component (τ = 4.7 ns). This τ value is consistent with previous (room temperature) estimates of donor–acceptor center to center distance of 25 Å. The most important result is that the simplified kinetics at room temperature argue that any structural states of the complex which are trapped at 77 K are largely equilibrated at 300 K within 5 ns. This result suggests that motion at the cytc/ccp interface can be quite rapid and offers experimental support for the rapid restricted dimensional diffusion model of the cytc–ccp complex suggested by Brownian dynamics.[8] With this information now available, more detailed insight into the nature of the binding sites in principle could be obtained by comparing the decay distributions for the native systems with those for site-specific mutants.[9,10] Such studies are in progress.

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Characterization of the Soluble All-Carbon Molecules C_{60} and C_{70}

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We report on the further physical and chemical characterization of the new forms of molecular carbon, C_{60} and C_{70}. Our results demonstrate a high yield of production (14%) under optimized conditions and reveal only C_{60} and C_{70} in measurable quantity, in an 85:15 ratio. These two new molecular forms of carbon can be completely separated in analytical amounts by column chromatography on alumina. Comparison among mass spectra obtained by the electron impact, laser desorption, and fast atom bombardment (FAB) methods allows a clear assessment of the composition of the mixed and pure samples, and of the fragmentation and double ionization patterns of the molecules. In addition, spectroscopic analyses are reported for the crude mixture by ^{13}C NMR and by IR spectroscopy in KBr pellet, and for pure C_{60} and C_{70} in solution by UV–vis spectroscopy.

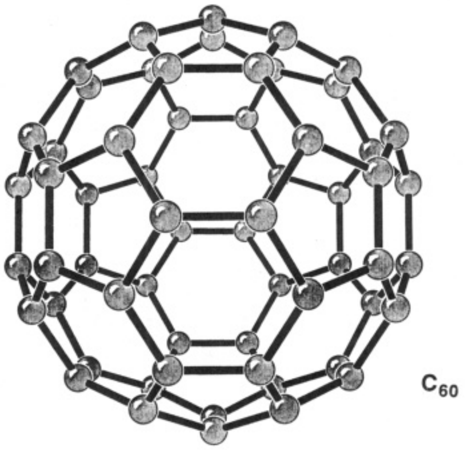
Introduction

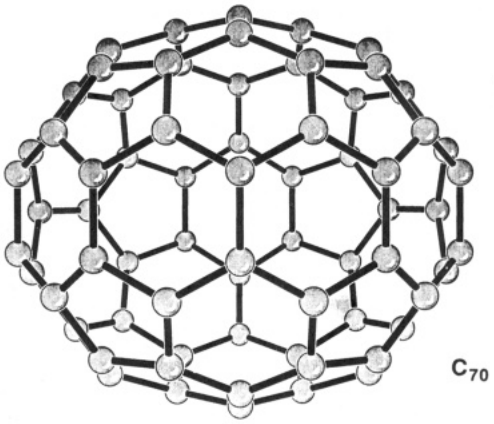
In a surprising recent development, Krätschmer et al.[1] have shown that certain all-carbon molecules are produced in large quantities in the evaporation of graphite and can be isolated as soluble, well-defined solids. The major species was identified as molecular C_{60} through mass spectrometry and by comparison of the infrared spectrum with theoretical predictions for the celebrated truncated-icosahedron structure, which had earlier been proposed to account for cluster beam observations.[2] The solid material, described as a new form of elemental carbon in a nearly pure state, has a disordered *hcp* lattice of packed quasi-spherical molecules, but determination of the precise molecular structure awaits diffraction from well-ordered crystals.

Kroto et al.[3] have followed this announcement with a partial chemical separation of the soluble all-carbon molecules generated by the same procedure. They used mass spectrometric evidence to conclude that other air-stable C_n molecules are present (n = 62, 64, 66, 68, 70). They reported that chromatographic separation yields C_{60} and C_{70} in a 3:1 ratio, in contrast to the 2–10% of C_{70} estimated in ref 1. The reported ^{13}C NMR spectrum of the C_{60} fraction, in particular, evidently confirms the existence of a species with all 60 carbon atoms chemically equivalent (proposed structures as shown in Chart I).

This paper describes the further physical and chemical characterization of these two new forms of molecular carbon.[4] Our results include the high-yield production (14%) of soluble material under optimized conditions, consisting of only C_{60} and C_{70} in measurable quantity. These have been separated in analytical amounts by column chromatography and have been characterized in pure or mixed forms by a combination of electron impact, fast atom bombardment (FAB), and laser desorption mass spectrometry. Spectroscopic characterization is reported including the ^{13}C NMR spectrum and the infrared absorption spectrum for the crude C_{60}/C_{70} mixture, and the UV–vis spectrum of pure C_{60} and C_{70} in solution. All five peaks of C_{70} in the ^{13}C NMR spectrum are

CHART I





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unambiguously found.

Preparation Method and Chromatographic Separation

Two sets of samples have been used in the experiments described below, i.e., one prepared in Heidelberg,[1] used in the earlier stage of this work, and samples newly collected in Los Angeles. We now describe in more detail the method used and yields obtained in the latter preparations. The samples have been prepared following closely the method described by Krätschmer et al.[1] A carbon rod is evaporated by resistive heating under partial helium atmosphere (0.3 bar). The best results were obtained from high-uniformity graphite rods (Poco Graphite, Inc., Type DFP-2, <4 μm grain size, 0.8 μm average pore size). The rods are 1/8 in. diameter and emit a faint gray-white plume when heated by a current of 140–180 A. The sootlike material, collected from the partial evaporation of rods onto a glass shield surrounding the electrodes, is extracted with boiling benzene or toluene to give, after filtration, a brown-red solution. Evaporation yields a brown-black crystalline material in 14% yield (30 mg, identified below to be C_{60} and C_{70}). This yield is higher than reported earlier (ca. 1%,[1b] or "up to 8 percent"[3]) and is believed to be related to the graphite quality and the higher He pressure used. Further evaluation of these methods and yields will follow in a subsequent paper. Chromatographic filtration of the concentrated solution of "crude" material on silica gel with benzene can be performed, but the material obtained remains identical, in all aspects (same C_{60}/C_{70} ratio, no other constituents), to the crude material obtained from the benzene extractions.

Separation of the mixture of C_{60}/C_{70} proved to be a challenging task, particularly because of the poor solubility of the material in most organic solvents. While the solubility in benzene is about 5 mg/mL at 25 °C, the compound is soluble with difficulty at the same temperature in chloroform, dichloromethane, tetrachloromethane, diethyl ether, tetrahydrofuran, *n*-hexane, *n*-pentane, and *n*-octane. The mixture of C_{60}/C_{70} dissolves appreciably better in boiling cyclohexane, from which small black cubes crystallize out on cooling. The material did not melt below 360 °C in a sealed tube; the resulting sample redissolves in benzene, showing no sign of decomposition.

Analytical thin-layer chromatography on silica gel indicated some separation with *n*-hexane or with *n*-pentane as eluents, but not with cyclohexane. Analytical HPLC performed with hexanes (5-μm Econosphere silica, Alltech/Applied Science) gave a satisfactory separation (retention times 6.64 and 6.93 min for C_{60} and C_{70}, respectively, at a flow rate of 0.5 mL/min; detector wavelength, 256 nm), indicating the content of C_{70} to be approximately 15% for the Los Angeles samples. Two other minor peaks, possibly other unidentified C_n species, were observed (retention times 5.86 and 8.31 min), but they constituted less than 1.5% of the total mass.

Column chromatography with hexanes on flash silica gel gave a few fractions of C_{60} with ≥95% purity, as determined by HPLC, along with later fractions containing mixtures of C_{60}/C_{70} in various ratios. Because of the poor solubility of C_{60} and C_{70} in these alkanes, only limited amounts of pure C_{60} were made available this way, in insufficient quantity for a reliable ^{13}C NMR spectrum to be measured (see below). However, column chromatography on neutral alumina with hexanes gave an *excellent* separation in analytical quantities. Thus, pure fractions containing C_{60} (99.85%) and C_{70} (>99%) were obtained, as indicated by mass spectrometric measurements described below.

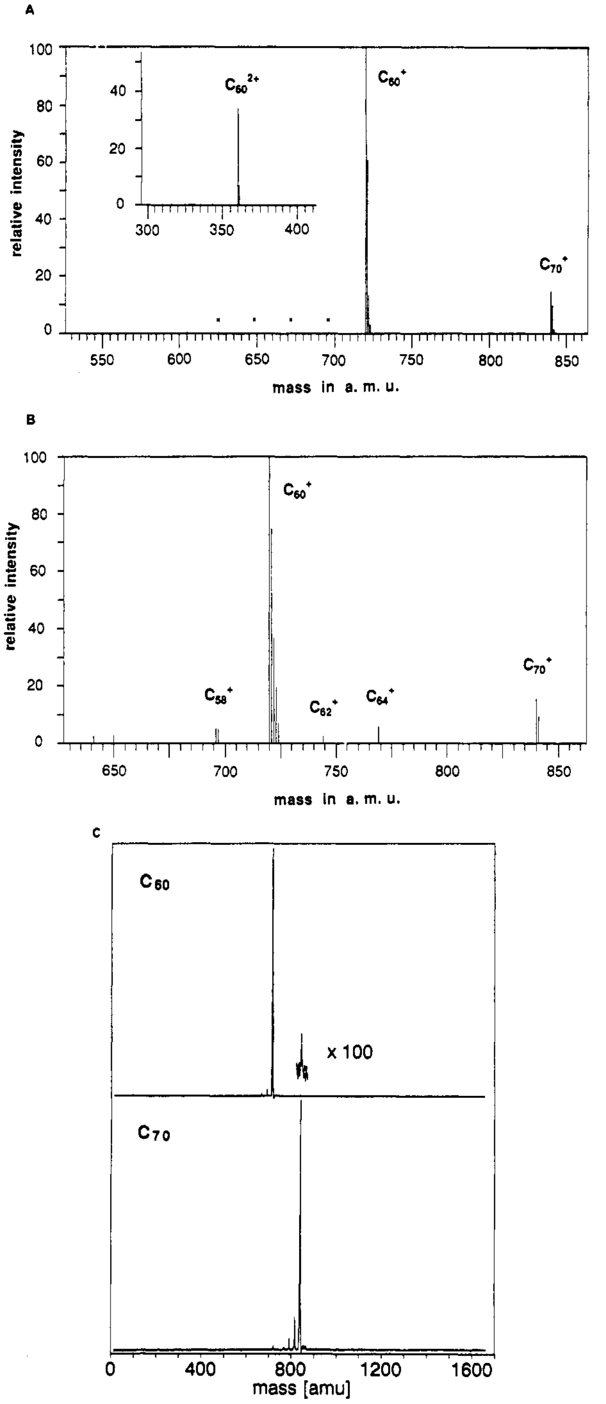

Figure 1. (A) EI MS spectrum of the C_{60} and C_{70} mixture at 70 eV, with a source temperature of 340 °C. Peaks marked with an × are for the ions of C_{58}, C_{56}, C_{54}, and C_{52} at m/z = 696, 672, 648, and 624, respectively. The insert shows the C_{60}^{2+} ion of the same sample. The C_{70}^{2+} ion which also appears in the spectrum is not shown. (B) FAB MS spectrum of the C_{60} and C_{70} mixture with NOBA as the matrix. (C) Laser desorption mass spectra of *pure* C_{60} (above) and C_{70} (below).

Mass Spectrometric Characterization

The 70-eV EI mass spectrometric measurements of the C_{60}/C_{70} mixture's vapor at a source/probe temperature of 340 °C gave exceptionally clean spectra for the samples (Figure 1A). The C_{60}^+ ion at m/z = 720 and the C_{70}^+ ion (m/z = 840) are dominant, each with precisely the expected isotopic patterns. The next larger peaks are the doubly charged species C_{60}^{2+} and C_{70}^{2+}, at about one-third of the base-peak intensities, indicating that they must be very stable species as well. At lower ionization energy (16 eV), the doubly charged peaks disappear. From several EI spectra, the average ratio of C_{60} to C_{70} was determined to be 87:13, in striking accordance with the HPLC and the ^{13}C NMR esti-

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(1) (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (b) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167.

(2) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Curl, R. F.; Smalley, R. E. *Science* **1988**, *242*, 1017.

(3) Private communication from H. W. Kroto.

(4) D. Bethune et al. have also reported a partial separation by sublimation and Raman spectra of C_{60} and C_{70}; Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. *Chem. Phys. Lett.*, in press.

mations (see below). It seems possible that previous estimates[1a] of the C_{70} content ($\sim$2%) of the crude C_{60} samples might have resulted from selective sublimation during the preparation of samples for IR and mass spectrometry. To examine this possibility, we have recorded the apparent abundances of the two molecules as the source/probe temperature is increased from 240 to 340 °C and find that the composition of the vapor changes from >99% C_{60} to the above ratio between 260 and 320 °C. A full analysis of the sublimation properties of these species will be reported separately.

The 70-eV EI spectrum of Figure 1A also contains peaks of C_{58}, C_{56}, C_{54}, and C_{52} at m/z = 696, 672, 648, and 624, respectively, corresponding to the expected fragmentation pattern.[5] Because they fail to appear at 16 eV, they must presumably result from fragmentation of the C_{60}^+ ion, yet their low abundance (0.8% summed together) suggests a very high stability to the carbon cage of C_{60}.

The fast atom bombardment (FAB) mass spectra of the *same* material were again astonishingly simple (Figure 1B), revealing only C_{58}, C_{62}, and C_{64} species besides the C_{60}^+ and the C_{70}^+ ions. No peaks were found beyond m/z = 840/841/842 (up to m/z = 1200), thus indicating the absence of higher mass C_n species. In agreement with the EI spectra of the high-temperature vapor, the FAB results indicated the C_{60}/C_{70} ratio to be 87:13. However, the minority species are more abundant than in the EI spectra and are probably the result of intermolecular reactions/fragmentations in the m-nitrobenzyl alcohol (NOBA) matrix used in FAB MS.

The laser desorption method is less destructive than the FAB method, but shares the feature of not requiring a continuous, long-time heating of the sample.[6b] Accordingly, the very clean LD mass spectra of C_{60} and C_{70} (Figure 1C) were obtained by time-of-flight analysis of the ions desorbed when 266-nm laser pulses were directed into a pulsed He jet flowing over the sample. On the crude mixture of C_{60}/C_{70}, it was found that all features of (0–2000 amu) except C_{60} and C_{70} vanished at the lowest laser fluences, and these exhibited the same ratio (88:12), within experimental uncertainty, as found in the high-temperature EI mass spectra. When applied to the samples of C_{60} and C_{70} separated by column chromatography on alumina, the C_{60} fraction was found to have a purity of 99.85%, with C_{70} as the residual. On the other hand, the C_{70} fraction had a purity of >99%; the minor peaks, corresponding to C_{68}, C_{66}, C_{64}, and C_{60}, are found by careful analysis of the laser-fluence dependence to all be fragmentation products of C_{70}. In particular, the relative intensity of the C_{60} peak increased directly with increasing laser fluence, thus demonstrating that it results from the fragmentation of C_{70}.

Carbon-13 NMR Spectra

The crude samples of C_{60}/C_{70} obtained from our two sources were independently investigated by ^{13}C NMR and gave identical results. Since it was expected that the spin-lattice relaxation time of the ^{13}C nuclei would be quite long, an inversion recovery experiment was performed to obtain a rough estimate of T_1. Thus, it was determined that T_1 for C_{60} was ≥20 s. The samples of C_{60}/C_{70} were dissolved in an excess of benzene-d_6 and evaporated at 25 °C until saturation was achieved. Using a 30-deg pulse and a 20-s pulse delay, a total of 5780 accumulations obtained over 32 h on a Bruker AM 360 instrument (90.56 MHz) gave a spectrum with an acceptable signal/noise ratio, showing clearly the presence of C_{60} and C_{70} only (Figure 2B). Thus, the peak corresponding to C_{60} is observed at 143.2 ppm (cf. ref 3), and the peaks at 130.9, 145.4, 147.4, 148.1, and 150.7 ppm are attributed to C_{70}, the number of carbons and the 10/20/10/20/10 peak ratio being as expected for the proposed molecular structure.

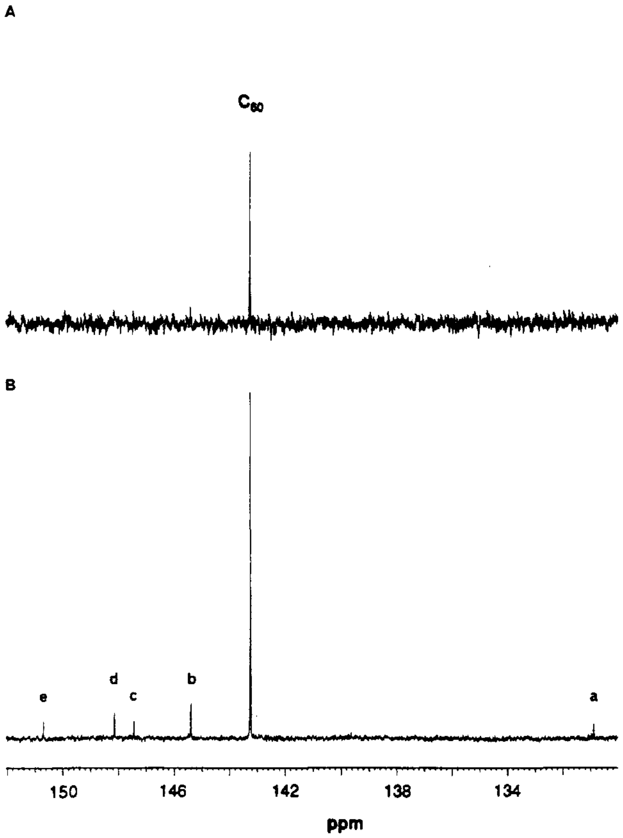

Figure 2. (A) ^{13}C NMR spectrum of a C_{60} and C_{70} mixture in benzene-d_6 at 296 K after 484 accumulations with a 2-s delay between 30-deg pulses. (B) Same sample after 5780 accumulations with a 20-s delay between pulses. Peaks labeled a, b, c, d, and e are assigned to C_{70}. Both spectra are plotted from 130 to 152 ppm.

The ^{13}C NMR spectrum shown in Figure 2A was performed on the same sample with only 484 accumulations with a 2-s delay between pulses. Thus it is possible to see the single C_{60} peak in a very short time during the experiment. This demonstrates that erroneous interpretations about the purity of the sample can be made if too few accumulations or a less sensitive instrument is used.

With relaxation times for the ^{13}C nuclei of C_{60} and C_{70} being probably very similar, an estimate of the ratio of the two compounds (Figure 2B) by comparison of the peak heights was expected to give a good estimate of the composition of the compound. Thus, the ratio was determined to be 82:18, in reasonable accordance with the HPLC and mass spectrometric determinations described above.

As expected, the proton NMR spectra of the samples dissolved in benzene-d_6 were devoid of any absorptions besides the C_6D_5H peak at 7.15 ppm and a few impurities at 0.3–1.4 ppm, also present in neat solvent.

Optical Absorption Spectra

In ref 1, the optical absorption spectrum in the ultraviolet and visible region was reported for the sublimed C_{60}/C_{70} mixture as a neat solid film. In our work, the spectra of pure C_{60} and C_{70} were recorded in n-hexane. Figure 3 shows the absorption spectra in the 200–800-nm region for C_{60} (99.85% purity) and C_{70} (>99%) at 25 °C. Compared with the spectrum of ref 1, one observes small hypsochromic shifts of the peak maxima of C_{60} and alterations in relative intensities as a result of removing the C_{70} contaminant. In addition, the spectrum of pure C_{70} appears to be distinct from any previously reported, including the brief list of maxima given for a sample of unstated purity in ref 3.

Absorption by C_{60} begins with an abrupt onset of 635 nm, followed by several bands of varying width (centered at 621, 598, 591, 568, 540, and 492 nm), and a highly transparent region at 420–440 nm. The structure of the visible absorption spectrum

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(5) Radi, P. P.; Bunn, T. L.; Kemper, P. R.; Molchan, M. E.; Bowers, M. T. *J. Chem. Phys.* **1988**, *88*, 2809.

(6) (a) For the gas-phase synthesis of another carbon allotrope, C_{18}, see: Diederich, F.; Rubin, Y.; Knobler, C. B.; Whetten, R. L.; Schriver, K. E.; Houk, K. N.; Li, Y. *Science* **1989**, *245*, 1088. (b) For a preparation of C_{60} and C_{70} starting from molecular precursors, see: Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.*, in press.

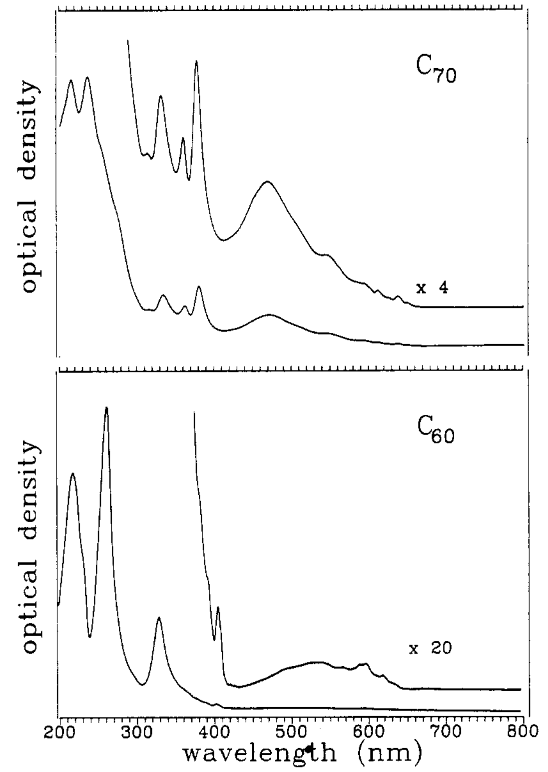

Figure 3. (A, top) Electronic absorption spectrum of dilute C_{70} in hexanes at 25 °C. The insert is the spectrum of the same sample at 4× concentration. (B, bottom) Electronic absorption spectrum of dilute C_{60} in hexanes at 25 °C. The insert is the spectrum of the same sample at 20× concentration.

is suggestive of vibrational structure from one or two forbidden electronic transitions. The combination of transparency in this blue region and in the red (>635 nm) gives dilute solutions a distinct purple color to the eye. A second onset leading to stronger absorption occurs in the form of a band at 404 nm, with a shoulder at 408 nm. These are followed by distinct shoulders at 396, 391, 377, and 365 nm, also suggestive of vibrational structure, appearing on a strong rise toward the first major maximum at 328 nm. The ultraviolet region is dominated by this feature and two other strong broad bands peaking at 211 and 256 nm, the former with a shoulder at 227 nm.

Based on these results, it seems unlikely that neutral C_{60} is the carrier of the interstellar 220-nm absorption band,[7] as the 255- and 330-nm peaks are not concurrently observed.

Absorption by C_{70} begins with a weak onset band at 650 nm, followed by a series of peaks (637, 624, 610, 600, and 594 nm) superimposed on a gradually rising continuum leading to stronger maxima at 544 and 469 nm. A broad minimum covers the blue-violet region, and maxima of intermediate strength appear in the near-ultraviolet region at 378, 359, and 331 nm. Following a weaker maximum at 313 nm, very strong absorptions appear with three shoulders leading to the dominant bands at 236 and 215 nm. Dilute C_{70} solutions are orange-red in color. Detailed comparison of the spectra indicates no coincidences between C_{70} and C_{60} bands, as would be expected from the purities stated above.

The FT-IR spectrum of the C_{60} and C_{70} mixture performed with a conventional KBr pellet showed the four strongest bands for C_{60} at 1430, 1182, 577, and 527 cm^{-1}, as observed previously by Krätschmer et al.[1] In addition, the strong peak at 673 cm^{-1} mentioned by these authors was present, together with a smaller peak at 795 cm^{-1}.

Conclusion

The new molecular forms of carbon, C_{60} and C_{70}, were prepared following the method of Krätschmer et al.[1] in a consistently high yield (14%).[1] The benzene-soluble material extracted from the graphite evaporation product is predominantly constituted of C_{60} and C_{70}. Three independent methods, namely HPLC, mass spectroscopy, and ^{13}C NMR, demonstrate that these two compounds are present in a ratio near 85:15. The two compounds can be separated by column chromatography on alumina, allowing as for now the purification of minute quantities of pure C_{60} and C_{70}. Support for the proposed symmetrical cage structures (fullerenes) of C_{60} and C_{70} is inferred from the simplicity of the ^{13}C NMR spectra and the strong presence of the C_{60}^{2+} and C_{70}^{2+} ions. Attempts at the X-ray determination of the C_{60} molecular structure are now actively pursued.[6]

Note Added in Proof. The soluble byproduct (HPLC retention time 8.31 min) has since been isolated and determined to be C_{84} by laser desorption MS. The ^{13}C NMR spectrum of *pure* C_{70} (in 1,1,2,2-tetrachloroethane-d_2) has *only* the five lines at 131.0, 145.4, 147.5, 148.2, and 150.8 ppm.

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(7) Huffman, D. R. *Adv. Phys.* **1977**, *26*, 129.