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A new form of carbon marks frontier in science

The "buckyball" is a carbon molecule of 60 atoms in the form of a hollow structure, called in geometry a truncated icosahedron. Mark Wilsey reports on fullerenes, the third form of carbon.

Recently, the element carbon has shown us an unexpected side to its nature. The fact that carbon is the basis of life on this planet and is familiar to us in at least a million known organic compounds makes this new find all the more surprising. To the known forms of carbon, diamond and graphite, add now a third: the fullerene, whose star member is the "buckyball."

While diamonds are made up of pyramidal structures, and graphite is comprised of sheets in a hexagonal pattern, fullerenes are a class of carbon molecules that have a hollow, cage-like structure where the carbon atoms form hexagonal and pentagonal faces. The most popular of these is the buckyball, which is made up of 60 carbon atoms forming a network of 12 pentagons and 20 hexagons. To a geometer, this is a truncated icosahedron or geodesic sphere; to most of us it resembles a soccer ball (**Figure 1**). "Buckyball" is a nickname for buckminsterfullerene, named after R. Buckminster Fuller, the inventor of the geodesic dome. It is represented by the chemical symbol C_{60}.

In 1985, chemists Richard Smalley of Rice University in Houston and Harold Kroto of the University of Sussex in England suggested this soccer ball structure for C_{60}. Smalley's research focuses on the field of atomic clusters, where he uses lasers to vaporize elements and then studies how the atoms "clump" back together. Cluster research seeks to determine the characterisics of those bits of matter that fall in between individual atoms and bulk molecules. Kroto, noting the existence of carbon molecules in interstellar dust and wanting to learn more about how those compounds are formed, suggested that Smalley use his laser vaporization technique on carbon. Kroto felt this would simulate the near-vacuum and high-temperature conditions that exist around carbon-rich stars.

The process Smalley uses involves striking a graphite target with a laser pulse. The carbon vapor is carried off by a jet of helium gas into a vacuum chamber, where the supersonic stream of carbon atoms recombines. Since helium is an inert gas, it does not react with the carbon, but rather serves as a cooling bath to moderate the thermal processes in the carbon vapor. The newly formed carbon clusters are then run though a mass spectrometer, which counts and weighs the bits of carbon that go by.

Smalley expected to find a random distribution of atomic clusters. Instead, he found a large spike at the atomic mass of 720, corresponding to 60 carbon atoms. One carbon atom has an atomic mass of 12, which is the total number protons and neutrons in its nucleus. While other researchers had previously noted this peak, the peaks produced by Smalley's experiments were prominent (**Figure 2**).

In these experiments, it seemed that, under proper conditions, carbon atoms "preferred" to run around in groups of 60, if possible, or at least in even-numbered groups, as the data also showed smaller peaks at C_{52}, C_{54}, C_{56}, C_{58}, C_{70}, and so on.

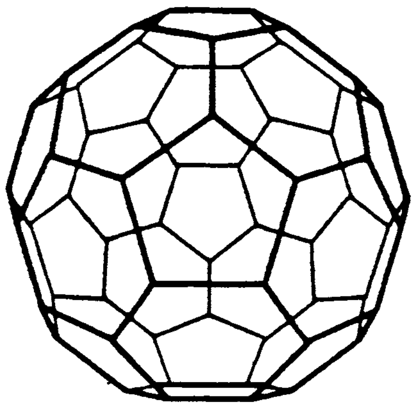
All these carbon clusters are fullerenes. In this range, only C_{60} is spherical; the others are more oblong in shape. In other words, instead of a soccer ball, C_{70} resembles a rugby ball.

Why is 60 so special? What organization would be involved to form this group? It was speculated that C_{60} had to have a very stable structure, one in which stresses on the atomic bonds are minimized. Moreover, the structure would be "closed," with no loose ends or edges for other atoms to grab onto, thus limiting the structure to 60 atoms. The sphere seemed natural, and this geodesic with 60 vertices seemed to fit; however, this is an oversimplification. The actual mechanism for the formation of fullerenes is still an open debate. Although other researchers had earlier predicted the existence

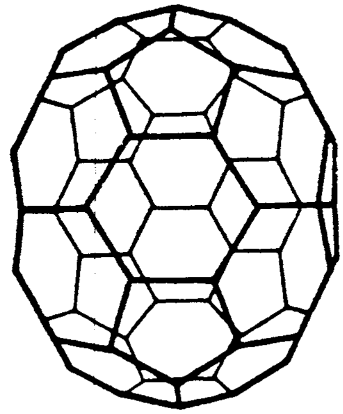
FIGURE 1

Truncated icosahedron structure for C_{60}, and its rugby ball-shaped cousin, C_{70}

Carbon, the basis for organic chemistry, is known to us in two forms: diamond and graphite. Now there is a third form, called fullerenes. One of these fullerenes, carbon-60, is the "buckyball"—short for "buckminsterfullerene," because these carbon cages are geodesic spheres, and were therefore named after R. Buckminster Fuller, who invented the geodesic dome.



Carbon-60



Carbon-70

of a hollow carbon structure, now it has been tagged and named.

The stability of C_{60} was put to the test, and it has been found that buckyballs can really take a punch. A strong jolt from Smalley's laser tended to reduce C_{60} to C_{58} by chipping off two carbon atoms, and C_{58} to C_{56}, and so on, until C_{32} was reached, after which the structure would shatter easily. Robert Whetten and his group at the University of California at Los Angeles have reported that buckyballs can survive collisions at speeds exceeding 20,000 miles per hour. No other molecule could take such an impact.

Carbon cages

In order to show that buckyballs are hollow spheres, Smalley set his machine to see what he could catch in his carbon cages. The graphite target was salted with the metal potassium chloride. The laser then vaporized both the metal and the carbon to form a buckyball containing an ion (a charged particle) of the metal. To see if the metal ion was, indeed, trapped inside the C_{60} structure, the laser was once again aimed at the buckyball. By chipping off carbon atoms as before, the buckyball was "shrink-wrapped" around the metal ion. Calculations showed that the structure should shatter when the carbon net was reduced to the size of the ion—i.e., being too small to contain it. In the case of a potassium, 44 atoms of carbon was the breaking point, as predicted.

In fact, the idea of placing various atoms and molecules inside these carbon cages is a very promising line of research. A new generation of fullerene-based materials may have a wide range of useful properties. Buckyballs could be used to encapsulate other materials for study or storage.

Reseachers theorize that much larger fullerenes are possible. Geodesics always contain 12 pentagons; the number of hexagons determines the size of the structure. The next largest possible geodesic would be C_{240}, then C_{540}, and C_{960}, at least in theory. Smalley has identified carbon clusters as large as 600 atoms which seem to be fullerenes. He would like to show, one day, that smaller fullerenes can be trapped inside larger fullerenes.

Buckyball research received a big boost in 1990 when scientists discovered that C_{60} is not so hard to produce. Donald Huffman of the University of Arizona and Wolfgang Krätschmer of the Max Planck Insitute in Germany had developed a way of making buckyballs in bulk with little more than an arc welder. They found that the electrical discharge between two graphite rods in controlled conditions could produce a larger quantity of fullerenes than had been seen before. Now, dozens of laboratories and hundreds of scientists are working with buckyballs, and the findings are coming out fast in the scientific literature.

Superconducting buckyballs

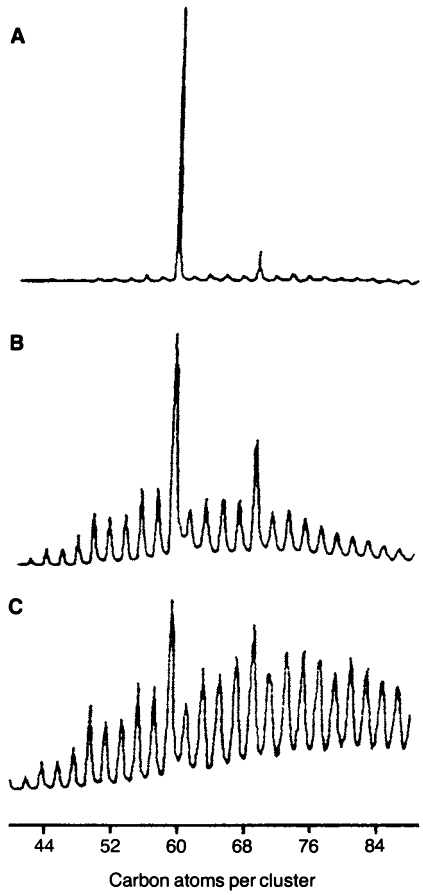
Earlier this year, scientists at AT&T Bell Laboratories, Nippon Electric Co. (NEC) of Japan, and elsewhere found that buckyballs can be used to make superconductors, in which resistance to electricity is zero. Buckyballs crystalize into a face-centered cubic (f.c.c.) crystal with one C_{60} at each corner of the cube and one in the center of each face. A buckyball crystal is called C_{60} fullerite. This fullerite, in its pure form, does not conduct electricity. However, when alkali metals, those elements in the first row of the periodic table (potassium, rubidium, and cesium, for example), were introduced into the buckyball crystal lattice in a process called "doping," the compounds became conductive. The alkali metal ions fill the spaces between the balls, one in the center of each edge of the cube, eight forming a smaller cube inside the larger, and another in the center of it all (**Figure 3**). These compounds, as chemical nomenclature goes, are called fullerides. Optimal conduction occurs at the chemical ratio of three metal ions per buckyball, e.g., for potassium, the formula is K_3C_{60}. When these compounds are cooled they become superconductive.

The temperatures at which these C_{60} fullerides, or buckides, become superconductive are much higher than expected: In the case of potassium, 18° Kelvin, which is twice as high as for the potassium metal itself. In similar experiments, the Japanese, using rubidium together with cesium, have demonstrated superconductivity at 33° Kelvin. In the United States, a group from Allied Signal's laboratory in New Jersey have reported superconductivity at 42° Kelvin, using thallium in both rubidium- and potassium-doped fullerenes.

Arthur Hebard, a scientist at AT&T, explains that not only are conducting electrons needed, which is what the alkaline metal contributes, to have superconduction, but also that the electrons must combine into pairs. This is the basis for the standard theory of superconductivity. The mechanism for this pairing involves the vibrations within the solid, called phonons. In this C_{60} system, it is thought that the vibration between the carbon atoms of the balls themselves are providing the phonons for this superconductivity.

As we become more familiar with buckyballs, speculation turns to the question: What uses could they have? Beyond gaining a new insight into the organization of matter, or the sheer novelty of the discovery, who knows? They may lead to new high-strength materials, better batteries, or super-slippery lubricants. They could be tailored to serve as catalysts in chemical reactions. Indeed, buckyballs may become the hottest thing in organic chemistry since the benzene ring (see box), giving chemists a new framework to build on. I.M.K. Ismail of the University of Dayton Research Institute in Ohio, suggests that C_{60} could be used in molecular sieves, for separating gases of differing sizes. Scientists at the Jet Propulsion Laboratory are interested in seeing if buckyballs, because of their high atomic weight and neat packaging, could be used in ion thrusters for satellites and other space vehicles.

FIGURE 2
Typical mass spectrometer readings



Increasing helium pressure and altering the nozzle configuration enhanced C_{60} formation, from early readings (c) to later ones (a).

FIGURE 3
The face-centered cubic (f.c.c.) buckyball

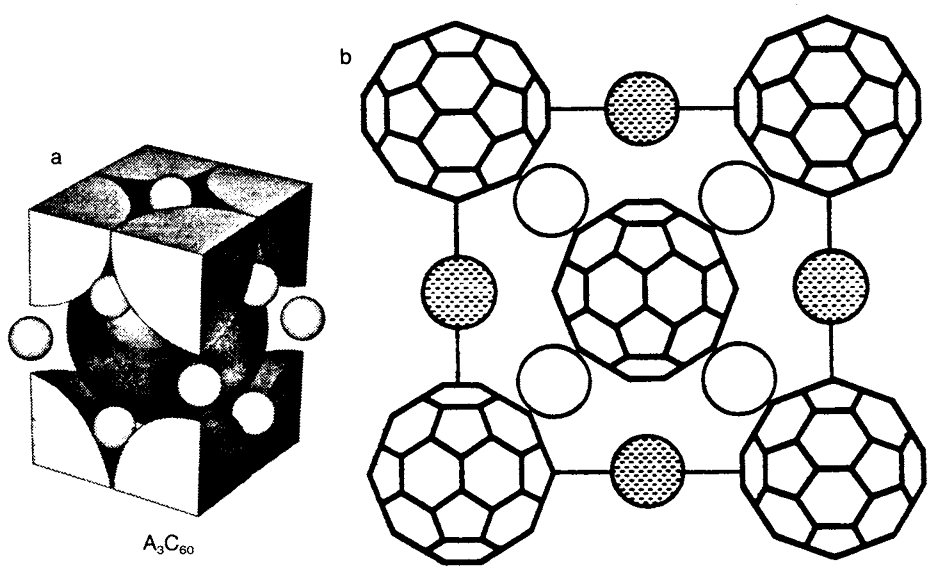


Figure 3b shows one face of the f.c.c. buckyball crystal, with a ball at each corner and one in the center of the face. The hatched circles are ions on the edge of the cube, the open circles are ions inside the cube. Figure 3a represents one quarter of the f.c.c. buckyball crystal rotated 45° to show the nesting of the ions. A diagonal plane through (a) will give you (b).