.0 kcal/mol higher in energy than **4a** at the HF/6-31G*//3-21G level, so we can conclude that **4** is exclusively represented by the bowl conformation under normal conditions.

The planar conformation of D_{2h} symmetry is 76.1 kcal/mol higher in energy than **4a** (6-31G*//3-21G); however, this structure is not the transition state (TS) for the bowl-to-bowl inversion of **4** since it exhibits two imaginary vibrational frequencies at the HF/3-21G level [150*i* (B_{2g}) and 126*i* (B_{3u})]. This led to consideration of the two-step pathway **4a** → TS → **4b** → TS → **4a** as the lowest energy process for bowl-to-bowl

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(13) Yellow needles (from benzene), decomposing over 300 °C. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 7.42 (s, 4H), 7.55 (d, J = 9.0 Hz, 4H), 7.91 (d, J = 9.0 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100.61 MHz): 125.5, 126.8, 127.3 (all three CH by DEPHT experiment); 128.2, 128.6, 136.8, 137.3, 142.0 ppm (quat). MS (*m/e*, rel intensity): 372 (100), 186 (30). HRMS: calcd for $C_{30}H_{12}$ 372.0939, found 372.0929.

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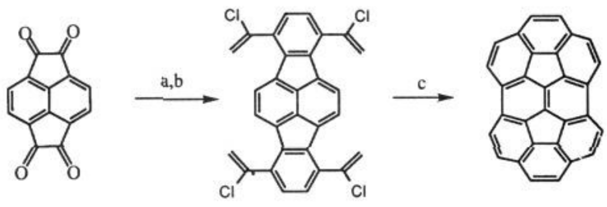
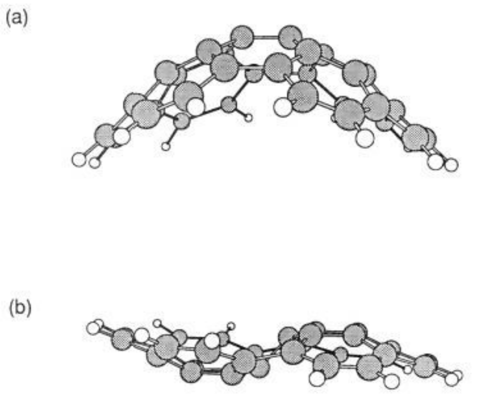
Scheme 1[a]



[a] (a) 2,4,6-Heptanetrione, glycine (catalyst), norbornadiene–toluene, reflux for 72 h; 15%. (b) PCl_5, toluene, reflux for 3 h; 30%. (c) Flash vacuum pyrolysis at 1000 °C; ca. 5%.



4a

4b

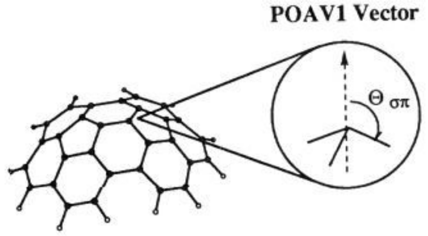
Figure 1. 3-21G optimized minimum energy structures of **4**: (a) global minimum of C_{2v} symmetry (**4a**) and (b) local minimum of C_{2h} symmetry (**4b**).

inversion, and while the TS could not be located by ab initio calculations, it was located by the semiempirical AM1 method.[17]

A structure of C_s symmetry was found that exhibited only one imaginary frequency, being 5.9 kcal/mol higher in energy than **4b**. Adding this number to the difference in energy between **4a** and **4b** from the ab initio results produces an estimation of the inversion barrier to be 57 kcal/mol. Although this transition state would be more easily reached than the D_{2h} structure, it is still very high in energy, and, as one would expect, the barrier for bowl-to-bowl inversion in **4** will be significantly higher than in either **2** or **3**.[6,7,18]

Of course an obvious question concerning semibuckminsterfullerenes is their potential dimerization to buckminsterfullerene itself. However, in the case of **4**, the icosahedral C_{60} cannot be formed without some bond reorganization. That is, even if dimerization could be achieved by sequential formation of the new bonds between the tertiary peripheral carbon atoms of **4** with retention of the bond pattern in the monomers, an isomer of buckminsterfullerene would be formed: an "imperfect" C_{60} cage of D_{2d} symmetry. While such a structure would have 20 six-membered and 12 five-membered rings like buckminsterfullerene, it would contain four pairs of adjacent (i.e., edge-sharing) pentagons. According to recent calculations, the energy of this isomer is expected to be 116 kcal/mol higher than that of icosahedral buckminsterfullerene.[19]

A major point of interest in synthesizing hydrocarbons along the buckminsterfullerene surface is to determine at what point the chemistry of these compounds becomes "fullerene-like". In this context, we note that two of the quaternary carbons of **4** have ^{13}C resonances at 142.0 and 145.4 ppm, very close to the value of 143 ppm for buckminsterfullerene.[1] Of course one of the most interesting features for comparison is curvature. Using the π-orbital vector analysis method,[20] (POAV1), the pyramidalization angle of buckminsterfullerene, defined as $\Theta_{\sigma\pi} - 90$, is 11.6; there is a single value since all of the carbons are identical.



In **4**, the curvature is expected to vary across the surface, and the maximum (and average) pyramidalization angle derived from the ab initio calculated structure is 11.4 (5.2). Hence the curvature of **4**, at least in the region of maximum curvature, is predicted to be quite comparable to that of buckminsterfullerene.

Although the chemistry of curved aromatic hydrocarbons is largely unexplored, these bowl-shaped compounds may be expected to resemble the fullerenes in some of their properties. The behavior of **4**, especially with its deep, bowl geometry, should be exciting.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, of the U.S. Department of Energy and by SNCC (Louisiana State University) for allocation of computer time. We also thank R. C. Haddon for the latest version of the POAV program.

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