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Palladium-Catalyzed C−H Activation Taken to the Limit. Flattening an Aromatic Bowl by Total Arylation

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Supporting Information

ABSTRACT: All 10 C−H positions on the rim of corannulene can be arylated by repetitive palladium-catalyzed C−H activation. To relieve congestion among the 10 tightly packed aryl substituents in the product, the central corannulene adopts a nearly planar geometry.

The arylation of aromatic compounds lies at the heart of organic chemistry, particularly in the field of π-conjugated aromatic materials. In recent years, the direct C−H arylation of aromatics catalyzed by a transition-metal complex has emerged as a practical alternative to the well-established palladium-catalyzed cross-coupling reactions of metalated and halogenated aromatic compounds.[1] Such a direct molecular activation−transformation technology not only streamlines the synthesis of useful molecular entities but also unlocks opportunities for markedly different reactivity and selectivity in synthesis.[2] During our studies aimed toward a controlled synthesis of nanographenes, we recently developed a $Pd(OAc)_2$/*o*-chloranil catalyst for the oxidative C−H arylation of polycyclic aromatic hydrocarbons with arylboron compounds, arylsilanes, or even unfunctionalized aromatic compounds.[3] For example, the C−H arylation of pyrene occurs with various arylboroxins to furnish the corresponding 4-arylpyrenes with complete regioselectivity (Figure 1, top).[3a] As illustrated by these examples, the $Pd(OAc)_2$/*o*-chloranil catalyst manifests unique regioselectivity, activating/arylating an exposed outer π-bond of aromatic compounds (K-region[4]). Herein we report that the palladium-catalyzed arylation reaction can be pushed all the way to per-arylation in the case of corannulene, a bowl-shaped polycyclic aromatic hydrocarbon that contains only K-regions (Figure 1, bottom). The ability to produce compounds as strained as **2**, which suffers from serious steric congestion (discussed further below), represents an important and previously unrecognized attribute of this powerful arylation method.

Under the original reaction conditions[3a] with 3.0 equiv of phenylboroxin, corannulene (**1**) takes on 1−5 phenyl groups in varying amounts, as expected. When larger amounts of phenylboroxin and $Pd(OAc)_2$ were employed to maximize the yield of pentaphenylcorannulene, however, we were surprised to observe the formation of significant amounts of higher polyphenylcorannulenes bearing more than five phenyl groups.

The introduction of six phenyl groups onto the corannulene rim requires that at least two phenyl groups end up located

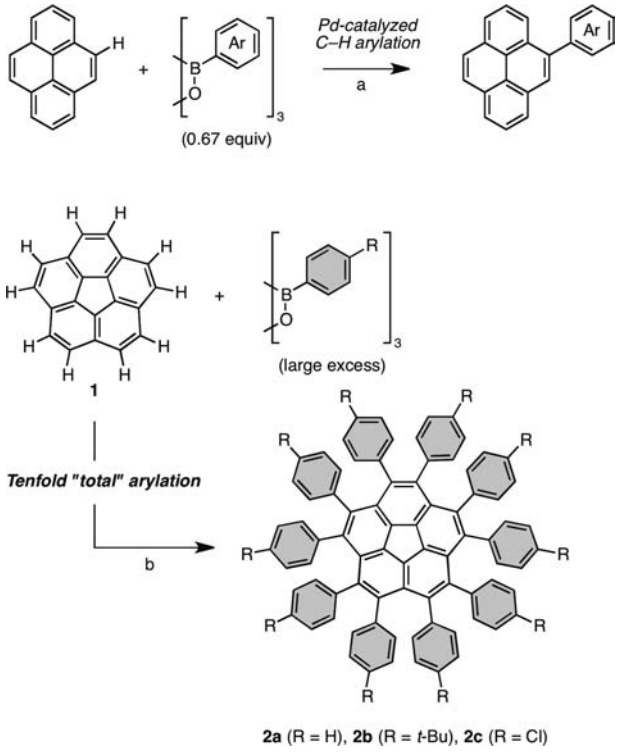

Figure 1. (a) $Pd(OAc)_2$ (2.5 mol %), *o*-chloranil (1.0 equiv), DCE, 80 °C, 2 h. (b) $Pd(OAc)_2$, *o*-chloranil, DCE, 80 °C, repeat 3−4 cycles.

ortho to one another on the same ring *and* that at least two phenyl groups end up located *peri* to one another on adjoining rings. *Both* structural features impose more steric congestion than we expected to find. This discovery immediately suggested that decaphenylcorannulene (**2a**) might be accessible by repetition of the reaction.

Indeed, a second round of phenylation adds more phenyl groups to the rim, and a third round pushes the reaction even further.[5] After the fourth round of phenylations, much to our delight, decaphenylcorannulene (**2a**) could be isolated by careful chromatography. The yield, unfortunately, was disappointingly low (6%), but we soon learned why.

Mass spectral analysis of the product mixtures obtained after multiple rounds of phenylation revealed that the reaction does not stop when it reaches 10 phenyl groups. By the fourth cycle,

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some of the molecules had already taken on as many as 17 phenyl groups![6] Although we have no proof concerning the sites of attachment of the "extra" phenyl groups, the palladium probably catalyzes arylation of the first circle of phenyl groups by C−H activation under the forcing conditions employed.

In harmony with this assumption, bulky *tert*-butyl substituents on the *para*-positions of the phenyl groups effectively shut down the overarylation chemistry and allow the reaction to be stopped at the point of decasubstitution. After four cycles of arylation, decakis(*p*-*tert*-butylphenyl)corannulene (**2b**) can be isolated as a pure solid in 23% yield. Even less bulky chlorine atoms suppress the overarylation chemistry and allow preparation of decakis(*p*-chlorophenyl)corannulene (**2c**) in 54% yield, after isolation and purification.

We were eager to obtain an X-ray crystal structure of decaphenylcorannulene or one of its derivatives, because DFT calculations (BMK/6-31G*)[7] predict that the corannulene nucleus should be dramatically flattened (Figure 2), rather than bowl-shaped, like the unsubstituted parent hydrocarbon (**1**).[8] Our inability to grow X-ray quality crystals of either decaphenylcorannulene (**2a**) or the *p*-*tert*-butyl derivative (**2b**), in fact, is what prompted us to synthesize the *p*-chloro derivative (**2c**), in the expectation that chlorine atoms might impart greater crystallinity. Gratifyingly, **2c** does crystallize well, and the X-ray crystal structure confirms the dramatic flattening of the corannulene bowl (Figure 3).

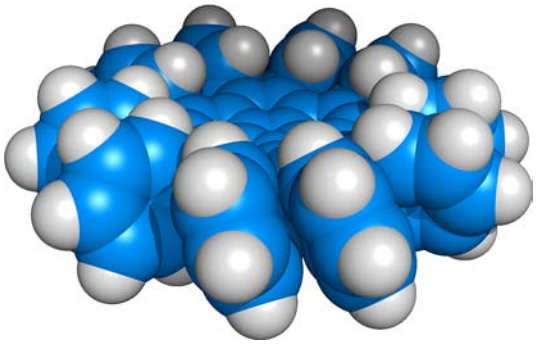

Figure 2. Calculated space-filling structure (BMK/6-31G*) for decaphenylcorannulene (**2a**).

Refinement of the X-ray diffraction data for **2c** indicates that the molecule adopts a very shallow bowl-shaped geometry, with a bowl depth of only 0.248(7) Å (Figure 3). The 10 aryl groups all twist in the same direction with average dihedral angles of 70.1°, and that makes the structure chiral in the crystal (approximately C_5-symmetric). The barrier for bowl-to-bowl inversion ($\Delta G^{\ddagger}$) is calculated (BMK/cc-pVDZ) to be only 2.5 kcal/mol at 100 K, the temperature at which the X-ray data were obtained.[6,9] Unlike the inversion of many other chiral corannulene derivatives, this inversion does not lead to racemization but produces the same enantiomer of the molecule (through a chiral transition state of D_5 symmetry). This chirality derives from *P* vs *M* twisting of the 10 aryl groups, which remain fixed in the crystal, and not on the concave vs convex geometry of the core. The two sites in the crystal for the five hub carbon atoms are thus each 50% occupied. The exceptionally low barrier for inversion and the absence of any steric impediments in the crystal suggest that the trampoline-like motion of the molecule is probably rapid even in the solid state, especially at room temperature, although we have no way of verifying this experimentally. The shallow bowl of decakis(phenylthio)corannulene is similarly disordered in the crystal.[10]

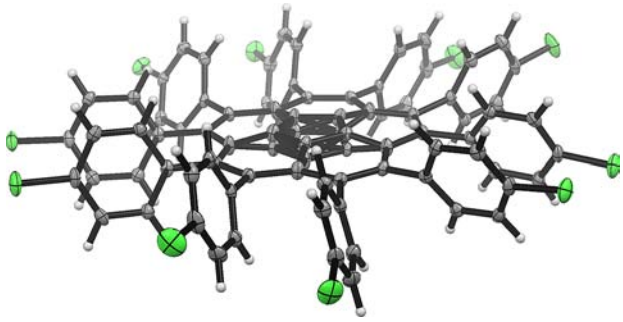

Figure 3. X-ray crystal structure of decakis(*p*-chlorophenylcorannulene (**2c**). Note the two sites for the five hub carbon atoms, each with 50% occupancy. Bowl depth = 0.248(7) Å.

The parent corannulene (**1**) has a bowl depth of 0.87 Å[8] and inverts through a planar transition state with a barrier of ∼11.5 kcal/mol.[9,11] To pay the energetic price for flattening the corannulene nucleus, decakis(*p*-chlorophenyl)corannulene (**2c**) must benefit from the relief of close to 10 kcal/mol of strain associated with compaction of the 10 phenyl groups in the bowl-shaped geometry. From the X-ray crystal structure of **2c**, it can be seen that the rim of the corannulene nucleus is stretched by nearly 0.5 Å, relative to that in the parent corannulene (**1**), and that the CCC bond angles at the quaternary carbons on the rim are expanded from an average value of 129.9° in corannulene to 136.6° in **2c**. Both of these structural changes create more room for the closely sandwiched aryl groups. We calculate (BMK/cc-pVDZ)[7] an *increase* in strain energy of 53.2 kcal/mol associated with the addition of 10 aryl groups around the rim of corannulene.[6]

Figure 4 shows the ^{1}H NMR spectrum of decakis(*p*-chlorophenyl)corannulene (**2c**). The sizable shift of the signals upfield from the normal region for hydrogens attached to "aromatic" hydrocarbons reflects the strong shielding of these hydrogens by the induced diamagnetic ring currents in the proximal benzene rings. The simplicity of the spectrum furthermore indicates a time-averaged D_{5h} symmetry of the molecule in solution. Not only is the trampoline-like motion of the corannulene core rapid on the NMR time scale, but so is rocking of the aryl groups between *M* and *P* twisted geometries. The ^{1}H NMR spectra of **2a** and **2b** show similarly large upfield shifts for the aryl hydrogen signals and reflect the same time-averaged D_{5h} symmetry.[6]

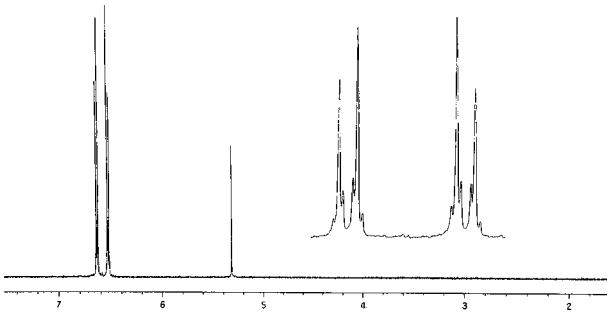

Figure 4. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of decakis(*p*-chlorophenyl)corannulene (**2c**).

Decaphenylcorannulene (**2a**) absorbs in the UV (CH_2Cl_2) at λ_{max} 274 ($\varepsilon = 5.0 \times 10^4$) and 317 nm ($3.5 \times 10^4$), with a tailing shoulder at 350 nm, and fluoresces at 373, 390, and 470 nm. From our TD DFT calculations[6] (BMK/cc-pVDZ), we assign the weak shoulder at 350 nm in the absorption spectrum to the forbidden HOMO−LUMO transition. The maximum at 317 nm most likely corresponds to the HOMO-2−LUMO, and the strongest absorption at 274 nm arises from the HOMO-3/HOMO-4−LUMO transition. By comparison, corannulene (**1**, EtOH) absorbs at λ_{max} 246 ($\varepsilon = 6.0 \times 10^4$), 249 ($5.4 \times 10^4$), 253 ($9.1 \times 10^4$), and 288 ($3.3 \times 10^4$), with a tailing shoulder at 320 nm,[12] and fluoresces (BuOAc) at 395 (sh), 419, and 434 nm.[13] The *p-tert*-butyl and *p*-chloro derivatives (**2b** and **2c**) give UV−vis absorption and fluorescence spectra similar to those of **2a**.[6]

Reduction in the curvature of the corannulene bowl has been seen before. Crowding of substituents on the rim of corannulene by *peri* interactions can be relieved by flattening, as in the present case. In 1,3,5,7,9-penta-*tert*-butylcorannulene,[14] the bowl depth is reduced to 0.72 Å (from 0.87 Å in corannulene), and in deca-substituted corannulenes, the bowl depths are reduced even further, e.g., decapentynylcorannulene (0.60 Å),[15] decachlorocorannulene (0.51 Å),[16] and decakis-(phenylthio)corannulene (0.49 Å).[10] Benzannulation likewise diminishes the curvature of corannulenes, although less dramatically so.[17] Dibenzo[*a,g*]corannulene has a bowl depth of 0.83 Å.[18] The only known corannulene derivative with an essentially flat ring system is $[(Cp^*Ru)_2(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-}C_{20}H_{10})][SbF_6]_2$, in which η^6-complexation of the π-system by one metal on each face causes planarization.[19] The decaarylcorannulenes reported here are significantly flatter than all other known, metal-free corannulene derivatives.

Totally arylated polycyclic aromatic hydrocarbons are rare and have unusual properties. Octaphenylnaphthalene, octaphenylbiphenylene, and decaphenylanthracene are the only known simple cases, prior to this work; the latter is twisted end-to-end by 63°.[20] Like **2a−c**, such systems also suffer great strain from the overcrowding of phenyl substituents.[21] Attempts to arylate naphthalene all the way to octa-substitution by the strategy that works for corannulene, unfortunately, has not been successful.

In conclusion, we have found that corannulene, the prototypical geodesic polyarene, can be flattened dramatically through the complete replacement of all 10 hydrogen atoms on its rim by phenyl groups or substituted phenyl groups. The arylation of polycyclic aromatic hydrocarbons by Pd-catalyzed C−H activation was not previously known to be capable of introducing so much steric strain.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures for the synthesis, isolation, and purification of **2a−c**; ^{1}H NMR, ^{13}C NMR, UV−vis absorption, fluorescence, and MALDI-TOF mass spectra for **2a−c**; X-ray crystal structure for **2c**; MALDI mass spectra showing over-phenylation of corannulene after multiple cycles; geometry and strain energy calculations for **2a**, octaphenylnaphthalene, and decaphenylanthracene; bowl-to-bowl inversion barrier calculations for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(5) Eventually, these reactions slow down and stop, which we tentatively ascribe to deactivation of the catalyst. Adding more catalyst, phenylboroxin, and *o*-chloranil is not as effective in promoting further reaction as starting fresh after a quick workup (see the Supporting Information for details).

(6) See the Supporting Information for details.

(7) The BMK/cc-pVDZ level of theory has been reported to produce more reliable structures than B3LYP/6-31G(d) for compounds with close face-to-face contact of arenes, because B3LYP/6-31G(d) often overestimates intramolecular close $\pi-\pi$ distances: Cozzi, F.; Annunziata, R.; Benaglia, M.; Baldridge, K. K.; Aguirre, G.; Estrada, J.; Sritana-Anant, Y.; Siegel, J. S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2686−2694. Our syntheses of compounds **2a−c** were originally motivated by calculations at the BMK/6-31G(d) level of theory, but our final calculations were performed with the cc-pVDZ basis set.

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