

Synthesis and Quantum Mechanical Structure of *sym*-Pentamethylcorannulene and Decamethylcorannulene

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The five-fold symmetric structure of corannulene (**1**, Figure 1) serves as an archetype of a series of bowl-shaped hydrocarbons.¹ Extension to *sym*-penta- and deca-substituted derivatives of **1** establishes a focal point for the design of higher homologues and multimeric constructs. *sym*-Pentamethylcorannulene (**2**) and decamethylcorannulene (**3**) are particularly important intermediates in such designs. We report the facile transformation of halo- to alkylcorannulenes using trimethylaluminum and catalytic nickel salts.

A number of routes to **1** have been developed,² and halogenation of **1** can be controlled to give monobromo- (**4**),^{3,4} *sym*-pentachloro- (**5**),^{3,4} and decachlorocorannulene (**6**).^{3–5} In general, bromo-to-alkyl transformations are straightforward via cross coupling methods.⁶ In the case of **4**, simple transformation to methylcorannulene (**7**) occurs cleanly. The lower reactivity of chlorides and the reduced solubility of highly chlorinated compounds make the same kind of transformation more difficult for **5** and **6**. An additional complication comes from the ease with which the corannulene fragment forms a radical anion by reduction.^{7,8} Strongly nucleophilic metal alkyls are often not effective because of significant amounts of reduction side products, but weakly nucleophilic reagents are unable to cause substitution. Trimethylaluminum (TMA) with catalytic 1,3-bis-(diphenylphosphino)propanenickel(II) chloride (NiCl₂dppp) turns out to be a useful and tunable reagent mixture.

TMA with 10% NiCl₂dppp in 1,2-dimethoxyethane (DME) cleanly transforms **4** into **7**⁹ in 2 h at 90 °C (Scheme 1). In contrast, under identical reaction conditions, 24 h is required in order to transform **5** into **2**,¹⁰ and **6** is left unreacted after 3 days. Thus, NiCl₂dppp is able to activate the chlorines of **5**, but **6** is

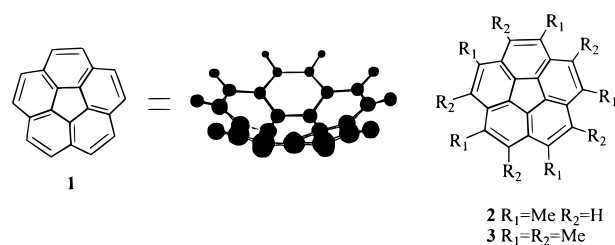
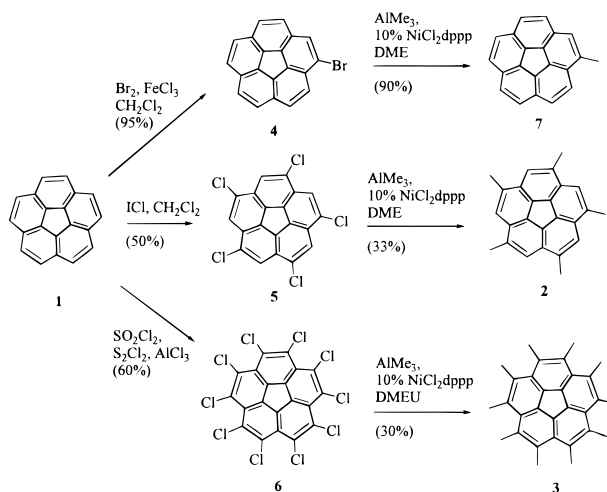


Figure 1. Corannulene (**1**), *sym*-pentamethylcorannulene (**2**), and decamethylcorannulene (**3**).

Scheme 1



resistant due to limited solubility in most organic solvents, including DME. Gratifyingly, TMA/NiCl₂dppp does not adversely react with *N,N'*-dimethylethyleneurea (DMEU) at 100 °C, and under such conditions **6** exhibits sufficient solubility for the reaction to proceed cleanly to **3**.^{11,12}

Structural computations of compounds **1**, **2**, and **3** were performed at the restricted Hartree–Fock (RHF) level of theory using the analytically determined gradients and search algorithms within GAMESS¹³ and, additionally, using hybrid density functional methods (HDFT) using GAUSSIAN98¹⁴ to uncover effects of dynamic correlation. The HDFT method employed Becke's three-parameter functional¹⁵ in combination with nonlocal correlation provided by the Lee–Yang–Parr expression^{16,17} that contains both local and nonlocal terms, B3LYP. Dunning's correlation consistent basis set, cc-pVDZ,¹⁸ a [3s2p1d] contraction

(11) Mp 310–312 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.89 (s, 30H). ¹³C NMR (125 MHz, CDCl₃): δ 20.5, 129.6, 130.5, 133.7. HRMS: calcd (C₃₀H₃₀) 390.2348, found 390.2347.

(12) One might speculate that a coordinative interaction between TMA and the oxygen of DMEU heightens the reactivity of TMA in the mixture.

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(9) Mp 123–129 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.92 (d, J = 0.8 Hz, 3H), 7.64 (d, J = 0.8 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.83–7.92 (m, 6H), 7.99 (d, J = 8.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 19.0, 124.7, 125.6, 126.4, 126.5, 126.7, 126.8, 126.88, 126.90, 130.2, 130.3, 130.7, 130.8, 131.3, 134.6, 135.4, 135.5, 135.6, 135.7, 135.8, 136.6. HRMS: calcd (C₂₁H₁₂) 264.0939, found 264.0926.

(10) Mp 179–182 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.78 (d, J = 0.8 Hz, 15H), 7.55 (d, J = 0.8 Hz, 5H). ¹³C NMR (100 MHz, CDCl₃): δ 19.1, 122.8, 130.5, 134.4, 136.1. HRMS calcd (C₂₅H₂₀) 320.1565, found 320.1560.

Table 1. Bowl Depth, Inversion Barrier, and Bond Lengths for 1–3

	1		1a calcd ^a	2 calcd ^a	3 calcd ^a
	exptl	calcd ^a			
bowl depth (Å)	0.87	0.88	0	0.85	0.58
ΔG^{\ddagger} (kcal/mol)	11.5	9.2	0	8.7	2.2
hub (Å)	1.42	1.42	1.40	1.42	1.41
spoke (Å)	1.38	1.39	1.37	1.38	1.38
flank (Å)	1.44	1.45	1.46	1.45	1.47
rim (Å)	1.39	1.39	1.41	1.40	1.42

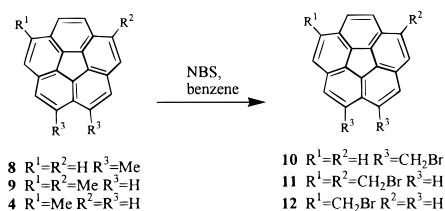
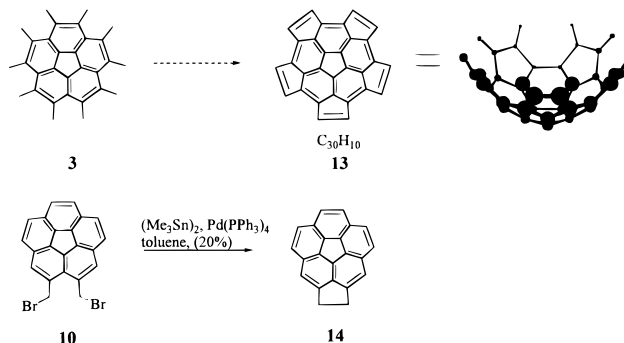
^a B3LYP/cc-pVDZ.

of a (9s4p1d) primitive set, was employed. These levels of theory have been shown previously to be reliable for the structure and frequencies of **1**.¹⁹ From the fully optimized structures, chemical and physical properties such as bond localization and bowl depth²⁰ were derived. More extensive comparison was done on **1** to determine the effects of basis set and correlation, including RHF, HDFT, and MP2-4²¹ levels of theory and basis sets of double- and triple- ζ quality with angular momentum functionality up through f type functions. We note a nontrivial sensitivity of predicted structure (especially bowl depth) and barrier with the inclusion of polarization functionality and with the extent and manner of including dynamic correlation. For example, in the case of **1**, dynamic correlation via HDFT predicts a barrier of 9.2 kcal/mol, whereas MP2 predicts 11.0 kcal/mol at the same basis set level.²²

Ab initio quantum mechanical computations predict a significant flattening of the bowl depth in **3** as compared to that in **1**, whereas the bowl depth of **2** is essentially the same as that of **1** (Table 1). With methyl groups across all peri positions, **3** can be considered a highly crowded aromatic molecule.²³ The predicted flattening is apparently in response to the steric repulsions across the peri positions, thus destabilizing the bowl conformations relative to the flat conformation. Support for the destabilization of the bowl conformation by alkyl substitution at the rim comes from the predicted inversion barriers of 8.7 and 2.2 kcal/mol for **2** and **3**, respectively, relative to 9.2 kcal/mol for **1** (experimental estimate of **1** is 11.5 kcal/mol, see below). Associated with the decrease in bowl depth, the average bond length increases from **1** to **3** by ca. 1–2 pm. Specifically, the rim and flank bonds lengthen by 3 pm each, the hub contracts by 1 pm, and the spoke remains essentially the same as in **1**. This lengthening of the peripheral bonds and contraction of the hub bonds is also predicted in the flat (**1a**) (D_{5h}) structure of **1**.

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(20) Bowl depth is defined as the distance from the best plane of hub carbons to the best plane of the rim carbons.

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To test the relationship among peri repulsions, bowl depth, and reduced barrier to inversion, 2,3-dimethylcorannulene (**8**) was prepared from 2,3-dichlorocorannulene using TMA/NiCl₂dppp.²⁴ Photobromination of **8**, 2,5-dimethylcorannulene (**9**),² and **4** with *N*-bromosuccinimide (NBS) gave bromomethyl derivatives **10**,²⁵ **11**,² and **12**.²⁶ Variable-temperature NMR spectroscopy revealed inversion barriers of 9.1, 10.5, and 11.0 kcal/mol for **10**, **11**, and **12**, respectively (Scheme 2). The barrier of **1** can be extrapolated from the barriers of **11** and **12**. Elimination of one of the bromomethyl groups from **11** raises the barrier 0.5 kcal/mol, from 10.5 to 11.0 kcal/mol for **12**. Assuming the effects of the bromomethyl groups are independent in **11**, an inversion barrier of 11.5 kcal/mol is estimated for **1**. The experimental inversion barrier for **10** is 2.4 kcal/mol less than **1** and 1.4 kcal/mol less than **11**. This reduction in barrier height reflects the added repulsion of peri methyl groups. Calculated bowl depths (B3LYP/cc-pVDZ) for **8**, **9**, and **4** follow the predicted trend (0.83, 0.86, and 0.87 Å respectively).

Extending **3** to the fullerene fragment C₃₀H₁₀ (**13**) requires the formation of bonds across each peri position (Scheme 3). A model reaction for this is the transformation of **10** to acacorannulene (**14**), and is accomplished by hexamethyldistannane with catalytic tetrakis(triphenylphosphine)palladium(0).²⁷ Ab initio quantum mechanical predictions on **14** corroborate the experimental findings of a higher inversion barrier and deeper bowl: 25.6 kcal/mol and 1.07 Å (calcd) vs 27.7 kcal/mol and 1.1 Å (expt²⁸). Ab initio calculations also predict a substantial increase in bowl depth for **13**.¹

In conclusion, halo and alkyl substitution as well as palladium-mediated ring closure represent methodologies that are useful and complementary to our previously developed low valent titanium ring closing methods.^{2a,24} Together, these open up avenues to a family of curved polynuclear aromatic compounds with tailored physical and structural features.

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