

Buckybowls: Polynuclear Aromatic Hydrocarbons Related to the Buckminsterfullerene Surface

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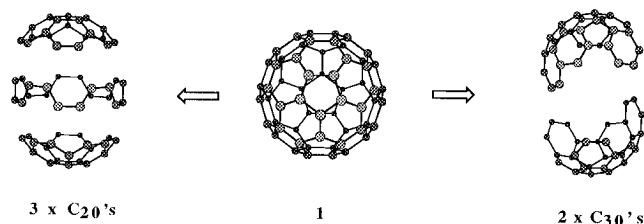
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Received October 30, 1995

Introduction

Buckminsterfullerene (**1**) was named “Molecule of the Year” by *Science* (Dec 20, 1991), and it is hard to imagine any area of chemical research in recent history that has attracted the kind of attention afforded to **1** and the related fullerene family. Kroto, Heath, O'Brien, Curl, and Smalley¹ made the remarkable discovery that buckminsterfullerene, C₆₀, is a stable molecule due to geodesic and electronic properties inherent in the truncated icosahedral cage structure. The subsequent isolation of macroscopic amounts of C₆₀ and C₇₀ from soots produced by the vaporization of graphite² has facilitated a flood of research activity.³ Buckminsterfullerene, or “buckyball”, is the most important member of this new family of three-dimensional carbon cages. It consists of 20 six-membered rings and 12 five-membered rings; the five-membered rings provide the curvature while strain is minimized since no two five-membered rings are adjacent.

Our own interests lie with the polynuclear aromatic hydrocarbons (PAHs) that result when buckminsterfullerene is “taken apart” and hydrogen is attached to the resulting dangling bonds. Of course many hydrocarbons can be generated in this way, including benzene and naphthalene, but it is not until C₂₀ is reached that they acquire the most interesting feature of buckminsterfullerene, its curvature. We have re-



ferred to these compounds as “buckybowls”,⁴ since, like buckyball, they consist of five- and six-membered rings with no two five-membered rings abutting, and the five-membered rings surrounded by six-membered rings provide curvature.

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Andrzej Sygula was born and educated in Poland. He received his M.S. in chemistry (1976) and Ph.D. (1982) from Jagiellonian University, Krakow, Poland. In 1982 he joined the faculty of the Department of Chemistry at Jagiellonian University. He spent two years (1985–86) with Professor P. W. Rabideau in Indianapolis as a postdoctoral researcher. In 1990 he returned to the U.S. where he is currently a research assistant professor of Chemistry at Louisiana State University.

These curved-surface, polynuclear aromatic hydrocarbons are of interest for a number of reasons. First, they serve as model compounds for fullerene structure and reactivity; it will be interesting to observe the progression from smaller to larger fragments on the fullerene surface to determine when the chemistry and properties of the hydrocarbons become fullerene-like. And, of course, there is a potential competition between fullerene-like reactivity at the sites of greatest pyramidalization vs typical PAH reactions at the periphery. Second, appropriate buckybowls have been suggested as potential substrates for the total synthesis of fullerenes.^{5–8} Although a broad spectrum of fullerenes are now commercially available from carbon soots, the importance of total synthesis goes beyond aesthetics for the synthetic organic chemists. For example, controlled isotope labeling, formation of higher energy isomers, and stuffing the cages with guest atoms may all be possible through total synthesis. Third, alkali-metal-doped fullerenes are low-temperature superconductors,⁹ and it is of interest to learn if bowl-shaped PAHs will exhibit similar behavior. Fourth, accessibility of both concave and convex faces may allow both endo and exo metal complexation (cf. exo- and endohedral complexation of the fullerenes). Fifth, because of the theoretical interest in the nature of aromaticity, the curved buckybowls—as well as the

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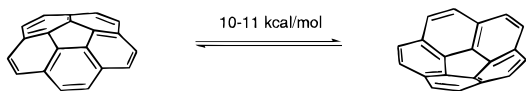
fullerenes—are very attractive systems since they manifest a compromise between strain and conjugation.

Corannulene

Until recently, the only known fullerene-related hydrocarbon was corannulene, $C_{20}H_{10}$. Corannulene (**2**) represents the polar cap of buckminsterfullerene, and as illustrated above, **1** can be separated into two C_{20} corannulene fragments with the remaining middle section corresponding to *all-trans*-cycloeicosadecaene. Surprisingly, **2** was not even mentioned in the literature prior to its synthesis by Barth and Lawton in 1966.¹⁰ However, its fascinating structure notwithstanding, the chemistry and properties of corannulene were not fully investigated due to the length and difficulty of the original synthesis. A major breakthrough occurred in 1991 when the Scott group announced a new synthetic method that opened the door for the exploration of fullerene-related hydrocarbons.¹¹ Subsequently, two alternative routes to corannulene were reported by the Siegel¹² and Zimmermann¹³ groups. While the Scott group has used several different precursors in the final pyrolysis step,^{11c} Scheme 1 shows a route that we have used successfully many times. Moreover, we have applied this route to the synthesis of larger fullerene-related systems to be described below.

Bowl Depth and Bowl-to-Bowl Inversion

Despite its considerable curvature, corannulene is surprisingly flexible. Bowl-to-bowl inversion barriers have been determined by NMR techniques for several appropriately substituted corannulenes with barriers found to be in the range of 10–11 kcal/mol,^{14,15} and it



is expected that substitution would have only a minor effect on the barrier relative to the parent hydrocarbon. X-ray crystallography shows a bowl depth of 0.87 Å as measured from the plane containing the five-membered ring to the plane containing the peripheral aromatic carbon atoms,¹⁶ and this is significantly more shallow than would be expected for the polar cap within the buckminsterfullerene geometry (ca. 1.5 Å; see below). Hence “release” from the spherical constraint allows for flattening of the system. Another interesting aspect of the crystal structure is the absence of any amount of bowl-stacking since this

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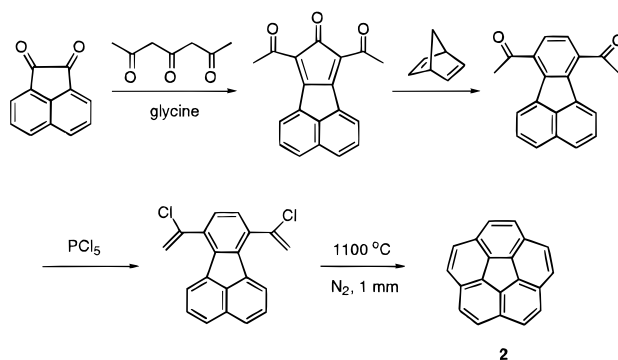
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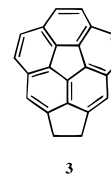
(16) Hanson, J. C.; Nordman, C. E. *Acta Crystallogr., B* **1976**, *B32*, 1147–1153.

Scheme 1

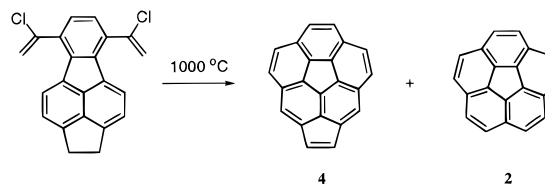


arrangement would seem ideal to allow close packing and attractive π – π interactions (however, see cyclopentacorannulene below).

In view of the surprising flexibility of corannulene, we became interested in learning how much additional elaboration of the structure along the buckminsterfullerene surface would be required to “lock” the bowl-shaped geometry. The most logical approach was incorporation of a second five-membered ring since this would introduce additional constraint, and so we undertook the synthesis of dihydrocyclopentacorannulene **3**. The obvious route was the Scott procedure



outlined in Scheme 1, but with an additional five-membered ring present in the starting material. This procedure was successful except that hydrogen was lost during the pyrolysis, and C_2H_2 was also lost although to a lesser extent (7:3 ratio of **4** to **2**). In any event, this route produced the first fullerene-related hydrocarbon beyond corannulene,¹⁷ and an opportunity to examine the effects of further constraint on the corannulene system.



The additional five-membered ring in **4** produces a significant increase in curvature relative to corannulene as demonstrated by X-ray crystal structure determination.¹⁸ The bowl depths of both **2** and **4** are illustrated in Figure 1 as the distance between the plane containing the central five-membered ring and the aromatic carbons at the rim. These values can be compared to a value of ca. 1.5 Å for the C_{20} polar cap within buckminsterfullerene as deduced from values

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in the range of 1.47–1.52 Å determined for the crystal structure of $C_{60} \cdot 3SbPh_3$.¹⁹

In addition to showing significantly more curvature than **2**, the crystal structure of **4** also revealed interesting long-range packing in the solid state. The bowl-shaped molecules are stacked in a concave–convex fashion in which there are 24 intermolecular C···C distances shorter than 3.8 Å for every 2 molecules in the crystal; such stacking is absent in the

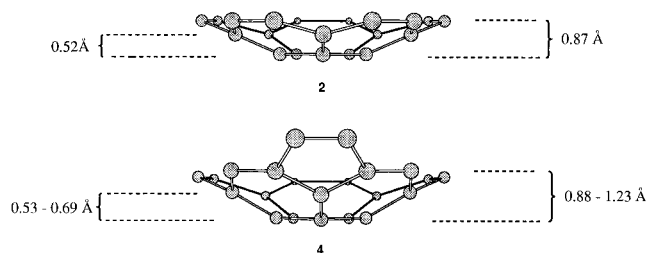
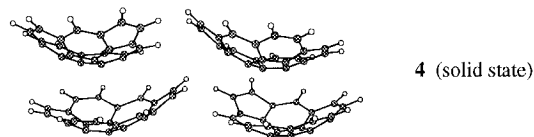
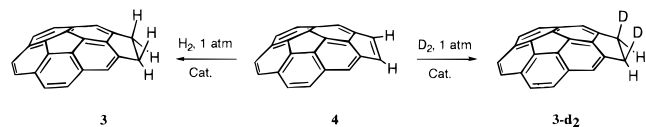


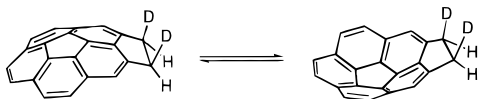
Figure 1. Relative bowl depths of corannulene (**2**) and cyclopentacorannulene **4**.

crystal structure of corannulene. Of course stacking may be a function of bowl depth, and it will not be known if this arrangement will be common for bowl-shaped hydrocarbons until other examples appear. Recently, analogous concave–convex structures were suggested for the gas-phase dimers of corannulene with radical cations of corannulene (Cor/Cor⁺) and C_{60} (Cor/ C_{60}^+).²⁰ It should also be noted that the cup-shaped compounds known as tribenzotriquinacenes also show stacking in the crystal although these structures have hydrogens or alkyl groups at the vertex of three fused five-membered rings that prevent close packing of the aromatic rings.²¹

Bowl-to-bowl inversion in **4** cannot be observed by NMR, and our original intention was the synthesis of **3** since it would show two sets of signals representing the exo (convex) and endo (concave) hydrogens under conditions of slow exchange. Hydrogenation of **4** was a simple matter, and **3** did indeed show two sets of benzylic protons. However, somewhat unexpectedly, the spectrum was unchanged upon heating to the spectrometer upper temperature limit, and it became obvious that the barrier to inversion was too high for measurement by NMR coalescence methods.¹⁷ Hence, another approach was needed, and given the substantial curvature of **3**, we wondered if deuteration of the double bond might not occur with some degree of selectivity. Indeed, this reaction proceeded with complete π -facial stereoselectivity to produce a single stereoisomer (**3-d₂**),²² and then determination of the



inversion barrier became possible by following the equilibration of **3-d₂** with its isotopomer by ¹H NMR.



Interestingly, the introduction of a single, additional

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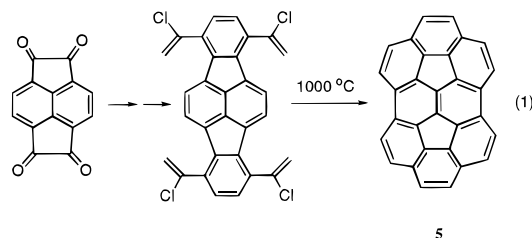
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five-membered ring to the rim of corannulene increased the barrier for inversion more than 2-fold! Barriers of 27.6–27.7 kcal/mol in the temperature range of 52.1–99.3 °C were determined for **3**²² as compared to the value of only 10–11 kcal/mol for monosubstituted corannulenes.

Semibuckminsterfullerenes

C_{2v} Semibuckminsterfullerene. Our success in being able to go beyond corannulene encouraged us to continue further along the C_{60} surface although we realized that systems beyond C_{20} involve a considerable amount of strain, and a number of conventional routes had already been tried without success. However, the strength of the Scott route (Scheme 1) lies in the high temperature involved in the ring closure step, and we recognized that extension of this procedure could, in principle, lead to the first fullerene-related $C_{30}H_{12}$. The route outlined in eq 1 required

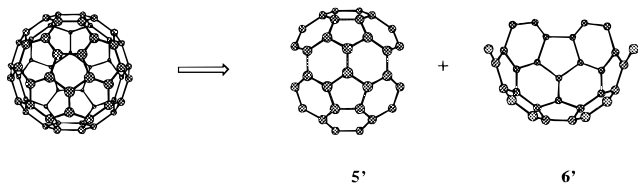


the then unknown 1,2,5,6-tetraketopyracene as a starting material, and it proved rather difficult to synthesize.²³ However, the tetrakis(chlorovinyl) precursor was eventually obtained, and pyrolysis was successful in producing **5**, albeit in milligram quantities, as the first known semibuckminsterfullerene.⁴ Compound **5** was crystallized as yellow needles from benzene and did not melt under 300 °C; the carbon NMR showed three methine and five quaternary carbons with two of the quaternary carbons at 142.0 and 145.4 ppm, very close to that of buckminsterfullerene (143 ppm). Although suitable crystals have not yet been obtained for an X-ray structure, **5** is expected to be considerably bowl-shaped, with its maximum curvature approximating that of C_{60} (see below). The bowl geometry is also expected to be quite rigid. Extrapolation from the experimentally determined barrier for bowl-to-bowl inversion in substituted corannulenes (10–11 kcal/mol), as well as that for **3** (27 kcal/mol), suggests a very high barrier for inversion in **5**. Indeed, calculations using a combination of *ab initio* (HF/6-31G**//3-21G) and AM1 semiempiri-

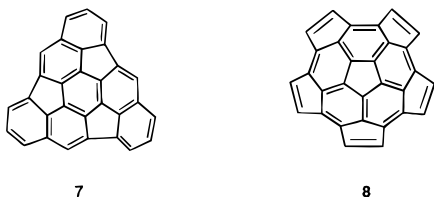
(23) Abdourazak, A. H.; Marcinow, Z.; Folsom, H. E.; Fronczek, F. R.; Sygula, R.; Sygula, A.; Rabideau, P. W. *Tetrahedron Lett.* **1994**, *35*, 3856–3860.

cal methods predict a barrier of ca. 57 kcal/mol for bowl inversion in **5** proceeding through an "s"-shaped transition state.⁴

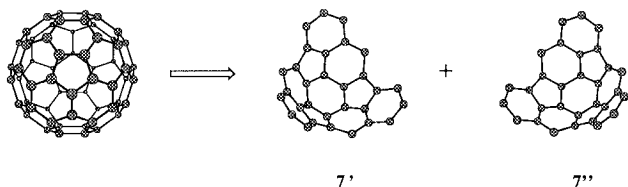
Other C₃₀H_n Synthetic Targets. Structure **5** may be regarded as a semibuckminsterfullerene⁶ or half of buckminsterfullerene by virtue of the fact that it has 30 carbons and exhibits a pattern of five- and six-membered rings identifiable on the surface of C₆₀. However, **5** is not an exact half of **1** since when buckminsterfullerene is "taken apart" to produce the carbon framework that leads to **5** (i.e., **5'**), the remaining C₃₀ carbon fragment (**6'**) is not identical with **5'**,



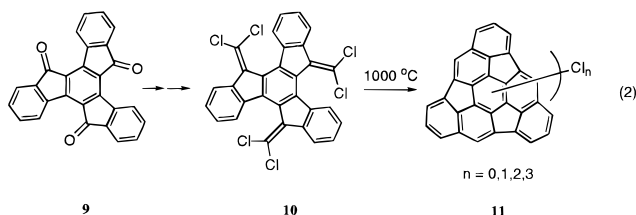
and it has two "dangling carbons" that translate to methylene units when hydrogens are added. On the other hand, there are a number of identical C₃₀ pairs that can be produced by halving C₆₀ and, when the dangling bonds are saturated with hydrogen atoms, produce reasonable synthetic targets. The most attractive of these are **7** and **8**, and in fact, the C₃₀



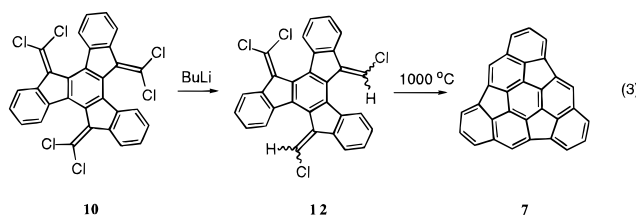
fragment with the bonding pattern in **7** was previously considered by McKee and Herndon as a potential intermediate in buckyball formation by the vaporization of graphite.²⁴ Interestingly, halving C₆₀ to produce carbon frameworks corresponding to hydrocarbon **7** results in a pair of enantiomers (**7'** and **7''**).



C₃ Semibuckminsterfullerene. Although hydrocarbon **7** attracted early attention as a possible intermediate to **1**, its synthesis proved to be elusive by conventional routes. Once again, our approach was to involve pyrolysis in the critical step where curvature is introduced into the molecule. Beginning with the readily available precursor **9**, we attempted to prepare the tris(chlorovinyl) derivative for pyrolysis. However, after a number of failed attempts, we found that it was much easier to synthesize the tris(dichlorovinyl) compound **10**. Pyrolysis of **10** did seem to produce some C₃₀H₁₂ by mass spectroscopy, but the major products still contained chlorine in varying amounts (eq 2). Unfortunately, removal of chlorine from **11** was



not successful since most of the effective reagents appeared to react with the hydrocarbon system as well as remove chlorine. We then shifted our strategy to the removal of chlorine before pyrolysis (eq 3), but



reaction of **10** with varying amounts of butyllithium was only successful in producing mainly a mixture of tetrachloro isomers (**12**). For reasons that we cannot explain, the trichloro derivative could not be produced in any significant amounts by this method, although it does appear to be present in the mixture (**12**) in small amounts. At any rate, pyrolysis did produce **7**, the first C₃₀ hydrocarbon representing exactly half of the buckminsterfullerene carbon framework.²⁵ The compound is an orange solid that does not melt below 340 °C.

With the present method, **12** is pyrolyzed in several runs of 80–90 mg each which are then combined and purified to produce ca. 5 mg of **7**. We hope that an efficient synthesis of the tris(chlorovinyl) analog will provide a considerable improvement in the yield of **7** during pyrolysis, and this has become a major goal of our continuing efforts.

The third semibuckminsterfullerene considered, compound **8**, is very attractive due to its high symmetry, but its synthesis is expected to be even more challenging than that of **7**. The six five-membered rings present in this C₃₀H₁₀ hydrocarbon introduce considerable strain that will likely destabilize the structure.

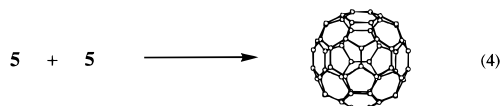
A Potential Synthetic Route to C₆₀

Perhaps the most exciting feature of C₃₀H_n buckybowls is the possibility of dimerization to C₆₀H_{2n} followed by the loss of hydrogen to afford a total synthesis of buckminsterfullerene. When considering dimerization to produce C₆₀H_n and/or C₆₀, it is assumed that the bonding pattern in the carbon networks of the substrates will remain unchanged, and that the new carbon-carbon bonds will be formed in a sequential mode between the tertiary rim carbon atoms. However, this process can lead to several different carbon cages, albeit of considerably different energies, depending on the docking pattern. Of course **5** is not a candidate for the production of buckminsterfullerene since its dimerization cannot produce icosahedral C₆₀ without some reorganization of the

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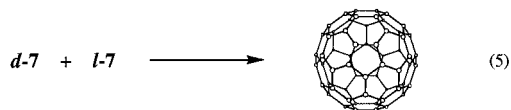
(25) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **1995**, *117*, 6410–6411.

carbon framework. Under the best docking conditions, dimerization of **5** would lead to an imperfect C₆₀ cage of D_{2h} symmetry (eq 4).⁴ According to recent *ab initio*



calculations at the HF/3-21G level, the energy of this isomer, which has four pairs of abutting pentagons, is expected to be 116 kcal/mol higher than that of buckminsterfullerene itself.²⁶

In the case of **7**, seven different C₆₀ cages could be formed.²⁷ Dimerization of the two enantiomers of **7** may formally yield three isomers of C₆₀, with the lowest energy structure being icosahedral buckminsterfullerene (eq 5). On the other hand, dimerization of two identical molecules of **7** leads to four isomers. In this case the lowest energy cage has D₃ symmetry (eq 6) with the same number of five-membered (12)



and six-membered (20) rings as buckminsterfullerene, but with three pairs of abutting five-membered rings. This "imperfect" structure is predicted to be higher in energy than **1** by 76 kcal/mol (or 1.26 kcal/mol per carbon atom) at the HF/3-21G level.²⁶

The dimerization reaction has yet to be fully explored except that neither C₆₀H₂₄ nor C₆₀ is produced simply on heating **5** or **7** to a melt. Hence, a variety of conditions including the use of catalysts need to be employed, and this will require more material than is available from the current synthetic route.

Evaluation of Curvature

Methods for the evaluation and comparison of curvature in π -conjugated carbon networks are of great importance for these systems, and the POAV1 (π -orbital axis vector) analysis approach²⁸ is conceptually simple and quite convenient (Figure 2). This method describes the local curvature of any carbon atom by construction of a vector that makes equal angles to the three attached σ -bonds assuming these bonds to lie along the internuclear axes. In an ideal case, this angle ($\Theta_{\sigma\pi}$) is 90° for planar sp² centers, and 109.2° for tetrahedral sp³ carbons. The pyramidalization angle is defined as $\Theta_{\sigma\pi} - 90$, and buckminsterfullerene has a single pyramidalization angle of 11.6°²⁸ since all of the carbons are equivalent. With buckybowls, however, the curvature varies across the

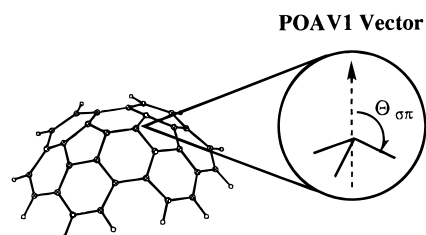


Figure 2. POAV1 π -orbital vector analysis method.

Table 1. Local Maximum and Overall Average POAV1 Pyramidalization Angles (deg) Based on *Ab Initio* Optimized Geometries^a

	2	4	5	7	8	C ₆₀
max angle	8.4	11.4	11.4	11.1	12.5	11.6
av angle for quat carbons	6.0	7.2	7.6	7.6	9.0	11.6

^a HF/3-21G.

surface and is best described by two values: the maximum pyramidalization angle and the average pyramidalization angle for all of the carbons that do not have hydrogens attached. The rim carbons are omitted since they are predicted to be only slightly pyramidalized with pyramidalization angles in the range of 1–2°.

Table 1 provides POAV1 analyses for corannulene (**2**), cyclopentacorannulene **4**, and the three semibuckminsterfullerenes **5**, **7**, and **8** based on *ab initio* optimized geometries. All of the buckybowls beyond corannulene exhibit a maximum local curvature quite comparable to the curvature of C₆₀ itself, although the average values are lower. In the buckybowls, the highest curvature occurs on the carbon atoms at the core, and then it gradually diminishes toward the rim. The predicted curvatures for **4**, **5**, and **7** are all quite similar, with a slightly higher curvature predicted for **8**. However, all four compounds are more curved than corannulene, and the curvature parallels the number of five-membered rings present which varies from one in **2**, two in **4** and **5**, three in **7**, and finally to six in **8**. The degree of curvature, both the maximum and the average, is very similar for **4** and **5** despite a significant difference in size; this is clearly a function of the number of five-membered rings which are responsible for the curvature. In any case, when the maximum curvature values are considered, these buckybowls are expected to be among the most pyramidalized of the presently known conjugated carbon networks.^{28c}

Reduction

Corannulene is easily reduced both electrochemically and by alkali metals,^{29–33} and the final reduction product by lithium in THF is the tetraanion **13**. It appears that this tetraanion may be an "anion within an anion", that is, a cyclopentadienyl anion inner core, with the remaining three excess electrons at the periphery producing an 18- π -trianion (**13**).³⁰ However,

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(27) Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; Jai Press Inc.: Greenwich, CT, 1995; Vol. 3, pp 1–36.

(28) (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137–142. (b) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243–249. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385–3389. (d) Haddon, R. C. *Science* **1993**, *261*, 1545–1550.

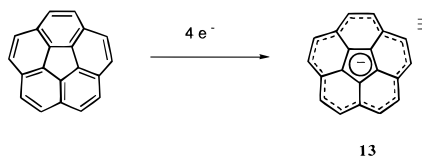
(29) Janata, J.; Gendell, J.; Ling, C.-Y.; Barth, W.; Backes, L.; Mark, H. B., Jr.; Lawton, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3056–3058.

(30) Ayalon, A.; Rabinovitz, M.; Cheng, P.-C.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1636–1637.

(31) Rabideau, P. W.; Marcinow, Z.; Sygula, R.; Sygula, A. *Tetrahedron Lett.* **1993**, *34*, 6351–6354.

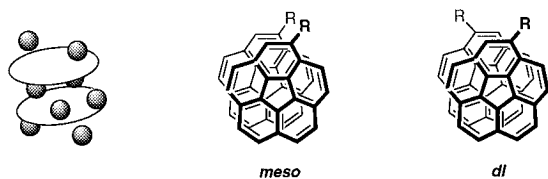
(32) Ayalon, A.; Sygula, A.; Cheng, P.-C.; Rabinovitz, M.; Rabideau, P. W.; Scott, L. T. *Science* **1994**, *265*, 1065–1067.

(33) Baumgarten, M.; Gherghel, L.; Wagner, M.; Weitz, A.; Rabinovitz, M.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **1995**, *117*, 6254–6257.



NMR data and *ab initio* calculations suggest somewhat less than the 1.0 excess electron density within the central ring that would be required for this model.^{31,34}

The radical anion, dianion, radical trianion, and tetraanion of corannulene have all been examined spectroscopically by NMR and/or EPR.³³ An especially interesting dimer of the tetraanion was uncovered by examination of the ⁶Li and ⁷Li NMR behavior of **13**.³² In both cases, two Li signals appeared at low temperature, one broad and one sharp, followed by coalescence to a singlet with increasing temperature. With **13** itself, this behavior might be attributed to the bowl-to-bowl inversion process, but examination of the proton NMR of *i*-Pr-**13** and *t*-Bu-**13** provided the unexpected observation of two sets of alkyl groups in each case in somewhat unequal abundance. This observation pointed to the presence of tightly complexed dimers. The four equivalent Li cations on the outside of the "sandwich" are solvent separated and give rise to a sharp signal in contrast to the broad signal from the inner four Li cations, which are contact ion pairs. At higher temperatures, the Li cations exchange, resulting in a single signal. On the other hand, exchange of the corannulene units to interconvert *meso* and *dl* isomers must be slow, at least on



the NMR time scale, since the alkyl NMR signals remain distinct up to the highest temperature possible without decomposition. Additional evidence for this model was achieved by the preparation of "mixed" dimers, and also the addition of lithium bromide, which averaged with the broad ⁷Li signal at low temperatures, but not with the sharp ⁷Li signal.³² A recent self-diffusion study further supports the existence of dimeric aggregates for tetralithio **13**.³⁵

Previous observations of lithium sandwiching in solution appear to be limited to the monolithium derivatives of cyclohexenyl or cyclopentadienyl systems. Hence, this behavior of corannulene tetraanion in sandwiching four lithiums is quite novel, and it remains to be seen if it will be observed with other bowl-shaped aromatic hydrocarbons. A comparison of the low-lying, unoccupied molecular orbitals of cyclopentacorannulene and semibuckminsterfullerenes **5** and **7** with corannulene suggests that at least tetraanions should be easily formed in each case.²⁷ Moreover, it appears that a hexaanion is quite feasible in the case of **7** (Figure 3).

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(35) Cohen, Y.; Ayalon, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 816–818.

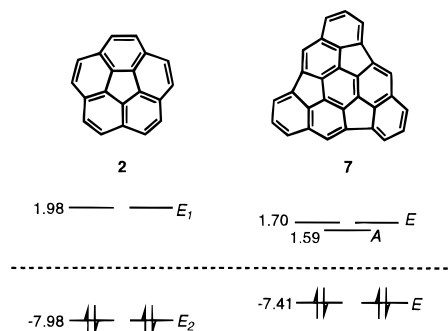
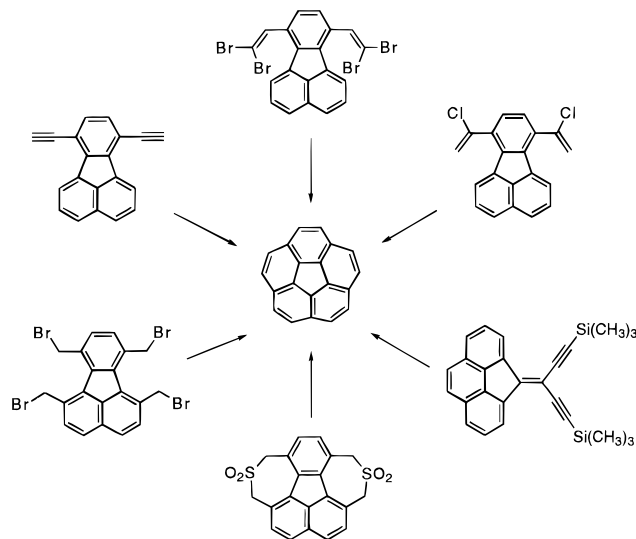
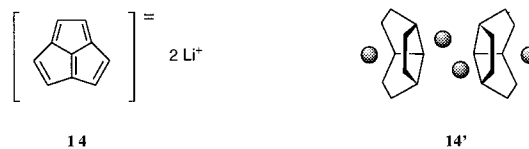


Figure 3. HOMO and low-lying LUMOs calculated by HF/6-31G*/3-21G with orbital energies in electronvolts.

Scheme 2



In a somewhat related case, a bowl-shaped dilithio dianion was prepared from acepentalene, and in the solid state, the bowls are oriented in pairs with a convex-to-convex arrangement with two lithiums in between. However, this arrangement does not appear to persist in solution.³⁶



Additional Synthetic Approaches

The production of new buckybowls will depend, of course, on the development of synthetic methods, and most of the recent routes have involved high-temperature reactions. Scott et al. reason that planar polynuclear aromatic systems may fluctuate drastically from their equilibrium geometries at high temperatures, and this allows folding that brings normally inaccessible reaction sites within reach.¹¹ In fact, aside from the original lengthy procedure, all of the successful syntheses of corannulene to date involve pyrolysis (Scheme 2).

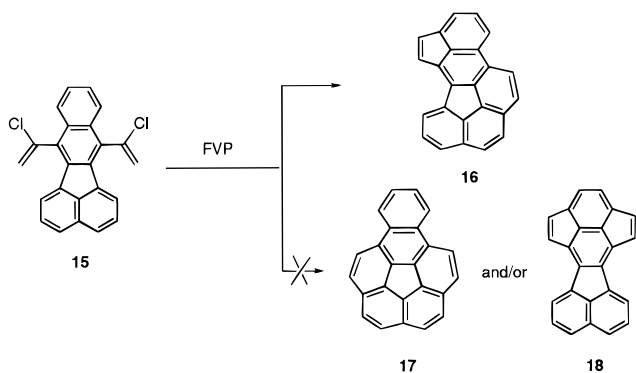
The mechanisms of ring closure under these conditions may involve electrocyclic reactions, carbene insertions, or free radical processes. One of the best procedures is the pyrolysis of terminal acetylenes, or

(36) Haag, R.; Fleischer, R.; Stalke, D.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1492–1495.

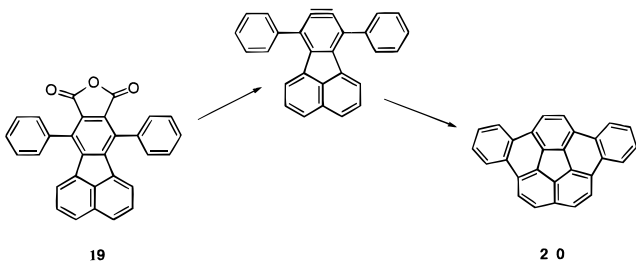
vinyl halides which may lose HX to form acetylenes. In this case a reversible pyrolytic rearrangement to vinylidenes followed by trapping of the transient carbene via intramolecular C–H insertion has been proposed.^{11,37}



An interesting aspect of this reaction, however, is that, drastic fluctuations in geometry at high temperatures notwithstanding, the reaction still appears to prefer planar products over curved ones, and perhaps six-membered rings over five-membered rings when there is such competition. At least that is the case with the pyrolysis of **15**, which leads only to planar **16**, with no benzocorannulene **17** and no pyracylene-type product **18**.³⁸



In other approaches, Bratcher and Scott recently prepared dibenzocorannulene **20** by the pyrolysis of anhydride **19** with a proposed mechanism involving an aryne intermediate.³⁹ Zimmermann et al.⁴⁰ ex-



plored the use of methylene-bridged polycyclics as precursors for bowl-shaped hydrocarbons. Pyrolysis of 9,9'-bi-9*H*-fluorenylidene provided **21** which produced only traces of **22** upon subsequent flow pyrolysis (FP) at 980 °C. The synthesis was compromised by a competing process: the isomerization of bifluorenylidene to the more thermodynamically stable **23**. This process, formally analogous to the Stone–Wales rearrangement, is known to be mediated by the presence of reactive radicals,⁴¹ so when the pyrolysis was performed in a stream of hydrogen, **23** was formed almost exclusively. On the other hand, significant

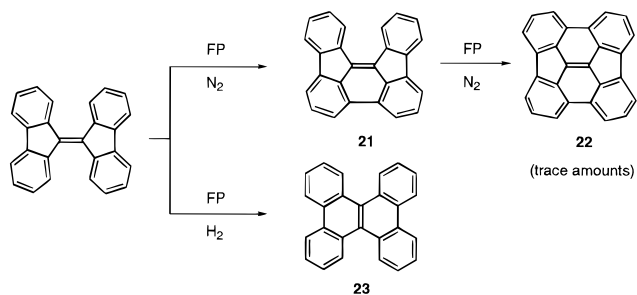
(37) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J.; McMullen G. L. *Aust. J. Chem.* **1974**, *27*, 2393–2402.

(38) Marcinow, Z.; Fronczek, F. R.; Liu, Y.-H.; Rabideau, P. W. *J. Org. Chem.* **1995**, *60*, 7015–7016.

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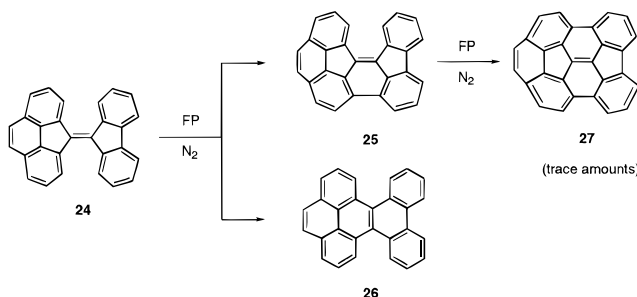
(40) Hagen, S.; Neuchter, U.; Neuchter, M.; Zimmermann, G. *Poly-cyclic Aromat. Compd.* **1995**, *4*, 209–217.

(41) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 712–713

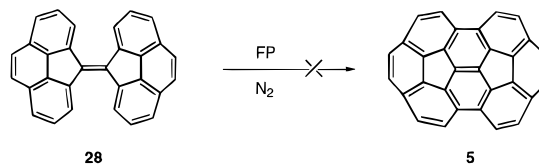


amounts of **21** were formed when either nitrogen or nitrogen/toluene was used as the carrier gas. Hydrocarbon **22** can certainly be regarded as a buckybowll since its carbon framework can be identified on the C₆₀ surface and, according to semiempirical calculations, it adopts a bowl-shaped conformation as its minimum energy structure. However, calculations predict **22** to be very flexible with an inversion barrier similar to that for corannulene (14.1 vs 15.3 kcal/mol, respectively, at the semiempirical PM3 level).

Flow pyrolysis of the related structure **24** produced similar results, affording **25**, along with **26**, and subsequent FP of **25** at 980 °C produced traces of **27**.⁴²



Hence, this method was recognized as a potential route for the synthesis of buckybowll **5** by pyrolysis of the higher homolog **28**. However, in this case, pyrolysis failed to produce even trace quantities of **5** with rearrangement, as above, as the major pathway.⁴³



An attempt to synthesize sumanene (**30**) by the pyrolysis of tris(bromomethyl)triphenylene **29** has also been reported.⁴⁴ Although this C₂₁H₁₂ hydrocarbon possesses three sp³ hybridized carbon atoms, it is presumably curved, and consequently its structure and flexibility are of interest. However, only the closure of two sides was possible (**31**), and no sumanene was detected.

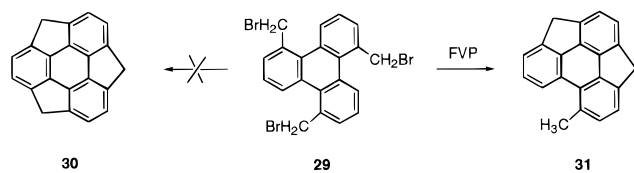
Conclusion

The synthesis, chemistry, and properties of curved-surface, polynuclear aromatics would be of great interest even if buckminsterfullerene had never been

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discovered. The presence of both convex and concave surfaces provides the potential for exceptional stereoselectivities, as well as attractive opportunities for some very interesting metal complexation.^{6,45,46} How-

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ever, the fullerenes have been discovered, and there can be no denying that this relationship adds an additional level of excitement to what is already an intriguing new class of aromatic compounds.

The authors would like to thank their talented co-workers, especially Atteye H. Abdourazak, Zbigniew Marcinow, and Renata Sygula. We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, for major support of this work. We also acknowledge a recent grant from the National Science Foundation. Finally a special thanks to Professor Larry Scott whose work and help allowed us entry into this exciting field.

AR950197D