

Geodesic polyarenes with exposed concave surfaces*

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) in which five-membered rings have been interspersed among the six-membered rings generally display curved π systems that can be either fully closed (fullerenes) or partially open (bowl-shaped fullerene fragments), depending on the number of five-membered rings. Both classes of compounds belong to the larger family we call 'GEODESIC POLYARENES.' Herein, we highlight the utility of high temperature aryl radical cyclizations as a general strategy for constructing strained geodesic polyarenes. We also report the first examples of reactions at the 'interior' carbon atoms of neutral PAHs that are not fullerenes, e.g. carbene additions, 1,3-dipolar cycloadditions, osmylation, nucleophilic addition of MeLi, and electrophilic addition of $\oplus\text{CHCl}_2$ and $\oplus\text{CCl}_3$.

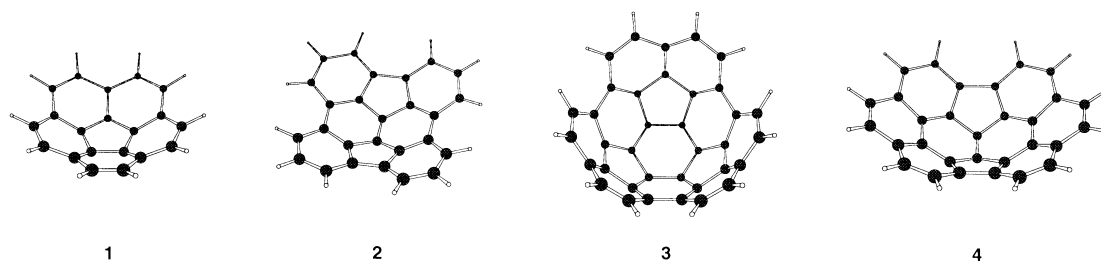
INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) composed entirely of fused benzene rings strive to maintain planar structures that can be regarded as subunits of two-dimensional graphite sheets, although steric factors sometimes override this tendency, as in the helicenes. Networks of trigonal carbon atoms harboring one or more imbedded five-membered rings, on the other hand, invariably show lower resistance to out-of-plane deformations and nearly always adopt nonplanar equilibrium geometries. When such networks of trigonal carbon atoms contain exactly 12 five-membered rings, closed-surface fullerenes result. Any number of five-membered rings fewer than 12 produces bowl-shaped molecules with convex and concave surfaces both exposed. Many such molecules comprise substructures of C_{60} and are sometimes referred to as 'fullerene fragments' or 'buckybowls', e.g. **1** [1–3], **2** [4,5], and **3** [6]. There is no absolute requirement, however, that the ring system of such molecules map onto that of C_{60} , and some do not, e.g. **4** (a substructure of C_{76}) [7]. We consider all PAHs that have curved surfaces resulting from the presence of one or more fully unsaturated five-membered (or smaller) rings to be 'GEODESIC POLYARENES', as they are all reminiscent of the geodesic structures of Buckminster Fuller, the architect for whom [60]fullerene was first named. The fullerenes constitute one family of geodesic polyarenes, and bowl-shaped PAHs constitute another.

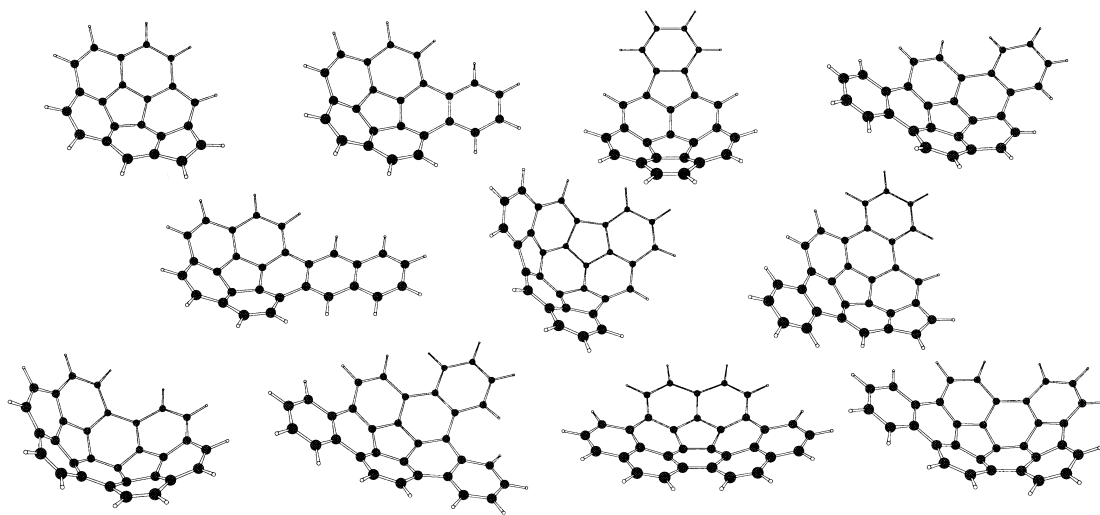
While research on the chemistry of C_{60} and the higher fullerenes has run at a furious pace in the 1990s, we have been busy developing new strategies for the synthesis of open geodesic polyarenes. Our approach takes advantage of the fact that the normal out of plane deformations of simple planar or nearly planar polyarenes become greatly amplified under conditions of flash pyrolysis. By catching such molecules in their temporarily distorted conformations, using cyclization reactions based on the intramolecular trapping of one or more strategically located carbenes [2a] or aryl radicals [5], we have been able to prepare and characterize a wide range of bowl-shaped fullerene fragments. More than a dozen of these novel aromatic hydrocarbons have now been prepared in our laboratory by this highly successful strategy (**1–4** and Fig. 1) [2,5–9], and their chemical behavior is under active investigation.

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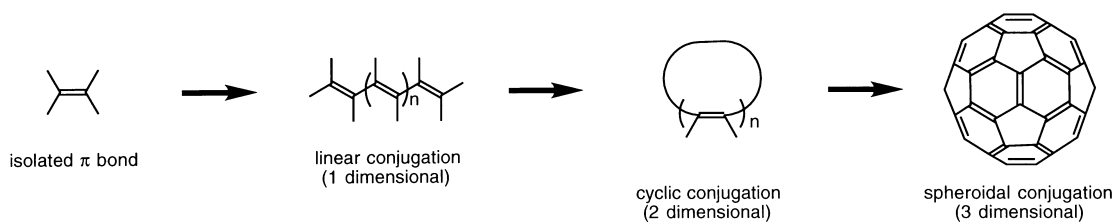
**Scheme 1**

Three of the compounds pictured in Fig. 1 have also been synthesized by others, using adaptations of our high temperature methods [10]. A striking parallel between the chemistry of bowl-shaped polyarenes and that of C_{60} has already begun to emerge, and some of our latest results in this area are presented below. Whether or not the concave surfaces of such bowl-shaped polyarenes can serve as hosts for convex guests of the appropriate dimensions and electrostatic character remains to be established.

**Fig. 1** Open geodesic polyarenes related to 1–4 that have also been synthesized recently in our laboratory.

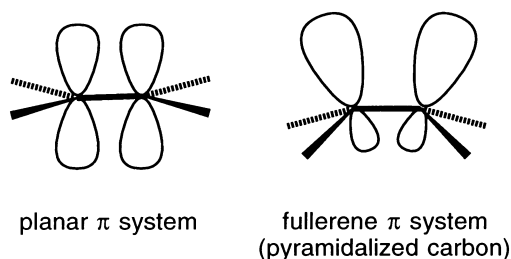
CONJUGATION AND CURVATURE

Unending π system that are conjugated in three-dimensions, with no edges, and large expanses of convex curvature stand out as the two most distinctive structural features of the fullerenes. Our bowl-shaped polyarenes share with fullerenes the curved geodesic arrays of unsaturated carbon atoms, but they have edges and are therefore conjugated, topologically, in only two dimensions. A brief digression to look at the dependence of molecular properties on both the dimensionality of conjugation and the degree of molecular curvature is in order at this point. Consider first the hierarchy of π systems as a function of their dimensionality outlined in Fig. 2.

**Fig. 2** Hierarchy of π systems as a function of their dimensionality.

Linear conjugated π systems (one-dimensional) exhibit properties that are distinctly different from those associated with isolated double bonds, e.g. longer wavelength electronic absorption maxima, higher lying HOMOs (lower ionization potentials, greater susceptibility to protonation, etc.), lower lying LUMOs (greater electron affinities, greater susceptibility to Birch reduction, etc.), a susceptibility to 1,4- and 1,6-addition reactions, and so on. Branched or cross-conjugated acyclic polyenes most closely resemble the linear, one-dimensional conjugated π systems. Joining (conceptually) the termini of a linear acyclic π system creates a monocyclic π system (two-dimensional) and turns on another set of new properties that have no counterpart in one-dimensional systems, e.g. aromaticity and the thermodynamic stabilization that it imparts, a bias toward substitution reactions rather than additions, induced ring currents, antiaromaticity, etc. Polycyclic aromatic hydrocarbons exhibit properties that most closely resemble those of the simplest two-dimensional π systems. Joining (conceptually) the edges of a polycyclic π system creates a polyhedral π system (three-dimensional), and it would seem reasonable to expect this move up the hierarchy to give rise to still another set of new properties that have no counterpart in two-dimensional conjugated π systems. As yet, we have nothing as straightforward as Hückel's rule for the fullerenes, although some trends are beginning to materialize [11].

All geodesic polyarenes, both open (e.g. bowls) and closed (fullerenes), are characterized by curved π systems composed of pyramidalized carbon atoms. Pyramidalization has several consequences. Obviously, the less parallel the alignment of p-orbitals, the poorer will be their overlap, and that will lead to weaker π bonds. Weakening a π bond tends to raise the energy of the bonding π MO and lower the energy of the antibonding π^* MO. The energetic cost of destroying a π bond, as in an addition reaction, is therefore diminished when the bond starts out weakened. A second important consequence of pyramidalization is the mixing in of s-orbital character with the p-orbitals that make up the π system. This lowers the energy of each atomic orbital and thereby lowers the energy of all the derived π MOs, including both the HOMO and the LUMO. This lowering of the HOMO due to the hybridization change approximately offsets the tendency of the HOMO to go up in energy as a consequence of poorer π overlap. The lowering of the LUMO due to the hybridization change, however, amplifies the lowering imposed by the weaker π bond. A major consequence of curvature therefore is a substantial lowering of the energy of the LUMO with relatively little change in the HOMO.



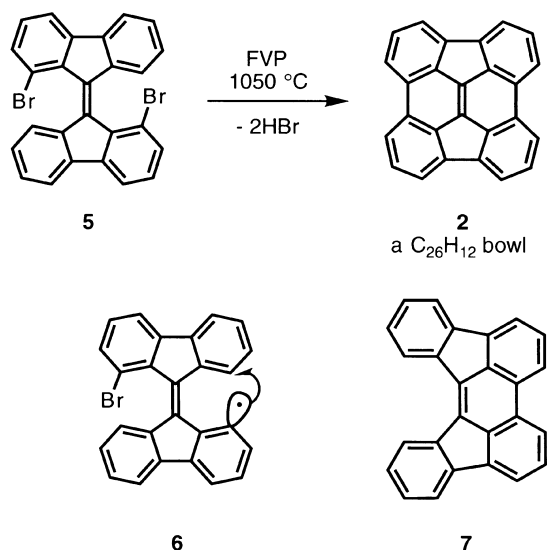
Scheme 2

We view open geodesic polyarenes as ideal probes for disentangling the separate roles of three-dimensional electron delocalization and molecular curvature as structural features responsible for the unusual properties of the fullerenes. Any special property of the fullerenes that shows up also in the open geodesic polyarenes cannot be a consequence of three-dimensional electron delocalization.

The following summary looks at three specific cases, starting with the $C_{26}H_{12}$ hydrocarbon **2**, the smallest bowl-shaped fullerene fragment with a central double bond. The point of greatest curvature in this hydrocarbon corresponds to the site where addition reactions take place on fullerenes, a so-called '6-6 double bond.'

DIINDENO[1,2,3,4-*defg*; 1',2',3',4'-*mno*]CHRYSENE (**2**)

We have found that flash vacuum pyrolysis (FVP) of 1,1'-dibromobifluorenylidene [5] at 1050 °C gives the alkene-centered fullerene fragment **2** in isolated yields of 25–35% (Scheme 3) [5]. This double cyclization is believed to follow a stepwise pathway involving initial homolysis of a C–Br bond, followed

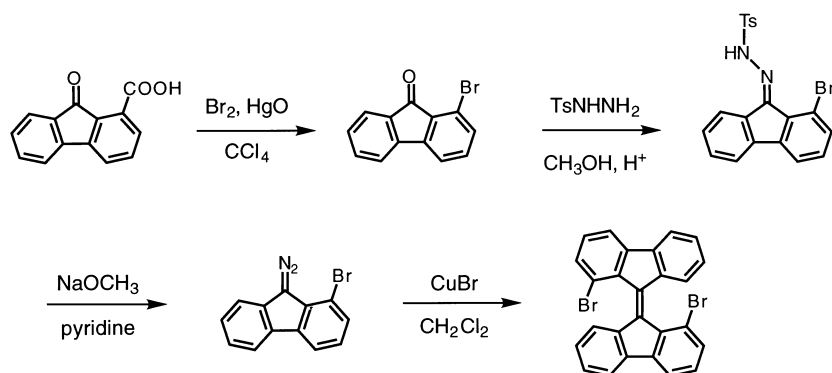


Scheme 3

by attack of the resulting aryl radical [6] on the aromatic ring across the fjord. Rearomatization and a repeat of the entire process then closes the other six-membered ring.

Without the bromine atoms on **5**, pyrolysis of the parent hydrocarbon, fluorenylidene, gives the product of one cyclization [7] but no trace of the doubly cyclized product **2** [4]. Re-pyrolysis of hydrocarbon **7** does produce the $\text{C}_{26}\text{H}_{12}$ bowl **2**, but only in 0.6% yield [4]. This case dramatically underscores the superiority of orchestrated aryl radical cyclizations over undirected cyclodehydrogenations as a method for constructing strained geodesic polyarenes.

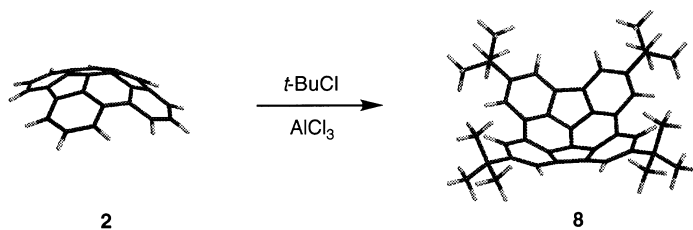
Scheme 4 summarizes the route by which the requisite dibromide [5] was prepared in four steps from commercially available starting materials.



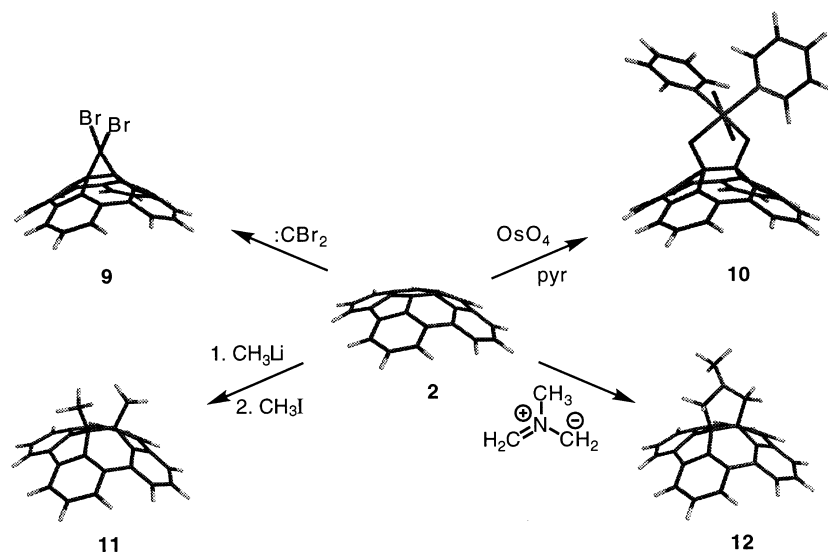
Scheme 4

Under Friedel–Crafts alkylation conditions, the bowl-shaped diindenochrysenes **2** behaves like an ordinary polycyclic aromatic hydrocarbon and is transformed into the symmetrical tetra-*t*-butyl derivative **8** (Scheme 5).

Toward reagents that react with fullerenes, on the other hand, **2** undergoes addition reactions at the central 6–6 ring junction, behaving just as C_{60} does with the same reagents (Scheme 6). Thus, dibromocarbene, generated *in situ* from bromoform and strong base, cyclopropanates the interior C=C bond to give **9**. Osmium tetroxide in pyridine gives the osmate ester at the interior C=C bond [10]. Methyl lithium adds in a nucleophilic fashion to the interior C=C bond, generating an anion that can be alkylated with methyl iodide to give **11**. And the 1,3-dipole generated from *N*-methylglycine and formaldehyde adds exclusively to the interior C=C bond to give the *N*-methylpyrrolidine [12].



Scheme 5



Scheme 6

To our knowledge, the reactions depicted in Scheme 6 represent the first examples ever observed in which reagents attack ‘interior’ carbon atoms [12] of a neutral polycyclic aromatic hydrocarbon, making new covalent bonds that permanently destroy the cyclic conjugation in two benzene rings. Until now, the chemistry of polyarenes could best be described as ‘edge chemistry’ [12], the only exceptions being the fullerenes, which have no edges. Hydrocarbon **2** thus constitutes the first bridge between the old flat world of traditional aromatic compounds and the new round world of fullerenes.

Clearly, the unusual addition chemistry of the fullerenes cannot be a consequence of three-dimensional conjugation, since an open geodesic polyarene that lacks this structural feature (**2**) exhibits the same unusual chemistry. Can we therefore conclude that this unusual reactivity is purely a consequence of molecular curvature, i.e. purely steric in origin with no electronic basis? No, such a conclusion is not justified. A close examination of the frontier molecular orbitals of diindenochrysene reveals unusual electronic characteristics that cannot be traced back to molecular curvature.

Figure 3 (top) shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of hydrocarbon **2** calculated at the HF/6-31G* level of theory, using the bowl-shaped geometry obtained by an AM1 optimization [13]. Here one can see the largest coefficients for the HOMO of **2** at the central 6–6 bond; this is the site where electrophiles should be expected to attack, and they do (Scheme 6: CBr_2 and OsO_4). We have also found, however, that flattening the bowl leads to remarkably little change in the character of the HOMO (Fig. 3 bottom); the maximum is still centered over the interior 6–6 bond. Thus, there appears to be an *intrinsic* reactivity at the center of this nonalternant PAH that is independent of molecular curvature. The antibonding LUMO likewise has its largest coefficients at the central 6–6 bond of **2** in the bowl-shaped geometry (Fig. 3 top), and flattening causes only a modest amount of ‘leakage’ toward the edge (Fig. 3 bottom).

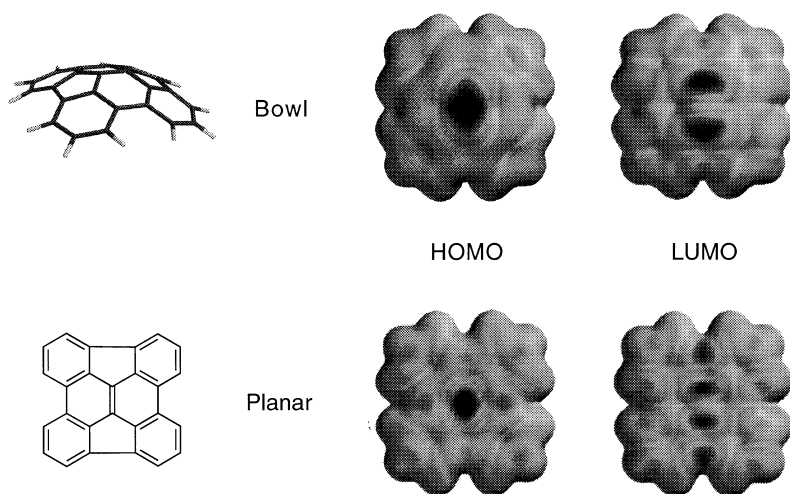


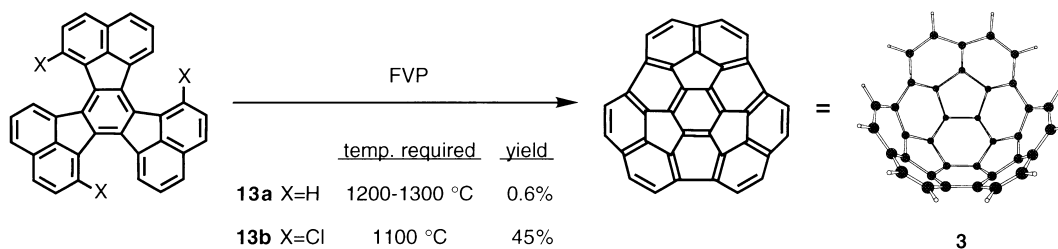
Fig. 3 Frontier molecular orbitals of diindeno[1,2-*b*]fluorene **2** (HF/6-31G**//AM1) [13] in both the bowl-shaped (top) and planar (bottom) geometries. The darkest shading corresponds to the largest MO coefficients.

We conclude that the fullerene-like reactivity of the open geodesic polyarene **2** is not entirely steric in origin but has a significant electronic component, one that is not coupled to the three-dimensional conjugation found in the fullerenes.

THE C₃₆H₁₂ BOWL (**3**)

The largest member of this family of compounds prepared to date is the C₃₆H₁₂ polyarene **3**, a deep bowl-shaped fullerene fragment with a central six-membered ring, constituting 60% of the C₆₀ ball. In 1996, we reported that flash vacuum pyrolysis of 'decacyclene' (**13a**) produces the C₃₆H₁₂ bowl [3,6]. Temperatures in the range of 1200–1300 °C were required, and the yield was only 0.2% (now up to 0.6%), but we did isolate the bowl, and its X-ray structure has since been published [14].

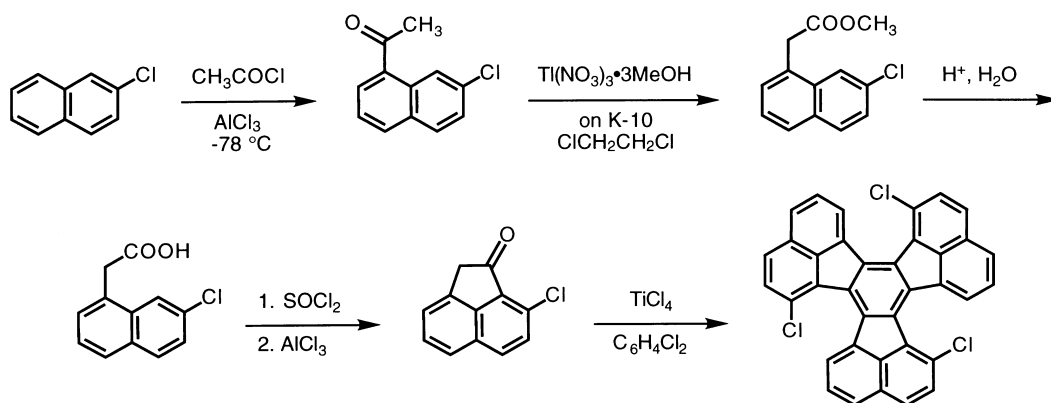
Obviously, this brute force triple-cyclodehydrogenation is not an efficient process. The incorporation of substituents capable of generating radicals in the fjord regions, however, would be expected to improve the synthesis. This dream has now been realized. We recently developed a synthesis of 1,7,13-trichlorodecacyclene (**13b**) and were gratified to find that the same C₃₆H₁₂ bowl (**3**) is produced in 45% yield by flash vacuum pyrolysis of this properly functionalized decacyclene at 1100 °C (Scheme 7) [9].



Scheme 7

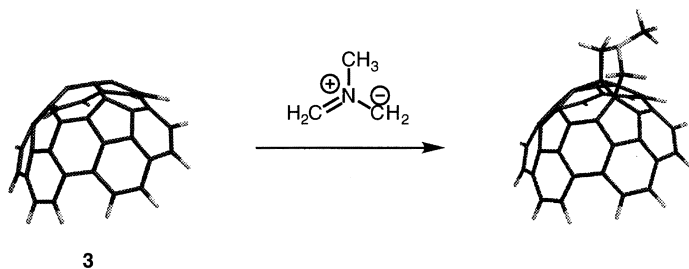
Scheme 8 summarizes the route by which 1,7,13-trichlorodecacyclene (**13b**) was prepared in five steps from commercially available 2-chloronaphthalene [9].

In light of the chemistry of the smaller C₂₆H₁₂ bowl **2** (Scheme 6), it came as no surprise that the more strongly curved C₃₆H₁₂ bowl **3** likewise undergoes 1,3-dipolar cycloaddition at a strained 6–6 bond (Scheme 9) [9]. Three distinct sets of 6–6 bonds can be found in hydrocarbon **3**, and it bears noting that the reaction is site-selective for the 6–6 bond located at the point of greatest curvature on the convex surface. Analogous selectivity has been seen in the chemistry of C₇₀, which has five different types of 6–6



Scheme 8

bonds, each characterized by a different degree of pyramidalization [15]. Again, our fullerene fragments exhibit chemistry reminiscent of that seen with the fullerenes.



Scheme 9

While much remains to be learned about chemistry on the convex surfaces and around the edges of open geodesic polyarenes, it is their exposed concave surfaces that now hold the greatest allure. The concave surfaces of fullerenes are hidden from external reagents, but they are accessible in bowl-shaped fullerene fragments. Density functional calculations (BP/DN**) [16] predict that the electrostatic potential on the inside surface of the $C_{36}H_{12}$ bowl **3** should closely resemble that of benzene, i.e. it should be electron-rich, whereas the outside surface is predicted to be relatively electrophilic, resembling that of C_{60} (Fig. 4).

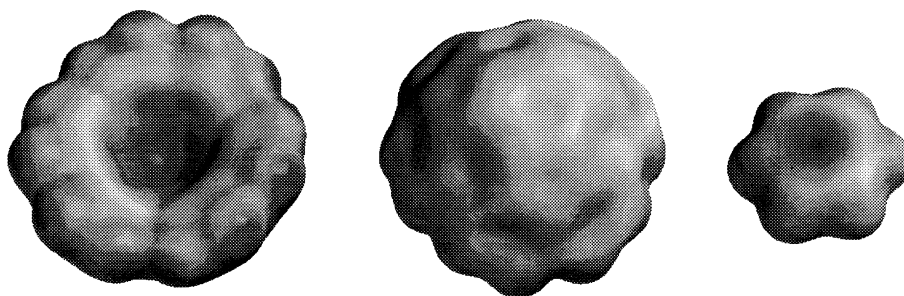


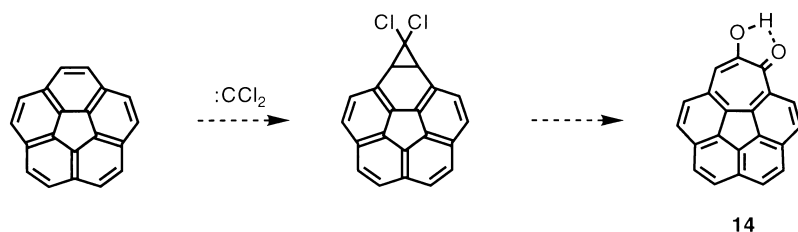
Fig. 4 Electrostatic potentials (BP/DN**) [16] on the surfaces of the $C_{36}H_{12}$ bowl **3** and benzene. The darkest shading at the center of benzene and the interior of the bowl corresponds to the most negative electrostatic potential.

Interestingly, AM1 calculations lead to precisely the opposite prediction [16], i.e. greater electron deficiency inside than out. Experiments designed to resolve this discrepancy have been initiated, but the results are still too preliminary (and puzzling) to report. A healthy interplay between theory and experiment continues to drive this research.

CORANNULENE (1)

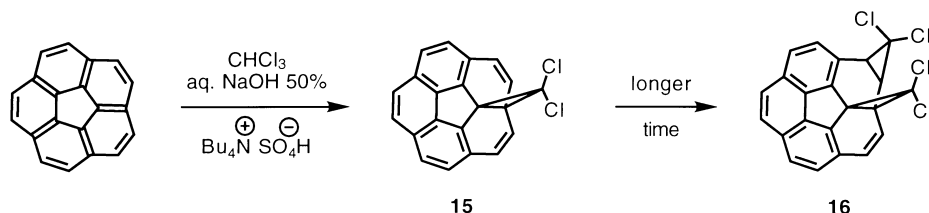
The smallest ($C_{20}H_{10}$) and least curved of the bowl-shaped fullerene fragments, corannulene (**1**) is built around a central five-membered ring. Our three-step synthesis of corannulene has already been published in full detail [2] and requires no further elaboration here. Instead, we will focus on two unusual reactions of corannulene discovered recently in our lab.

The first of these concerns the addition of dichlorocarbene to corannulene. We anticipated that dichlorocarbene would add to the phenanthrene-like perimeter ‘double bond’ of corannulene, as it does with phenanthrene [17], and that opening of the resulting cyclopropane would lead to a ring-expanded product, from which we could synthesize the novel tropolone **14** (Scheme 10). Heats of combustion measurements [18] allow one to derive a strain energy of nearly 50 kcal/mol for corannulene (**1**), and much of that strain would be released by the illustrated ring expansion. We fancied tropolone **14** to be a fitting tribute to the memory of Tetsuo Nozoe, the late father of tropolone chemistry in whose name this lecture was given, and therefore set out to effect this ‘Nozoelation of corannulene.’



Scheme 10

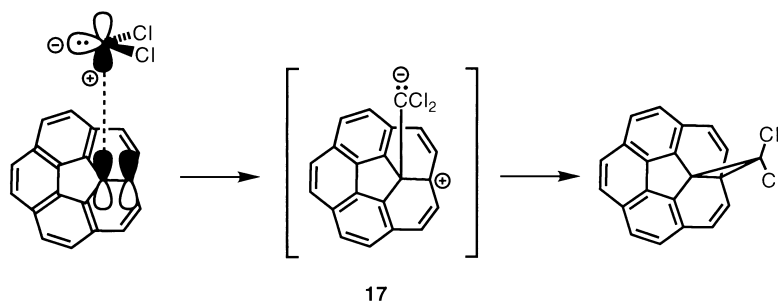
To our surprise, dichlorocarbene totally ignores the perimeter double bonds of corannulene and adds exclusively to one of the radial bonds, giving the unusual propellane **15** as the sole primary product (Scheme 11). As the reaction progresses, the olefinic bonds in **15** begin to compete with corannulene for the carbene, and the 2:1 adduct **16** starts to appear. Exactly the same behavior is seen for the addition of dibromocarbene, but the addition of diiodocarbene to corannulene stops after the first step, giving only the propellane corresponding to **15** [9].



Scheme 11

As one possible rationalization for this unforeseen behavior of corannulene toward dichlorocarbene, we entertained the possibility that the cyclopropanation reaction might occur in a stepwise manner by way of zwitterionic intermediate **17** (Scheme 12). Electrophilic attack at an interior carbon atom of corannulene would relieve all the pyramidalization strain at that atom and would generate a highly stabilized carbocation. Furthermore, the degenerate HOMO and HOMO-1 of corannulene have their largest coefficients at the interior carbon atoms (BP/DN** density functional calculations), so attack there should be favored kinetically also on electronic grounds. Finally, there is good evidence for the stepwise nature of dichlorocarbene additions to other target molecules in at least two cases [19].

It did concern us, however, that with ordinary electrophiles, corannulene undergoes a wide variety of classical electrophilic aromatic substitution reactions, including formylation, Friedel-Crafts alkylation and acylation, nitration, iodination, bromination, and chlorination [5,8b,9]. Why should dihalocarbenes go to the interior carbon atoms of corannulene, while all other electrophiles examined so far lead to products from attack on the rim? We speculated that perhaps all electrophiles react fastest at the interior

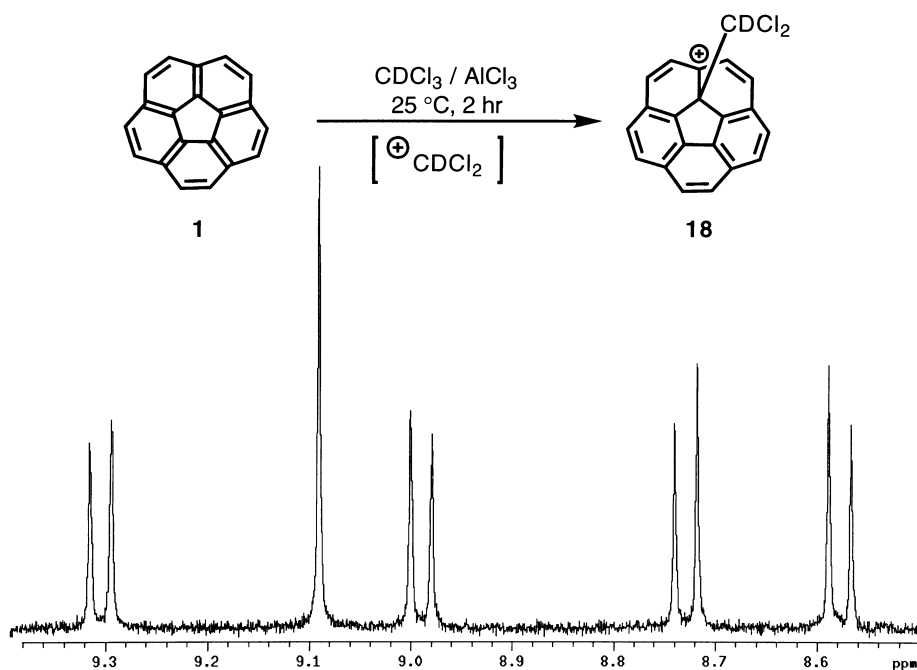


Scheme 12

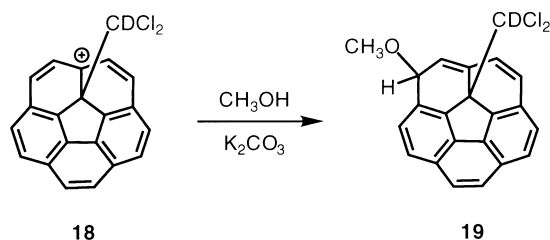
carbon atoms of corannulene but that the initial attack is reversible for relatively stable cations, such as the *t*-Bu cation, acylium ions, the nitronium ion, etc. Given multiple opportunities, these electrophiles could eventually attack a methine position on the rim to generate an arenium ion that could rearomatize by deprotonation. Our postulated zwitterionic intermediate **17**, on the other hand, would be unlikely to expel a high-energy carbene; it also has a pathway available to consummate the reaction that does not require an alpha-hydrogen.

To test this hypothesis, we began searching for highly reactive electrophiles that would attack one of the interior carbon atoms of corannulene irreversibly to give a persistent arenium ion analogous to **17**. Success came quickly. The dichloromethyl cation provides a particularly striking example.

When solid AlCl_3 is added to a solution of corannulene (**1**) in CDCl_3 at room temperature, a blue color appears immediately. An $^1\text{H-NMR}$ spectrum recorded at this point shows predominantly unreacted corannulene, but over a period of about two hours at room temperature, the NMR signal for corannulene slowly disappears (7.8 p.p.m. singlet), and a new set of signals for a single new species grows in at lower field (8.6–9.3 p.p.m.). From the simplicity of the spectrum (Fig. 5), the downfield shift of the signals, and the subsequent quenching studies (Scheme 13), it is clear that the new species corresponds to the carbocation derived from addition of the CDCl_2 cation to an interior carbon atom of the corannulene ring system (**18**).

Fig. 5 Electrophilic attack at an interior carbon atom of corannulene (**1**).

Quenching the reaction mixture with methanol and potassium carbonate gives methyl ether **19**. The C–O bond formation is site selective, completing a net 1,4-addition to the benzene ring. Weaker nucleophiles, e.g. benzene, fail to quench this unusually stable carbocation, which can be viewed as a pentadienyl cation that is tertiary in the center and benzylic at both ends.



Scheme 13

The trichloromethyl cation derived from carbon tetrachloride and AlCl_3 behaves in the same manner as the dichloromethyl cation and likewise attacks an interior carbon atom of corannulene [9]. To the best of our knowledge, the attachments of $\oplus\text{CHCl}_2$ and $\oplus\text{CCl}_3$ to corannulene represent the first examples ever seen of covalent bond formation at an interior carbon atom of a polycyclic aromatic hydrocarbon by the attack of an external cation.

Clearly, the open geodesic polyarenes comprise a family of novel hydrocarbons with novel properties that rival those of the fullerenes, and we can expect more surprises as the story continues to unfold.

ACKNOWLEDGEMENTS

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