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A National Historic Chemical Landmark

The Discovery of Fullerenes

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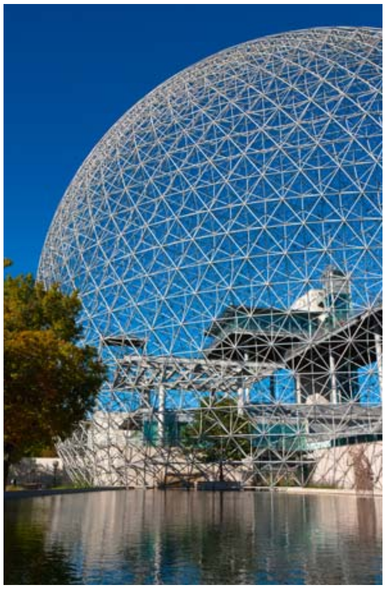
American Chemical Society

“Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal.” — From the abstract of a famous letter to *Nature* (Vol. 318, 14 November 1985) describing the dramatic discovery of the first known molecular form of carbon.

AN IDEA AND A MACHINE

Truncated icosahedron: technical term for a soccer ball in the United States, a football everywhere else. The scientists who vaporized graphite to produce C_{60} dubbed the new allotrope buckminsterfullerene (shortened to fullerene or buckyballs) because the geodesic domes designed by inventor and architect Buckminster Fuller provided a clue to the molecule's structure.



Buckminster Fuller's Biosphere — U.S. Pavilion at the 1967 World Exposition in Montreal

Carbon, the basis of life, is one of the most common elements and certainly the most studied. A new study of pure carbon would not seem all that exciting to most chemists. In 1984 Richard Smalley found himself less than thrilled when Harry Kroto, a chemist at the University of Sussex, asked to use equipment in Smalley's laboratory at Rice University to study a special kind of carbon molecule.

Kroto wanted to investigate long linear chain molecules of carbon that he, together with Canadian radio astronomers, had discovered in interstellar space. Kroto was convinced that these unusual, long flexible molecules had been created in the atmospheres of carbon-rich red giant stars and wanted to prove this contention using Smalley's laser-supersonic cluster beam apparatus. This experiment also could be a preliminary pilot for a rather more complicated experiment that might solve a long-standing puzzle in astronomy – the carriers of the mysterious diffuse interstellar bands.

Clusters of any element could be studied in the AP2 (pronounced app-two), the colloquial name of Smalley's machine. Operators fire an intense laser pulse at a target, which creates a hot vapor above it. The laser generates temperatures reaching tens of thousands of degrees, hotter than the surfaces of most stars. As the vapor cools, the evaporated atoms align in clusters. A high pressure burst of gas sweeps the vapor into a mass spectrometer, where the clusters are analyzed. Kroto's request to use AP2 came during a visit to Robert Curl in Houston in March 1984. Smalley, busily studying semiconductor clusters with Curl, initially declined to free up time on the machine for Kroto to explore his theory about the formation of carbon chains in the atmosphere of stars.

SEPTEMBER 1985

A year later, Smalley agreed to give Kroto time on the cluster beam apparatus, and Curl telephoned to ask whether Kroto wanted the Rice team to carry out the experiments and send him the data or if he wanted to come to Houston. Kroto says “one thing was certain in my mind: I had not waited this long to have my experiments carried out by others...” He borrowed money from his wife, packed his bags, and arrived in Houston a few days later, in late August 1985.

Kroto, Smalley, and Curl conducted the study, with the assistance of graduate students James Heath, Sean O'Brien, and Yuan Liu. The students ran the machine with Kroto directing the experiments. Two significant results emerged from the feverish ten days of experiments: first, the team found, as Smalley put it, “Kroto's long carbon snakes”; second, the scientists observed a previously unknown carbon molecule.

The lab book for September 2 first notes the molecule. Then on Wednesday, September 4, using helium as the carrier gas, the team noticed, in Kroto's words, “something remarkable taking place,” an odd peak in the mass spectra of the molecules that formed in the vapor. The peak occurred at sixty carbon atoms (a smaller peak also occurred at seventy atoms). Yuan Liu noted in the lab book, “C_{60} and C_{70} are very strong,” adding an exclamation mark and underlining the entry.

From the beginning of the experiments, the team met regularly to analyze the data. Now the scientists focused their discussions on the mystery of C_{60}. At first, the group referred to it as a wadge, a British term for “a handful of stuff,” with Smalley referring to the mother wadge, Kroto to the godwadge.

DOMES

Since Kroto was scheduled to return to England early the following week, Heath and O'Brien spent the weekend trying to plumb the mystery molecule's properties. One thing became apparent: C_{60} formed very readily and exhibited extraordinary stability; in one instance, AP2 produced forty times more C_{60} than either C_{58} or C_{62} carbon clusters.

What was the structure of these clusters? The scientists were stumped at first by the stable, sixty-carbon molecule that did not react with other molecules, which suggested it had no dangling bonds. All known carbon-containing molecules, even benzene, a very stable ring of carbon atoms, have edges that terminate with other elements. But C_{60} was chemically inert; it did not need hydrogen, or any other element, to tie up its bonds.

The team considered two candidates for C_{60}'s structure: a so-called flatlander model where carbon was stacked in hexagonal sheets, similar to the structure of graphite, with the dangling bonds tied up in some fashion; or a spherical form where the hexagonal graphite sheet curled around and closed. A closed structure, a cage, would have no dangling bonds.

Monday, September 9 was climactic. Spheroids dominated the discussion. At some point during the previous week Buckminster Fuller and his geodesic domes had been raised. Kroto and Smalley thought hexagons made up the surface of geodesic domes. Then Kroto remembered a stardome he once made for his children; he told Smalley it had pentagonal facets as well as hexagonal ones. Kroto also remembered visiting Fuller's famous geodesic dome at Expo 67 in Montreal.

At one point the team viewed a photograph of one of the architect's domes; its grid appeared to be entirely composed of hexagons. Curl, who brought a healthy dose of skepticism to the entire project, questioned whether hexagons alone would do the trick.

With the daytime discussion seemingly reaching a dead end, part of the group went to a favorite Mexican restaurant to celebrate the discovery of C_{60}. During the meal, Smalley wondered how a sheet of hexagons could close; perhaps, the only way to find out was to build one.

Smalley worked into the night at his home computer trying to generate a structure. When that failed, he turned to low-tech tools: paper, tape, and scissors. He remembered that Kroto had mentioned the presence of pentagons in his stardome. He began interspersing pentagons among the carbon hexagons (many carbon compounds have five- and six-membered rings), which resulted in a geodesic dome with sixty vertices. Smalley had stumbled through trial-and-error on a mathematical truth Fuller employed in his domes: a sheet of hexagons can be made to curl by using twelve pentagons. Sixty, it turned out, was the only number of atoms that could form a nearly perfect sphere.

When Smalley tossed the paper model of twelve pentagons and twenty hexagons on a table in his office the next day, Kroto "was ecstatic and overtaken with its beauty." Smalley called Bill Veech, chair of Rice's mathematics department to ask if he was familiar with the form. The answer came a few minutes later in a return call: "I could explain this to you in a number of ways, but what you've got there, boys, is a soccer ball."

AFTERMATH

The *Nature* letter describing C_{60} was attractive and logical, but seeing a line in a mass spectrum did not convince all scientists of the discovery of a new allotrope of carbon. During the period 1985-1990, the Curl/Smalley team at Rice and Kroto at Sussex managed to amass a wide range of circumstantial evidence to support the fullerene structure proposal. Full acceptance came when Wolfgang Krätschmer of the Max Planck Institute for Nuclear Physics in Heidelberg, Germany, and Donald Huffman of the University of Arizona, with their students Konstantinos Fostiropoulos and Lowell Lamb, succeeded in synthesizing C_{60} in sufficient quantities to allow structural characterization.

In 1996 Curl, Kroto, and Smalley won the Nobel Prize in Chemistry. The presenter of the Nobel noted that the discovery of fullerenes has implications for all the natural sciences. It was born of astronomy, by the wish to grasp the behavior of carbon in red giant stars in interstellar gas clouds and by the work of Curl and Smalley in cluster chemistry at Rice University. It has expanded knowledge of chemistry and physics. Fullerenes have been found in geological formations and in sooty flames.

Research on fullerenes has resulted in the synthesis of a steadily increasing number of new compounds, already more than one thousand. The discovery of fullerenes also led to research in carbon nanotubes, the cylindrical cousins of buckyballs, and the development of new fields of advanced materials. Carbon nanotubes' unique structural and bonding properties, whereby inner tubes in a multi-walled nanotube can slide within an outer tube, suggest uses in tiny motors and as ball bearings and lubricants. Twenty-five years after their discovery, fullerenes provide abundant research opportunities in pure chemistry, materials science, pharmaceutical chemistry, and nanotechnology.

The Fullerene Discovery Team in front of Space Science Building at Rice University. Shown from left to right: Sean O'Brien, Richard Smalley, Robert Curl, Harry Kroto, and James Heath.

National Historic Chemical Landmark

The American Chemical Society designated the discovery of fullerenes as a National Historic Chemical Landmark in a ceremony at the Richard E. Smalley Institute for Nanoscale Science and Technology at Rice University in Houston, Texas, on October 11, 2010. The text of the plaque commemorating the development reads:

In this building in early September 1985, a team of scientists discovered a previously unknown pure carbon molecule, C_{60}, which they dubbed buckminsterfullerene. The name was chosen because the geodesic domes of Buckminster Fuller provided a clue that the molecule's atoms might be arranged in the form of a hollow cage. The structure, a truncated icosahedron with 32 faces, 12 pentagonal and 20 hexagonal, has the shape of a soccer ball. Nicknamed buckyballs, this first known stable molecular form of carbon not only opened up a new field of organic chemistry but also, through the development of carbon nanotubes, a new field of materials science. In 1996, Robert Curl, Harold Kroto, and Richard Smalley won the Nobel Prize in Chemistry for the discovery of the fullerenes.

About the National Historic Chemical Landmarks Program

The American Chemical Society, the world's largest scientific society with more than 161,000 members, has designated landmarks in the history of chemistry since 1993. The process begins at the local level. Members identify milestones in their cities or regions, document their importance, and nominate them for landmark designation. An international committee of chemists, chemical engineers, museum curators, and historians evaluates each nomination. For more information, please call the Office of Public Affairs at 202-872-6214 or 800-227-5558, ext. 6214, e-mail us at nhclp@acs.org, or visit our web site: www.acs.org/landmarks.

A nonprofit organization, the American Chemical Society publishes scientific journals and databases, convenes major research conferences, and provides educational, science policy, and career programs in chemistry. Its main offices are in Washington, DC, and Columbus, Ohio.

Acknowledgments

Written by Judah Ginsberg

Photo credits: Richard E. Smalley Institute for Nanoscience and Technology at Rice University and Anne-Katrin Purkiss.

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