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Aromatic π-Systems More Curved Than C_{60}. The Complete Family of All Indenocorannulenes Synthesized by Iterative Microwave-Assisted Intramolecular Arylations

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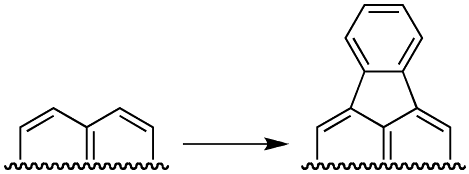
Abstract: Syntheses and X-ray crystal structures are reported for all seven members of the indenocorannulene family, comprising indenocorannulene, both isomers of diindenocorannulene, both isomers of triindenocorannulene, tetraindenocorannulene, and pentaindenocorannulene. With each additional indenoannulation, the pyramidalization of the trigonal carbon atoms at the hub of the corannulene increases. Five of the seven indenocorannulenes contain carbon atoms at the hub that are actually more pyramidalized than the carbon atoms of C_{60}. This work demonstrates, for the first time, that extended π-systems with curvatures exceeding those of the most curved stable fullerenes and carbon nanotubes can be prepared by ordinary laboratory methods in solution, without recourse to high-temperature gas phase methods, such as flash vacuum pyrolysis. This proof of principle presages the days when scientists will be able to synthesize isomerically pure fullerenes and single-chirality nanotubes by well-understood, controlled chemical methods. Pentaindenocorannulene, itself, represents an attractive precursor to the C_{5v} end-cap of an all-carbon, single-walled, "armchair" [5,5]nanotube.

Introduction

Any chemical synthesis of an isolable fullerene will require the embedding of 12 fully unsaturated five-membered rings into a lattice of condensed six-membered rings (Euler's theorem[1] and the isolated pentagon rule, IPR[2]). It is the five-membered rings encircled by fused benzene rings that give IPR-fullerene surfaces their curvature.[3] Most of the strain energy in fullerenes (all of it in C_{60}) is also associated with the carbon atoms of the five-membered rings, in which the internal angles (108° for a regular pentagon) deviate significantly from the 120° natural angle of unstrained sp^2-hybridized carbon atoms. Unfortunately, synthetic methods remain scarce even for the simple annulation of fully unsaturated five-membered rings onto the perimeters of appropriately constituted polycyclic aromatic hydrocarbons (PAHs) (Scheme 1).[4−6]

Scheme 1. Indenoannulation: Bridging *peri*-Positions with an *ortho*-Phenylene Unit



Faced with this shortcoming in the toolbox of synthetic organic chemistry, our laboratory has undertaken a program to develop indenoannulation methods that are not only versatile but also amenable to multiple indenoannulations within the same molecule in a single laboratory operation. As an initial step in that direction, the tandem Suzuki−Heck-type coupling cascade

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(1) Fowler, P. W.; Manolopoulos, D. E. *Atlas of Fullerenes*; Oxford University Press: Oxford, U.K., 1995. A discussion of Euler's theorem can be found in Chapter 2.

(2) Hirsch, A.; Brettreich, M. *Fullerenes*; Wiley-VCH: Weinheim, 2005. A discussion of the isolated pentagon rule, IPR, can be found in section 1.5.1.

(3) Corannulene (**5**), the $C_{20}H_{10}$ hydrocarbon with a five-membered ring completely encircled by fused benzene rings, represents the smallest subunit of a fullerene that retains a curved π-system:(a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380–1. (b) Lawton, R. G.; Barth, W. E. *J. Am. Chem. Soc.* **1971**, *93*, 1730–45. (c) Hanson, J. C.; Nordman, C. E. *Acta Crystallogr., Sect. B* **1976**, *32*, 1147–53.

(4) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997. (b) Harvey, R. G. *Curr. Org. Chem.* **2004**, *8*, 303–323.

(5) (a) Preda, D. V.; Scott, L. T. *Polycyclic Aromat. Compd.* **2000**, *19*, 119–131. (b) Wu, Y.-T.; Hayama, T.; Baldridge, K. K.; Linden, A.; Siegel, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 6870–6884.

(6) (a) Wegner, H. A.; Scott, L. T.; de Meijere, A. *J. Org. Chem.* **2003**, *68*, 883–887, and references therein. (b) Quimby, J. M.; Scott, L. T. *Adv. Synth. Catal.* **2009**, *351*, 1009–1013.

(7) (a) Wegner, H. A.; Reisch, H.; Rauch, K.; Demeter, A.; Zachariasse, K. A.; de Meijere, A.; Scott, L. T. *J. Org. Chem.* **2006**, *71*, 9080–9087. (b) Aprahamian, I.; Wegner, H. A.; Sternfeld, T.; Rauch, K.; de Meijere, A.; Sheradsky, T.; Scott, L. T.; Rabinovitz, M. *Chem.−Asian J.* **2006**, *1*, 678–685. (c) de Meijere, A.; Stulgies, B.; Albrecht, K.; Rauch, K.; Wegner, H. A.; Hopf, H.; Scott, L. T.; Eshdat, L.; Aprahamian, I.; Rabinovitz, M. *Pure Appl. Chem.* **2006**, *78*, 813–830.

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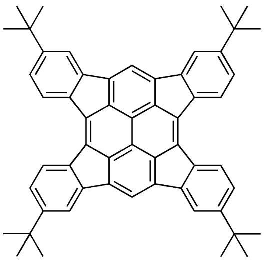

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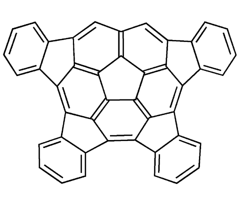
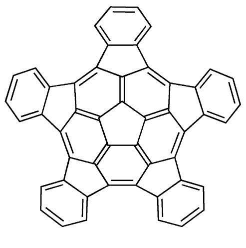


tetra-IC



penta-IC

that we introduced in 2003[6a] was successfully applied to the first synthesis of a tetraindenopyrene (**1**) from pyrene in 2006.[7] More recently, we succeeded in synthesizing tetraindenocorannulene[8] (**tetra-IC**) and pentaindenocorannulene[9] (**penta-IC**) by a powerful stepwise indenoannulation method.[10] [Descriptive nicknames that are easier to recognize than bare numbers will be used when referring to the indenocorannulenes in this paper].

This new method has now been extended to provide all seven members of the family of indenocorannulenes, including both isomers of triindenocorannulene (**1,2,3-tri-IC**[11] and **1,2,4-tri-IC**[12]), both isomers of diindenocorannulene (***ortho*-di-IC**[13] and ***para*-di-IC**[14]), and the parent indenocorannulene (**mono-IC**[15]). Figure 1 shows three-dimensional structural representations of all seven indenocorannulenes, generated from the X-ray crystal structures of the individual compounds (discussed further below).

This sizable family of aromatic hydrocarbons provides an exquisite opportunity for testing the reliability of modern computational methods as applied to geodesic polyarenes, by allowing comparisons to be made between theoretically calculated geometric parameters, NMR spectra, etc., and those obtained experimentally.[16,17] The bowl-shaped PAHs in this family range in size from $C_{26}H_{12}$ to $C_{50}H_{20}$, and they all map onto the geodesic framework of C_{60}.

Most importantly, this work demonstrates for the first time that solution phase chemical methods can be used to synthesize fused networks of five- and six-membered rings with curvatures equaling, *and even surpassing,* that of the most curved, stable fullerene, C_{60}. As revealed by X-ray crystallography, the pyramidalization of trigonal carbon atoms at the centers of all but two of the indenocorannulenes actually *exceeds* that observed for the carbon atoms of C_{60} (see X-ray section). Prior to this work, such acutely curved aromatic π-surfaces had been accessible only by high-temperature gas phase methods such as flash vacuum pyrolysis.[18] Our findings make the impediments to synthesizing fullerenes and carbon nanotubes entirely by solution phase chemical methods no longer appear insurmountable.

Syntheses of the Indenocorannulenes

General Strategy. The indenoannulations performed in this work all begin with the preparation of suitably halogenated corannulenes. Suzuki−Miyaura couplings of these haloarenes with *ortho*-chlorophenyl boronic acid then introduce all of the carbon atoms required for the final target molecules, and palladium-catalyzed intramolecular arylations close all of the five-membered rings (Scheme 2). The details of how the reactions were conducted to accomplish these transformations are described in the sections below.

Halogenated Corannulenes: Functionalized Scaffolds on Which to Build. The most reliable method we have found for preparing bromocorannulene (**2**) in high yield, uncontaminated by dibromocorannulene (**3**) and tribromocorannulene (**4**), involves the direct bromination of corannulene (**5**) with IBr in dichloromethane at room temperature (99% yield[19]). The deactivating effect of the first bromine substituent prevents overbromination until the ratio of product to starting material climbs to a high level. Interrupting the reaction before all of the starting material is consumed yields a product containing minor amounts of corannulene as the only significant contaminant. Chromatographic separation can be achieved at this stage but has proven unnecessary. Corannulene is inert during the next reaction and can easily be recovered and recycled virtually quantitatively after the bromocorannulene has been carried through the Suzuki−Miyaura coupling.

Pushing the bromination of corannulene with more IBr at higher concentrations attaches a second bromine atom onto the rim,[20] and the reaction conveniently stops there, even when a large excess of IBr is used at room temperature (87% yield). The complex mixture of dibromocorannulenes obtained from this reaction may contain as many as seven possible positional

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(8) Complete name: tetraindeno[1,2,3-*bc*; 1′,2′,3′-*ef*; 1″,2″,3″-*hi*; 1‴,2‴,3‴-*kl*]corannulene.

(9) Complete name: pentaindeno[1,2,3-*bc*; 1′,2′,3′-*ef*; 1″,2″,3″-*hi*; 1‴,2‴,3‴-*kl*; 1⁗,2⁗,3⁗-*no*]corannulene.

(10) Jackson, E. A.; Steinberg, B. D.; Bancu, M.; Wakamiya, A.; Scott, L. T. *J. Am. Chem. Soc.* **2007**, *129*, 484–485.

(11) Complete name: triindeno[1,2,3-*bc*; 1′,2′,3′-*ef*; 1″,2″,3″-*hi*]corannulene.

(12) Complete name: triindeno[1,2,3-*bc*; 1′,2′,3′-*ef*; 1″,2″,3″-*kl*]corannulene.

(13) Complete name: diindeno[1,2,3-*bc*; 1′,2′,3′-*ef*]corannulene.

(14) Complete name: diindeno[1,2,3-*bc*; 1′,2′,3′-*hi*]corannulene.

(15) Complete name: indeno[1,2,3-*bc*]corannulene. For prior syntheses of variously substituted indenocorannulenes, see ref 5b.

(16) We have previously demonstrated that X-ray quality geometries of relatively rigid geodesic polyarenes can be obtained from theoretical calculations at the B3LYP/6-31G* level of theory: Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. *J. Org. Chem.* **2005**, *70*, 5713–5716.

(17) Higher levels of theory with more extensive basis sets than B3LYP/6-31G* have been used to gain more reliable insight into the properties and dynamics of geodesic polyarenes:(a) Baldridge, K. K.; Siegel, J. S. *Theor. Chem. Acc.* **1997**, *97*, 67–71. (b) Seiders, T. J.; Grube, G.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517–25. (c) Hayama, T.; Wu, Y.-T.; Linden, A.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 1583. (d) Yao-Ting Wu, Y.-T.; Bandera, D.; Maag, R.; Linden, A.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 10729–39.

(18) (a) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743–8744. (b) Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5766–5767. (c) Ansems, R. B. M.; Scott, L. T. *J. Am. Chem. Soc.* **2000**, *122*, 2719–2724.

(19) The 99% yield is based on corannulene consumed (details can be found in the Supporting Information). For alternate syntheses of bromocorannulene, see: (a) Seiders, T. J.; Baldridge, K. K.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439–7440. (b) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804–7813. (c) Mack, J.; Vogel, P.; Jones, D.; Kaval, N.; Sutton, A. *Org. Biomol. Chem.* **2007**, *5*, 2448–2452.

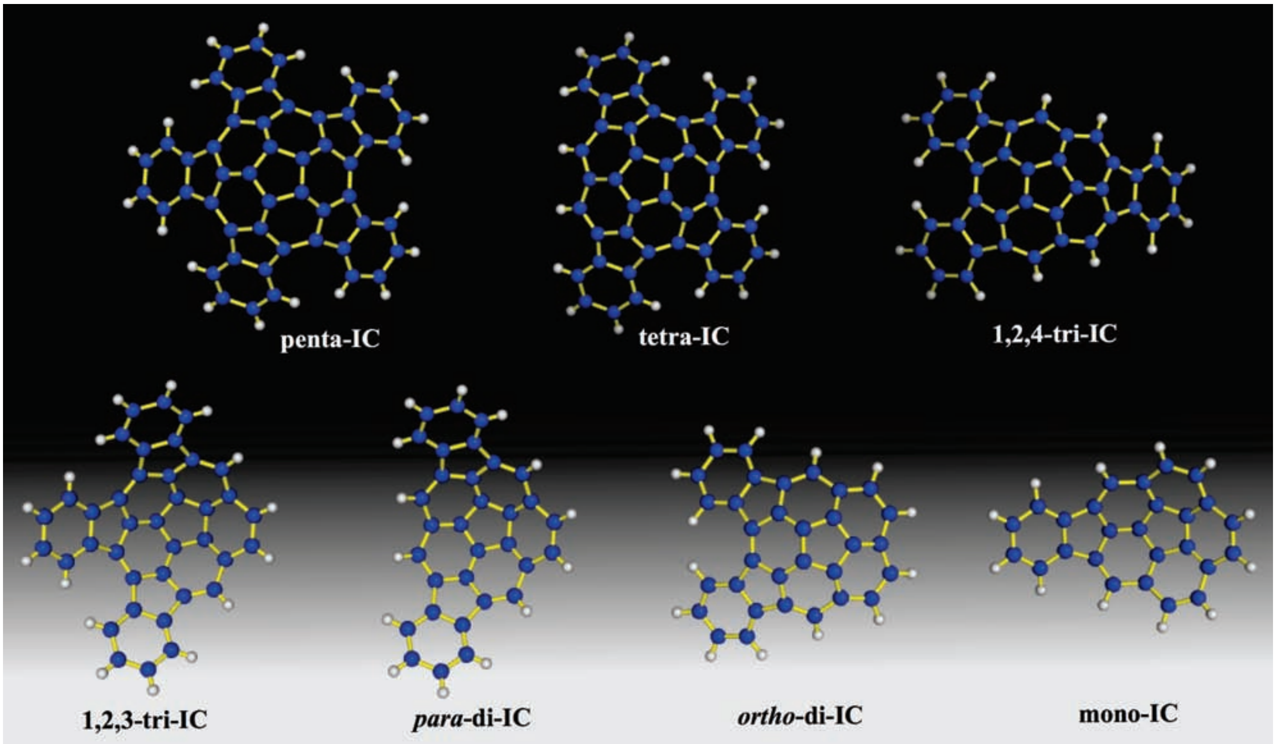
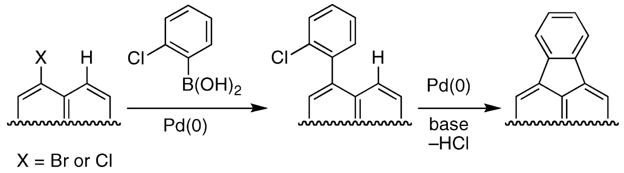


Figure 1. The complete family of all seven indenocorannulenes.

Scheme 2



isomers;[21] however, we made no attempt to separate the individual components. Application of the indenoannulation sequence outlined in Scheme 2 was expected to convert all seven dibromocorannulenes into diindenocorannulenes, and the latter has only two isomers (***ortho*-di-IC** and ***para*-di-IC**). As discussed below, this isomer proliferation−reconvergence plan works just fine, and the two diindenocorannulenes can be separated, isolated, and individually characterized at the end.

Triindenocorannulene likewise has only two isomers (**1,2,3-tri-IC** and **1,2,4-tri-IC**), so every positional isomer of tribromocorannulene subjected to the indenoannulation sequence in Scheme 2 would be expected to give either **1,2,3-tri-IC** or **1,2,4-tri-IC**.[22] Consequently, we decided to push the bromination further and to continue ignoring the lack of site selectivity. As mentioned above, excess IBr and long reaction times fail to attach a third bromine atom onto the rim of dibromocorannulene at room temperature; however, gentle heating of the reaction mixture (38 °C for 24 h) gives tribromocorannulene as a mixture of positional isomers in 92% yield. Higher levels of bromination by IBr pose no problem under these conditions.[23] Scheme 3 summarizes these bromination reactions.

As a starting point for the synthesis of tetraindenocorannulene (**tetra-IC**), we chose 1,2,5,6-tetrabromocorannulene (**6**), a useful corannulene derivative that is readily available by the method of Sygula et al. (Scheme 4, top).[24] For the synthesis of pentaindenocorannulene (**penta-IC**), 1,3,5,7,9-pentachlorocorannulene (**7**) proved to be the most convenient precursor. The direct 5-fold chlorination of corannulene with ICl to give this symmetrical derivative (Scheme 4, bottom) was discovered in our laboratory many years ago,[25] and the compound has found considerable use since then.[19a,b,26] No conditions for the direct bromination or iodination of corannu-

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(20) The five interior carbon atoms of corannulene are often referred to as the "hub" carbon atoms, and the 15 outer carbon atoms comprise the "rim"; see, for example: (a) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921. (b) Samdal, S.; Hedberg, L.; Hedberg, K.; Richardson, A. D.; Bancu, M.; Scott, L. T. *J. Phys. Chem. A* **2003**, *107*, 411–417. (c) Petrukhina, M. A.; Sevryugina, Y.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 7208–7210.

(21) In principle, bromocorannulene could acquire a second bromine atom at any of the nine remaining CH positions in the molecule. Because the two substituents are the same, however, the 1,3- and the 1,9-isomers are identical, and the 1,5- and the 1,7-isomers are also identical.

(22) The one exception to this assertion would be 1,2,3-tribromocorannulene, but its formation is considered highly unlikely on both steric and electronic grounds.

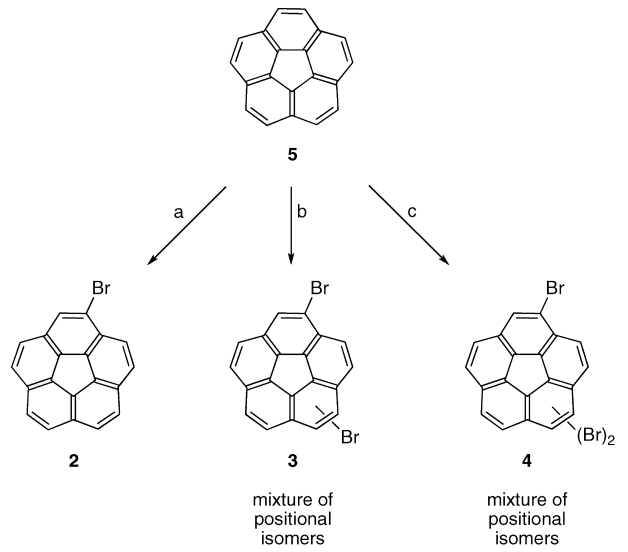
(23) Under sufficiently forcing conditions with elemental bromine, even decabromocorannulene can be prepared: (a) Prinzbach, H.; Weiler, A.; Landenberger, P.; Wahl, F.; Wörth, J.; Scott, L. T.; Gelmont, M.; Olevano, D.; v. Issendorff, B. *Nature* **2000**, *407*, 60–63. (b) Prinzbach, H.; Wahl, F.; Weiler, A.; Landenberger, P.; Wörth, J.; Scott, L. T.; Gelmont, M.; Olevano, D.; Sommer, F.; Issendorff, B. *Chem.−Eur. J.* **2006**, *12*, 6268–6280.

(24) (a) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323–6324. (b) Sygula, A.; Xu, G.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron* **2001**, *57*, 3637–3644.

(25) Cheng, P.-C. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 1996.

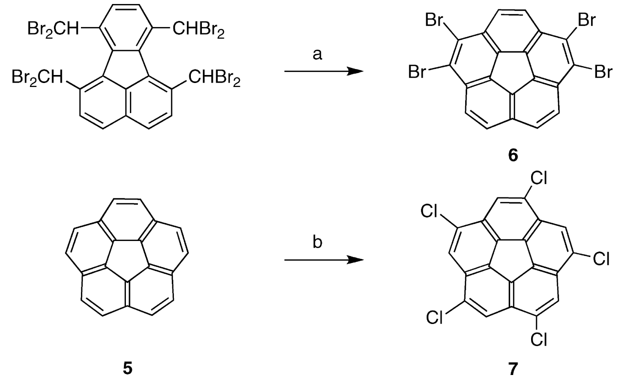
(26) (a) Mizyed, S.; Georghiou, P. E.; Bancu, M.; Cuadra, B.; Rai, A. K.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **2001**, *123*, 12770–12774. (b) Grube, G. H.; Elliott, E. L.; Steffens, R. J.; Jones, C. S.; Baldridge, K. K.; Siegel, J. S. *Org. Lett.* **2003**, *5*, 713–716. (c) Bancu, M.; Rai, A. K.; Cheng, P.-C.; Gilardi, R. D.; Scott, L. T. *Synlett* **2004**, 173–176. (d) Mori, T.; Grimme, S.; Inoue, Y. *J. Org. Chem.* **2007**, *72*, 6998–7010.

Scheme 3. Bromination of Corannulene Using IBr[a]



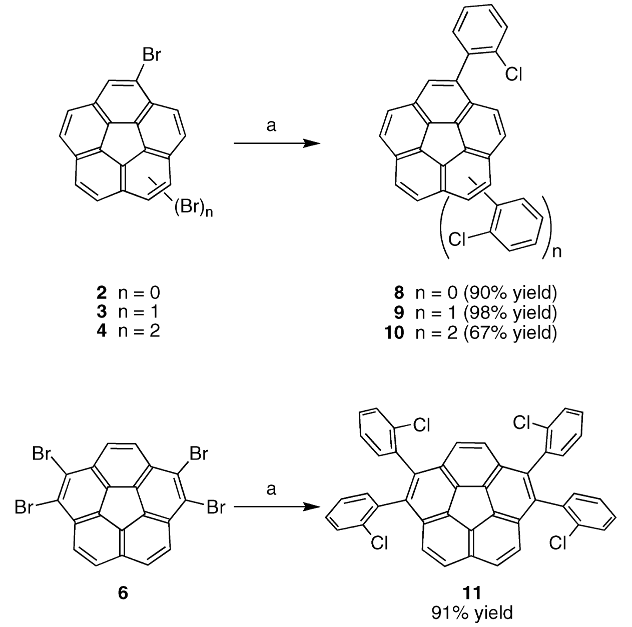
[a] (a) IBr (1.9 molar equiv, 0.1 M in CH_2Cl_2), rt, 24 h, 99% yield; (b) IBr (9.0 molar equiv, 0.25 M in CH_2Cl_2), rt, 5 h, 87% yield; (c) IBr (9.0 molar equiv, 0.25 M in CH_2Cl_2), 38 °C, 24 h, 92% yield.

Scheme 4[a]



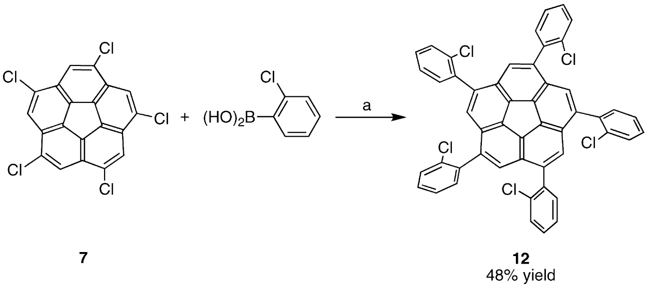
[a] (a) NaOH, dioxane/water (3:1), 100 °C, 15 min, 83% yield; (b) ICl (12.5 molar equiv, 1.0 M in CH_2Cl_2), rt, 2 days, 37% yield.

Scheme 5. Suzuki−Miyaura Couplings with Brominated Corannulenes[a]



[a] (a) 2-Chlorophenylboronic acid, Pd(0), K_2CO_3, heat, 24 h.

Scheme 6. Suzuki−Miyaura Couplings with 1,3,5,7,9-Pentachlorocorannulene[a]



[a] (a) $Pd_2(dba)_3$, 1,3-bis(2,6-di-isopropylphenyl)imidazolium, Cs_2CO_3, 1,4-dioxane, 80 °C, 2 days.

lene have been found that exhibit the same fortuitous site selectivity as this chlorination.[17c,d,27]

Adding the New Six-Membered Rings by Suzuki−Miyaura Coupling. We have previously shown that bromocorannulene (**2**) can be converted to indenocorannulene (**mono-IC**) in a single step by our Suzuki−Heck-type cascade method;[6a] however, the yield by that procedure was just 40%, which we did not consider adequate for multiple indenoannulations. Fortunately, the stepwise alternative proved highly effective. Standard Suzuki−Miyaura conditions (catalytic $Pd(PPh_3)_4$ and K_2CO_3) work well to cross-couple *ortho*-chlorophenylboronic acid with the variously brominated corannulenes. Thus, *ortho*-chlorophenylcorannulene (**8**), bis(*ortho*-chlorophenyl)corannulene (**9**), tris(*ortho*-chlorophenyl)corannulene (**10**), and 1,2,5,6-tetrakis(*ortho*-chlorophenyl)corannulene (**11**)[28] were prepared in 90%, 98%, 67%, and 91% isolated yields, respectively (Scheme 5). The bis- and tris(*ortho*-chlorophenyl)corannulenes (**9** and **10**) both consist of collections of many isomers, for the reasons discussed in the previous section, but we encountered no difficulty in carrying these isomer mixtures through the final reaction without separation.

To cross-couple *ortho*-chlorophenylboronic acid with the less reactive 1,3,5,7,9-pentachlorocorannulene (**7**), we resorted to the conditions introduced by Nolan et al. (catalytic $Pd_2(dba)_3$, Cs_2CO_3, and 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride).[29] In this manner we were able to obtain 1,3,5,7,9-pentakis(*ortho*-chlorophenyl)corannulene (**12**)[30] in 48% isolated yield (86% average per C−C coupling) (Scheme 6).

The fact that *ortho*-chlorophenylboronic acid does not simply polymerize or form cyclic oligomers, such as triphenylene, by self-coupling under these reaction conditions deserves a comment. We believe that the cross-coupling is favored because oxidative addition to the Pd(0) occurs faster at the rim of corannulene than oxidative addition at the Ar−Cl bond of *ortho*-chlorophenylboronic acid. This difference in reactivity holds

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(27) (a) Corpuz, E. M.S. Thesis, Boston College, Chestnut Hill, MA, 1997. (b) Bancu, M. Ph.D. dissertation, Boston College, Chestnut Hill, MA, 2004.

(28) Sygula et al. have previously prepared 1,2,5,6-tetraphenylcorannulene also from **6**.[24b]

(29) Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866–2873, and references therein.

(30) Other 1,3,5,7,9-pentaarylcorannulenes have been prepared from **7** by Siegel et al.[17d,26b]

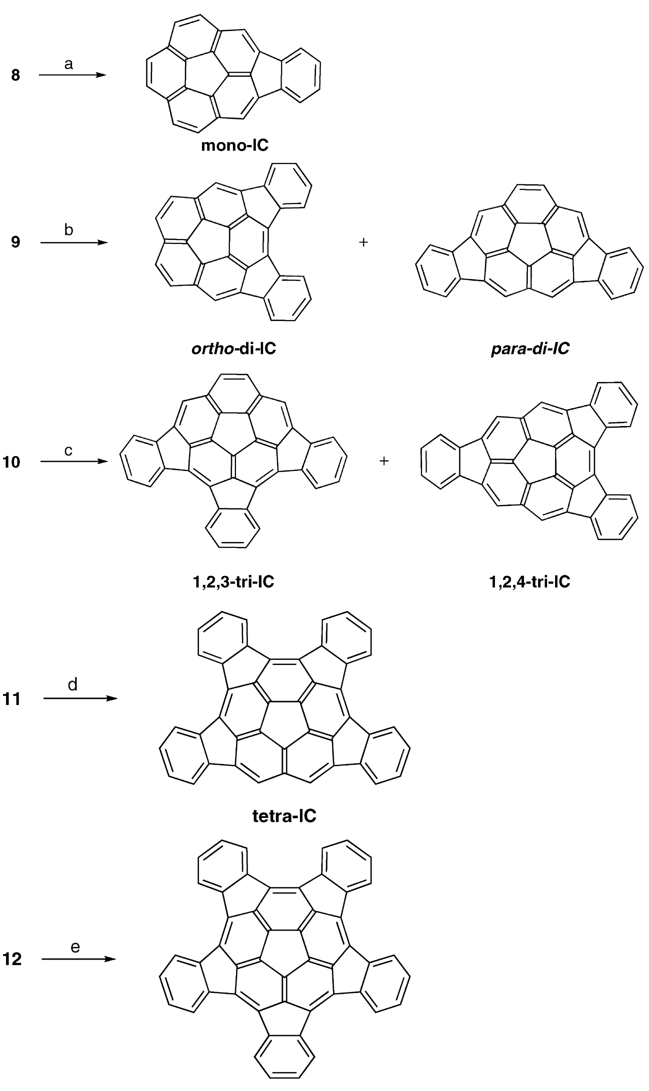
even for the chlorinated corannulene **7**, because the boronic acid group is both bulky and anionic under the basic conditions of the reaction, and that deactivates the Ar−Cl bond of *ortho*-chlorophenylboronic acid toward oxidative addition both sterically and electronically. After the cross-coupling has occurred, the Ar−Cl bond on the phenyl group loses its electronic protection, but it gains new steric protection as an *ortho*-chlorobiaryl. The differential reactivity is not perfect, but it is enough to give us the products we needed. With all the necessary arylated corannulenes in hand we could now explore the final cyclization step to form the new polyarenes.

Closing the New Five-Membered Rings by Microwave-Assisted Intramolecular Arylations. Some years ago, we found that palladium-catalyzed intramolecular arylation reactions could be used to impose curvature on planar PAH π-systems.[31,32] By applying this method to the *ortho*-chlorophenyl-substituted derivatives of corannulene, we learned that curved PAHs can also be made even more curved through this chemistry. Thus, **8** was cyclized to indenocorannulene (**mono-IC**) in 95% yield by heating it to 160 °C for 1 h in dimethylacetamide (DMAc) with a catalytic amount of $Pd(PCy_3)_2Cl_2$ and several equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 7).[27b] These same conditions were used to convert the mixture of bis(*ortho*-chlorophenyl)corannulene isomers (**9**) into the isomeric diindenocorannulenes (***ortho*-di-IC**:***para*-di-IC** = 45:55), also in 95% yield (Scheme 7), and the two new $C_{32}H_{14}$ polyarenes could be separated by chromatography.[27b]

Unfortunately, these reactions were discovered to be highly capricious,[33] and the need for a more dependable method became critical. Extensive efforts to stabilize and optimize these intramolecular arylations eventually led to testing microwave-assisted variants, and those results proved most satisfying. In just 30 min at 170 °C in a microwave oven with excess DBU and a catalytic amount of $Pd(PCy_3)_2Cl_2$ in DMAc, the monosubstituted corannulene **8** cyclizes to indenocorannulene (**mono-IC**) in 99% yield (Scheme 7). Likewise, **9** cyclizes to the two diindenocorannulenes (***ortho*-di-IC**:***para*-di-IC** = 30:70) in 89% yield (Scheme 7). These reactions are totally reliable and work every time.

Molecular geometry calculations predict, and X-ray structural analyses confirm (*vide infra*), that indenoannulations of corannulene force the interior carbon atoms of the ring system to become more pyramidalized. Consequently, we were eager to test the limits of this chemistry and to find out if it could be used to provide access to even larger, more strained polyarenes. Gratifyingly, microwave heating with the same catalytic system converts **10** into the two new triindenocorannulene in 48% yield (**1,2,3-tri-IC**:**1,2,4-tri-IC** = 25:75, Scheme 7), and the two isomers could be separated by chromatography and individually characterized. Tetraindenocorannulene (**tetra-IC**) is likewise obtained from **11** under the microwave conditions, but the yield drops to only 13%. The lower yield in this case can be attributed, in part, to the intervention of a competing side reaction, whereby some of the proximal phenyl groups couple with each other instead of with the *peri*-positions on the corannulene rim. On the other hand, we were delighted to find that the microwave-assisted intramolecular arylation of **12** produces the highly strained pentaindenocorannulene (**penta-IC**) in 35% yield (86% average yield per C−C coupling, Scheme 7). We never encountered problems of irreproducibility with the microwave-assisted cyclizations.[34]

Scheme 7. Intramolecular arylations[a]



[a] (a) $Pd(PCy_3)_2Cl_2$, DBU, DMAc, 170 °C (microwave), 30 min, 99% yield; (b) $Pd(PCy_3)_2Cl_2$, DBU, DMAc, 170 °C (microwave), 30 min, 89% yield (30:70); (c) $Pd(PCy_3)_2Cl_2$, DBU, DMAc, 180 °C (microwave), 40 min, 48% yield (25:75); (d) $Pd(PCy_3)_2Cl_2$, DBU, DMAc, 170 °C (microwave), 40 min, 13% yield; (e) $Pd(PCy_3)_2Cl_2$, DBU, DMAc, 180 °C (microwave), 45 min, 35% yield.

Closing the New Five-Membered Rings by Flash Vacuum Pyrolysis. Flash vacuum pyrolysis (FVP) has been used since the early 1990s for the preparation of more than two dozen geodesic polyarenes, ranging in size from corannulene to

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[31] Reisch, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427–1430.

[32] For excellent reviews and leading references to other intramolecular arylation reactions, see: (a) Echavarren, A. M.; Gomez-Lor, B.; Gonzalez, J. J.; de Frutos, O. *Synlett* **2003**, 585–597. (b) Pascual, S.; de Mendoza, P.; Echavarren, A. M. *Org. Biomol. Chem.* **2007**, *5*, 2727–2734.

[33] Cyclized materials were always formed cleanly as the only products detectable by ^1H NMR analysis; however, the reactions run with conventional heating would often come to a halt, for reasons that we were never able to discern, or overcome, leaving varying amounts of unchanged starting material. The microwave-assisted cyclizations proved to be much more reproducible.

[34] Under bone dry conditions in the winter, these intramolecular arylations sometimes falter, but traces of water added to the reaction mixture restore the normal reliability.

fullerene-C_{60}.[35−38] In the present case, however, it has proven to be inferior to the solution phase methods. FVP of the tetrakis(*ortho*-chlorophenyl)corannulene **11** at 1100 °C, for example, gives tetraindenocorannulene (**tetra-IC**) in only 2% isolated yield (isolated by HPLC), along with a host of other products. Both of the triindenocorannulenes (**1,2,3-tri-IC** and **1,2,4-tri-IC**), both of the diindenocorannulenes (***ortho*-di-IC** and ***para*-di-IC**), and even the simplest indenocorannulene (**mono-IC**) were also isolated from the same pyrolysate by tedious HPLC, all in low yield. The presence of these lower molecular weight products clearly points to aryl group loss, by rupture of corannulene−aryl bonds, as a significant side reaction in these FVP experiments. Such "aryl group loss" products are not uncommon when the FVP starting material has parts of the molecule linked by only a single bond.[39]

Analysis of the Stepwise Introduction of Strain Energy. In our synthesis of pentaindenocorannulene (**penta-IC**), the most strained member of this family, the severe deformation of the trigonal carbon atoms away from their natural geometries is not achieved all at once. Rather, it is built in gradually, in a stepwise manner. Each new five-membered ring closure adds a little more strain and causes a little more pyramidalization of the interior carbon atoms (see X-ray section below). This strategy of introducing a large amount of strain little by little over many steps has been used numerous times before, Eaton's synthesis of cubane being a prime example.[40] In our case, the price for the increase in strain is paid for by the energy released in the intrinsically exothermic reductive elimination of Pd(0) in the final step of each intramolecular arylation. Multiplied 5 times over, that intrinsic exothermicity pays for a considerable increase in strain.

To get a sense of how much strain is associated with each ring closure, we have calculated minimum energy geometries at the B3LYP/6-31G* level of theory[16,17,41] for 1,3,5,7,9-pentakis(*ortho*-chlorophenyl)corannulene (**12**) and for all of the partially closed intermediates along the various pathways leading from there to **penta-IC**. Figure 2 summarizes the results. The strain energy increases shown over each arrow correspond to the *extra energy costs* for the cyclizations indicated, compared to the "strain-free" reference system of benzene coupling with chlorobenzene to make biphenyl.[42] Chlorine atoms have been arbitrarily located *exo* to the bowl in this analysis to circumvent the obfuscation of the bewildering conglomeration of noninterconverting rotamers. At this level of theory, the rotamer of *ortho*-chlorophenylcorannulene (**8**) with the chlorine atom *exo* is more stable than the *endo* rotamer by 0.36 kcal/mol.

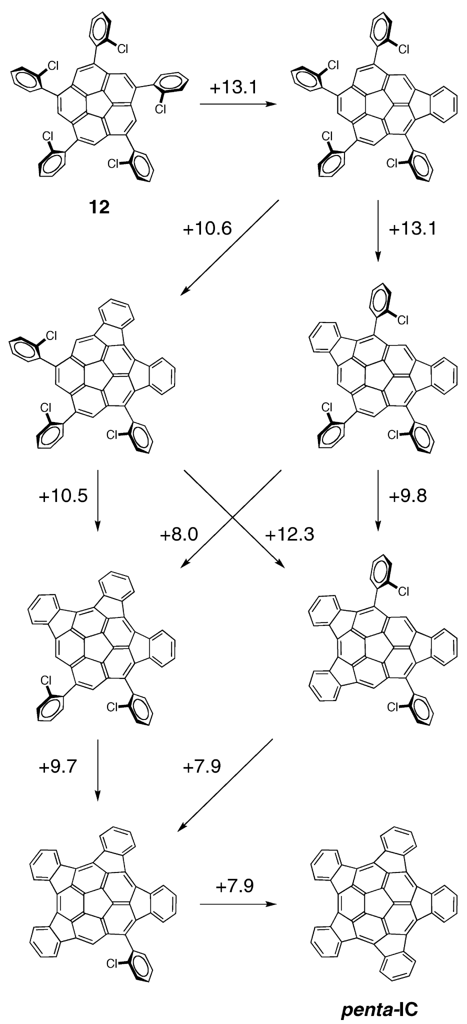

Figure 2. Values over the arrows indicate the extra energy cost (kcal/mol) calculated for each cyclization at the B3LYP/6-31G* level of theory, compared to the strain-free reference system of benzene coupling with chlorobenzene to make biphenyl.[41,42]

According to this analysis, five indenoannulations on corannulene add another 51.8 kcal/mol of strain energy to the already strained ring system. The strain is introduced gradually, and the first ring closure actually appears to be the most difficult (13.1 kcal/mol of strain added). Closing the fifth ring to make **penta-IC** introduces only 7.9 kcal/mol of additional strain. The intrinsic exothermicity associated with reductive elimination of Pd(0) from a diaryl palladium has never been determined

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(35) (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082–7084. (b) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963–10968.

(36) (a) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291–300. (b) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209–219. (c) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868–4884.

(37) (a) Boorum, M. M.; Vasil'ev, Y. V.; Drewello, T.; Scott, L. T. *Science* **2001**, *294*, 828–831. (b) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500–1503. (c) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4995–5007.

(38) (a) Aprahamian, I.; Hoffman, R. E.; Sheradsky, T.; Preda, D. V.; Bancu, M.; Scott, L. T.; Rabinovitz, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1712–1715. (b) Aprahamian, I.; Preda, D. V.; Bancu, M.; Belanger, A. P.; Sheradsky, T.; Scott, L. T.; Rabinovitz, M. *J. Org. Chem.* **2006**, *71*, 290–298.

(39) (a) Bratcher, M. S. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 1996. (b) Peng, L.; Scott, L. T. *J. Am. Chem. Soc.* **2005**, *127*, 16518–16521. (c) Xue, X. Ph.D. Dissertation, Boston College, Chestnut Hill, MA, 2008. (d) Amsharov, K. Y.; Jansen, M. *J. Org. Chem.* **2008**, *73*, 2931–2934. (e) FVP of the pentakis(*ortho*-chlorophenyl)corannulene **12** at 1100 °C produces only ca. 1% yield of pentaindenocorannulene (**penta-IC**), which was positively identified by HPLC with a UV-diode array detector but was not isolated.

(40) (a) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157–3158. (b) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421–1436.

(41) *Spartan*. software; Wavefunction, Inc.: Irvine, CA92612.

(42) Homodesmic reaction used for the first cyclization: **12** + Ph−Ph → product + PhH + Ph−Cl.

(43) High-level NMR calculations on geodesic polyarenes include: (a) Baldridge, K. K.; Siegel, J. S. *J. Phys. Chem. A* **1999**, *103*, 4038–4042. (b) Baldridge, K. K.; Siegel, J. S. *Theor. Chem. Acc.* **2008**, *120*, 95–106.

experimentally, to the best of our knowledge, but it must be worth at least 13 kcal/mol (lower limit), according to our calculations.

Properties of Indenocorannulenes

NMR Spectra of the Indenocorannulenes. In the ^{1}H NMR spectrum of corannulene, the 10 equivalent protons give rise to a single peak at δ 7.82 (CD_2Cl_2). One indenoannulation causes the signals for the corannulene rim hydrogens all to shift upfield by 0.2 ppm or more, and an even larger shielding is seen for the corannulene rim hydrogens of the higher indenocorannulenes. Whenever two indeno moieties are introduced "*ortho*" to one another (i.e., attached to the same benzene ring of corannulene), a fjord region results, and the sterically congested hydrogens located therein become strongly deshielded. The effect is greatest in **penta-IC** (δ 8.10).

The rigidity of the indenocorannulenes fixes the locations of the hydrogens and makes these molecules excellent candidates for NMR chemical shift calculations. We have chosen to test the B3LYP/6-31G* level of theory against our new data set, primarily because this computational method has gained considerable popularity among practicing chemists, and calibration points such as these are valuable, despite the fact that higher levels of theory can give more reliable results.[17,43] Using the computationally optimized geometries, we find that gauge-invariant atomic orbital calculations (GIAO)[44] reproduce the experimental NMR spectra with remarkable accuracy (±0.09 ppm average deviation between experiment and theory, Table 1). The calculations slightly overestimate the shielding of the hydrogens in all cases except for **tetra-IC**, for which it underestimate the shielding. We have no explanation at the moment for the nonconformity of **tetra-IC**. This is the first such assessment of NMR chemical shift calculations on geodesic polyarenes that draws from such a large experimental data set.

The low solubility of some of these indenocorannulenes, the high density of ^{13}C NMR signals in the aromatic region, and the long relaxation times associated with interior carbon atoms made it difficult to obtain a complete set of experimental ^{13}C NMR spectral data. A listing of all the calculated ^{13}C NMR chemical shifts for the seven indenocorannulenes can be found in the Supporting Information. The hub[20] carbon signals are all predicted to fall in the narrow range 139.5−143.4 ppm (cf. 143.2 ppm for fullerene-C_{60}). The lowest field chemical shift in each spectrum invariably comes from one of the carbon atoms attached to the hub, usually at the site of an indenoannulation (147.1−157.8 ppm), whereas the highest field chemical shifts are always associated with α-carbon atoms on the indeno groups (122.5−127.3 ppm).

UV−Vis Spectra of the Indenocorannulenes. As expected for such highly conjugated systems, all of the indenocorannulenes exhibit rich UV−vis spectra. None have absorption maxima in the visible region of the spectrum, but all of the long-wavelength absorptions tail well beyond 400 nm, and some extend beyond 500 nm. Figure 3 shows the UV−vis spectra of all the indenocorannulenes superimposed for comparison; larger individual spectra of each family member can be found in the Supporting Information. Successive indenoannulations impart progressive red shifts in the spectra. The mono- and diindenocorannulenes appear yellow in color; the triindenocorannulenes begin to take on an orange tinge, **tetra-IC** is distinctly orange, and **penta-IC** is dark orange. We have not examined the emission spectra of these new chromophores.

Table 1. Experimental ^{1}H NMR Chemical Shifts of the Indenocorannulenes and Theoretical Values Calculated by the GIAO Method Using Geometries Optimized by Density Functional Theory (B3LYP/6-31G*)

compound	experimental ^{1}H NMR (ppm)	calculated ^{1}H NMR (ppm)	deviation[a] (ppm)
indenocorannulene	7.63	7.59	−0.04
	7.62	7.55	−0.07
	7.62	7.53	−0.09
	7.56	7.52	−0.04
	7.52	7.44	−0.08
	7.19	7.12	−0.07
ortho-diindenocorannulene	7.98	7.85	−0.13
	7.66	7.55	−0.11
	7.56	7.40	−0.16
	7.46	7.36	−0.10
	7.38	7.27	−0.11
	7.29	7.17	−0.12
	7.29	7.17	−0.12
para-diindenocorannulene	7.59	7.53	−0.07
	7.59	7.50	−0.09
	7.55	7.43	−0.12
	7.47	7.41	−0.06
	7.46	7.30	−0.16
	7.18	7.14	−0.04
	7.18	7.13	−0.05
1,2,3-triindenocorannulene	8.05	7.94	−0.11
	8.00	7.91	−0.09
	7.61	7.53	−0.08
	7.38	7.27	−0.11
	7.37	7.25	−0.12
	7.31	7.24	−0.07
	7.28	7.20	−0.08
	7.28	7.19	−0.09
1,2,4-triindenocorannulene	7.96	7.81	−0.15
	7.66	7.53	−0.13
	7.63	7.52	−0.11
	7.54	7.36	−0.08
	7.48	7.30	−0.18
	7.32	7.17	−0.15
	7.32	7.17	−0.15
	7.25	7.15	−0.10
tetraindenocorannulene	7.98	8.02	+0.04
	7.89	7.93	+0.04
	7.86	7.90	+0.04
	7.52	7.56	+0.04
	7.27	7.30	+0.03
	7.25	7.29	+0.04
	7.23	7.27	+0.04
	7.19	7.23	+0.04
	7.19	7.23	+0.04
pentaindenocorannulene	8.10	8.04	−0.06
	7.37	7.33	−0.04
		average |dev|	0.09

[a] Deviation = calculated − experimental.

X-ray Crystal Structures of the Indenocorannulenes. After a considerable investment of time and energy, we were ultimately rewarded with X-ray quality crystals of all seven indenocorannulenes (Figure 1). Tables of experimental bond lengths, bond angles, etc., can be found in the Supporting Information; however, two aspects of the observed molecular structures deserve special attention, namely, (1) the degree of pyramidalization of the interior trigonal carbon atoms in each molecule and (2) the depth of the corannulene bowl in each.

The pyramidalization of trigonal atoms is most conveniently quantified using Haddon's widely adopted p-orbital axis vector

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(44) NMR chemical shifts were calculated by the GIAO method incorporated into the Gaussian 03 suite of programs, using the chemical shift of tetramethylsilane calculated at the same level of theory as the reference point: Frisch, M. J.; et al. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.

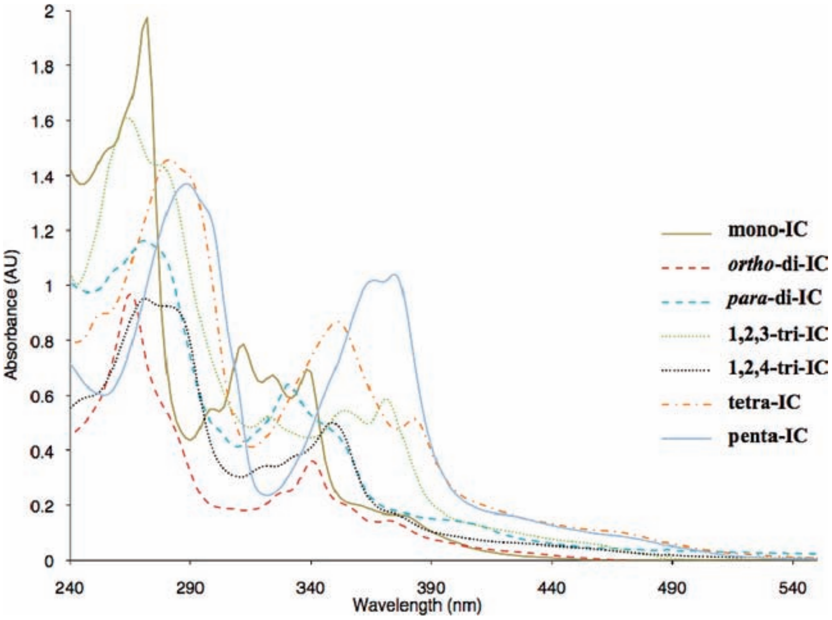

Figure 3. UV−vis spectra of the indenocorannulenes in CH_2Cl_2.

(POAV) analysis.[45] Planar trigonal carbon atoms, such as those in benzene, have POAV angles of 0.0°, whereas the hub[20] carbon atoms of corannulene have POAV angles of 8.2°, and the more highly pyramidalized atoms of C_{60} (all identical) have POAV angles of 11.6°. The largest POAV angles in each of the indenocorannulenes were found to range from 11.2° in monoindenocorannulene up to 12.7° in pentaindenocorannulene, as determined from the crystal structures. Bridging a pair of *peri*-positions on the rim of corannulene or any of its derivatives with an *ortho*-phenylene unit (i.e., indenoannulation) invariably squeezes the *peri*-positions closer together and imposes greater pyramidalization on the nearest hub carbon atom.[17a] The B3LYP/6-31G* geometry optimizations described above do a good job of predicting the observed POAV angles at the central five-membered ring carbon atoms of the indenocorannulenes (±0.2° average deviation from experiment, Table 2). It is important to note that five of the seven indenocorannulenes contain carbon atoms that are *more severely pyramidalized than the carbon atoms of C_{60}*, which is the most curved of the stable fullerenes. From high-level theoretical calculations, Baldridge and Siegel predicted curvatures greater than that in C_{60} for several other geodesic polyarenes that have a corannulene base.[17a]

Corannulene is characterized by a “bowl depth” of 0.870 Å.[3c,16,46] This metric corresponds to the distance between the plane containing the five carbon atoms at the hub of corannulene and the plane containing the 10 methine carbon atoms on the rim. For the indenocorannulenes of lower symmetry, the mean planes defined by these two sets of carbon atoms are used to determine the bowl depths. Table 3 lists the experimental bowl depths of all seven indenocorannulenes, as determined from their X-ray crystal structures, along with the values calculated from the B3LYP/6-31G*-optimized geometries. It is gratifying to see that density functional theory does a good job also of predicting these bowl depths (±0.015 Å average deviation between experiment and theory). For comparison purposes, the bowl depth of the parent corannulene molecule is included in Table 3.

Table 2. POAV Angles at the Interior Five-Membered Ring Carbon Atoms of the Indenocorannulenes As Determined Experimentally by X-ray Crystallography and Theoretically by Geometry Optimizations Using Density Functional Theory (B3LYP/6-31G*)

compound	X-ray POAV[a] (deg)	DFT POAV (deg)	deviation[b] (deg)
indenocorannulene	8.91	8.96	+0.05
	9.83	9.85	+0.02
	11.15	11.00	−0.15
ortho-diindenocorannulene	8.87	9.44	+0.57
	9.79	10.13	+0.34
	11.75	11.80	+0.05
para-diindenocorannulene	10.41	10.30	−0.11
	10.93	11.09	+0.16
	11.20	11.40	+0.20
1,2,3-triindenocorannulene	10.28	10.41	+0.13
	11.81	11.85	+0.04
	12.41	12.37	−0.04
1,2,4-triindenocorannulene	11.09	11.20	+0.11
	11.52	12.12	+0.60
	12.01	12.63	+0.62
tetraindenocorannulene	11.43	11.17	−0.26
	12.07	12.02	−0.05
	12.45	12.39	−0.06
pentaindenocorannulene	12.69	12.42	−0.27
		average |dev|	0.20
C_{60} (for comparison)	11.64	11.64	

[a] The X-ray POAV angles reported here are the values obtained by averaging the POAV angles of symmetry-related carbon atoms, assuming C_s symmetry for all compounds except for pentaindenocorannulene, which was treated as C_{5v} symmetrical. [b] Deviation = calculated − experimental.

Some of the indenocorannulenes arrange themselves like stacks of bowls in the solid state, while others prefer less regular orientations. All are characterized by significant intermolecular π,π-contacts. A thorough discussion of these crystal-packing patterns and the possible influences they may have on various solid-state properties exhibited by these novel carbon-rich

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(45) (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385–3389. [erratum p 8217].

Table 3. Bowl Depths from the Five-Membered Ring Hub to the 10 Carbon Atoms of the Corannulene Rim in the Indenocorannulenes As Determined Experimentally by X-ray Crystallography and Theoretically by Geometry Optimizations Using Density Functional Theory (B3LYP/6-31G*)

compound	bowl depth X-ray (Å)	bowl depth DFT (Å)	deviation[a] (Å)
indenocorannulene	1.065	1.060	−0.005
ortho-diindenocorannulene	1.157	1.190	+0.033
para-diindenocorannulene	1.209	1.224	+0.015
1,2,3-triindenocorannulene	1.272	1.283	+0.011
1,2,4-triindenocorannulene	1.298	1.309	+0.011
tetraindenocorannulene	1.378	1.366	−0.012
pentaindenocorannulene	1.433	1.418	−0.015
		average |dev|	0.015
corannulene (for comparison)	0.870	0.858	−0.012

[a] Deviation = calculated − experimental.

materials will comprise the primary focus of our forthcoming paper on the crystallography of these compounds.

Conclusions

The family of indenocorannulenes is now complete and offers a wealth of new experimental data on fullerene fragments that all map onto the geodesic framework of C_{60} and range in size from $C_{26}H_{12}$ to $C_{50}H_{20}$. The rigidity of these fully unsaturated hydrocarbons makes them ideal candidates for testing the reliability of geometry calculations and NMR chemical shift predictions as applied to large, conformationally locked, strongly curved π-systems. The widely used B3LYP/6-31G* density functional method was found to successfully predict the degree of pyramidalization at the innermost carbon atoms of all seven indenocorannulenes (POAV angles, average deviation ± 0.2°), bowl depths (average deviation ± 0.015 Å), and ^{1}H NMR chemical shifts (GIAO method, average deviation ± 0.09 ppm). The UV−vis absorption spectra of these extended π-systems are rich in detail but have not been analyzed.

The most important conclusion to be drawn from this work is the proof of principle that highly distorted π-systems, with curvatures surpassing that of C_{60}, can be synthesized by well-understood chemical reactions *in solution*, without any recourse to flash vacuum pyrolysis or other high-energy gas phase methods. Our syntheses of the indenocorannulenes constitute the first demonstration that the stepwise introduction of curvature can be pushed all the way to produce a level of curvature equal to that of C_{60} and even beyond. Since all carbon nanotubes and fullerenes that are expected to exist as stable entities under ambient conditions are less severely curved than C_{60}, this work provides assurance, for the first time, that they can all be considered realistic targets for chemical synthesis by ordinary laboratory methods.[47]

Finally, we note that stitching the five arms of **penta-IC** together would yield a $C_{50}H_{10}$ hydrocarbon hemisphere that represents the C_{5v} end-cap of a [5,5]nanotube with an armchair rim.[17a] Growing a long [5,5]nanotube from this end-cap has considerable appeal as a method for obtaining single-chirality carbon nanotubes of uniform diameter, and we are pursuing this objective.[48]

Acknowledgment. This paper is dedicated to Amir H. Hoveyda on the occasion of his 50th birthday. We thank Dr. Bo Li for solving the X-ray crystal structure of **1,2,4-tri-IC**, Stephanie Ng for solving the X-ray crystal structures of ***ortho*-di-IC** and **1,2,3-tri-IC**, and Dr. Mihail Bancu for early studies on conventional intramolecular arylations. We are grateful to the National Science Foundation for financial support of this work (grants no. CHE-0414066 and CHE-0809494) and for funds to purchase mass spectrometers (grant no. DBI-0619576). Generous support of our X-ray Crystallography Facility by Schering-Plough is gratefully acknowledged. We thank AstraZeneca for a graduate fellowship awarded to B.D.S.

Supporting Information Available: Experimental details, spectroscopic characterization data for new compounds, crystallographic information files (CIF), XYZ coordinates for all calculated structures, calculated ^{13}C NMR chemical shifts, and complete ref 44. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) The bowl depth of corannulene has actually been determined independently four times by X-ray crystallography, and the results vary slightly as a function of the temperature at which the data were collected. The reported values (Å) are as follows (temp K): 0.877 (90),[16] 0.876 (173),[16] 0.872 (203),[3c] 0.862 (293−303).[3c] The average bowl depth from all these different temperature experiments is calculated to be 0.870(8), accounting for the temperature effect in the estimated standard deviation (temperature error). The crystal structures of the seven indenocorannulenes were all determined at temperatures between 90 and 193 K.

(47) Scott, L. T. *Angew. Chem., Int. Ed.* **2009**, *48*, 436–437.

(48) For related work, see: (a) Hill, T. J.; Hughes, R. K.; Scott, L. T. *Tetrahedron* **2008**, *64*, 11360–11369. (b) Steinberg, B. D.; Scott, L. T. *Angew. Chem., Int. Ed.* Published Online: May 28, 2009 (DOI: 10.1002/anie.200901025).