

New carbon materials

Recent research with carbon has amplified knowledge of fullerenes, especially the C_{60} molecule and nanotubes. Carbon is an important element occurring in a staggering number of compounds, many with extensive industrial uses. Carbon is found in nature in two pure crystalline forms: as diamond, an insulator that is the hardest material known; and as graphite, a soft, electrically conducting material. Graphite is used in pencil lead and as a lubricant, among other things.

The difference between diamond and graphite lies in the bonding configuration of the carbon atoms. In diamond the carbon-carbon bonds lock the atoms into a strong three-dimensional (3D) covalently bonded network, while in graphite the carbon atoms are covalently bonded only into two-dimensional (2D) sheets. The sheets then stack one on top of the other to form a 3D solid. The binding between the sheets in graphite is due to relatively weak van der Waals bonds, and it is the easy sliding of one sheet over the next that gives graphite its slippery feel and lubricating qualities. Interestingly, the carbon-carbon bonds within a single sheet of graphite (sometimes called a graphene sheet) are even stronger than the 3D bonds in diamond, and so an ideal defect-free graphene sheet is theoretically the strongest (stiffest) material known. This property of graphite is exploited in graphite fibers, which can be made in different forms but often approximate sheets of (unfortunately highly defected) graphite scrolled up into long fibers with diameters of the order of micrometers.

Pieces of graphite sheets can be arranged to form small and perhaps more perfect carbon structures. In a graphite sheet, the carbon atoms are arranged in a honeycomblike lattice (Fig. 1). The bonds between the atoms form hexagons. It turns out to be geometrically impossible to roll or fold such a sheet, containing just hexagons, into a perfectly closed hol-

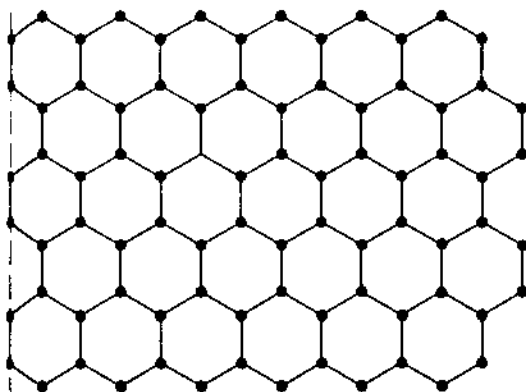


Fig. 1. Hexagonal "honeycomb" network, representative of arrangement of carbon atoms in a graphene sheet. The carbon atoms (dots) are at the vertices of the bonds. The broken lines delineate a strip that could be rolled into a tube; the particular tube segment thus formed would have six hexagons around its waist.

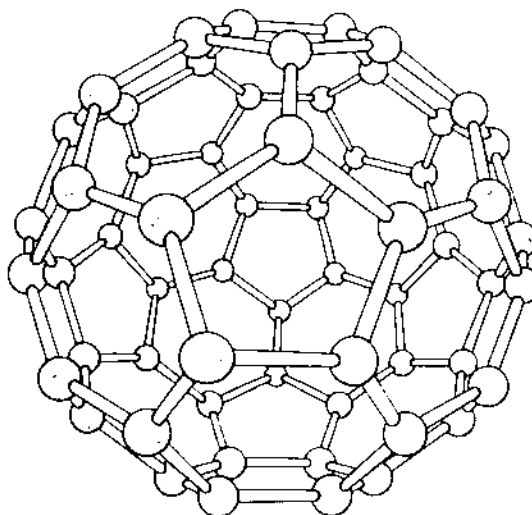


Fig. 2. Model of the buckyball, C_{60} . In this highly symmetrical carbon molecule, all 12 pentagons are isolated from each other.

low form. To accomplish closure, one must introduce pentagons. According to a theorem by Euler, one must introduce 12 pentagons to achieve a closed object. Surprisingly, this is independent of the number of hexagons in the final structure. The pentagons introduce the curvature needed for closure.

It might seem, then, that nature should abound with a huge number of different shell-like pure-carbon molecules, formed from various hexagon and pentagon arrangements of carbon atoms. This is certainly not the case. The reason is that the introduction of pentagons into a hexagonal carbon network is energetically very costly. Particularly costly is placing pentagons adjacent to one another. Therefore, the structures most likely to form would be those obeying an "isolated pentagon rule." Synthesizing even such isolated pentagon pure-carbon structures would necessarily require nonequilibrium methods, as graphite is the lowest-energy form of carbon and would be the natural product of any equilibrium growth process ("nonequilibrium" methods are of course also needed to produce diamond, which has a higher energy than graphite and is again, strictly speaking, metastable).

The field of pure-carbon cage molecules was born a decade ago when scientists synthesized and characterized small numbers of such structures in molecular beam experiments. An intense laser was used to vaporize a graphite target and create a nonequilibrium plasma or "soup" of hot isolated carbon atoms and carbon dimers, which upon rapid cooling coalesced into pure-carbon cage molecules. The most abundant and most stable of these molecules contained 60 carbon atoms in a highly spherical arrangement (Fig. 2). This molecule, C_{60} , was named buckminsterfullerene, or buckyball for short, by its discoverers (in honor of R. Buckminster Fuller, a practitioner of geodesic dome architecture). This discovery initiated the field of fullerenes, the name

given to this entire class of pure-carbon cage molecules.

Higher- and lower-order fullerenes. The laser-vaporization synthesis method described above for fullerenes yields not only C_{60} but structures containing an even number N of carbon atoms less than or greater than 60. The structures with $N > 60$ are termed higher-order fullerenes, while those with $N < 60$ are termed lower-order fullerenes. C_{60} holds a special place in the fullerene family: it is the smallest fullerene which obeys the isolated pentagon rule. In fact, it has been suggested that C_{60} might be the smallest stable fullerene possible.

The laser-produced molecular beam experiments yield a rich spectrum of gas-phase fullerene molecules, including those with N greater than and less than 60, but that alone does not ensure that such molecules are stable enough to be produced in bulk, that is, in sufficient quantity that the molecules can be packed together into a solid. Achieving a solid (usually crystalline) arrangement of the molecules is of great importance for many characterization experiments, and having bulk quantities available is necessary for most applications as well.

Bulk quantities of fullerenes may be produced using a carbon-arc-generated plasma. This method easily produces significant amounts of C_{60} , and its application has been instrumental in the production and study of bulk samples of C_{60} . The solid form of pure C_{60} , which can be viewed as a molecular solid, is precisely that expected from close-packing hard spheres into a minimum volume. The diameter of a single C_{60} molecule is about 0.71 nanometer, and in the face-centered-cubic packing arrangement the C_{60} crystal lattice constant is 1.417 nm. The C_{60} crystal is held together by weak van der Waals bonds, and as such the overall solid is soft (although the buckyballs themselves are quite robust and hard). Interestingly, at room temperature the C_{60} molecules in the solid appear to be freely spinning about their equilibrium positions. Although it was first believed that these weak bonding properties might lead to superior lubrication properties, it turns out the the C_{60} molecular units are simply too small to act as efficient roller bearings between commonly machined surfaces.

The above method is currently the most efficient one not only for producing C_{60} but for producing bulk amounts of higher-order fullerenes as well, such as C_{70} , C_{76} , C_{82} , and C_{84} . It was believed that lower-order fullerenes were simply too unstable to be produced in bulk.

C_{36} fullerene. Lower fullerenes necessarily violate the isolated pentagon rule. However, a theoretical study determined that a spherical shell arrangement of 36 carbon atoms should nevertheless be stable. Of the many arrangements possible for placing 36 atoms in a shell using hexagons and pentagons, two have a particularly low energy and are thus the most likely to form. They are designated d_{6h} and d_{2d} (Fig. 3) to identify the particular symmetry of the molecule. The d_{6h} structure is simple: it consists of six hexagons wrapped around the belly of the molecule, followed

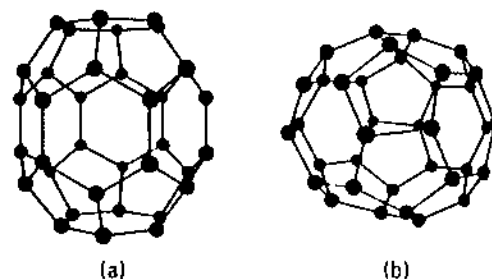


Fig. 3. Two isomers of C_{36} . (a) d_{6h} , (b) d_{2d} . Both versions contain adjacent pentagons. (Courtesy of J. Grossman)

by six adjacent pentagons on each cap. The very top and bottom of the caps are again a hexagon. The adjacent pentagons close the structure quickly, but at the expense of introducing much strain energy into the structure. The highly strained pentagon bonds are expected to be chemically very reactive. Thus, if C_{36} were formed, it should be particularly susceptible to bonding (with itself and with other atoms and molecules). This interesting (and possibly useful) feature has earned C_{36} the nickname "stickyball." In fact, because of its aggressive bonding nature, a solid formed from pure C_{36} is predicted to be very different from the van der Waals-bonded C_{60} solid. The C_{36} solid would be more covalently bonded, resulting in much greater mechanical strength. From theoretical predictions, the C_{36} molecule is 0.52 nm tall and 0.49 nm across at the waist. These dimensions make C_{36} significantly smaller than the C_{60} molecule (Fig. 4).

Bulk amounts of C_{36} can be synthesized using the nonequilibrium arc-plasma method. Scientists using such an approach, by "detuning" the synthesis conditions far away from those for optimal C_{60} production, were able to generate bulk quantities of C_{36} . One problem in producing the C_{36} is its propensity toward forming chemical bonds. If not handled properly, the material reacts with impurities in the environment, or even itself spontaneously polymerizes into a fused network of C_{36} molecules. This is of course exactly what is expected, given the high curvature and reactivity of the molecule.

So far, on an absolute scale only modest amounts of C_{36} have been produced, and many more experiments are needed to fully understand the properties of the isolated molecules and the C_{36} -based covalently bonded polymers and 3D solids. Interestingly, when thin films of C_{36} were produced, they were found to be extremely hard and scratch-resistant, quite unlike typical fullerene films or those based on other carbon types, such as amorphous carbon. This may have important industrial applications.

Additional theoretical studies have shown that C_{36} holds more surprises. It is predicted that for a particular crystal structure (arrangement of the molecules) of solid C_{36} , the material in its pure form will be electrically conducting, yielding an all-carbon metal. Furthermore, because of a favorable combination of

suitable electronic states and interactions between the electrons and atomic vibrations within the solid. C_{36} might display superconductivity (the complete loss of electrical resistance) at moderately high temperatures. These predictions have not yet been confirmed. See SUPERCONDUCTIVITY.

Carbon nanotubes. If one of the caps of the d_{60} C_{60} molecule is removed and an extra belt of hexagons is inserted, the molecule will be extended. Successive additions of such belts of hexagons will lead to a tubular structure, a carbon nanotube.

Geometrically, nanotubes can be constructed by cutting a strip from a graphite sheet and rolling this into a perfect seamless cylinder. The nanotube derived from the C_{60} molecule will be formed by using the strip outlined by the broken lines of Fig. 1. Obviously, this nanotube is not the only possibility. The geometry of a graphite sheet allows strips to be cut out not only with different (quantized) widths but also at different angles, leading to nanotubes with different diameters and chirality. An example of a chiral system is a barber pole or candy cane design: there is a certain helicity as one advances along the axis of the tube. As it turns out, the electrical properties of a carbon nanotube are extremely sensitive to the diameter and chirality of the tube. Some nanotubes are semiconductors, while others are metals.

A seamless defect-free nanotube would be a physical realization of the idealized graphite fiber discussed earlier. Such a system would have, in addition to the unusual electrical properties, outstanding mechanical and thermal properties.

Carbon nanotubes were first experimentally observed in high-resolution transmission electron microscopy studies of fullerene by-products. The non-equilibrium synthesis methods previously described for fullerenes are also quite efficient at nanotube production. Depending on the synthesis conditions (such as type of catalyst used), nanotubes with different geometries are produced (Fig. 5). Some are multiwalled, where many tubes are arranged coaxially and fit perfectly one inside the other (much like the collapsed segments of an old-fashioned mariner's telescope); others are single-walled. Often the single-walled tubes arrange themselves in an ordered bundle, resembling the closely packed strands of a steel cable. Nanotubes have also been produced from elements other than carbon, such as combinations of boron and nitrogen.

Typically, carbon nanotubes have an extremely high aspect ratio. They might be about 1–10 nm in diameter but many hundreds of micrometers in length. For comparison, if a typical garden hose of diameter 2 cm (0.8 in.) had the same aspect ratio, it would be several kilometers long. Despite their long relative length, nanotubes as currently produced are still too short for many mechanical applications, such as structural reinforcements. However, the unusual electronic properties have been exploited to form nanoscale electronic devices, such as rectifiers and transistors. Nanotubes might also be useful for energy storage systems. See NANOCHEMISTRY.

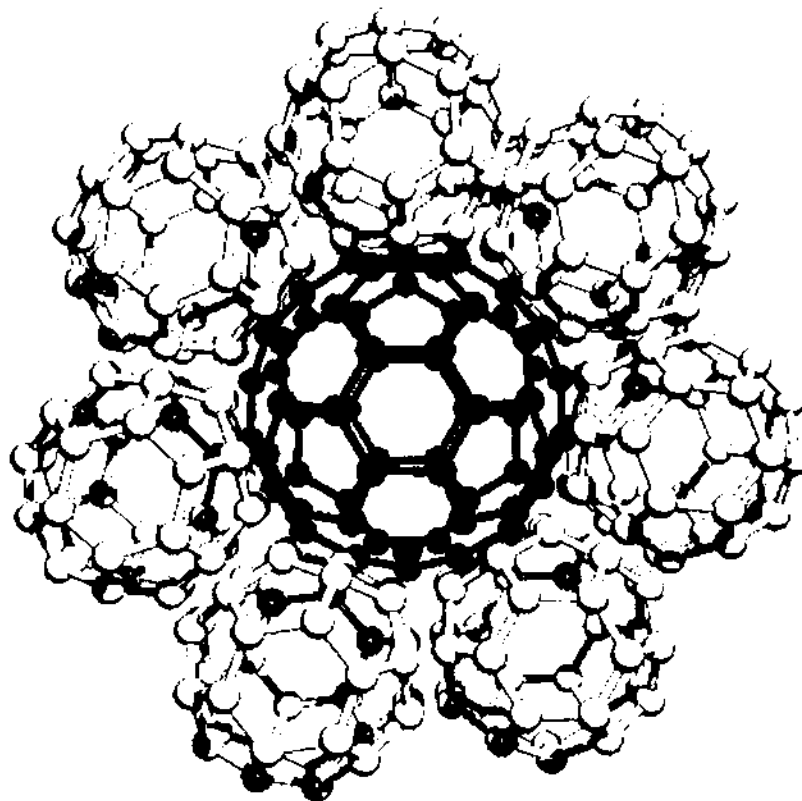


Fig. 4. Schematic representation of a C_{60} molecule surrounded by seven C_{36} molecules. C_{36} is significantly smaller than its buckyball cousin. (Courtesy of C. Piskoti)

Cut tubes. Part of the problem in exploiting nanotubes for many useful applications is that they often form a highly entangled mat. Untangling the mat is difficult, if not impossible, by known mechanical means. It is as if one had a hopelessly tangled ball of ultra-high-strength nylon fishing line. To extract useful pieces of the fishing line, it would be tempting to snip away at the ball with scissors and thus free up (shorter) pieces of the line.

The goal of systematically shortening tubes was recently achieved. Ultrasonic and chemical means were used to "cut" long pieces of nanotubes into shorter, manageable pieces. The cut tubes begin to resemble fullerene molecules. This molecular form for the tubes has tremendous advantages. For example, the short tubes dissolve in (or at least appear to be suspended in) various solvents, making available

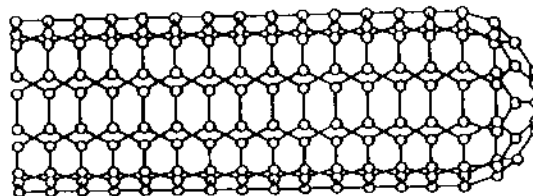


Fig. 5. Model of a carbon nanotube. The cylindrical body contains only hexagons, while the end cap contains some pentagons. Each end cap in a perfect tube would include six pentagons. (After M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, 1996)

many of the powerful techniques of wet chemistry. This allows, for example, different chemical species to be attached to the walls or ends of the tubes (such modifications are called functionalization), or it allows tubes to be easily mixed with other materials to form composites. It may even be possible, using appropriate templates or functionalization, to coax nanotubes in solution to self-assemble into useful patterns. This might be one way to make use of their unusual electronic and mechanical properties.

For background information see CARBON; FULLERENE; GRAPHITE; NANOCHEMISTRY; NANOSTRUCTURE; SCANNING TUNNELING MICROSCOPE; SEMICONDUCTOR; SUPERCONDUCTIVITY in the McGraw-Hill Encyclopedia of Science & Technology. A. Zettl

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Nobel prizes

The Nobel prizes for 1998 included the following awards for scientific disciplines.

Chemistry. Walter Kohn received one-half of the prize for his development of the density-functional theory. John A. Pople received the other half for his development of computational methods in quantum chemistry. Kohn is professor of physics at the University of California, Santa Barbara, and Pople is professor of chemistry at Northwestern University.

The theoretical work developed by Kohn helped to simplify the mathematics used to describe the bonding of atoms. Ignoring the motion of each individual electron, Kohn was concerned with the average number of electrons located at any one point in space. Called the density-functional theory, it is a computationally simpler method, allowing for the study of very large molecules.

In 1964 Kohn was able to demonstrate a correlation between the total energy for a system as related to the known electrons' spatial distribution (electron density). He was able to theoretically calculate the energy depending on the density. It took several decades and modifications to this theory before the

equation for determining the energy could be used to study molecular systems of increased size. The density-functional theory is used in various chemical applications, from calculating the geometrical structure of molecules (providing bonding distance and angles) to outlining chemical reactions (such as enzymatic reactions).

Pople developed quantum-chemical methodology currently used in various branches of chemistry. His computational methods allowed for the theoretical study of molecules, their properties, and their behavior in chemical reactions. A computer is fed input data regarding specific details of a molecule or a chemical reaction. The output describes molecular properties or how a chemical reaction might take place. Results are generally used to explain or illustrate the outcome of various experiments.

As theoretical methodology was significantly improved at the end of the 1960s, Pople designed a computer program which was superior to others in a number of significant points. He made his computational methods easily accessible to researchers by designing the GAUSSIAN-70 computer program, first published in 1970. He refined the methodology during the 1970s and 1980s while producing advanced chemistry models. Pople included Kohn's density-functional theory in the GAUSSIAN program in the 1990s. The GAUSSIAN program is now used by chemists in universities and commercial companies the world over. These improvements are enabling chemists to analyze increasingly complicated molecules.

Physics. The physics prize was awarded to Robert B. Laughlin of Stanford University, Horst L. Störmer of Columbia University and Bell Laboratories (Murray Hill, New Jersey), and Daniel C. Tsui of Princeton University for their discovery of a new form of quantum fluid with fractionally charged excitations. This fluid is manifested in the fractional quantum Hall effect, which was discovered by Störmer and Tsui in 1982 and explained by Laughlin the following year. (All three were then at Bell Laboratories.)

If a strip of conducting material is placed in a magnetic field perpendicular to its surface, an electric current along the strip produces a voltage across it. This phenomenon, the Hall effect, results from the force of the magnetic field on the moving charge carriers (electrons or holes), and the Hall voltage is normally proportional to the magnetic field strength. However, in 1980 Klaus von Klitzing discovered that at low temperatures and high magnetic fields the Hall voltage of samples whose electrons are confined to motion in a plane varies with magnetic field strength in a series of steps. The values of the Hall resistance (the ratio of the Hall voltage to the current) are extremely close to a combination of fundamental physical constants divided by integers. This integer quantum Hall effect can be explained in terms of the quantum behavior of individual electrons, and reflects the filling of an integral number of quantum levels.

Störmer and Tsui studied the Hall effect using samples of very high purity, and at even lower