

# Beyond C<sub>60</sub>: The Higher Fullerenes

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## Introduction

In 1990, Krätschmer, Huffman, et al. reported the preparation of macroscopic quantities of buckminsterfullerene (C<sub>60</sub>), the third allotropic and first molecular form of carbon, named after Buckminster Fuller, an architect renowned for his geodesic dome structures, by resistive heating of graphite under an inert atmosphere.<sup>1</sup> In following vigorous developments, the cage-like truncated icosahedral structure of C<sub>60</sub>, resembling a soccer ball, has been firmly established.<sup>2</sup> This structure had been predicted in 1985 by Kroto, Smalley, et al. at Rice University to account for the exceptional stability of the C<sub>60</sub> species in carbon cluster beams produced by laser vaporization of graphite.<sup>3</sup> Since 1981, Chapman et al. at UCLA had pursued the preparation of this carbon sphere in a total synthesis approach, which is documented in four Ph.D. theses.<sup>4</sup> However, it was only after the 1985 communication by the Rice group that a broad range of chemists and physicists became interested in theoretical calculations to predict the structure and properties of buckminsterfullerene.<sup>2c,5</sup> Perhaps the most important data generated between 1985 and 1990 was the four-line IR spectrum of C<sub>60</sub>, which was crucial for the discovery of the compound in the soot produced by resistive heating of graphite.<sup>6</sup>

Prior to the studies at Rice University, experiments at Exxon Research on the abundances of carbon clusters generated by laser vaporization of graphite resulted in the surprising observation that only even-numbered clusters were present in the C<sub>40</sub>-C<sub>200</sub> ion range.<sup>7</sup> Following their landmark 1985 paper, Kroto, Smalley, et al. explained the abundance of these even-numbered species with the formation of an entire family of carbon cages containing a central cavity called the *fullerenes*.<sup>8</sup> Specifically, it was proposed that these molecules with the composition C<sub>20+2m</sub> can take the stable form of hollow closed nets composed of 12 pentagons (five-membered rings, 5MRs) and *m* hexagons (6MRs). Krätschmer, Huffman, et al. found that C<sub>70</sub> was the second most abundant all-carbon molecule formed by

resistive heating of graphite, in agreement with the earlier Rice studies which reported C<sub>70</sub> to be the second most prominent carbon cluster in the molecular beams generated by laser vaporization of graphite.<sup>2b,3</sup> Like C<sub>60</sub>, the larger C<sub>70</sub> molecule is also a member of the fullerene family, and its ellipsoidal cage shape of a rugby ball has been confirmed by <sup>13</sup>C NMR spectroscopy<sup>2c,9,10</sup> and recently also by X-ray crystallographic analysis of an iridium derivative.<sup>11</sup> For some of the *higher fullerenes* beyond C<sub>60</sub> and C<sub>70</sub>, structures had been calculated; however, most theoretical studies did not predict structures for those derivatives that could actually be isolated.<sup>12</sup>

In September 1990, we isolated macroscopic quantities of C<sub>60</sub> and C<sub>70</sub> from soot prepared according to Krätschmer and Huffman.<sup>13</sup> To characterize the two fullerenes in pure form, we developed a chromatographic separation protocol which uses neutral alumina as the support and toluene/hexane mixtures as an eluent.<sup>9</sup> At the same time, we obtained mass spectrometric evidence for the presence of the higher fullerenes C<sub>76</sub>/C<sub>78</sub> and C<sub>84</sub> in the toluene-soluble soot extract.<sup>13</sup> Chromatography on alumina subsequently enabled us to isolate the first enriched samples of C<sub>76</sub>/C<sub>78</sub> and

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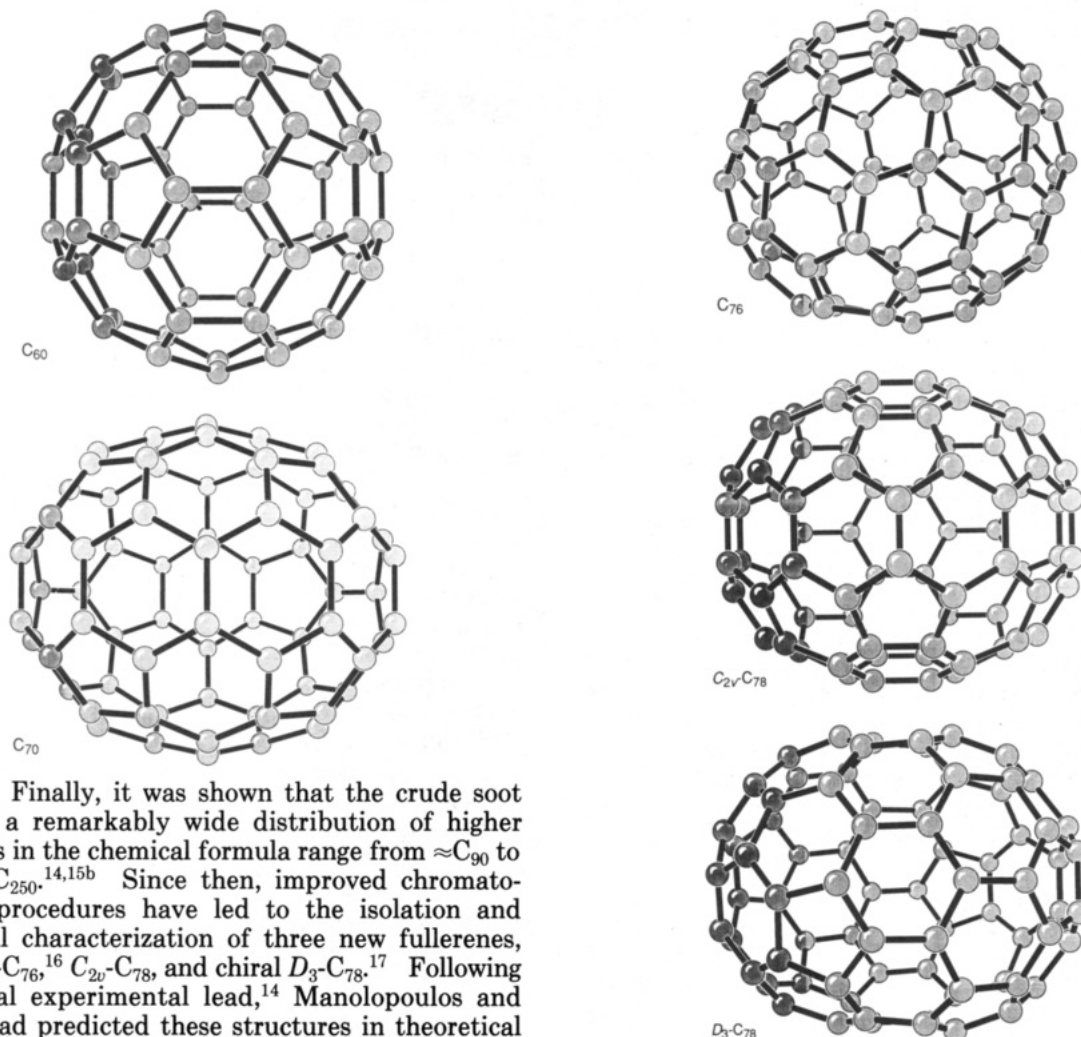
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François Diederich was born in Ettelbruck in the Grand-Duchy of Luxembourg on July 9, 1952. He received his diploma in chemistry in 1977 and his doctoral degree in 1979 from the University of Heidelberg working with Professor Heinz A. Staab. After postdoctoral research with Professor Orville L. Chapman at UCLA in 1979-1981, he became a research associate at the Max Planck Institute for medical research in Heidelberg. Following the Habilitation at the University of Heidelberg in 1985, he joined the faculty at UCLA, where he is currently a professor of organic and bioorganic chemistry. His research interests are in the chemistry of all-carbon molecules and network polymers, in molecular recognition, and in the general area of supramolecular chemistry.

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C<sub>84</sub>.<sup>14,15</sup> Finally, it was shown that the crude soot contains a remarkably wide distribution of higher fullerenes in the chemical formula range from  $\approx$ C<sub>90</sub> to beyond C<sub>250</sub>.<sup>14,15b</sup> Since then, improved chromatographic procedures have led to the isolation and structural characterization of three new fullerenes, chiral *D*<sub>2</sub>-C<sub>76</sub>,<sup>16</sup> *C*<sub>2v</sub>-C<sub>78</sub>, and chiral *D*<sub>3</sub>-C<sub>78</sub>.<sup>17</sup> Following the initial experimental lead,<sup>14</sup> Manolopoulos and Fowler had predicted these structures in theoretical work which applied a spiral algorithm to the search for fullerene structures.<sup>18</sup>

This Account describes the isolation and separation of stable higher fullerenes in late 1990–1991.<sup>13b</sup> The spectral data which support the structural assignments for these carbon spheres are compared to the data for C<sub>60</sub> and C<sub>70</sub>. Finally, perspectives of future research on higher fullerenes beyond C<sub>60</sub> are outlined.

### Separation of Fullerenes and Their Isomers

The fullerene soot at UCLA is prepared by resistive heating of graphite in a conventional evaporator, ordinarily employed for depositing amorphous carbon

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(17) Diederich, F.; Whetten, R. L.; Thilgen, C.; Ettl, R.; Chao, I.; Alvarez, M. M. *Science (Washington, D.C.)* **1991**, *254*, 1768–1770.

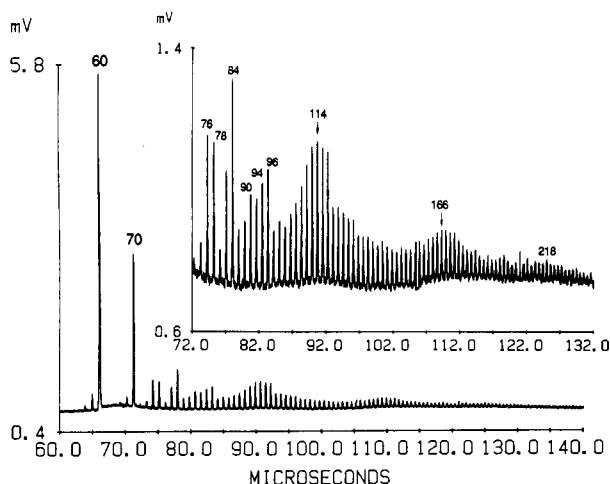
(18) (a) Manolopoulos, D. E. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2861–2862. (b) Fowler, P. W.; Manolopoulos, D. E.; Batten, R. C. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3103–3104. (c) Manolopoulos, D. E.; Fowler, P. W. *Chem. Phys. Lett.* **1991**, *187*, 1–7.

films on microscopy samples. Figure 1 shows laser-desorption time-of-flight (LD-TOF) spectra recorded of the crude material. Besides C<sub>60</sub> and C<sub>70</sub>, the C<sub>76</sub>, C<sub>78</sub>, and C<sub>84</sub> ions, which correspond to the most abundant higher fullerenes in the soot, give the most prominent peaks in the spectra.

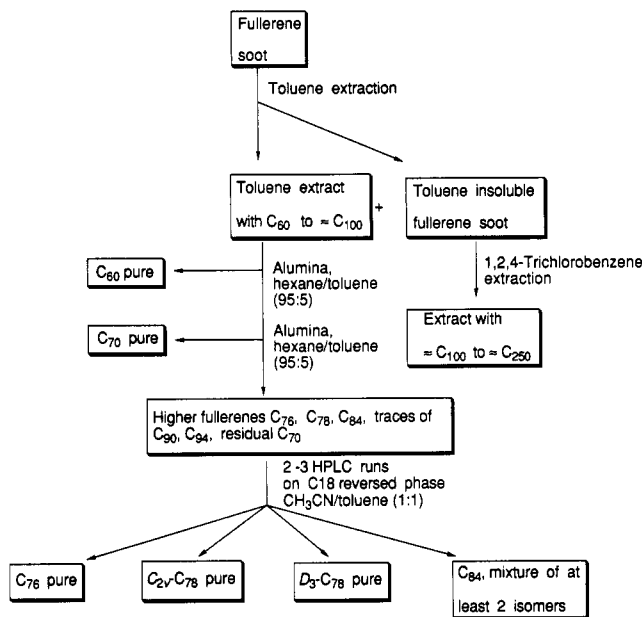
Soxhlet extraction of the soot with toluene affords a soluble extract, usually in yields above 20% and sometimes reaching 35–40% (Figure 2). This extract contains approximately 65% of C<sub>60</sub>, 30% of C<sub>70</sub>, and 5% of higher fullerenes, mainly C<sub>76</sub>, and two C<sub>78</sub> isomers, and C<sub>84</sub> (Figure 3A). Analysis of the remaining black toluene-insoluble material by LD-TOF and FAB mass spectrometry shows that it contains larger fullerenes in the range between  $\approx$ C<sub>100</sub> and C<sub>250</sub> in addition to some residual C<sub>60</sub> and C<sub>70</sub>. Fullerenes of this size can be solubilized in high-boiling solvents like 1,2,4-trichlorobenzene (bp 214 °C) or 1,2,4,5-tetramethylbenzene (bp 197 °C).<sup>14,15b</sup> We believe that the portion of the soot that is insoluble even in these high-boiling solvents contains very large, high-molecular-weight fullerenes. The formation of “giant fullerenes”<sup>19</sup> with molecular formulas up to C<sub>400</sub> had previously been observed in the laser vaporization not only of graphite<sup>7</sup> but also of other carbon-rich materials like PAHs<sup>20a</sup> and higher oxides of carbon.<sup>20b</sup>

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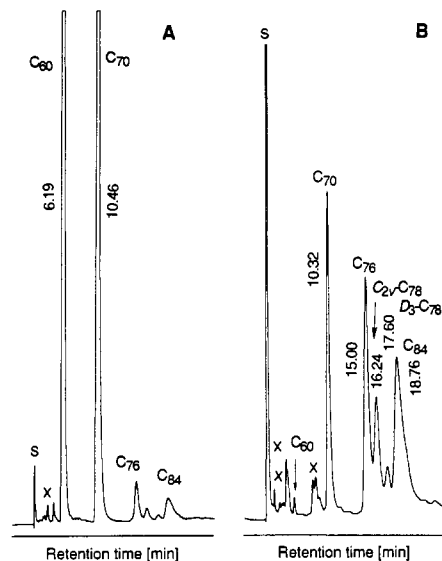
**Figure 1.** LD-TOF mass spectrum recorded of the crude fullerene soot produced by resistive heating of graphite under inert atmosphere. The insert shows the sensitivity-enhanced portion of the spectrum containing the higher fullerene ions beyond C<sub>70</sub>. Under the experimental conditions (laser wavelength 308 nm, fluence < 1 mJ/cm<sup>2</sup>, helium nozzle), the relative intensities of the mass spectral peaks reflect the relative concentrations of the individual fullerenes present in the soot as verified by independent experiments on known mixtures.



**Figure 2.** A protocol for fullerene isolation and separation.

Early attempts to separate the higher fullerenes by chromatography on alumina led to highly enriched 1–2-mg samples of C<sub>76</sub>, C<sub>78</sub>, C<sub>84</sub>, C<sub>90</sub>, and C<sub>94</sub> in addition to C<sub>70</sub>O, an oxide of D<sub>5h</sub>-C<sub>70</sub>.<sup>14</sup> Pure samples of higher fullerenes were finally obtained by high-performance liquid chromatography (HPLC) on a Vydac 201 TP C18 reversed-phase column<sup>21</sup> with the unusual solvent mixture acetonitrile/toluene (1:1, v/v) as the eluent.<sup>17</sup> Following the separation of C<sub>60</sub> and C<sub>70</sub> on alumina (Figure 3B), repeated runs on the reversed-phase column yielded C<sub>76</sub>, C<sub>2v</sub>-C<sub>78</sub>, and D<sub>3</sub>-C<sub>78</sub> in purities greater than 98% each besides a pure C<sub>84</sub> fraction containing at least two isomers. Fullerene C<sub>76</sub> is the most abundant, and as much as 10 mg of pure material has already been isolated. The two C<sub>78</sub> isomers form in a ratio of

(21) Vydac C<sub>18</sub> reversed-phase column: The Separations Group, 17434 Mojave St., Hesperia, CA 92345.



**Figure 3.** HPLC profiles (C18 reversed phase, acetonitrile/toluene, 1:1, 310-nm UV detection) (A) of the crude toluene extract of the fullerene soot and (B) of the higher fullerene mixture obtained after removal of all C<sub>60</sub> and most of the C<sub>70</sub>. S = solvent, X = unknown impurities. Separations were obtained on a 250 × 10 mm column (flow rate 5 mL/min, pressure 650 psi); retention times are given in minutes.

**Table I**  
IPR-Satisfying Structures of the Closed-Shell and Partially Closed-Shell<sup>a</sup> Fullerenes between C<sub>60</sub> and C<sub>78</sub>.<sup>b,c</sup>

structure	<sup>13</sup> C NMR lines (intensity)	$\Delta H_f^\circ$ (kcal mol <sup>-1</sup> )
I <sub>h</sub> -C <sub>60</sub>	1 (60 C)	573.8
D <sub>5h</sub> -C <sub>70</sub>	3 (10 C), 2 (20 C)	
D <sub>6h</sub> -C <sub>72</sub>	2 (24 C), 2 (12 C)	
D <sub>3h</sub> -C <sub>74</sub>	1 (2 C), 4 (6 C), 4 (12 C)	
D <sub>2</sub> -C <sub>76</sub>	19 (4 C)	
C <sub>2v</sub> -C <sub>78</sub>	18 (4 C), 3 (2 C)	695.7
D <sub>3</sub> -C <sub>78</sub>	13 (6 C)	697.8
C <sub>2v</sub> '-C <sub>78</sub>	17 (4 C), 5 (2 C)	694.3
D <sub>3h</sub> '-C <sub>78</sub>	5 (12 C), 3 (6 C)	702.3
D <sub>3h</sub> '-C <sub>78</sub>	5 (12 C), 3 (6 C)	697.8

<sup>a</sup> Contains a slightly bonding LUMO. <sup>b</sup> Reference 18c. <sup>c</sup> The numbers of independent resonances in the <sup>13</sup>C NMR spectra are given as well as selected gas-phase heats of formation  $\Delta H_f^\circ$  (298 K) calculated by the molecular mechanics program MM3.

approximately 5:1, and so far, we have isolated  $\approx 2$  mg of pure C<sub>2v</sub>-C<sub>78</sub> and  $\approx 0.2$  mg of the pure D<sub>3</sub> isomer.<sup>17</sup> The successful separation of the two C<sub>78</sub> isomers reflects an amazing molecular shape selectivity of the chromatographic phase. Over more than a year, nearly identical fullerene product distributions were found in the soot generated at UCLA. No fullerene between C<sub>70</sub> and C<sub>76</sub> could be isolated, and C<sub>82</sub>, which has recently been reported to form an endohedral complex with lanthanum ions,<sup>22</sup> has been absent in each run.<sup>23</sup>

### Fullerene Structure Elucidation: Interplay between Theoretical Prediction and <sup>13</sup>C NMR Experiment

According to the original definition, fullerenes C<sub>20+2m</sub> obey Euler's rule and are hollow closed nets with 12 pentagonal faces and *m* hexagonal faces.<sup>24</sup> Even within

(22) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wand, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* 1991, 95, 7564–7568.

(23) Fullerene soot from the Materials and Electrochemical Research (MER) Corporation, 7960 S. Kolb Rd., Tucson, AZ 85706, gave a similar product distribution.

**Table II**  
Line Positions (Intensity) and Centers of Gravity in the  $^{13}\text{C}$  NMR Spectra of  $\text{C}_{60}$  and  $\text{C}_{70}$  in  $\text{CDCl}_2\text{CDCl}_2$  and of  $\text{C}_{76}$ ,  $\text{C}_{20}\text{-C}_{78}$ , and  $\text{D}_3\text{-C}_{78}$  in  $\text{CS}_2$

peak no.	$\delta$ (ppm)				
	$\text{C}_{60}$	$\text{C}_{70}$	$\text{C}_{76}$	$\text{C}_{20}\text{-C}_{78}$	$\text{D}_3\text{-C}_{78}$
1	143.2 (60)	130.8 (10)	129.56 (4)	132.31 (4)	132.18 (6)
2		144.4 (20)	133.40 (4)	132.63 (2)	132.90 (6)
3		147.8 (10)	135.67 (4)	133.98 (4)	134.85 (6)
4		148.3 (20)	137.06 (4)	136.49 (4)	139.55 (6)
5		150.8 (10)	141.35 (4)	137.67 (4)	140.45 (6)
6			142.11 (4)	138.08 (4)	140.82 (6)
7			142.15 (4)	138.39 (4)	140.91 (6)
8			142.79 (4)	138.41 (4)	141.83 (6)
9			142.86 (4)	142.19 (2)	142.88 (6)
10			143.61 (4)	143.34 (4)	144.53 (6)
11			144.05 (4)	143.89 (4)	145.45 (6)
12			144.14 (4)	144.49 (4)	148.14 (6)
13			145.92 (4)	144.72 (4)	149.45 (6)
14			146.50 (4)	144.89 (4)	
15			146.65 (4)	144.99 (2)	
16			147.19 (4)	145.96 (4)	
17			147.66 (4)	146.04 (4)	
18			147.96 (4)	146.12 (4)	
19			150.03 (4)	146.99 (4)	
20				147.56 (4)	
21				147.62 (4)	
center of gravity: <sup>a</sup>	143.2	145.0	142.7	141.9	141.1

<sup>a</sup>The center of gravity in the spectrum for the isomeric mixture of pure  $\text{C}_{84}$  is  $\approx 140.3$  ppm. We measure the following 31 resonances for  $\text{C}_{84}$ : 133.84; 134.99; 135.49; 137.42; 137.52; 137.97; 138.48; 138.61; 138.90 (2 $\times$ ), 139.65; 139.72; 139.78 (2 $\times$ ); 140.01; 140.30; 140.36; 140.52; 140.62; 141.02; 141.35; 141.60; 142.15; 142.58; 142.91; 143.81; 143.83; 144.01; 144.50; 144.61; 144.63.

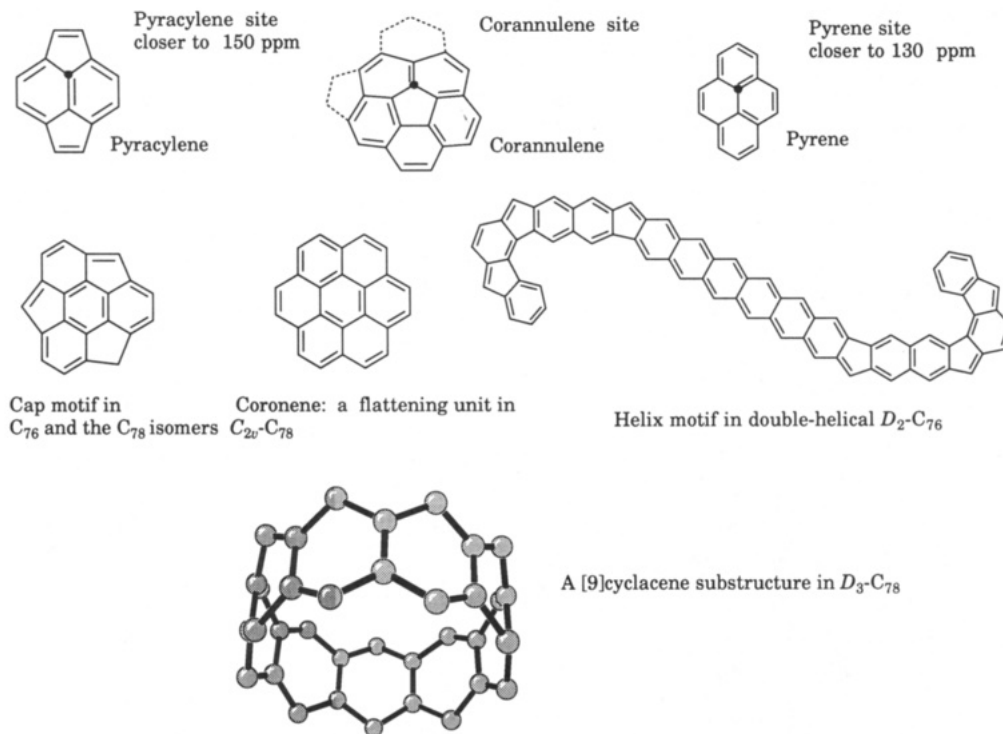
the constraints of this definition, a very large number of structures is conceivable for each one of the higher fullerenes. By applying a spiral algorithm, Manolopoulos and Fowler found 21 822 fullerene structures for  $\text{C}_{78}$ .<sup>18b</sup> However, as shown in Table I, the number of isomers decreases dramatically when the "isolated pentagon rule (IPR)"<sup>8,24</sup> is applied. In stable fullerene structures, all pentagons are fully annelated by hexagons, yielding corannulene substructures. The fusion of two pentagons to form pentalene substructures is energetically unfavorable as a result of increased  $\sigma$ -bonding ring strain and the formation of  $8e^-$  perimeters.<sup>18a</sup> The isolated pentagon rule has found strong experimental verification by the structures of the fullerenes that have been isolated. Qualitative Hückel molecular orbital theory allows identification of those structures that are closed-shell or partially closed-shell (partially since they contain a slightly bonding LUMO) electronic systems and therefore should have higher stability compared to open-shell systems.<sup>18</sup> For example,  $\text{C}_{76}$  prefers the partially closed-shell chiral  $D_2$  structure over the  $T_d$  symmetrical structure with an open-shell electron configuration. However, predictions of relative stabilities among closed-shell fullerene isomers that are based on the magnitude of the HOMO-LUMO gap have been less successful. The prediction that the closed-shell  $D_{3h}$  isomer of  $\text{C}_{78}$  would be the most stable<sup>18b</sup> is inconsistent with the experimental findings. The number of IPR-satisfying isomers grows rapidly with fullerene size: it increases from 5 for  $\text{C}_{78}$  to 24 for  $\text{C}_{84}$  and to 46 for  $\text{C}_{90}$ .<sup>18c</sup>

All five fullerenes have been structurally characterized in an unambiguous way by  $^{13}\text{C}$  NMR spectroscopy. Table II shows the  $^{13}\text{C}$  NMR data of the higher fullerenes recorded in carbon disulfide, a remarkable solvent for these large molecules. The data are uniquely

consistent with the spectral characteristics predicted by Fowler and Manolopoulos (Table I).

In  $I_h\text{-C}_{60}$ ,<sup>9b,13,25</sup> all carbon atoms are at identical sites, which we named pyracylene sites, since these carbon atoms participate in the bonds between two five-membered rings in pyracylene substructures (Figure 4). The  $D_{5h}$ -symmetrical ellipsoidal cage structure of  $\text{C}_{70}$  is supported by its five-line  $^{13}\text{C}$  NMR spectrum (Table II).<sup>9</sup> A 2D INADEQUATE  $^{13}\text{C}$  NMR experiment by Johnson et al.<sup>10</sup> showed that the most shielded resonance at 130.8 ppm (Table II) originates from the 10 carbon atoms lying at the intersection of three hexagons, in what we call a pyrene-type environment. The three least shielded signals between 137.8 and 150.8 ppm originate from carbons in the three different pyracylene sites. The remaining signal at 144.4 ppm is due to carbon atoms in what we named a corannulene site, defined by the intersection of one 5MR and two 6MRs but not connected to another 5MR. Starting from these assignments for  $\text{C}_{70}$ , we conducted a more detailed analysis of the  $^{13}\text{C}$  NMR data for the three higher fullerenes and obtained additional support for the structural assignments made.<sup>16,17</sup> The spectra of each higher fullerene showed the correct number and intensities of signals in the three environments, pyrene, corannulene, and pyracylene sites (Figure 4). Fullerenes  $\text{C}_{76}$  and  $\text{D}_3\text{-C}_{78}$  have four and three, respectively, sets of carbon atoms at pyrene-type sites, and accordingly, four and three, respectively, distinctively upfield shifted resonances between 130 and 135 ppm are observed in the spectra of these compounds.

The resistive heating of achiral graphite leads to chiral all-carbon molecules. Fullerene  $\text{C}_{76}$  has  $D_2$  symmetry and consists of a spiraling double helical arrangement of two identical edge-sharing helical fragments, shown in Figure 4.<sup>16</sup> Figure 5A shows a view on



**Figure 4.** Structural motifs in the fullerenes and the three different kinds of atomic environments of fullerene carbon atoms.

the flat face of the molecule, looking down one of the three  $C_2$  axes. A second chiral molecule is the minor  $D_3$ -symmetrical isomer of  $C_{78}$ .<sup>17</sup> Figure 5B shows a view onto one of the three symmetry-related smoothly curved faces in  $D_3$ - $C_{78}$  that are capped by two triphenylene caps. The same cap motif, illustrated in Figure 4, is shared by all three higher fullerenes. In the central part of  $D_3$ - $C_{78}$ , perpendicular to the  $C_3$  axis, one finds the interesting structural motif of a [9]cyclacene<sup>26</sup> (Figure 4), a circular acene formed of nine linearly annelated benzene rings. The major  $C_{78}$  isomer,  $C_{2v}$ - $C_{78}$ , has one flat coronene face (Figure 4), and if a paper model is placed on this face, the molecule resembles a helmet or a turtle's shell (Figure 5C).

We performed MM3 force-field calculations on the five IPR-satisfying  $C_{78}$  structures and found that the two isolated isomers are much more stable than the  $D_{3h}$  isomer predicted by qualitative MO theory (Table I).<sup>17,18b</sup> Also, model building clearly shows that the  $D_{3h}$  isomer with three flat coronene faces separated by rather sharp edges is much more strained than the  $C_{2v}$  isomer, which has only one quasi-planar coronene face and a more uniform curvature over two-thirds of the helmet-shaped ball surface. Strain is better delocalized in the  $C_{2v}$  than in the  $D_{3h}$  isomer.

Interestingly, the predicted  $D_{3h}$  isomer and the observed dominant  $C_{2v}$  isomer of  $C_{78}$  are interchangeable by 90° rotation of a single  $C_2$  unit in the *pyracylene rearrangement* (Figure 6) first suggested by Stone and Wales<sup>27</sup> for  $C_{60}$  and subsequently proposed as the first step in the degradation of  $C_{60}$  to smaller fullerenes via consecutive  $C_2$  losses.<sup>28</sup> This rearrangement is very

general on the  $C_{78}$  fullerene hypersurface: all except the  $D_3$  isomer of  $C_{78}$  may be interchangeable in single-step rearrangements.<sup>17</sup>

The pure fraction of fullerene  $C_{84}$  gave 31 unique resonances in its <sup>13</sup>C NMR spectrum (Table II). Although expanded HPLC profiles of this fraction seemed to indicate a mixture consisting of only two isomers, it may well contain three or more isomers.<sup>18c,29</sup>

Table II shows that the <sup>13</sup>C NMR peaks in all fullerene spectra fall in a range between 130 and 151 ppm, which we define as the fullerene region. The center of spectral gravity shifts smoothly to higher field with increasing fullerene size, e.g., from 145 ppm for  $C_{70}$  to ≈140.3 ppm for  $C_{84}$ . An exception to this strong trend is the pyracylene-type resonance for  $C_{60}$ , which must now be viewed as being particularly shielded, possibly due to some local and  $\pi$ -system anisotropic effects.<sup>30</sup> The upfield shift of the center of spectral gravity into the more common benzenoid aromatic region of the <sup>13</sup>C NMR spectrum reflects the incorporation of an increasing number of benzenoid, pyrene-type carbon atoms into the higher fullerenes, while the sum of the pyracylene and corannulene resonances in all fullerenes remains identical and equal to 60.

### Electronic Absorption Spectra of the Fullerenes

The fullerenes demonstrate a rich variety of colors. Buckminsterfullerene ( $C_{60}$ ) is intensely purple in apolar solvents and in the crystal. Fullerene  $C_{70}$  gives deep orange-red solutions. Chiral  $C_{76}$  shows a bright yellow-green color both in solution and in the crystalline state. The  $C_{2v}$  isomer of  $C_{78}$  produces chestnut-brown solutions whereas solutions of the chiral  $D_3$  isomer are golden-yellow. Solutions of the  $C_{84}$  fraction are olive-

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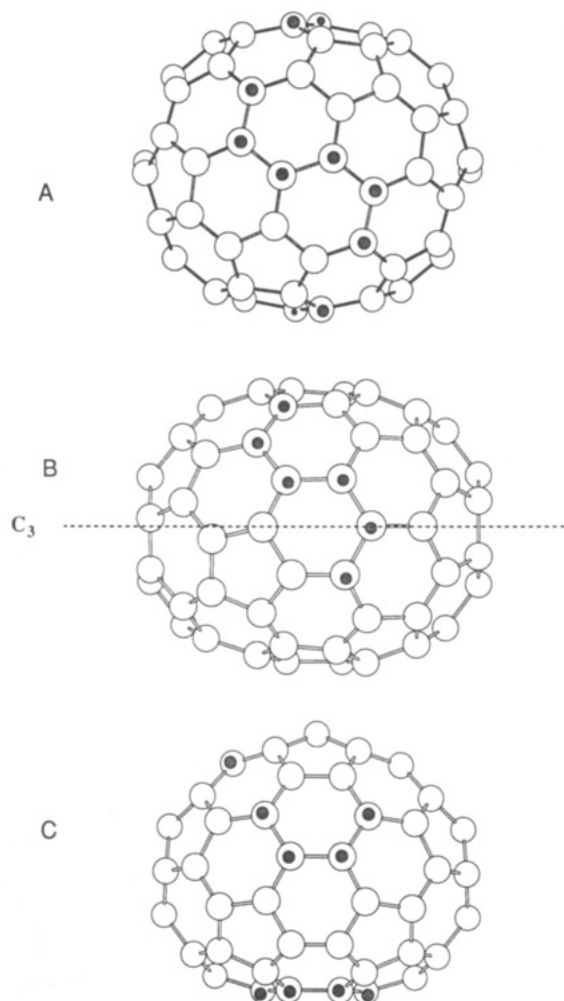
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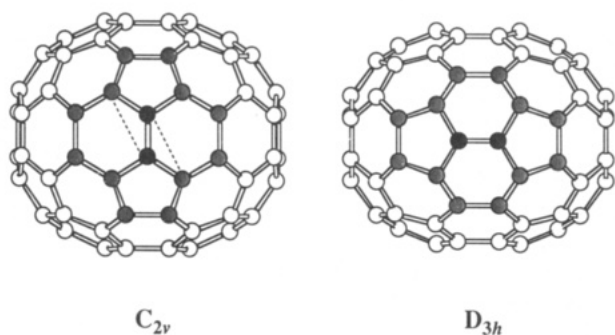
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**Figure 5.** Views of (A)  $C_{76}$ , (B)  $D_3-C_{78}$ , and (C)  $C_{2v}-C_{78}$  showing the pyrene-type carbon sites in the molecules. The view of  $C_{76}$  is along one of the three  $C_2$  axes,  $D_3-C_{78}$  is shown in a view onto one of the three symmetry-related smoothly curved faces, and  $C_{2v}-C_{78}$  is placed on its flat coronene base to show its helmet-type shape.



**Figure 6.** Interconversion between the  $C_{2v}$  and  $D_{3h}$  isomers of  $C_{78}$  via the  $4e^-$  pyraclyene rearrangement.

greenish. Figure 7 shows the electronic absorption spectra at the origin of these colors. All spectra are characterized by bands of weak to intermediate strength in the visible region and strong bands with molar extinction coefficients around  $100\,000\text{ L mol}^{-1}\text{ cm}^{-1}$  in the UV range below 300 nm. A loss of fine structure is observed with increasing fullerene size. For  $C_{60}$  and  $C_{70}$ , the absorption onset is seen at 635 and 650 nm, respectively.<sup>13a</sup> The onset of the absorption by the higher fullerenes occurs at longer wavelengths and is shifted into the near infrared. The maximum of the longest

wavelength band in  $C_{2v}-C_{78}$  is located around 700 nm, with the end absorption tailing to  $\approx 900$  nm, and the  $D_3$  isomer of  $C_{78}$  shows a set of distinct bands between 700 and 850 nm.<sup>17</sup>

Even further shifted into the near infrared is the absorption of chiral  $C_{76}$ . The onset of the strong long-wavelength transition ( $\epsilon = 3080\text{ L mol}^{-1}\text{ cm}^{-1}$  at 715 nm) is seen near 920 nm (1.39 eV) and therefore at a much lower energy than the onset of the longest wavelength transition in  $C_{60}$  (near 2.0 eV). Semi-empirical molecular orbital calculations qualitatively reproduce the smaller HOMO-LUMO gap<sup>31</sup> in  $C_{76}$  compared to  $C_{60}$  and suggest that  $C_{76}$  should be both a better donor and a better acceptor than  $C_{60}$ .<sup>16</sup> The prediction that  $C_{76}$  is a better donor than  $C_{60}$  and also  $C_{70}$  was recently confirmed experimentally by cyclic voltammetry.<sup>32</sup> In contrast to  $C_{60}$  and  $C_{70}$ , which only show high electron affinity,<sup>9a,33</sup>  $C_{76}$  is capable of both accepting and releasing electrons. A cyclic voltammogram in THF exhibits four reversible reduction steps as well as two reversible oxidation steps leading to a monocation and a dication, respectively. Similarly, four reversible reduction steps and one oxidation step are seen in the cyclic voltammogram of  $C_{2v}-C_{78}$ .<sup>32</sup>

### Perspectives of Research on Higher Fullerenes

Research on the higher fullerenes does not simply provide results similar to those obtained in the ongoing studies with  $C_{60}$ . On the contrary, the exploration of these molecular carbon allotropes leads to true discovery. Two of the isolated higher fullerenes are chiral, and many more chiral structures will be found. The preliminary electrochemical data on  $C_{76}$  and  $C_{2v}-C_{78}$  suggest that the chemistry of the higher fullerenes will be diverse and distinctively different from the chemistry of buckminsterfullerene and  $C_{70}$ .<sup>32</sup> Chemical conversions and electron-transfer processes passing through cationic intermediates could not be exploited with  $C_{60}$  and  $C_{70}$  but are now in reach with the larger carbon spheres. Recent results in the laboratory of Smalley et al.<sup>22</sup> suggest that metal ions induce, under endohedral complex formation, the generation of higher fullerene cages like  $C_{82}$  which we do not observe in our pure carbon soot. An important question is whether resistive heating of graphite gives the same products in the same ratio all over the world. Reports from the Japanese group of Achiba et al. describe a product distribution that differs from the one isolated in our laboratory; in an arc heating process, these researchers have obtained evidence for the formation of a third isomer of  $C_{78}$  ( $C_{2v}'$  in Table I) and for  $C_{82}$ .<sup>15d,34</sup>

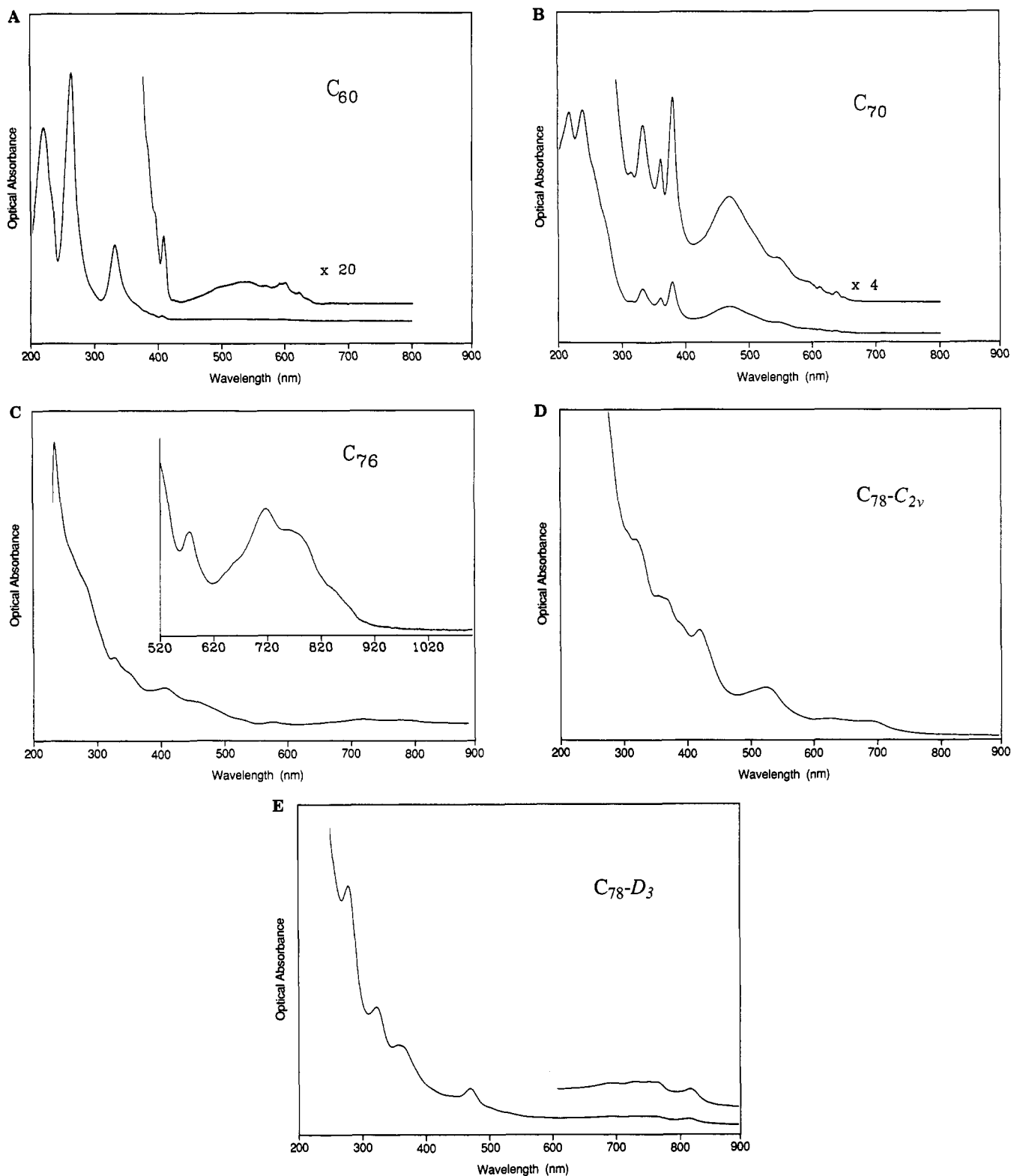
To advance the chemistry and physics of the higher fullerenes, the conditions for their formation need to be optimized. Closely related to this problem is the elucidation of the unprecedented mechanism for fullerene production. Although the initially proposed sequential shell closure mechanism<sup>2b,c</sup> seems very attractive to explain the formation of  $C_{60}$ , it is probably not a reasonable pathway under the harsh conditions of the production process. At temperatures of several

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**Figure 7.** Electronic absorption spectra recorded in hexane (C<sub>60</sub> and C<sub>70</sub>) and in dichloromethane (C<sub>76</sub> and C<sub>78</sub> isomers).

thousand degrees at the graphite electrodes, the assembly of ordered, entropically constrained structures is unlikely. Rather, we believe that the initial step involves the formation of a hot gas containing carbon atoms that react to give small reactive fragments like C<sub>2</sub> and C<sub>3</sub>. After thermal transport into less hot environments, these small carbon fragments could further react to give larger fragments, e.g., all-carbon chains and rings like C<sub>14</sub>, C<sub>18</sub>, and others. Intermolecular reactions of these intermediate-sized compounds could lead to a

whole variety of larger spheroidal compounds which eventually generate via rearrangement and fragmentation steps the stable fullerenes that are now isolated. This mechanistic picture, which finds indirect support in a variety of our experiments,<sup>14,17,20b</sup> awaits testing in challenging experimentation.

What are the structures of the giant fullerenes? Although the supersphere structures with large hollow cavities, proposed by Kroto for very large fullerenes,<sup>19</sup> are fascinating geometries, their formation does not

seem very probable. Nature generally does not create a vacuum and leave large empty spaces. Alternative types of structures for the larger fullerenes, with better space occupancy, have emerged from theoretical studies. Good space occupancy would be reached in molecular shapes that incorporate two stacking, large, planar, graphite-like segments connected by a sharply curved band incorporating the 12 fullerene pentagons.<sup>12c</sup> By extrapolating from the chiral  $D_2$  structures found for  $C_{76}$  and predicted for  $C_{84}$ ,<sup>29</sup> Labastie et al. constructed models for an infinite series  $D_2-C_{76+4m}$  of chiral double-helical fullerenes with quasi-cylindrical structures capped by bisections of  $I_h-C_{60}$ .<sup>35</sup> Similar to  $D_2-C_{76}$ , all members of this series can be bisected into two equivalent helical strands of edge-sharing pentagons and hexagons. Other series of low-strain cylindrical "carbon fiber" structures have also been generated,<sup>35</sup> and a

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theoretical study has raised the question of whether fullerene tubules have metallic character.<sup>36</sup> Already, such structures seem to have become a reality, since Iijima et al. recently reported on the isolation of needlelike microtubules of graphitic carbon.<sup>37</sup> It is clear from this brief outlook that fullerene research beyond  $C_{60}$  will provide unprecedented discovery in the years to come.

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