Synthesis and Characterization of a $C_{36}H_{12}$ Fullerene Subunit

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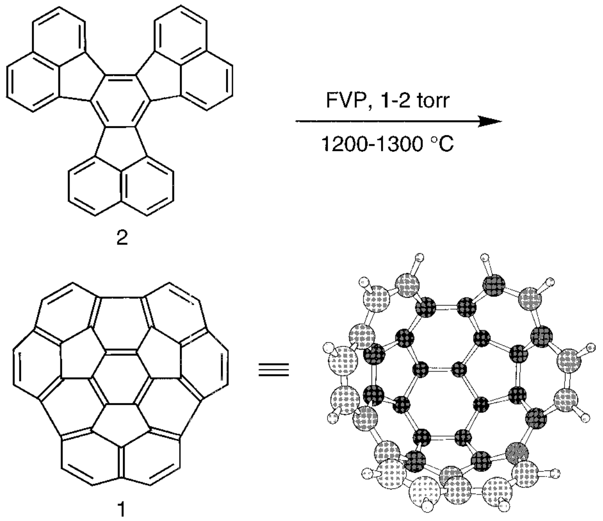
Curved polycyclic aromatic hydrocarbons (PAH) composed of five- and six-membered rings organized in the same arrangement as those found on the surface of a fullerene have attracted considerable attention since the first isolation of C_{60} in 1990.[1,2] Corannulene ($C_{20}H_{10}$)[3] stands out as both the oldest and the smallest member of this family of bowl-shaped PAH, but larger representatives have begun to appear in recent years, i.e., cyclopentacorannulene ($C_{22}H_{10}$),[4] benzocorannulene ($C_{24}H_{14}$),[5] diindenochrysene ($C_{26}H_{12}$),[6] dibenzo[*a,g*]corannulene ($C_{28}H_{14}$),[7] two isomeric $C_{30}H_{12}$ "buckybowls," [8] and cyclopenta[*kl*]dibenzo[*a,g*]corannulene ($C_{30}H_{14}$).[5] We are now pleased to report the first synthesis and characterization of a fullerene fragment comprising 60% of the C_{60} ball: triacenaphthotriphenylene, **1** ($C_{36}H_{12}$).[9] A most gratifying aspect of this work is that this new fullerene fragment can be prepared in just one step by flash vacuum pyrolysis (FVP) of "decacyclene," **2**, a compound that has been known to chemists for more than 100 years[10] and is commercially available today in kilogram quantities.[11]



Our first attempts to effect cyclodehydrogenation of **2** to **1** under ordinary FVP conditions at 1100 °C a number of years ago invariably gave unchanged decacyclene back as the only recoverable monomeric material, and other investigators have independently experienced the same disappointment. Higher temperatures (1200−1300 °C) and a better method for introducing samples of low volatility, however, ultimately proved to be the key to success. Although the yield in this uncatalyzed thermal cyclodehydrogenation still leaves much room for improvement (0.2%), it can be conveniently performed on a 5.0 g scale to give 10 mg of purified **1** in a single 5 h run.[12] By good fortune, the basket-shaped **1** (a triple corannulene) travels faster on chromatography[12] than any of the other components in the pyrolysate and can be isolated as a pale yellow solid (mp > 300 °C) from the early fractions off the column.[13] Unlike most large planar PAH, triacenaphthotriphenylene (**1**) exhibits exceptionally good solubility in common organic solvents. It is also stable under ordinary laboratory conditions and, like C_{60}, can be handled without difficulty in the light and air.

In agreement with the assigned structure, the ^1H NMR spectrum of **1** consists of just two doublets in the "aromatic region:" (400 MHz, $CDCl_3$) δ 7.58 (d, 6H, $J = 9.1$ Hz), 7.20 (d, 6H, $J = 9.1$ Hz), and the ^{13}C NMR spectrum shows the expected seven lines: (100 MHz, $CDCl_3$) δ 152.2, 139.4, 136.8, 135.1, 127.2, 126.8, 125.4. The strong ^{13}C NMR signals at 127.2 and 125.4 ppm were identified as the two associated with the methine carbon atoms by an NMR Attached Proton Test.

The mass spectrum of **1** is characterized by a dominant molecular ion ($M^+ =$ base peak), little fragmentation, and a prominent doubly charged molecular ion;[14] a high resolution mass measurement on the molecular ion confirmed the molecular formula as $C_{36}H_{12}$.[14] The UV absorption spectrum of **1** bears a striking resemblance to that of C_{60} (Figure 1).[14] As the

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(1) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−8.

(2) For recent reviews on bowl-shaped fullerene subunits, see: Siegel, J. S.; Seiders, T. J. *Chem. Britain* **1995**, 313−6. Faust, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1429−32. Rabideau, P. W.; Sygula, A. *Adv. Theor. Interesting Mol* **1995**, *3*, 1−36. Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−42.

(3) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380−1. Lawton, R. G.; Barth, W. E. *J. Am. Chem. Soc.* **1971**, *93*, 1730−45. Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082−4. Scott, L. T.; Cheng, P.-C.; Bratcher, M. S. *Seventh International Symposium on Novel Aromatic Compounds*, abstr. no. 64, Victoria, British Columbia, Canada, July 19−24, 1992. Cheng, P.-C. M. S. thesis, University of Nevada, Reno, 1992. Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921−3. Zimmermann, G.; Nuechter, U.; Hagen, S.; Nuechter, M. *Tetrahedron Lett.* **1994**, *35*, 4747−50.

(4) Cyclopenta[*bc*]corannulene: Abdourazak, A. H.; Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1993**, *115*, 3010−11. Sygula, A.; Abdourazak, A. H.; Rabideau, P. W. *J. Am. Chem. Soc.* **1996**, *118*, 339−43. Cheng, P.-C. Ph.D. Dissertation, Boston College, 1996.

(5) Benzocorannulene and cyclopenta[*kl*]dibenzo[*a,g*]corannulene: Scott, L. T.; McComas, C. C. results presented at the *National Meeting of the American Chemical Society*, New Orleans, LA, March, 1996. McComas, C. C. B.S. Thesis, Boston College, 1996.

(6) Diindeno[1,2,3,4-defg; 1′,2′,3′,4′-mnop]chrysene: Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycyclic Arom. Comp.* **1995**, *4*, 209−17. Scott, L. T.; Choi, N.; Bronstein, H. Unpublished results.

(7) Dibenzo[*a,g*]corannulene: Scott, L. T.; Bratcher, M. S. results presented at the *National Meeting of the American Chemical Society*, San Diego, CA, March, 1994. Bratcher, M. S. Ph.D. Dissertation, Boston College, 1996.

(8) Rabideau, P. W.; Abdourazak, A. H.; Folsom, H. *J. Am. Chem. Soc.* **1994**, *116*, 7891−2. Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **1995**, *117*, 6410−11.

(9) The complete name for **1** is triacenaphtho[3,2,1,8-c,d,e,f,g; 3′,2′,1′,8′-i,j,k,l,m; 3″,2″,1″,8″-o,pq,r,a]triphenylene.

(10) Rehländer, P. Ph.D. dissertation, University of Berlin, 1893, cited by Rehländer, P. *Chem. Ber.* **1903**, *36*, 1583−7. Dziewonski, K. *Chem. Ber.* **1903**, *36*, 962−71. Ho, D. M.; Pascal, R. A. *Chem. Mater.* **1993**, *5*, 1358−61.

(11) Decacyclene is currently available for $120.85/500 g from Aldrich Chemical Co., Milwaukee, WI.

(12) The pyrolysis apparatus used in these experiments consists of an unpacked horizontal quartz tube (28 mm I. D.) heated in a single zone electric furnace (Lindberg model 54233; hot zone length 55 cm) and connected to a vertical product trap cooled with liquid nitrogen. A carrier gas inlet head was constructed to admit a steady flow of nitrogen through a 15 cm length of capillary glass tubing (0.32 mm I. D.) from a reservoir maintained at 1 atm by means of a bubbler. With mechanical pumping downstream from the product trap (Precision Vac Torr 150 Model 69151) and the nitrogen leaking in, an operating pressure of 1−2 Torr was measured during pyrolysis runs. In a typical pyrolysis, 5.0 g of decacyclene was distributed over a bed of quartz chips inside the quartz pyrolysis tube about 7 cm back from the hot zone. The section of tube containing the sample was wrapped with heating tape that was connected to a variable AC controller. When the sample was heated to ca. 300 °C with the pump on and the carrier gas flowing, products began to appear in the trap. The time required for a typical pyrolysis was ca. 5 h. The crude pyrolysate was dissolved in CH_2Cl_2 and chromatographed on alumina with hexane/benzene (8:1) to give 10 mg (0.2%) of the $C_{36}H_{12}$ bowl (1) and 16 mg (0.3%) of the $C_{36}H_{14}$ product of double ring closure (3) eluting in that order.

(13) The high mobility of bowl-shaped polycyclic aromatic hydrocarbons on alumina chromatography, relative to that of planar PAH of comparable size, has previously been noted: Hagen, S.; Christoph, H.; Zimmermann, G. *Tetrahedron* **1995**, *51*, 6961−70. Similar behavior on reverse phase HPLC has likewise been reported: Sander, L. C.; Wise, S. A. *J. Chromatogr.* **1993**, *97*, 13539−43. Fetzer, J. C.; Biggs, W. R.; Jinno, K. *Chromatogr.* **1986**, *21*, 439−42.

S0002-7863(96)02151-8 CCC: $12.00

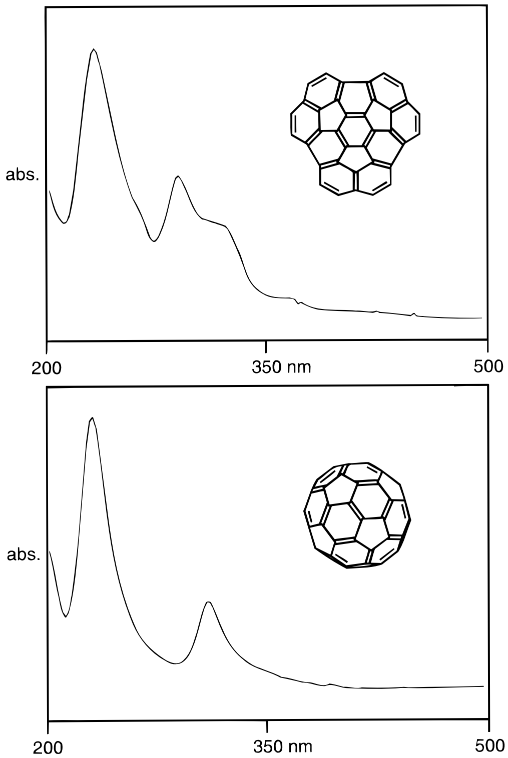

Figure 1. UV−vis absorption spectra of triacenaphthotriphenylene (**1**) and C_{60}.

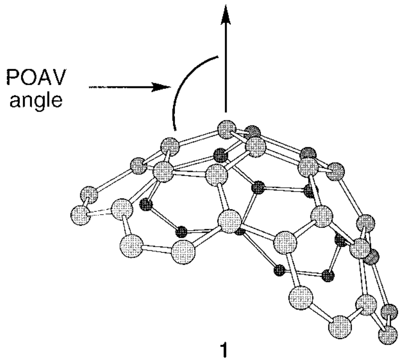

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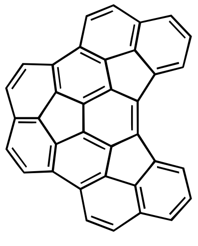
Figure 2. The p-orbital axis vector (POAV) angle[16] at the most pyramidalized carbon atoms of triacenaphthotriphenylene (**1**) is calculated[15] to be 102.42° (PM3), 102.43° (AM1), and 102.37° (MNDO); cf. 101.64° for C_{60} (by symmetry).

network of rings increases from corannulene ($C_{20}H_{10}$) to **1** ($C_{36}H_{12}$), fullerene fragments appear to take on more and more of the electronic character of C_{60}.

We have not yet obtained X-ray quality crystals of **1**, but theoretical calculations by several of the common semiempirical methods[15] all point to a structure with steep curvature. Analysis of these energy-minimized structures by the p-orbital axis vector (POAV) method[16] reveals a predicted degree of pyramidalization at the six central carbon atoms in **1** that actually exceeds that of the carbon atoms in C_{60} by a small amount (Figure 2). Experiments have been initiated to look for fullerene-like chemical reactivity at the highly-strained interior carbon atoms of **1**.

Other products formed in the FVP of decacyclene at 1200−1300 °C include the doubly closed $C_{36}H_{14}$ hydrocarbon **3**, the singly closed $C_{36}H_{16}$ hydrocarbon **4**, and a trace of C_{60}. The doubly closed compound also moves fast on chromatography and can be isolated from the second fraction. It is obtained in slightly higher yield than **1** at these temperatures and has been characterized so far only by ^{1}H NMR, UV−vis, and low and high resolution mass spectroscopy.[17] The singly closed compound (**4**) travels more slowly on chromatography and cannot be separated from the large amount of unchanged decacyclene and other products, but it has been positively identified in the mixture by comparison of its HPLC-UV properties with those of a sample prepared by an independent method.[18]



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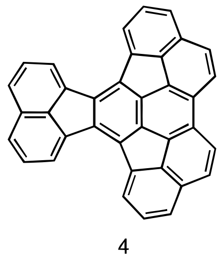

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With authentic samples of decacyclene (**2**) and the products of one, two, and three ring closures (**4**, **3**, and **1**, respectively) all available, we reexamined the FVP of decacyclene at 1100 °C using the nitrogen carrier gas method at 1−2 Torr but still detected no more than a faint trace of the triply closed bowl (**1**); hydrocarbons **2**, **3**, and **4** were obtained in a ratio of approximately 15:1:6, along with other products that remain to be characterized. Thus, it seems that the energy required to effect 3-fold cyclodehydrogenation of decacyclene simply is not available under FVP conditions at 1100 °C.

We believe that the high temperature chemistry described here bears an important relationship to that operating in fuel-rich flames wherein fullerene production has been observed.[19] Novel chemical transformations of several other polycyclic aromatic hydrocarbons at temperatures in the 1200−1300 °C range have also been uncovered and will be reported shortly.

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(14) Compound **1**: Mass spec (70 eV): *m/z* (rel abundance) 445 (37, M + 1), 444 (100, M^+), 443 (10), 442(15), 222.5 (10), 222 (28, M^{++}), 221 (15). HRMS calcd for $C_{36}H_{12}$: 444.0939, found: 444.0938. UV: (CH_3CN) λ_{max} (ϵ): 368 (sh, 4000), 322 (sh, 16 000), 290.5 (25 000), 232.5 (37 000).

(15) Semiempirical molecular orbital calculations were performed using the Spartan program, version 4.0 from Wavefunction, Inc., Irvine CA.

(16) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137−42. Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385−9. We thank Dr. Haddon for kindly supplying a copy of the POAV program.

(17) Hydrocarbon **3**: pale yellow solid, mp > 300 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.01 (d, 2H, $J = 8.9$ Hz), 7.97 (d, 2H, $J = 7.1$ Hz), 7.78 (d, 2H, $J = 9.0$ Hz), 7.64 (d, 2H, $J = 8.9$ Hz), 7.62 (d, 2H, $J = 7.9$ Hz), 7.45 (d, 2H, $J = 9.0$ Hz), 7.43 (dd, 2H, $J = 7.9$ and 7.1 Hz). HRMS: M+ calcd for $C_{36}H_{14}$: 446.1096, found: 446.1098. UV−vis (CH_3CN) λ_{max} (ϵ): 460 (sh, 2100), 387 (11 100), 373 (11 500), 359 (11 100), 323 (59 100), 242 (sh 57 000), 228 (60 500).

(18) An authentic sample of hydrocarbon **4** was prepared by catalytic cyclodehydrogenation of 0.5 g of **2** with 1 g of 5% Pd on charcoal (450−480 °C, 3 h). The products were extracted with *o*-dichlorobenzene to give a solution from which 123 mg of unreacted **2** was removed by crystallization. The solvent of the mother liquor was evaporated under reduced pressure, and the resulting solid was subjected to column chromatography on alumina with hexane/toluene (gradient) as eluant. The target compound (**4**) was dominant in the early fractions, which gave a total yield of 4.3%, in addition to more unchanged **2**. Recrystallization from chloroform gave an analytically pure sample of **4** as a sparingly soluble red solid: mp > 340 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, $J = 7.0$ Hz, 2H), 8.21 (d, $J = 8.7$ Hz, 2H), 8.19 (d, $J = 7.0$ Hz, 2H), 7.95 (d, $J = 7.9$ Hz, 2H), 7.86 (d, $J = 8.7$ Hz, 2H), 7.83 (dd, $J = 7.0$ Hz and 8.2 Hz, 2H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 7.0$ Hz and 8.1 Hz, 2H). Mass spec (70 eV): *m/z* (rel abundance) 449 (39, M + 1), 448 (100, M^+), 447 (14), 446 (30), 224.5 (20), 224 (49, M^{++}), 223 (31) 222 (19). HRMS: M^+ calcd for $C_{36}H_{16}$: 448.1252, found: 448.1255. UV−vis (CH_2Cl_2) λ_{max} (ϵ): 497 (8800), 464 (7200), 390 (29 600), 377 (27 000), 358 (29 300, sh), 343 (47 900), 329 (38 200, sh), 286 (97 900), 238 nm (76 400, sh).

(19) Gerhardt, Ph.; Löffler, S.; Homann, K.-H. *Chem. Phys. Lett.* **1988**, *88*, 1588. Howard, J. B.; Lafleur, A. L.; Makarovsky, Y.; Mitra, S.; Pope, C. J.; Yadav, T. K. *Carbon* **1992**, *30*, 1183−201. Pope, C. J.; Marr, J. A.; Howard, J. B. *J. Phys. Chem.* **1993**, *97*, 11001−13. Ahrens, J.; Bachmann, M.; Baum, Th.; Griesheimer, J.; Kovacs, R.; Weilmünster, P.; Homann, K.-H. *Internat. J. Mass Spectr. Ion Proc.* **1994**, *138*, 133−48 and references cited therein.