

Pentaindenocorannulene and Tetraindenocorannulene: New Aromatic Hydrocarbon π Systems with Curvatures Surpassing That of C_{60}

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It gives us great pleasure to report syntheses and X-ray crystal structures of two new geodesic polyarenes, pentaindenocorannulene¹ (**1**, $C_{50}H_{20}$) and tetraindenocorannulene² (**2**, $C_{44}H_{18}$) (Figure 1). These extended aromatic π systems constitute the largest curved subunits of C_{60} ever prepared.³ In agreement with theoretical predictions, the trigonal carbon atoms at the cores of these new hydrocarbons suffer even greater pyramidalization than that exhibited by the carbon atoms of C_{60} .

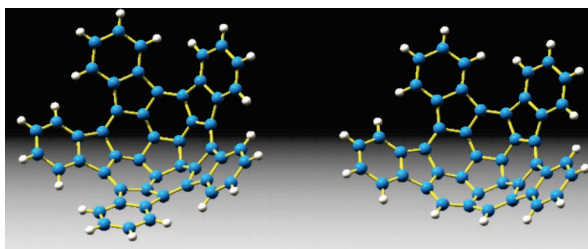
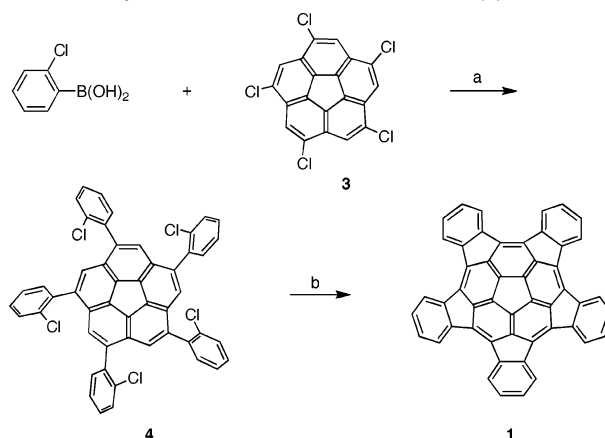


Figure 1. Pentaindenocorannulene (**1**) and tetraindenocorannulene (**2**); geometries taken from their X-ray crystal structures.

Our synthesis of pentaindenocorannulene (**1**) begins with 1,3,5,7,9-pentachlorocorannulene (**3**), an exquisitely functionalized building block that is readily available by direct chlorination of corannulene.^{3a,4} Five-fold Suzuki–Miyaura coupling of **3** with 2-chlorophenylboronic acid under the conditions introduced by Nolan et al.⁵ (Scheme 1) gives 1,3,5,7,9-pentakis(2-chlorophenyl)corannulene (**4**) in 48% isolated yield (86% average yield per C–C coupling).⁶ Subsequent conversion of **4** to pentaindenocorannulene (**1**) was achieved in 35% isolated yield (81% average yield per C–C coupling) by a 5-fold intramolecular arylation reaction (Scheme 1). The conditions used for the final 5-fold cyclization closely resemble those reported previously in our nonpyrolytic synthesis of dibenzo[*a,g*]corannulene,⁷ except that we now use microwave heating. For these two palladium-catalyzed C–C coupling reactions, the final recipes that work are simple. As is often the case, however, finding those conditions required extensive experimentation with countless combinations of palladium source, ligand, base, stoichiometry, solvent, temperature, time, and other variables.

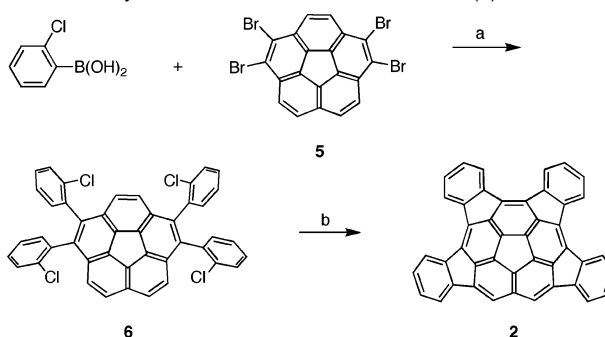
Pentaindenocorannulene (**1**) is a deep orange, thermally robust, air stable, crystalline solid (needles from toluene/dichloromethane, mp >400 °C) with a rich UV–vis spectrum and an absorption tail in the visible region that extends beyond 500 nm (see Supporting Information). Dilute solutions of **1** in common organic solvents appear golden yellow. This highly symmetrical bowl is very sparingly soluble in solvents such as chloroform, benzene, toluene, 1,1,2,2-tetrachloroethane, and carbon disulfide and is only slightly

Scheme 1. Synthesis of Pentaindenocorannulene (**1**)^a



^a Conditions: (a) $Pd_2(dba)_3$, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, Cs_2CO_3 , dioxane, 80 °C, 48 h, 48% isolated yield; (b) $Pd(PCy_3)_2Cl_2$, DBU, DMAc, 180 °C (microwave), 45 min, 35% isolated yield.

Scheme 2. Synthesis of Tetraindenocorannulene (**2**)^a



^a Conditions: (a) $Pd(PPh_3)_4$, K_2CO_3 , toluene/EtOH/ H_2O , 85 °C, 24 h, 91% isolated yield; (b) $Pd(PCy_3)_2Cl_2$, DBU, DMAc, 170 °C (microwave), 40 min, 13% isolated yield.

more soluble in *ortho*-dichlorobenzene, nitrobenzene, and bromoform.⁸ As expected, its ¹H NMR spectrum exhibits just a simple AA'BB' pattern (δ 8.10 and 7.37 ppm in $CDCl_3$), and its ¹³C NMR spectrum consists of only six signals (δ 144.65, 136.97, 136.86, 136.35, 126.65, and 123.25 ppm in $CDBr_3$).

Our synthesis of tetraindenocorannulene (**2**) follows the same course as that taken in the synthesis of **1** but starts from 1,2,5,6-tetrabromocorannulene (**5**), another readily available polyhalocorannulene.⁹ Four-fold Suzuki–Miyaura coupling of **5** with 2-chlorophenylboronic acid gives 1,2,5,6-tetrakis(2-chlorophenyl)corannulene (**6**) in 91% isolated yield.¹⁰ The subsequent 4-fold cyclization to tetraindenocorannulene (**2**) was achieved in 13% isolated yield (Scheme 2). The superior yield for the Suzuki–

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Miyaura coupling in this case presumably reflects the greater reactivity of the Ar–Br bonds in **5**, relative to that of the Ar–Cl bonds in **3**.^{9b} The inferior yield for the intramolecular arylation step, on the other hand, appears to result, at least in part, from competitive couplings between the proximal phenyl rings.¹¹

Tetraindenocorannulene (**2**) is also an orange, thermally robust, air stable, crystalline solid (needles from benzene/carbon disulfide/ethanol, mp >400 °C) that likewise has a rich UV–vis spectrum with a long absorption tail in the visible region (see Supporting Information). This less highly symmetrical bowl exhibits somewhat greater solubility than **1** in solvents such as chloroform and benzene and is significantly more soluble in carbon disulfide and bromoform.⁸ Its ¹H NMR and ¹³C spectra are more complex than those of **1** but are completely consistent with the assigned structure (see Supporting Information).

Flash vacuum pyrolysis (FVP) of the tetrakis(2-chlorophenyl)corannulene (**6**) also produces tetraindenocorannulene (**2**), albeit in lower yield and admixed with numerous other products,¹¹ including several derived from loss of one or more of the 2-chlorophenyl groups.^{12–14} By a combination of chromatography on alumina and semipreparative reverse phase HPLC, tetraindenocorannulene (**2**) was isolated from the FVP of **6** in 1–2% yield. Pentaindenocorannulene (**1**) was tentatively identified in the product mixture derived from FVP of **4**, but it was not isolated.

Considerable difficulty was encountered with growing crystals of **1** and **2** suitable for X-ray analysis. Both new bowls form very thin needles that diffract only weakly. Ultimately, the crystal structure of **1** was determined on a crystal of dimensions 0.20 × 0.01 × 0.01 mm (see Supporting Information).

One particularly noteworthy aspect of the X-ray crystal structures is the greatly enhanced pyramidalization of the carbon atoms comprising the central five-membered rings of **1** and **2** (Figure 1). Bridging the *peri*-positions of corannulene with *ortho*-phenylene units tightens up the external CCC angles on the rim and deepens the bowl.

To quantify the degree of pyramidalization, we have used the widely adopted p-orbital axis vector (POAV) analysis of Haddon.¹⁵ A planar trigonal carbon atom, as in benzene, has a POAV angle of 0.0°, whereas the highly pyramidalized carbon atoms of C₆₀ (all identical) have POAV angles of 11.6°. The POAV angles of open geodesic polyarenes typically fall somewhere between these two extremes (e.g., corannulene: 8.3°). It is striking, therefore, to see that the average POAV angle is 12.1° for the carbon atoms comprising the central five-membered ring of tetraindenocorannulene (**2**) and 12.6° for those in pentaindenocorannulene (**1**).

This point has important long-range implications. Our syntheses of indenocorannulenes **1** and **2** from the halogenated corannulenes **3** and **5**, as well as the syntheses of those intermediates, in turn, from planar aromatic hydrocarbons, have all been accomplished by solution chemical methods. *Taken together, these achievements demonstrate unequivocally that rational chemical syntheses of fullerenes, carbon nanotubes, and related carbon-rich molecules should all be possible using exclusively solution chemical methods!* Recourse to high-temperature gas-phase pyrolysis^{3c,f} should not be necessary.

Finally, we note that calculations using density functional theory (B3LYP/6-31G**) predict average POAV angles of 12.0 and 12.4° for the carbon atoms comprising the central five-membered rings in **2** and **1**, respectively.¹⁶ This represents a very close agreement between theory and experiment, demonstrating once again the ability of B3LYP/6-31G** DFT calculations to provide geometries for geodesic polyarenes that are essentially identical to those obtained

from X-ray crystal structures.¹⁷ We have come to rely increasingly on such calculations to guide our planning of syntheses in this area. Work currently underway in our laboratory is directed toward stitching up pentaindenocorannulene (**1**), or derivatives thereof, to the corresponding 50-carbon [5,5]nanotube end cap.¹⁸

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Supporting Information Available: ¹H NMR spectra, ¹³C NMR spectra, other characterization data, and experimental details for the synthesis of compounds **1**, **2**, **4**, and **6**; UV–vis spectra, X-ray crystal structure data, CIF files, and B3LYP/6-31G** xyz coordinates for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Although higher concentrations of hydrocarbons **1** and **2** can be achieved in bromoform than in carbon disulfide or in other ordinary organic solvents, the compounds either decompose or react with the bromoform (or dissolved impurities) over time.
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- (10) The NMR spectra of 1,2,5,6-tetrakis(2-chlorophenyl)corannulene (**6**) reveal that the product obtained is also a mixture of atropisomers. One isomer of C₂ symmetry (or time-averaged C₂ symmetry) can be separated by preparative thin layer chromatography on alumina, but it reverts to the original mixture of stereoisomers on standing in solution at room temperature for 1 month.
- (11) Other products that are isomeric with **2** (*m/z* 546) have been isolated by semipreparative HPLC but have not been thoroughly characterized.
- (12) Both isomers of triindenocorannulene have been tentatively identified among the pyrolysis products of **6**, and together they complete the set of all possible indenocorannulenes bearing one, two, three, four, or five indeno groups. These results will be included in our full paper on this work.
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