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# **Buckyballs**

**by Clair Wood**

Buckyballs—the soccer ball-shaped molecules that have taken the scientific world by storm—had a beginning that was literally out of this world. Harold Kroto, professor at the University of Sussex, England, had long been interested in the molecules found in deep space. In 1984 he visited Rice University in Texas, where Robert Curl and Richard Smalley had constructed a device that produced clusters by using a laser to vaporize even highly refractory materials, such as graphite, silicon, and germanium, which must be heated to a high temperature to vaporize significantly.

The clusters form as the atoms cool and condense in an inert gas atmosphere, and the distribution of cluster sizes is then analyzed with a mass spectrometer. Kroto hoped to use the device to prepare chains of carbon atoms similar to ones he believed resulted from chemistry taking place in red-giant stars. In particular, Kroto hoped that the carbon chains would solve the mystery of the Diffuse Interstellar Bands, a well-known feature of many stellar spectra that had puzzled astronomers for more than half a century.

### **Soccer ball science**

Initially, Smalley was not interested in trying up research time on his cluster machine by pursuing Kroto's dream of interstellar molecules. "It seemed like a stupid idea at the time," said Smalley. "After all, we know the chemistry of carbon better than any other element." Besides, the Rice University group was committed to research on silicon and germanium clusters and their relation to computer chips. Thus it was not until late August 1985, 18 months after Kroto's initial visit, that Curl telephoned Kroto to say that he could have a few days' research time on

the machine. Those few days were to prove to be some of the most exciting and productive in modern chemistry.

On September 1, 1985, Kroto, along with two Rice University graduate students, began to produce carbon clusters and immediately noted that something remarkable was taking place. A huge peak was seen at 720 atomic mass units in the mass spectrometer, corresponding to a species having 60 carbon atoms (C-60), along with a smaller peak corresponding to C-70. The researchers set out to determine the optimum conditions to produce the strange C-60 peak and soon produced one that was off-scale.

What could be the structure of a strange molecule that contained 60 carbon atoms? Here accounts differ somewhat. The group was brainstorming possible structures for the molecule. Kroto claims to have first thought of a structure similar to the geodesic dome invented by Buckminster Fuller that he had first seen at the Montreal EXPO '67. Smalley's version is that he used the 18th-century mathematician Euler's rule that geometrical closed structures would have to consist of exactly 12 pentagons and however many hexagons were needed to produce the size structure desired. At any rate, Smalley went home that evening and made a paper model of a spherical molecule. The model contained 60 carbons with all bonds equivalent.

Later that week Smalley took his model to a colleague in the mathematics department and was told, "What you've got there is a soccer ball!" The paper describing their momentous discovery appeared in the journal *Nature* along with a picture of a soccer ball to describe the proposed structure for buckyballs.

## **Great balls of carbon!**

The spherical structure proposed for buckminsterfullerene (the technical name for a buckyball) is known as a truncated icosahedron in geometry. Smalley has described several methods by which the structure was proven. The accepted structure for buckminsterfullerene is shown in the photo below. The negative ion of C-60 gives an ultraviolet photoelectric spectrum that is a detailed match to the theoretical energy levels calculated for the proposed structure. Nuclear magnetic resonance studies revealed that all carbon atoms in the molecule are equivalent. The C-60 molecule could be made to lose carbon atoms two at a time until, at C-32, the molecule shattered precisely at the point where theory predicted bond strain would make it unstable. Because C-60 is a hollow sphere, it should be possible to trap metal ions within it. The molecule would then shatter at a higher carbon number, depending upon the size of the trapped ion. The results of laboratory experiments conformed

exactly to the theory when the molecule shattered at C-44 when a potassium ion was trapped and at C-48 for the slightly larger cesium ion.

### **Disappointment and...**

Kroto's excitement at having been part of the team to discover a new family of carbon molecules was tempered by the fact that the discovery failed to prove his original hypothesis. When sufficient quantities of C-60 were prepared, the visible and ultraviolet spectra did not match the Diffuse Interstellar Band observed in space. The matter is not entirely dead, however, because astronomer Adrian Webster of the Royal Observatory in Edinburgh thinks the band may be due to saturated  $C_{60}H_{60}$  or partially saturated  $C_{60}H_{36}$ .

### **Jubilation!**

The amount of C-60 and other fullerenes produced by the laser technique was too small for most experiments. In fact, it was not certain that the fullerene idea was right, or whether fullerenes would be stable as bulk chemical substances. This changed overnight when Donald Huffman at the University of Arizona, in conjunction with co-workers at the Max Planck Institute, Germany, discovered a simple method of mass-producing the elusive molecules. Huffman found that he could vaporize graphite electrodes in a low-pressure helium atmosphere to produce a soot that contained about 10% fullerenes by weight. The fullerenes dissolved readily in benzene to give a solution that varied from red to brown depending upon concentration. The larger soot particles were insoluble, so the smaller fullerenes were easily separable from the remaining soot. Evaporation of the benzene solutions gave a material that was mainly C-60, with a trace of C-70. Huffman dubbed the crystals "fullerite." The buckyball fraction was found to sublime (change from a solid to a gas) in a near vacuum at 400 °C, making it easy to obtain pure C-60. A group at IBM's Almaden Research Center used this method to make samples for Raman spectroscopy, which revealed that the C-60 molecules vibrate just as theory had predicted, providing one early confirmation of the "soccer ball" structure.

The IBM group also found that although Buckminsterfullerene, or C-60, is an undistinguished-looking material, it has the astonishing feature that each spherical buckyball in a solid crystal is rotating at an incredible 20 billion revolutions per second!

Recently a group at MIT found that they can produce a gram of fullerene mixture (mostly C-60) per hour from soot that is about 2% fullerene by weight. They made a significant departure from others by producing their product from a sooty benzene flame. Today fullerite is

selling for about \$1250 per gram purified, or enough soot can be bought to yield one gram of fullerite at \$200 per gram of soot. These prices should start to drop shortly as further improvements are made on preparative techniques.

One writer has compared the buckyball to a major league baseball player who, everyone agrees, has great potential but has not yet lived up to it. Even though it is true that no major use for buckyballs has yet been announced, they have shown unexpected potential in two very important areas: magnetism and superconductivity.

### **Supermagnet, superconductor**

It has long been the dream of chemists to make a strongly magnetic material from nonmetals. Fred Wudl, professor of physics and chemistry at the University of California, Santa Barbara, now reports his research group has created an organic material that displays magnetic behavior at higher temperatures than ever before recorded. The solid, made up of buckballs plus an organic reducing agent, was able to generate magnetic fields at 16 K. This is about eight times warmer than the previous record set by a combined organic-metallic compound. Wudl terms the compound a "soft ferromagnet" because it loses its magnetization when the external magnetic field is cut off. Wudl says that the discovery has no immediate application but that "the possibilities are huge. It's just the beginning."

Interest in superconductivity exploded in 1987 when rare-earth oxides exhibited near-zero resistance to current passage at temperatures higher than 77 K. The first hint that buckyballs might be contenders in the race for the highest temperature at which superconductivity is exhibited came in 1991 when Art Hebard and colleagues at AT&T Bell Laboratories found that the molecule, when "doped" with potassium atoms (a small amount of potassium was mixed with the carbon), became superconducting at 18 K and reached nearly zero electrical resistance at 5 K. Hebard says that each of the three potassium atoms donates its single valence electron to a C-60 molecule, producing a [C-60]<sup>3-</sup> ion and creating a conducting band in the process.

This record was immediately challenged by a team of Japanese researchers who found that doping the buckyballs with either cesium or rubidium would elevate the superconducting limit to 33 K. The latest entry into the superconductivity race comes from Allied-Signal Corporation in New Jersey, where buckyballs doped with thallium became superconducting at 45 K. No one will hazard a guess on the upper temperature limit of fullerene superconductivity.

Buckyballs have demonstrated many other fascinating properties whose future applications can only be guessed at. Robert Whetten of UCLA has fired buckyballs at speeds in excess of 17,000 miles per hour into steel walls only to have the resilient molecules bounce off. A white solid produced from reacting buckminsterfullerene with fluorine is fully fluorinated  $C_{60}F_{60}$ , according to a team of chemists at the University of Leicester in England. The compound should be valuable for heat-resistant lubricants and waterproofing, according to the discoverers.

Hollow cylinders synthesized from buckyballs, known as "buckytubes," may conduct electricity as well as many metals, say researchers at the Naval Research Laboratory in Washington. Buckytubes resemble a sheet of graphite rolled into a tube.

When spherical buckyballs pack into a crystal, there is a lot of space between neighboring spheres, and gas molecules can pack into these spaces. Researchers at Sandia National Laboratories have found that small molecules, such as hydrogen and helium, absorb readily; larger ones, such as oxygen, more slowly; and any larger than methane not at all. Thus, buckyballs might prove useful as gas filters.

Finally, fullerenes, particularly C-70, have proven to be an ideal substrate upon which to grow extremely thin diamond films. The films, which form when carbon vapor is deposited on the surface of the fullerene crystal, can be used as tough diamond coatings on tools, ball bearings, razor blades, surgical blades, and dozens of other products. The National Research Council has said that the thin diamond films may prove to be the buckyball's most economically valuable use.

## Looking to the future

Fullerenes are so new that we can only guess at their full potential. Giant fullerenes, up to 700 atoms, are being predicted. A positive ion of C-350 has already been identified. Buckytubes, bucky fibers, semiconductors, superconductors and even buckyballs strung on a hydrocarbon chain like a string of pearls have all been postulated or are being made. "Fuzzyballs" ( $C_{60}H_{60}$ ) have just been reported, as has a new class of "fulleroids" consisting of buckyballs with various organic side chains. Smalley has characterized other derivatives as "bucky-babies" (C-32 to C-58) and "bunny-balls" (C-60 molecules with two short organic side chains). Several groups are now making significant amounts of metallofullerenes—fullerenes containing metal atoms or clusters. No one knows what other unique molecules lie just ahead.

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## SIDE BAR

### C-60 Buckyball Model

Buckminsterfullerene, named after the architect Buckminster Fuller, is a revolutionary form of carbon. C-60 Buckminsterfullerene consists of 60 carbon atoms arranged in hexagons and pentagons that fit together to form a sphere. In this model the hexagons are printed on paper, the pentagons will appear as five-sided holes in the model, and each corner represents a carbon atom. This model is on heavy paper, but the design works satisfactorily when photocopied on regular weight paper.

To Make Your Own Buckyball...

- 1 Cut out the three strips of hexagons by cutting only on the *solid* lines.
- 2 Crease the strips by folding down on the dotted lines.
- 3 Match the two edges labeled "AA" and tape them together.
- 4 Match the two edges labeled "BB" and tape together. This will give you a shape like a crooked Y.
- 5 Match the two edges numbered "1" and tape them, then match the two edges numbered "2" and tape. Continue this in numerical order. Your buckyball model is now ready to throw, hang from the ceiling, or sit on your desk for you to admire.

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## CAPTIONS

The classic buckyball contains 60 carbon atoms joined by covalent bonds. The pattern of bonds is identical to the seams on a soccer ball. This style model shows the bonds only; a carbon atom would be located at each junction.

Buckminster Fuller, architect and visionary, in front of the dome that he designed to serve as the United States pavilion at the 1967 World's Fair. The dome has become a Montreal landmark. The newly discovered spherical molecules of carbon were named *buckyballs* because they reminded one researcher of this geodesic dome.

The buckyball may realize the longstanding dream of chemists to make a strongly magnetic material from nonmetals.

Buckyballs may become a leading contender in the superconductivity race.

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