

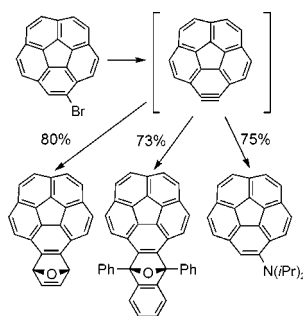
The First Buckybowl Aryne. Corannulyne: A Nonplanar Benzyne

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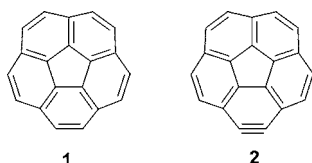
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ABSTRACT



Treatment of bromocorannulene with NaNH₂/tBuOK in THF in the presence of furans or amines leads to formation of addition products in good yields, presumably through formation of 1,2-didehydrocorannulene (corannulyne). HDFT calculations predict that corannulyne exists as a bowl-shaped entity and that the didehydrogenation energy of corannulene is slightly lower than that of benzene.

Bowl-shaped polycyclic aromatic hydrocarbons (buckybowls) represent a novel and fascinating class of compounds, and the development of practical, gram-scale synthetic methods has allowed for systematic studies of their chemistry.¹ Several derivatives of the smallest buckybowl, corannulene **1**, have recently been synthesized.² However, it is the use of readily available buckybowl, like corannulene, as precursors for the synthesis of larger buckybowl that holds enormous potential for advances in this field.



An especially attractive possibility would be the aryne **2** derived from corannulene, since it would open a number of synthetic possibilities. Consequently, our success with the high-yield synthesis of dimethyl 1,2-corannulenedicarboxylate (**3**)³ led us to pursue the formation of corannulyne by the well-known anthranilic acid route;⁴ that is, conversion

of **3** to the imide **4** followed by either Hoffman or Curtius-type rearrangement to the corresponding amino acid **5** (Scheme 1). Of course, **5** should serve as a precursor for corannulyne **2** by diazotization followed by thermal decomposition to the benzyne.⁴ However, despite numerous attempts we failed to find a synthetically useful procedure for

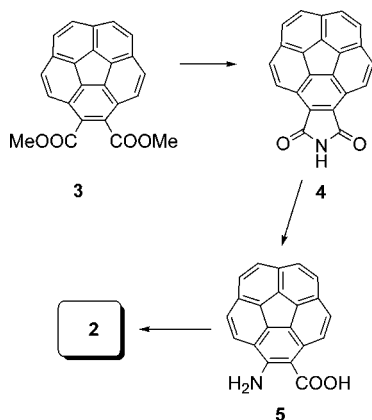
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Scheme 1

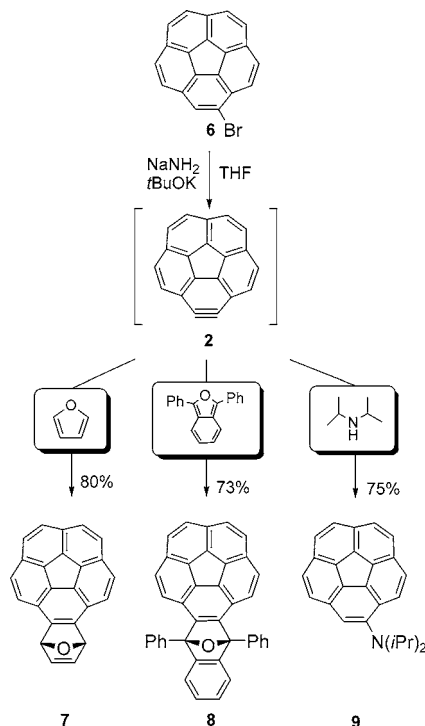


the conversion of **4** to **5**. Therefore, we turned our attention to alternative methods of benzyne generation starting with other derivatives of corannulene.

The ortho-deprotonation of monohalogenated aromatics has been known to successfully generate benzyne.⁴ And while fluoroaromatics are usually employed for this purpose, there have been recent examples of benzyne generation from monobrominated aromatic systems.⁵ Since bromocorannulene **6** is now easily accessible by the bromination of corannulene,⁶ it became a reasonable candidate for the generation of **2**. While preliminary attempts employing *n*BuLi as a base failed, we learned that treatment of **6** with an excess of sodium amide and a catalytic amount of potassium *tert*-butoxide in THF at room temperature leads to the expected corannulyne, as evidenced by the isolation of trapping products in good yields (Scheme 2).⁷ For example, in the presence of excess furan this procedure gives the Diels–Alder adduct **7**⁸ in 80% yield along with traces of corannulene and benzocorannulene. Similarly, generation of corannulyne in the presence of 3 equiv of diphenylisobenzofuran produces adduct **8**⁹ in 73% yield.

Since nucleophilic addition to benzyne constitutes a large part of their chemistry, we examined the behavior of **2** in the presence of excess of diisopropylamine and found the

Scheme 2



expected *N,N*-diisopropylaminocorannulene **9**¹⁰ to be formed in ca. 75% yield.

The above examples illustrate that base-induced generation of corannulyne **2** represents a promising route for the synthesis of novel derivatives of corannulene. Cycloaddition reactions of **2** with various dienes are of special interest since they could lead to efficient syntheses of large PAH systems with embedded corannulene subunit(s). Diels–Alder adducts such as **7** and **8** are useful as intermediates in syntheses of PAHs since the endoxone bridge can be readily cleaved.⁴ For example, we quantitatively converted **7** into known benzocorannulene¹¹ by refluxing it with $\text{Fe}_2(\text{CO})_9$ in benzene.

Computational studies¹² give a deeper insight into the nature of corannulyne. Similarly to the parent **1**, **2** exists in a bowl-shaped conformation (Figure 1). The average distance of the 10 rim carbon atoms from the plane of the central five-membered ring (bowl depth) in **2** is calculated as 0.84

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(7) **General Procedure.** To a solution of 33 mg of **6** (0.1 mmol) in 2–3 mL of dry THF with the appropriate trapping agent was added in one portion ca. 80 mg of NaNH_2 and ca. 4 mg of *t*BuOK. The reaction mixture was stirred at rt under argon until starting material is no longer detectable by TLC. Methanol was added to quench the reaction, and the products were extracted with benzene, washed well with water and chromatographed on silica gel.

(8) **7**: oily yellow solid; ^1H NMR (600 MHz, CDCl_3) δ 6.32 (2H, s), 7.11 (2H, bs), 7.62–7.81 (8H, two overlapping AB systems); ^{13}C NMR (75 MHz, CDCl_3) δ 81.62, 123.59, 127.21, 127.23, 127.33, 127.65, 130.58, 131.09, 134.37, 134.92, 136.01, 144.06, 150.55. MS m/z (rel intensity) 317 (23), 316 (100), 288 (22), 287 (73), 207 (42); HRMS (EI, 25 eV) calcd for $\text{C}_{24}\text{H}_{20}\text{O}$ 316.0888, found 316.0886.

(9) **8**: yellow solid (from EtOH); dec gradually over 190 °C; ^1H NMR (600 MHz, CDCl_3) δ 6.07 (2H, m), 7.20 (2H, m), 7.39 (2H, d, J = 8.9 Hz), 7.56–7.72 (12H, m), 8.38 (4H, d, J = 7.2 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 93.27, 121.85, 124.32, 125.20, 127.28, 127.47, 128.86, 129.10, 130.00, 130.83, 131.02, 134.50, 134.95, 135.54, 136.11, 151.28, 152.43; MS m/z (rel intensity) 519 (26), 518 (69), 502 (41), 441 (51), 413 (51), 411 (39), 231 (30), 230 (23), 117 (100); HRMS (EI, 25 eV) calcd for $\text{C}_{40}\text{H}_{22}\text{O}$ 518.1671, found 518.1666.

(10) **9**: yellow solid (from EtOH); mp 149 °C; ^1H NMR (600 MHz, CDCl_3) δ 1.20 (12H, d, J = 6.4 Hz), 3.95 (2H, m), 7.47 (1H, s), 7.73 (1H, d, J = 8.6 Hz), 7.76–7.84 (6H, m), 8.08 (1H, d, J = 8.8 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 22.10, 50.50, 121.29, 126.50, 126.60, 127.07, 127.11, 127.14, 127.16, 130.29, 130.93, 131.01, 131.55, 133.30, 135.48, 135.89, 136.27, 136.34, 136.54, 147.69; MS m/z (rel intensity) 349 (36), 335 (21), 334 (100), 292 (77), 264 (24), 250 (25), 249 (26); HRMS (EI, 25 eV) calcd for $\text{C}_{26}\text{H}_{23}\text{N}$ 349.1830, found 349.1832.

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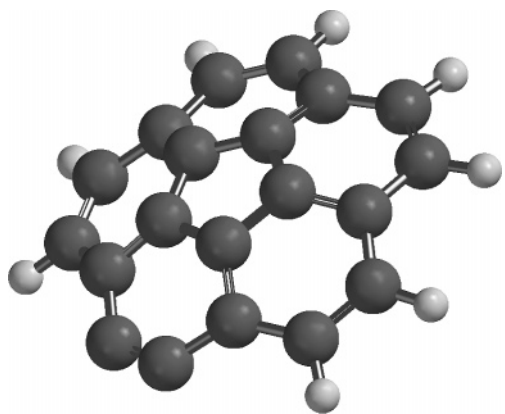


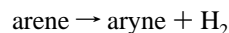
Figure 1. Becke3LYP/6-31G(d)-optimized structure of corannulyne **2**.

Å at the Becke3LYP/6-31G(d) level of theory,¹³ very close to 0.86 Å calculated for corannulene. The calculated triple CC bond length is 1.247 Å, slightly shorter than the analogous bond length in benzyne (1.251 Å). The bowl-shaped structure of **2** is indeed a minimum energy conformation as demonstrated by all positive molecular vibrations. The calculated frequency associated with the stretching of the triple CC bond in **2** is 2000–2010 cm⁻¹, depending on the basis set used.

The calculated energy differences between the bowl-shaped **2** with *C_s* symmetry and its planar *C_{2v}* conformer representing a Transition State for the bowl-to-bowl inversion gives an estimation of its inversion barrier. At the highest level of theory applied here (Becke3LYP/6-311G-(d,p)) the difference is 9.8 kcal/mol, again very similar to the calculated and experimental inversion barrier for parent

corannulene. Therefore we conclude that corannulyne **2** represents a first example of an aryne with a bowl-shaped minimum energy structure (a buckybowl aryne).

To assess the relative stability of corannulyne as compared to benzyne, we calculated the 1,2-didehydrogenation energies, i.e., the energies of the formal process



Since the process is not isodesmic, accurate inclusion of electron correlation effects as well as zero point energies (ZPE) is necessary to obtain reliable predictions. Results of benchmark calculations on benzyne at various levels of theory performed earlier¹⁴ show that HDFT calculations give dehydrogenation energies in good agreement with both the experimental estimate of ca. 87 kcal/mol¹⁵ as well as with high quality calculations such as MP2 and CCSD(T). Our calculations at the Becke3LYP/6-311G(d) level give an energy of 88.9 kcal/mol for the dehydrogenation of benzene and 85.9 kcal/mol for 1,2-didehydrogenation of corannulene. Therefore, considering the very similar dehydrogenation energies, we conclude that the stability of **2** should be similar to the stability of benzyne itself.¹⁶

In conclusion, we show that treatment of bromocorannulene with strong bases in the presence of trapping agents leads to the formation of adducts with good yields, presumably through formation of 1,2-dehydrocorannulene (corannulyne). The procedure offers new possibilities for syntheses of large PAH systems with the bowl-shaped corannulene unit. HDFT calculations predict that corannulyne **2** retains the bowl shape of parent corannulene, which makes it the first reported buckybowl aryne. Its relative stability should be similar to the stability of benzyne as demonstrated by similar dehydrogenation energies calculated for the two arene to aryne conversions.

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(12) (a) Hybrid density functional theory (HDFT) calculations were performed at the Becke3LYP level, i.e. Becke's three-parameter hybrid exchange functional in combination with the Lee–Yang–Parr nonlocal correlation functional.^{12b} Various basis sets were employed, including 6-31G(d), 6-31G(d,p), 6-311G(d), and 6-311G(d,p). The calculations were done using Gaussian 03^{12c} and Spartan'04^{12d} program suites. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (c) Gaussian 03, Revision B.03: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, **2003** (d) Spartan'04; Wavefunction, Inc.; Irvine, CA.

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(16) Following the reviewer's suggestion we calculated the energy of the isodesmic process: corannulyne + benzene → corannulene + benzyne. At the Becke3LYP/6-311G(d) level of theory, this process is slightly endothermic (+3 kcal/mol), again indicating that corannulyne is only slightly more stable than benzyne.