

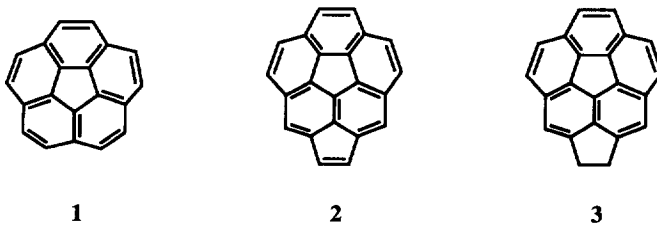
Synthesis of a New C₃₂H₁₂ Bowl-Shaped Aromatic Hydrocarbon

Mark D. Clayton and Peter W. Rabideau*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

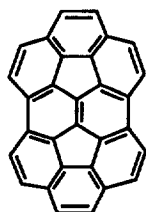
Abstract: 7,10-Bis(2-bromophenyl)benzo[k]fluoranthene undergoes pyrolysis to afford a number of polynuclear aromatics including a new bowl-shaped C₃₂H₁₂ hydrocarbon having a carbon framework that can be identified on the buckminsterfullerene surface. © 1997, Elsevier Science Ltd. All rights reserved.

The discovery of C₆₀ and the other fullerenes has led to considerable interest in polynuclear aromatic hydrocarbons that have carbon frameworks corresponding to some portion of the buckminsterfullerene surface.¹ The simplest example is corannulene (**1**), corresponding to the polar cap of buckminsterfullerene, and **1** stood as the only such hydrocarbon known for many years since its original synthesis by Barth and Lawton in 1966.² The development of a new synthesis of **1** by Scott, et al.³ led to the discovery that the bowl conformation of corannulene is not fixed, and bowl-to-bowl inversion takes place as a relatively low energy process with a barrier of ca. 10-11 kcal/mol. Our synthesis of **2** represented the first buckminsterfullerene

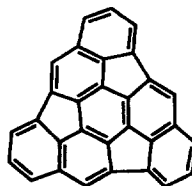


related, bowl-shaped aromatic hydrocarbon, or "buckybowl," beyond corannulene on the C₆₀ surface.⁴ Subsequent hydrogenation to **3** confirmed that the addition of a second five-membered ring adds both considerable curvature and resistance to bowl-to-bowl inversion. The barrier for **3** was determined to be in excess of 27 kcal/mol.⁵

More recently, we have used variations of the Scott pyrolytic method to synthesize the first semibuckminsterfullerenes, **4**⁶ and **5**,⁷ that represent half of the buckminsterfullerene carbon framework. Semibuckminsterfullerene **5** had been sought after for some time because of its potential for dimerization to C₆₀H₂₄ with loss of hydrogen leading to an overall organic synthesis of buckminsterfullerene itself.⁸

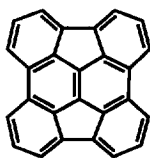
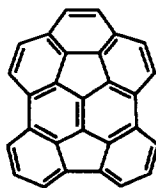
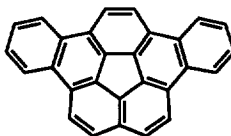
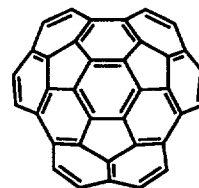


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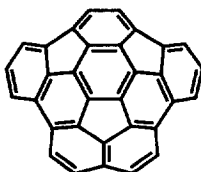
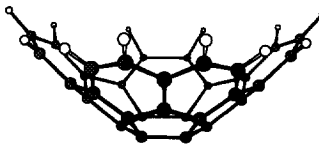


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A number of other buckminsterfullerene-related, bowl-shaped hydrocarbons have appeared, **6**,^{1e} **7**,⁹ **8**,^{1e} and very recently the previous limit of 30 carbons was exceeded for the first time with the synthesis of **9**.¹⁰

6; C₂₆H₁₂7; C₂₈H₁₂8; C₂₈H₁₄9; C₃₆H₁₂

Herein we report the synthesis of the second “buckybowl” possessing more than 30 carbons: the C₃₂H₁₂ hydrocarbon **10**.

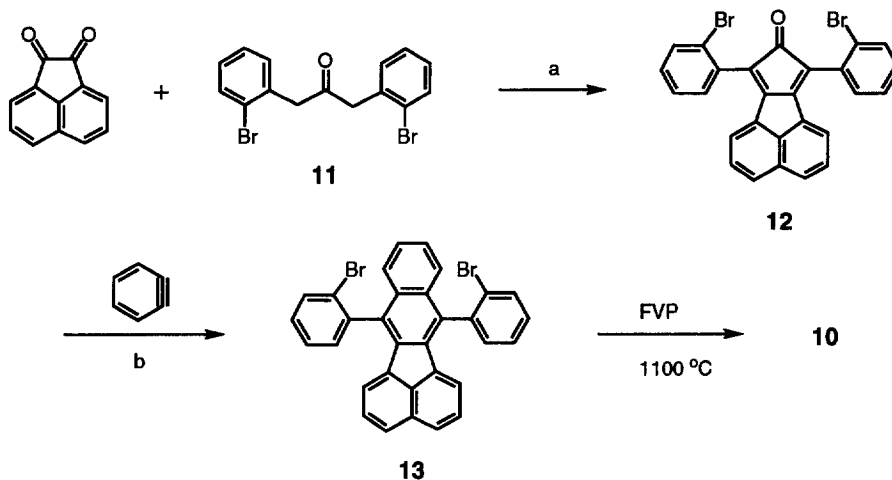
10; C₃₂H₁₂

MM Calc Structure

As outlined in Scheme 1, acenaphthaquinone was condensed with **11**¹¹ using one equivalent of sodium hydroxide in 150 mL methanol to give **12** in 96% yield.¹² Ketone **12** was then reacted with benzyne formed in situ from two equivalents of anthranilic acid and isoamyl nitrite respectively, to give **13** in 77% yield.¹³ Flash Vacuum Pyrolysis of **13** at 1100 °C (5.1 g in ca. 200 mg portions) gave 187 mg of crude material after removal of the insoluble component. Chromatography over silica gel using cyclohexane as an eluent gave three main fractions. The first fraction, after washing with ethanol, yielded 5 mg of **10**.¹⁴ The identification of **10** was straight forward since no other hydrocarbon of mass 396 has its symmetry. ¹H NMR showed the expected AB quartet, a singlet, two doublets and a doublet of doublets. ¹³C NMR showed six methine carbons although due to solubility, only 9 of the 11 quaternary signals were observed even after 3 days of accumulation. The second fraction yielded 70.7 mg which, after recrystallization from toluene, gave a mixture of two hydrocarbons with a

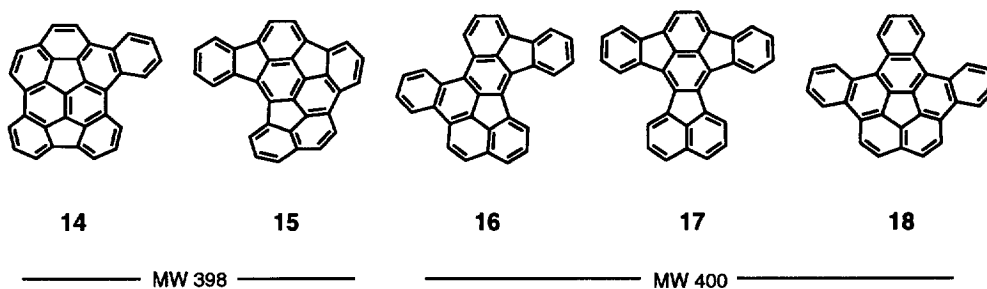
molecular weight of 398. The third fraction gave 65.5 mg which was recrystallized from toluene to give 27 mg of a mixture of hydrocarbons with molecular weight 400.

Scheme 1



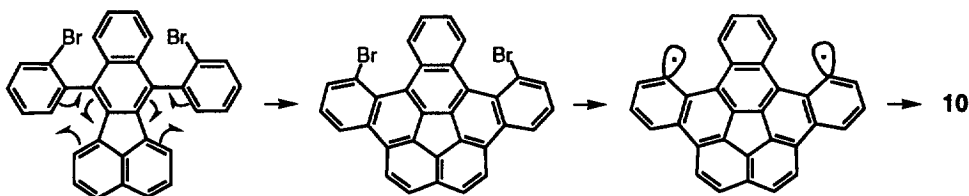
a. NaOH/MeOH, 25 °C, overnight; 96%. b. Anthranilic acid, isoamyl nitrite, DCM/acetone, reflux 24 h; 77%.

Until such time that they can be isolated and characterized, we can only speculate about the identity of the other hydrocarbons formed in the pyrolysis reaction. However, the logical products are **14** and **15** at molecular weight 398, and **16-18** at a molecular weight of 400. Efforts are underway to separate the respective isomers, although this does not appear to be possible by simple silica gel chromatography.



The likely mechanism for the formation of **10** from **11** is cyclodehydrogenation to form two sets of rings, and loss of bromine to produce aryl radicals resulting in formation of the second set of rings. Since cyclodehydrogenation would seem more likely for six-membered ring formation, we suggest the path shown in Scheme 2. Of course the order of reactions, cyclodehydrogenation vs. loss of bromine, cannot be discerned.

Scheme 2



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- Dark blue solid, mp 238-239 °C. ^1H NMR (250 MHz), δ 7.88 (d, $J = 7.2$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.44 (m, 10H); ^{13}C NMR (2 rotational isomers), δ 199.65, 155.99, 155.80, 145.28, 133.54, 133.49, 133.02, 132.97, 132.29, 131.95, 131.82, 131.40, 130.01, 128.63, 128.05, 127.41, 124.26, 124.11, 123.44, 123.17, 121.97, 121.79. MS (m/e , rel intensity): 162(100), 324(40), 435(37), 433(37), 326(34), 216(20), 217(19), 514(19). Anal. Calcd for $\text{C}_{27}\text{H}_{14}\text{Br}_2\text{O}$: C, 63.07; H, 2.74. Found: C, 62.84; H, 2.65.
- Yellow solid, mp 300-301 °C. ^1H NMR (300 MHz), δ 7.95 (d, $J = 7.8$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.56 (m, 12 H), 6.60 (d, $J = 7.1$ Hz, 2H); ^{13}C (NMR 250 MHz), δ 139.76, 136.52, 135.76, 135.19, 134.06, 133.64, 132.27, 131.97, 130.45, 130.05, 128.51, 128.30, 126.56, 126.42, 124.81, 121.93. MS (m/e , rel intensity): 199(100), 400(31), 562(31). Anal. Calcd. for $\text{C}_{32}\text{H}_{18}\text{Br}_2$: C, 68.35; H, 3.23. Found: C, 68.05; H, 3.55.
- Orange solid, softens with increased darkening above 300 °C. ^1H NMR (400 MHz, acetone- d_6), δ 8.21 (d; $J = 9.1$ Hz, 2H), 8.11 (d; $J = 8.3$ Hz, 2H), 7.75 (d; $J = 9.1$ Hz, 2H), 7.51 (d; $J = 7.2$, 2H), 7.44 (s; 2H), 7.38 (dd; $J = 7.2$, 8.3); ^{13}C NMR (300 MHz), 152.45, 150.34, 149.08, 141.48, 140.92, 140.56, 138.53, 134.18, 133.57, 128.87, 127.50, 126.92, 126.23, 125.85, 123.54, 119.61. HRMS required 396.0939. Found 396.0930.

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