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Synthesis and Properties of *sym*-Pentasubstituted Derivatives of Corannulene

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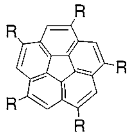
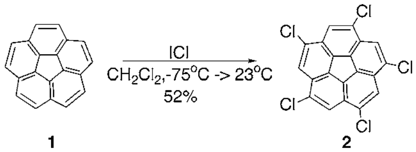
ABSTRACT



Alkyl, aryl, and alkynyl as well as heteroatom derivatives of *sym*-pentasubstituted corannulenes have been synthesized from *sym*-pentachlorocorannulene. These units form potential building blocks for future work on superstructures based on corannulene. Absorption/emission properties follow expected trends from the parent 1. *sym*-Pentasubstitution gives rise to variations in the chemical dynamics of bowl inversion. van der Waals attraction is cited to explain an anomalously high barrier to bowl inversion in 10.

The 5-fold symmetry and novel electronic and dynamic properties of corannulene make its *sym*-pentasubstituted derivatives attractive targets as building blocks for larger molecular architectures.[1,2] Regiochemical control and functional group generality are two hurdles to overcome in the synthesis of superstructures such as dendrimers and discotic liquid crystals based on the 5-fold symmetry of corannulene (**1**).[3] Fortuitously, chlorination of **1** with iodine monochloride yields *sym*-pentachlorocorannulene[3,4] (**2**), thus providing a starting point for further synthetic transformation (Scheme 1). The systematic conversion of **2** into a variety of *sym*-pentasubstituted corannulene derivatives and the study of their dynamic properties uncovers a special cooperative interaction of functional groups around the rim of the bowl.

Scheme 1



1 **2**

Formation of new carbon−carbon bonds through the use of palladium-catalyzed cross-coupling methods has become an extremely powerful synthetic tool.[5] Although relatively unreactive partners in such chemistry, aryl chlorides represent an important pool of substrates for such methods and have recently been the focus of extensive examination.[6] Along these lines, a general method for the conversion of the aryl pentachloride **2** into alkyl, vinyl/aryl, and alkynyl derivatives is a key milestone in this area.

Synthesis. Previously, we reported the transformation of **2** into *sym*-pentamethylcorannulene (**3**), via nickel-catalyzed cross-coupling with trimethyl aluminum, in 33% yield.[7] Extension of this method to the formation of longer chain

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[1] (a) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *Tetrahedron* **2001**, *57*, 3737−3742. (b) Seiders, T. J.; Baldridge, K. K.; Siegel, J. S.; Gleiter, R. *Tetrahedron Lett.* **2000**, *41*, 4519−22.

[2] Prefix *sym*- is used here to mean the C_5-symmetric substituted corannulene corresponding to 1,3,5,7,9-pentasubstitution.

[3] Seiders, T. J.; Elliott, E.; Grube, G.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804−7813.

[4] (a) Cheng, P. Ph.D. Dissertation, Boston College, Boston, MA, 1996; pp 212. (b) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300.

[5] (a) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F. N., Stang, P. J., Eds.; Wiley-VCH, Weinheim, Germany, 1998; (b) Tsuji, J. *Palladium Reagents and Catalysts, Innovations in Organic Synthesis*; Wiley: New York, 1995.

[6] Littke, A. F.; Fu, G. C. *Angew. Chem.* **2002**, *41*, 4176−4211.

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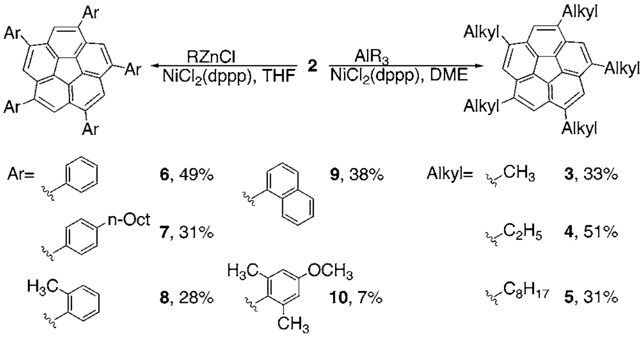
derivatives has now been accomplished by simple variation of the organoaluminum reagent (Scheme 2). Treatment of **2** with either triethyl- or trioctylaluminum in the presence of 1,3-bis(diphenylphosphino) nickel(II) chloride ($NiCl_2$(dppp)) provides *sym*-pentaethyl- (**4**) or *sym*-pentaoctylcorannulene (**5**) in 51 and 31% yield, respectively.

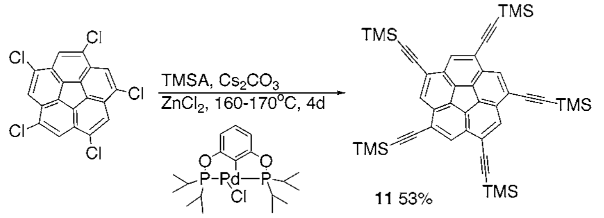
Scheme 2



In the case of aryl substituents, the zinc-based Negishi chemistry worked reasonably well.[8] The synthesis of *sym*-pentaphenylcorannulene (**6**) was achieved via nickel-catalyzed cross-coupling with phenylzinc chloride in an overall 49% yield (cf. Scheme 2). In a similar manner, aryl derivatives (**7**−**9**) were obtained in yields ranging from 25−40%. The lower yield for **10** (ca. 7%) likely results from the steric hindrance at the organometallic reaction center. In contrast to the arylzinc chemistry, similar reagents based on aluminum, magnesium, boron, and tin proved to be unsuccessful for pentasubstitution.

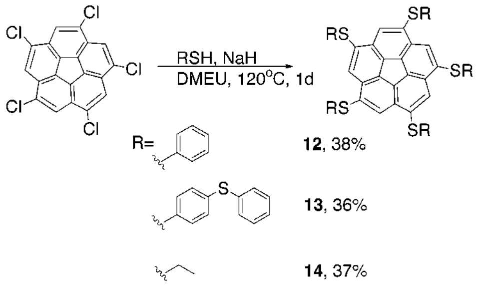
The above work demonstrated that sp^3 and sp^2 carbons could be installed selectively onto the corannulene rim in 5-fold symmetry. Synthesis of *sym*-pentakis-(trimethylsilyl-acetylene)corannulene (**11**) had been previously claimed by Scott and Cheng.[3] Independently, we have found that TMS acetylene in large excess can be coupled with **2** using the pincer catalyst of Eberhard et al.[9] to give **11** in good yield (Scheme 3). Thus, the milestone of converting **2** into pentasubstituted corannulenes with carbon substituents of sp, sp^2, and sp^3 hybridizations has been achieved.

Scheme 3



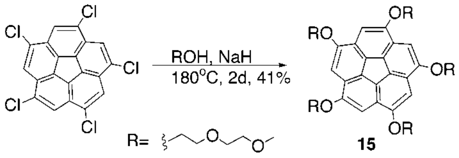
Direct nucleophilic aromatic substitution of chloro corannulenes is possible in the presence of good nucleophiles without the use of a catalyst.[10,11] We reported a series of such reactions on 2,3-dichlorocorannulene.[12] Scott and coworkers prepared *sym*-pentakis(4-methoxyphenylthio)-corannulene and *sym*-pentakis(2-naphthylthio)-corannulene from **2** and the respective thiolate in 1,3-dimethylimidazolin-2-one (DMEU) at ambient temperature for 2 days.[13] From our experience, the analogous reaction with sodium phenylthiolate to form *sym*-pentakis(thiophenyl)corannulene (**12**), or the more elaborate **13**, required a substantially elevated reaction temperature (120 °C) (Scheme 4). Analogously, treatment of **2** with sodium ethylthiolate in DMEU at 120 °C yielded *sym*-pentakis(1-thiapropyl)corannulene (**14**) in 37% yield.

Scheme 4



Nucleophilic substitution with alkoxides proved to be more challenging. Reaction of **2** with sodium diethyleneglycolate monomethyl ether in diethyleneglycol monomethyl ether required reaction temperatures of 180 °C for 2 days to prepare *sym*-pentakis(1,4,7-trioxaoctyl)corannulene (**15**) in 41% (Scheme 5).

Scheme 5



The high reaction temperature combined with the strength of the base/nucleophile raises the question of substitution

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(7) Seiders, T. J.; Baldridge, K. K.; Elliott, E.; Grube, G.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439−7440.

(8) (a) Negishi, E. *J. Org. Chem.* **1977**, *42*, 1821. (b) Negishi, E.; Takahashi, T.; King, A. O. *Org. Synth.* **1988**, *66*, 67.

(9) (a) Eberhard, M. R.; Wang, Z.; Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **2002**, 818−19. (b) Morales-Morales, D.; Grause, C.; Kasaok, K.; Redon, R.; Cramer, R. E.; Jensen, C. M. *Inorg. Chim. Acta* **2000**, *300*−*302*, 958−963.

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(11) (a) Tucker, J. H. R.; Gingras, M.; Brand, H.; Lehn, J.-M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1303−1307. (b) Mayor, M. Lehn, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 11231−11232.

(12) (a) Steffens, R.; Baldridge, K. K.; Siegel, J. S. *Helv. Chim. Acta* **2000**, *83*, 2644−2654. (b) Seiders, T. J.; Grube, G.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 517−25.

(13) Mizyed, S.; Georghiou, P. E.; Bancu, M.; Cuadra, B.; Rai, A. K.; Cheng, P.; Scott, L. T. *J. Am. Chem. Soc.* **2001**, *123*, 12770−12774.

via a Meisenheimer complex[14] versus an aryne intermediate. At first glance, it would seem that the high symmetry of the product (i.e., the regiospecificity of the reaction) would exclude the aryne mechanism; however, stabilization of the ortho anion, reminiscent of that seen in the Hart reaction,[15] could be a controlling factor. Specific evidence disfavoring the aryne mechanism comes from the regiospecific substitution of 2,3-dichlorocorannulene by sodium diethyleneglycolate monomethyl ether to give 2,3-bis(1,4,7-trioxaoctyl)-corannulene. An ortho anion-directed mechanism, analogous to the Hart reaction, would have predicted a mixture of 1,3- and 1,4-disubstituted products, but that is not seen. Therefore, it is a reasonable working hypothesis that the reaction mechanism proceeds through a Meisenheimer complex.

Properties. Simple alkyl derivatives of corannulene, **3**−**5**, display small red shifts of the $\pi-\pi^*$ absorption band in the UV−vis spectra of 9−10 nm, similar to that seen for alkyl substitution on benzene (Table 1). This red shift suggests a slight increase of the electron density in the aromatic system. Pentaphenylcorannulene, **6**, has a substantially larger red shift of 31 nm, which suggests conjugation between the corannulene nucleus and the phenyl substituents. As the steric size of the ortho substituent on the aryl group increases, it is likely that the aryl ring will twist out of conjugation. The decreasing red shift across the series (**9** < **8** < **10**) supports this hypothesis. A large red shift of the $\pi-\pi^*$ absorption of the polyether-substituted corannulene **15** correlates with the greater electron π-donating power of alkoxy over alkyl groups. The sulfur substituted corannulenes **12**−**14** each display a significant red shift in the $\pi-\pi^*$ absorption compared to corannulene, a classical effect of sulfur substitution.[16]

Table 1. UV−vis Absorption and Emission Data for **1**−**15**[a]

compd	absorption λ_{max}	emission λ_{max}	excitation λ
1[b]	251	421	247, 286
2	288		
3[b]	295	431	261, 297
4	297	431	262, 298
5	298	433	263, 299
6	319	447	286, 321
7	324	452	291, 326
8	308	440	273, 308
9	311	445	321
10	305	439	262, 310
11	337, 366_{sh}	474	337
12	349		
13	356	508	254, 296,357
14	337		
15	308	433	274

[a] Absorption/emission measurements in acetonitrile, wavelengths in nm. [b] See ref 3.

Emission spectra were recorded for a number of derivatives. The Stokes' shift across the series was about 130 nm. Thus, the emission wavelengths were reported primarily between 420 and 450 nm. One exception was the emission from **13**, which absorbed at a much longer wavelength and gave a correspondingly longer emission.

The bowl shape of corannulene and derivatives raises the possibility of a dynamic process in which the bowl inverts and thereby exchanges the concave and convex faces of the bowl. Previously we had demonstrated a structure−energy correlation for bowl inversion that allows us to put these results into the context of "normal" behavior for such systems.[12b] Compounds **4**, **10**, **14**, and **15** are useful for investigating the inversion barrier of the corannulene nucleus further by variable-temperature ^{1}H NMR.

In the case of **4**, **14**, and **15**, the enantiotopic methylene protons become diastereotopic below a certain temperature. Therefore, dynamic NMR methods could be used to assess the barriers to bowl inversion. By decoupling the protons adjacent to the methylene closest to the corannulene nucleus, a simple AB to AA′ coalescence analysis was possible.[17] The ethyl (**4**), ethylmercapto (**14**), and trioxaoctyl (**15**) substitutents gave rise to inversion barriers of 11.0, 10.5, and 11.5 kcal/mol, respectively.[18] The values for the inversion barriers of the alkyl, mercapto, and alkoxy compounds are consistent with the relative steric nature of a methylene group, a sulfur atom, and an oxygen atom.

In **10** we observe at room-temperature one singlet for each kind of proton, at 6.65 ppm for the phenyl ring proton and at 1.95 ppm for the *ortho*-methyl group. Below the coalescence temperature (T_c), we observe two singlets for each site, 6.53 and 6.69 ppm for the ring proton (T_c = 253 K) and 1.49 and 2.34 ppm for the *ortho*-methyl group (T_c = 268 K). From the coalescence temperature and the $\Delta\nu$, the inversion barrier of the molecule can be calculated, 12.1 kcal/mol in the case of the ring protons and 12.0 kcal/mol in the case of the *ortho*-methyl protons.[17,18] Thus, the inversion barrier of **10** is about 0.5 kcal/mol higher than the calculated barrier of 11.5 kcal/mol for **1**.[12b]

The high barrier to inversion for **10** is anomalous, on the basis of the relationship between bowl depth and barrier height, published previously;[12b] on the basis of that analysis, one would have expected a barrier around 9−10 kcal/mol. Density functional computations at the B3LYP/cc-pVDZ level of theory[19,20] were carried out and predicted a barrier to inversion of 8.5 kcal/mol, substantially lower than what was found experimentally. As reported in our earlier works, addition of dynamic correlation is essential for realistic prediction of barriers in this system, and thus MP2/cc-pVDZ//B3LYP/cc-pVDZ computations were also performed. These

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[14] Buncel, E.; Crampton, M. R.; Strauss, T. J.; Terrier, F. *Electron Deficient Aromatic and Heteroaromatic-Base Interactions*; Elsevier: New York, 1984.

[15] Vinod, T.; Hart, H. *J. Org. Chem.* **1990**, *55*, 881.

[16] Woodward−Fieser Rules would predict a red shift for substitutents in the order alkyl < alkoxy < mercapto = π-conjugation; see: Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Strucutral Spectroscopy*; Prentice Hall: Upper Saddle River, New Jersey, 1998; Chapter 11.

[17] Anet, F. A. L. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982, Chapter 7.

[18] In each of these experiments, temperature control is the single largest source of error, and as such, we estimate the error to be ±0.3 kcal/mol.

computations predicted a barrier of 14.6 kcal/mol, our most realistic assessment of the barrier.

One interpretation of this computational result is that the anomalous increase in barrier height is coming from van der Waals (vdW) attractive forces among the *endo* methyl groups in **10**. These attractive interactions are not present among the methyls of the *exo* face or the methyls in the transition state structure; therefore, breaking such "noncovalent" bonds would contribute to the higher barrier to inversion (Figure 1).

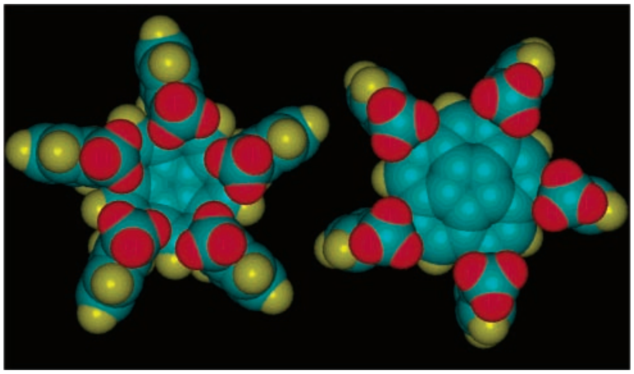

Figure 1. View of *endo* (left) and *exo* (right) faces of **10**. Methyl hydrogens are colored red for emphasis.

In an attempt to follow up the anomalous dynamic behavior of **10**, monomanisylcorannulene was prepared from manisyl zinc chloride and bromocorannulene.[21] At room temperature, the ^{1}H NMR spectrum displays only one *ortho*-methyl group and one *meta*-aryl hydrogen for the manisyl ring. Cooling to below 220 K gives rise to two *ortho*-methyl and two *meta*-aryl signals. From the coalescence temperature, the barrier to bowl inversion is calculated to be ca. 11.1 kcal/mol.[17,18] The lower barrier for the monomanisylcorannulene compared to the parent corannulene and **10** lends further support to the idea that there exists some cooperative interaction among the substitutents in **10**. It is our belief that the vdW attractive force provides the best basis to account for all the facts so far collected.

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Supporting Information Available: Detailed descriptions of experimental procedures and compound characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] Structural computations were performed using hybrid density functional methods (HDFT) using GUASSIAN98.[20a] The HDFT method employed Becke's three-parameter functional[20b] in combination with nonlocal correlation provided by the Lee−Yang−Parr expression[20c,d] that contains both local and nonlocal terms, B3LYP. Dunning's cc-pvdz (correlation consistent polarized valence double-ζ) basis set ([4s3p1d/3s2p1d/2s1p]) was used.[20e] Single-point energy computations were performed on optimized structures using MP2[20f] dynamic correlation treatment giving superior energetic barrier analysis. We have previously shown this combination of methods is very reliable for these compounds.[12b]

[20] (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett* **1989**, *157*, 200. (e) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (f) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622.

[21] Manisyl = 2,6-dimethyl-4-methoxyphenyl; see: Loren, J. C.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 754−57.