limited, we hope that this framework can stimulate investigations on the deep connection between condensed-matter and elementary particle physics.

References and Notes

1. P. W. Anderson, *Basic Notations of Condensed Matter Physics* (Addison-Wesley, Menlo Park, CA, 1997).
2. H. Bethe, *Z. Phys.* **71**, 205 (1931).
3. R. Laughlin, *Phys. Rev. Lett.* **50**, 1395 (1983).
4. R. Prange, S. Girvin, *The Quantum Hall Effect* (Springer Verlag, Berlin, Germany, 1990).
5. S. C. Zhang, *Int. J. Mod. Phys.* **B6**, 25 (1992) and references therein.
6. E. Witten, *Comm. Math. Phys.* **117**, 353 (1988).
7. B. Halperin, *Phys. Rev. B* **25**, 2185 (1982).
8. X. Wen, *Phys. Rev. Lett.* **64**, 2206 (1990).
9. M. Stone, *Phys. Rev. B* **42**, 8399 (1990).
10. F. D. M. Haldane, *Phys. Rev. Lett.* **51**, 605 (1983).
11. E. Demler, S. C. Zhang, *Ann. Phy.* **271**, 83 (1999) and references therein.
12. C. N. Yang, *J. Math. Phys.* **19**, 320 (1978).
13. R. Jackiw, C. Rebbi, *Phys. Rev. D* **14**, 517 (1976).
14. A. Belavin, A. Polyakov, A. Schwartz, Y. Tyupkin, *Phys. Lett. B* **59**, 85 (1975).
15. C. N. Yang, *J. Math. Phys.* **19**, 2622 (1978).
16. J. Talman, *Special Functions, A Group Theoretic Approach* (Benjamin, Reading, MA, 1968).
17. R. Feynman, *Feynman Lectures on Gravitation* (Addison Wesley, Boston, MA, 1995).
18. S. Weinberg, *Phys. Rev.* **138**, 988 (1965).
19. M. Fierz, W. Pauli, *Proc. R. Soc. London* **173**, 211 (1939).
20. J. Bjorken, *Ann. Phys.* **24**, 174 (1963).
21. H. Nielsen, I. Picek, *Nucl. Phys. B* **242**, 542 (1984).
22. G. Volovik, gr-qc/0101111 at http://xxx.lanl.gov.
23. G. Chapline, E. Hohlfeld, R. B. Laughlin, D. I. Santiago, gr-qc/0012094 at http://xxx.lanl.gov.
24. L. Susskind, hep-th/0101029 at http://xxx.lanl.gov.
25. Detailed calculations appear as supplementary Web material on *Science* Online at www.sciencemag.org/cgi/content/full/294/5543/823/DC1.

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REPORTS

Groundwork for a Rational Synthesis of C_{60}: Cyclodehydrogenation of a $C_{60}H_{30}$ Polyarene

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A $C_{60}H_{30}$ polycyclic aromatic hydrocarbon (PAH) that incorporates all 60 carbon atoms and 75 of the 90 carbon-carbon bonds required to form the fullerene C_{60} has been synthesized in nine steps by conventional laboratory methods. Laser irradiation of this $C_{60}H_{30}$ PAH at 337 nanometers induces hydrogen loss and the formation of C_{60}, as detected by mass spectrometry. A specifically labeled $[^{13}C_3]C_{60}H_{30}$ retains all three ^{13}C atoms during the cage formation process. A structurally related $C_{48}H_{24}$ PAH that lacks the three peripheral benzene rings cannot be transformed into C_{60}, whereas the next higher homolog, a $C_{80}H_{40}$ PAH, degrades to the $C_{60}H_{30}$ PAH, which then loses hydrogen to give [60]fullerene. These control experiments verify that the C_{60} is formed by a molecular transformation directly from the $C_{60}H_{30}$ PAH and not by fragmentation and recombination in the gas phase.

Despite more than a decade of intensive research on fullerenes (*1*), chemists worldwide still have no general methods or strategies available for the rational synthesis of these polyhedral carbon allotropes as discrete, preselected targets. Under carefully controlled conditions, the vaporization of graphite generates substantial amounts of C_{60} and C_{70}; however, this complicated process remains poorly understood and is intolerant to alteration (*2*). Higher fullerenes can be obtained from this source only in minuscule amounts through tedious chromatographic separations (*3*) and likely will never be available in quantity except by rational synthesis.

Before we can hope to develop rational syntheses of individual higher fullerenes, the goal of synthesizing C_{60} by rational methods must first be met. In this connection, the research groups of Diederich and colleagues (*4*), Rubin *et al.* (*5*), and Tobe *et al.* (*6–8*) have all prepared macrocyclic polyalkynes that shed multiple appendages when subjected to laser desorption/ionization (LDI), and the high-energy intermediates thus generated collapse to C_{60} in a mass spectrometer. The considerable ambiguity about which atoms in these molecular precursors become bonded to which other atoms as the fullerene takes shape, however, precludes characterization of these processes as entirely "rational" syntheses. Prinzbach *et al.* (*9*) recently reported a genuinely rational synthesis of icosahedral [5]fullerene-C_{20}, in which substituents were removed from a preformed dodecahedrane cage, but extensions of this approach to syntheses of fullerenes comprising 60 or more carbon atoms are likely to be difficult. In LDI experiments, the reactive C_{20} entities prepared in this way can be made to oligomerize and fuse into C_{60} (*10*).

Here, we report the synthesis of a stable polycyclic aromatic hydrocarbon (PAH) that incorporates all 60 of the carbon atoms and 75 of the 90 carbon-carbon bonds required to form C_{60}, and its laser-induced cyclodehydrogenation to C_{60} (Fig. 1). Control experiments establish that the C_{60} formed in the final step comes from a direct molecular transformation (or "zipping up") of the synthetic PAH **6**, as suggested in Fig. 1, and not by a laser-induced degradation of the hydrocarbon to smaller fragments that recombine in a thermodynamically driven manner, as in the laser-induced vaporization of graphite (*2*).

Several research groups have independently conceived of a laboratory synthesis of C_{60} from **6** or structurally related 60-carbon compounds. Wang and Shevlin in Alabama were the first to report preliminary experimental work in this direction (*11*). Their approach can be traced back to an earlier proposal from the same laboratory (*12*); however, they encountered difficulty in assembling the 60-carbon fullerene precursor. Our synthesis of **6** was designed to ensure a regioregular head-to-tail cyclotrimerization of a sickle-shaped 20-carbon precursor, **5**. While our work was under way, Sarobe *et al.* in the Netherlands found that attempts to synthesize **6** from a different precursor without controlling the head-to-tail regiochemistry gave the C_3-symmetric PAH **6** only as a minor component in an inseparable mixture of $C_{60}H_{30}$ regioisomers (*13*). Gomez-Lor *et al.* in Spain later prepared **6** as a single regioisomer by threefold annulation of truxene, a venerable 27-carbon, C_{3v}-symmetric PAH (*14, 15*). Neither Sarobe *et al.* nor Gomez-Lor *et al.*, however, were able to convert their synthetic $C_{60}H_{30}$ material to C_{60}.

Our synthesis of **6** (*16*) began with commercially available (1-bromoethyl)benzene, **1**, and 2-naphthaldehyde (*17*). These were joined by a Wittig reaction to give alkene **2** as a mixture of (*E*)- and (*Z*)-isomers in a combined yield of 79% after purification. Oxidative photocyclization of **2** under standard conditions

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(*18*) then gave a 98% isolated yield of the tetracyclic hydrocarbon **3** (*19–22*). Separation of the two geometric isomers of **2** before photocyclization was unnecessary, because they interconvert photochemically. Bromination of **3** with *N*-bromosuccinimide and subsequent displacement of the resulting benzylic bromide with potassium cyanide converted this intermediate to nitrile **4** in 94% yield over the two steps. Basic hydrolysis of **4** then gave the corresponding carboxylic acid in 65% yield, and conversion to the acid chloride followed by Friedel-Crafts cyclization produced ketone **5** in 70% yield from the acid.

Regiospecific head-to-tail cyclotrimerization of **5** to the C_3-symmetric $C_{60}H_{30}$ PAH **6** was accomplished in 80% yield by heating **5** with 2.4 molar equivalents of titanium tetrachloride in *ortho*-dichlorobenzene at 100°C for 2 hours. Purification of **6** was initially impeded by its exceptionally low solubility in all common organic solvents, but this property was ultimately turned to our advantage. The crude reaction mixture was adsorbed onto alumina and placed in the thimble of a Soxhlet extractor. Extraction with hot methylene chloride first removed some darkly colored, soluble impurities, which were set aside for later analysis (see below). Extraction for an additional 18 hours then slowly leached trimer **6** from the alumina. The extraction was terminated when the characteristic yellow color and bright green fluorescence of **6** could no longer be seen in fresh extracts.

To convert the $C_{60}H_{30}$ PAH **6** into fullerene-C_{60}, we performed a series of LDI experiments. A toluene solution of **6** was spotted onto a stainless steel sample holder and air-dried before introduction into the ion source of the mass spectrometer. A nitrogen laser (337 nm, 3 ns) was used to activate the sample surface, and the resulting ions were detected by means of reflectron time-of-flight mass spectrometry [for other recent applications of this apparatus, see (*23, 24*)]. In a typical experiment, 200 single-laser-shot events were accumulated for each mass spectrum. At a laser fluence adjusted slightly above the threshold for ion formation, essentially only the molecular ion of $C_{60}H_{30}$ is observed (Fig. 2A). With higher laser fluence (Fig. 2B), fragmentations begin to occur, featuring hydrogen losses and the expulsion of small hydrocarbon units. These fragmentations resemble the recently reported decay of hydrogenated fullerenes of similar elemental composition (*25*). Although differences can be seen in the overall fragmentation patterns, owing to the distinctly different structures of these two $C_{60}H_n$ hydrocarbons, the most striking difference is the much greater resistance of **6** toward dehydrogenation than is seen for the $C_{60}H_{36}$ hydrofullerene. In fact, hydrogen loss from hydrofullerenes occurs so readily that many years passed before suffi-

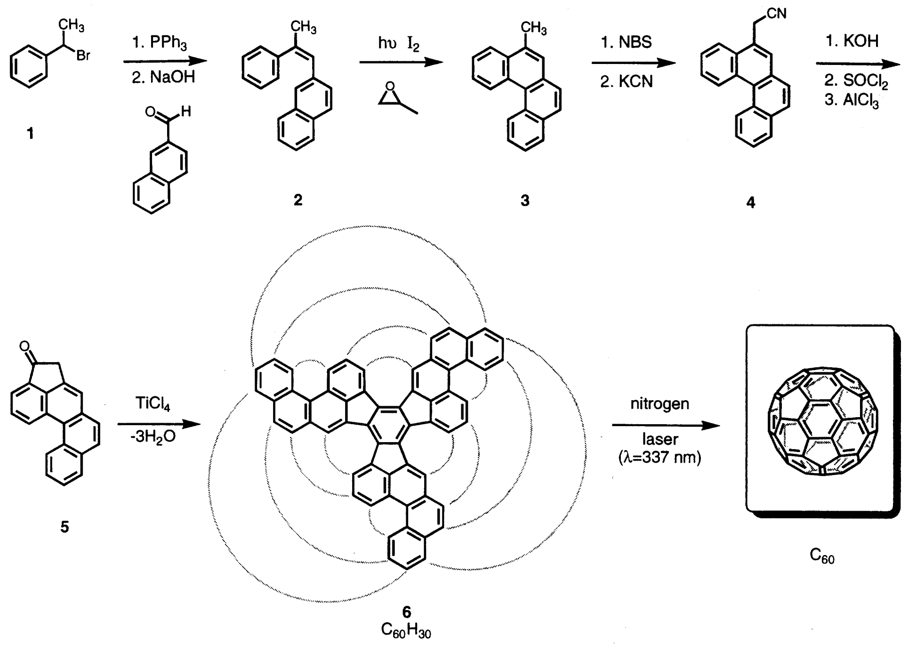

Fig. 1. Synthetic route to the $C_{60}H_{30}$ PAH **6** and its laser-induced conversion into fullerene-C_{60}.

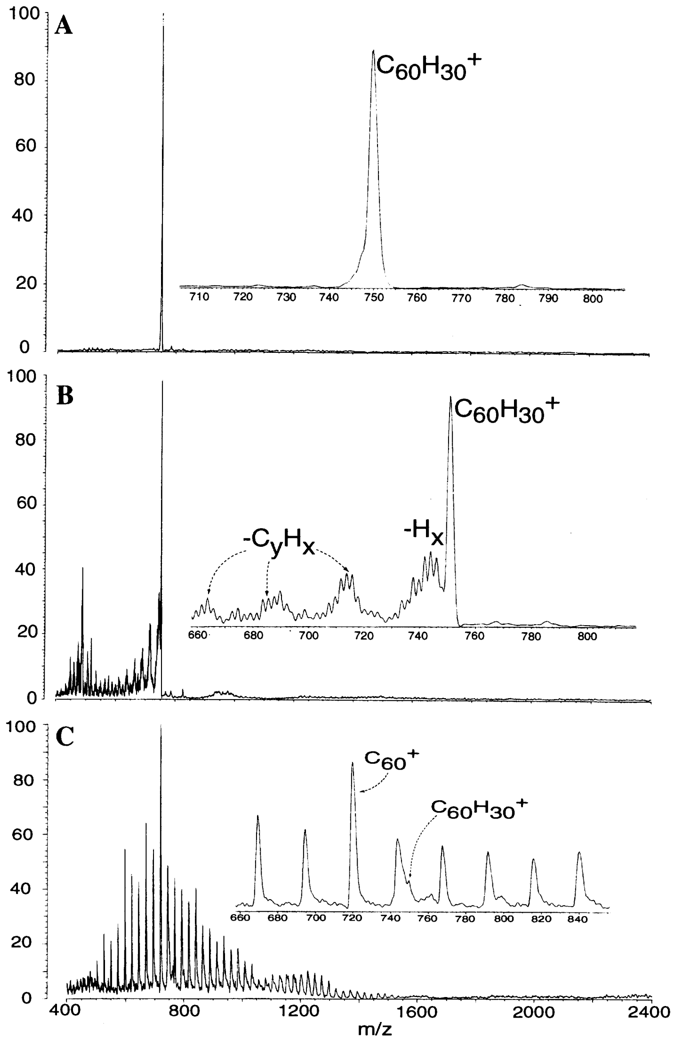

Fig. 2. Positive-ion LDI mass spectra using **6** as the target with increasing laser fluences. (**A**) The pronounced molecular ion signal is observed at a laser fluence slightly above the threshold for ion formation. (**B**) At increased laser fluence, fragmentations by losses of hydrogen and small hydrocarbon units are observed. (**C**) Upon further increase of the laser fluence, efficient conversion of the target material into C_{60} is observed, accompanied by loss and uptake of C_2 units.

ciently gentle conditions could be found to solve the long-standing dilemma regarding the true Birch-reduction product from C_{60} (*26*). Conversely, dehydrogenation of **6** is clearly a more energy-demanding process. By increasing the laser fluence further, however, the efficient formation of fullerenes can be achieved, leaving only traces of the PAH molecular ion still detectable (Fig. 2C).

C_{60} is the most abundant fullerene observed. The distribution of low-mass fullerenes, showing enhanced formation of C_{58}, C_{50}, and C_{44} (which are typical "magic numbers" in dissociations of C_{60}), strongly suggests that these fullerenes are in fact decomposition products of an initially generated fullerene-C_{60}. The fullerene distribution at the high-mass end showed a gradually declining abundance with increasing size and very little excess abundance of C_{70}. The observed pattern strongly indicates that the fullerenes in this region were generated predominantly via the uptake of C_2 units by C_{60}, rather than by processes involving the preferred formation of a particular higher fullerene directly from the PAH precursor. Notwithstanding the appeal of this simple mechanistic picture, additional experiments were conducted to evaluate whether **6** is truly acting as a direct precursor for the [60]fullerene, as opposed to suffering laser-induced decomposition to smaller fragments that subsequently recombine to form C_{60}, as in the laser-induced vaporization of graphite.

The first control experiment used the $C_{48}H_{24}$ PAH **7**, a truncated relative of the $C_{60}H_{30}$ PAH **6**. This compound embodies the same geometrical arrangement for its 48 carbon atoms as those in the core of **6** but lacks the outer fused benzo ring on each of the three blades. As a fullerene precursor, the 48-carbon PAH **7** should therefore function as well as the 60-carbon PAH **6**, if a fragmentation-recombination mechanism is operating that involves formation and recombination of fragments smaller than the 20-carbon units of which **6** is composed. Conversely, if a molecular transformation of **6** into fullerene-C_{60} represents the primary pathway followed, as depicted in Fig. 1, then the absence of the essential fourth fused benzo ring at the end of each blade would preclude a laser-induced conversion of **7** into C_{60}.

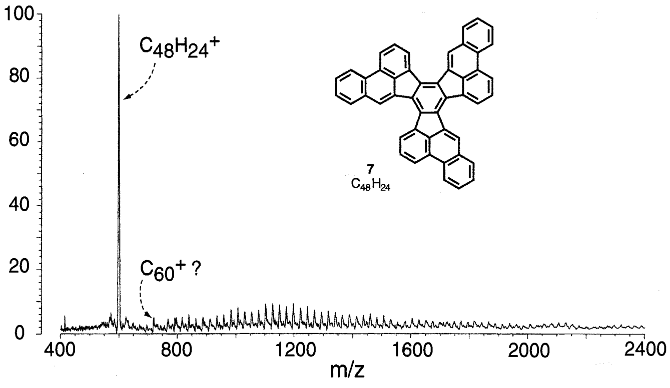

Fig. 3. Structure and positive-ion LDI mass spectrum of the $C_{48}H_{24}$ PAH **7** displaying the minuscule production of fullerenes and revealing C_{60} as an insignificant product.

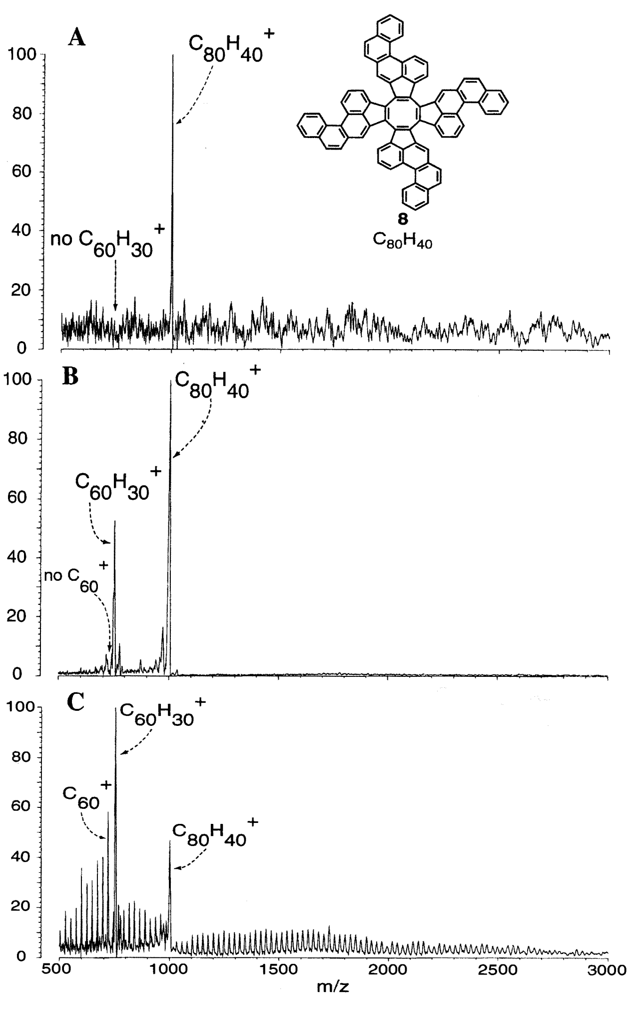

Fig. 4. Positive-ion LDI mass spectra using the $C_{80}H_{40}$ PAH **8** as the target with increasing laser fluences. (**A**) At the threshold of ion formation, only the molecular ion is observed. (**B**) At higher laser fluence, $C_{60}H_{30}$ is efficiently formed. (**C**) $C_{60}H_{30}$ is converted into C_{60} upon further increase of the laser fluence.

We synthesized the $C_{48}H_{24}$ PAH **7** in a manner completely analogous to that used for preparation of the larger $C_{60}H_{30}$ PAH **6** (*27, 28*) and attempted to induce its conversion to C_{60} by laser irradiation over a wide range of conditions. The best result achieved (Fig. 3) required conditions that were practically identical to those used for the production of C_{60} from **6** (Fig. 2C). Indeed, the formation of fullerenes is also observed in these experiments, albeit to a very minor extent. The robust 48-carbon framework of **7** remains largely intact. The ratio of fullerenes generated to unconverted PAH is two to three orders of magnitude smaller than when **6** is subjected to LDI, and, most remarkably, C_{60} appears as one of the least abundantly formed fullerenes. These findings argue strongly against a fragmentation-recombination mechanism as the major pathway for C_{60} formation from **6** and provide a reasonable estimate of the "background" level of fullerene production by minor pathways.

We also used a larger $C_{80}H_{40}$ PAH, **8**, as the target material. This cyclic tetramer of ketone **5** is the main side product found in the darkly colored extracts obtained from purification of the $C_{60}H_{30}$ PAH **6** (see above). The positive-ion LDI mass spectra of this compound are shown for increasing laser fluences in Fig. 4. Figure 4A was obtained at the threshold of ion formation and shows only the molecular ion of $C_{80}H_{40}$. Upon increasing the laser fluence (Fig. 4B), this $C_{80}H_{40}$ PAH decomposes predominantly into $C_{60}H_{30}$. It is only after $C_{60}H_{30}$ has been formed from $C_{80}H_{40}$ that further increases in laser fluence lead to the formation of fullerenes. The resulting spectrum (Fig. 4C) appears almost identical to that obtained when **6** was used as the target (Fig. 2C). The fullerene

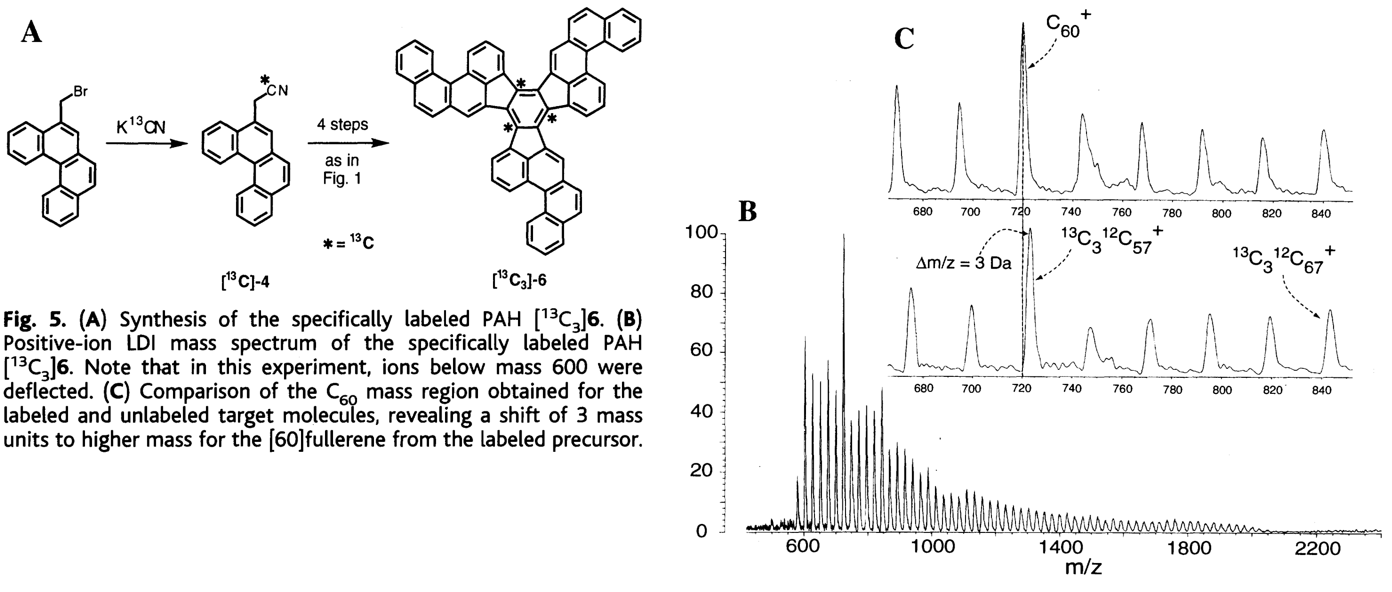

Fig. 5. (**A**) Synthesis of the specifically labeled PAH [$^{13}C_3$]**6**. (**B**) Positive-ion LDI mass spectrum of the specifically labeled PAH [$^{13}C_3$]**6**. Note that in this experiment, ions below mass 600 were deflected. (**C**) Comparison of the C_{60} mass region obtained for the labeled and unlabeled target molecules, revealing a shift of 3 mass units to higher mass for the [60]fullerene from the labeled precursor.

formation in this case resulted from a direct conversion of **6** into C_{60} after the release of one $C_{20}H_{10}$ unit from the $C_{80}H_{40}$ PAH **8**. The latter process has previously been observed for cyclic tetramers of related PAHs, which jettison one monomer unit at elevated temperatures and collapse back to the corresponding cyclic trimer (*29*).

The observation of a much stronger $C_{60}H_{30}$ signal in Fig. 4C when $C_{80}H_{40}$ is used as the target than when pure $C_{60}H_{30}$ is used (Fig. 2C) superficially appears to indicate a much lower conversion rate into C_{60}. In separate tandem mass spectrometry experiments using a deflector electrode (ion gate) for precursor ion selection, however, we showed that the energized $C_{60}H_{30}$ population produced inside the ion source of the mass spectrometer is almost completely converted into fullerene-C_{60}, just as when pure PAH **6** is used as the target. Thus, the $C_{60}H_{30}$ signal observed in Fig. 4C results almost entirely from decompositions of larger PAHs inside the flight tube of the mass spectrometer, leading to less energized $C_{60}H_{30}$ species that survive. Such low-energy species cannot be produced from the pure $C_{60}H_{30}$ target that is free of larger PAH impurities, as in the case shown in Fig. 2C.

As a final control, we synthesized **6** using KCN that was 99% enriched in ^{13}C, so that the $C_{60}H_{30}$ PAH contained three ^{13}C labels located at alternating positions around the central benzene ring (Fig. 5A). Any fragmentation-recombination mechanism involving degradation down to fragments smaller than the 20-carbon subunits of **6** would necessarily lead to a considerable amount of C_{60} containing either more or fewer than three ^{13}C atoms. The LDI mass spectrum of [$^{13}C_3$]$C_{60}H_{30}$ (Fig. 5B) bears a strikingly similar appearance to that obtained for the unlabeled compound (Fig. 2C). Figure 5C compares the spectra for the labeled and unlabeled targets. Although the mass resolution in our experiments is insufficient to resolve the individual isotopic pattern of each carbon cluster, no perceptible peak broadening is observed for the labeled target, and the clear shift of each signal in Fig. 5C corresponds to exactly 3 mass units. Like the C_{60} signal, the fullerene fragment ions from $^{13}C_3{}^{12}C_{57}$ also show a mass shift of 3 units to higher masses, as the loss of $^{12}C_2$ is much more probable than the release of $^{12}C^{13}C$. Similarly, those signals in Fig. 5C beyond the [60]fullerene are also shifted by 3 mass units. This shift reflects the fact that $^{12}C_2$ is much more abundantly available for uptake by the initially formed $^{13}C_3{}^{12}C_{57}$. On the basis of these findings, a fragmentation-recombination mechanism must be rejected.

We have synthesized the $C_{60}H_{30}$ PAH **6** and have closed it up to fullerene-C_{60} by activation with a nitrogen laser. By adaptations of the reaction pathway outlined in Fig. 1, it should now be possible to prepare halogenated derivatives of **6** that can be used for a rational synthesis of C_{60} in isolable quantities. Our previous experience has shown that the strategic incorporation of halogen atoms on PAHs invariably improves the preparative yields of geodesic polyarenes obtained from synthetic precursors, often by more than two orders of magnitude over what can be achieved by direct cyclodehydrogenations of unfunctionalized PAHs (*30, 31*).

References and Notes

1. R. Taylor, *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists* (Imperial College Press, London, 1999), and references therein.
2. N. S. Goroff, *Acc. Chem. Res.* **29**, 77 (1996).
3. K. Jinno, Y. Sato, H. Nagashima, K. Itoh, *J. Microcolumn Sep.* **10**, 79 (1998) and references therein.
4. S. W. McElvany, M. M. Ross, N. S. Goroff, F. Diederich, *Science* **259**, 1594 (1993).
5. Y. Rubin *et al.*, *Angew. Chem. Int. Ed.* **37**, 1226 (1998).
6. Y. Tobe *et al.*, *J. Am. Chem. Soc.* **120**, 4544 (1998).
7. Y. Tobe, H. Nakanishi, N. Nakagawa, R. Furukawa, *Proc. Electrochem. Soc.* **99–12**, 146 (1999).
8. Y. Tobe *et al.*, *Tetrahedron* **57**, 3629 (2001).
9. H. Prinzbach *et al.*, *Nature* **407**, 60 (2000).
10. E. E. B. Campbell, R. Tellgmann, F. Wahl, H. Prinzbach, *Int. J. Mass Spectrom. Ion Processes* **136**, 209 (1994).
11. L. Wang, P. B. Shevlin, in *Abstracts of Papers*, 212th National Meeting of the American Chemical Society, Orlando, Florida (American Chemical Society, Washington, DC, August 1996).
12. T. M. Chang, A. Naim, S. N. Ahmed, G. Goodloe, P. B. Shevlin, *J. Am. Chem. Soc.* **114**, 760 (1992).
13. M. Sarobe *et al.*, *Chem. Phys. Lett.* **313**, 31 (1999).
14. B. Gomez-Lor, O. de Frutos, A. M. Echavarren, *Chem. Commun.* **1999**, 2431 (1999).
15. F. S. Kipping, *J. Chem. Soc.* **65**, 269 (1894).
16. Detailed experimental procedures for the synthetic transformations reported here and characterization data for all the synthetic intermediates can be found in (*32*).
17. Both purchased from Aldrich Chemical Co., Milwaukee, WI.
18. L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **56**, 3769 (1991).
19. For alternative syntheses of 5-methylbenzo-[c]phenanthrene, **3**, see (*20–22*).
20. D. Muller, D. Cagniant, *Bull. Soc. Chim. Fr.* (1968), p. 334.
21. D. L. Nagel, R. Kupper, K. Antonson, L. Wallcave, *J. Org. Chem.* **42**, 3626 (1977).
22. S. Chowdhury, B. Zaho, V. Snieckus, *Polycyclic Aromat. Compd.* **5**, 27 (1994).
23. N. L. Clipston *et al.*, *J. Phys. Chem.* **104**, 9171 (2000).
24. Y. V. Vasil'ev, R. R. Absalimov, S. K. Nasibullaev, A. S. Lobach, T. Drewello, *J. Phys. Chem.* **105**, 661 (2001).
25. M. Möder *et al.*, *J. Chem. Soc.* **195–196**, 599 (2000).
26. Y. Vasil'ev *et al.*, *Chem. Commun.* **2000**, 1233 (2000).
27. B. J. McMahon, thesis, Boston College (1997). See also (*16*).
28. For an alternative synthesis of tribenzo[*a*,*l*,*w*]decacyclene, **7**, see (*33*).
29. E. Clar, *Polycyclic Hydrocarbons* (Academic Press, New York, 1964), chap. 43.
30. L. T. Scott, M. S. Bratcher, S. Hagen, *J. Am. Chem. Soc.* **118**, 8743 (1996).
31. R. B. M. Ansems, L. T. Scott, *J. Am. Chem. Soc.* **122**, 2719 (2000).
32. M. M. Boorum, thesis, Boston College (2001).
33. O. De Frutos *et al.*, *Angew. Chem. Int. Ed.* **38**, 204 (1999).
34. Supported by NSF, the U.S. Department of Energy, the Russian Foundation for Basic Research, INTAS, and the Leverhulme Trust (UK).

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