

Current Comments®

EUGENE GARFIELD

INSTITUTE FOR SCIENTIFIC INFORMATION®
3501 MARKET ST., PHILADELPHIA, PA 19104

The Birth of Fullerene Chemistry: Harold W. Kroto Discusses New Lines of Buckyball Research in a *Science Watch*® Interview

Number 37

September 13, 1993

A Star Is Born: Discovering the Third Form of Carbon

Last week in the engineering and physics/chemistry editions of *Current Contents*® (CC®), we published a *Citation Classic*® commentary by Harold W. Kroto, University of Sussex, Brighton, England, on the 1985 *Nature* paper describing the discovery of buckminsterfullerene.^{1,2} Working with a team of colleagues at Rice University, Houston, led by Richard E. Smalley, Kroto was interested in learning more about the interstellar formation of long carbon chains in red giant stars. An unexpected result of their effort was the serendipitous discovery of a third natural form of carbon—the stable C₆₀ molecule named after R. Buckminster Fuller for its novel geodesic “soccer ball” structure.

The discovery has turned out to be one of the rare research breakthroughs that fundamentally alters conventional scientific wisdom and triggers an explosion of multidisciplinary research. It upset centuries-old chemical tradition that just two forms of carbon existed, graphite and diamond. It has since opened up new research areas in chemistry, physics, materials science, medicine, and other disciplines. And it shows significant commercial potential for industrial applications as catalysts, lubricants, high strength fibers, pharmaceutical magic bullets, optical switches, superconductors, etc. Recent laboratory tests also indicate that “buckyballs” may inhibit an enzyme necessary for the AIDS virus to reproduce.³⁻⁵

Not surprisingly, buckyballs and the new field of fullerene chemistry have attracted much attention in the press. For example, *Science* selected the buckyball as its Molecule of the Year in 1991,⁶ and the *Economist* called it the Renaissance Molecule in 1992.⁷ It was first featured in CC in a 1988 essay on the most-cited 1985 chemistry papers.⁸

In addition, Kroto was interviewed in *Science Watch*®, ISI®'s newsletter that tracks quantitative trends in research.⁹ The 1992 interview, reprinted below, focused on new directions in fullerene research and its applications in various fields. It is a useful companion piece to Kroto's *Citation Classic* commentary,¹ because both represent “oral histories” or autobiographies of breakthrough research. Interested readers should also refer to Smalley's personal account of the discovery in *The Sciences*.¹⁰

In conclusion, it should be noted that there is some controversy about who on the research team envisioned the geodesic spherical structure of buckminsterfullerene.¹¹ Kroto and Smalley differ in their recollections on this point. Such differences are not unusual in an era of intensively collaborative research, especially when a major scientific breakthrough is involved. In these instances, personal accounts by the authors—such as *Citation Classic* commentaries or *Science Watch* interviews—become even more valuable as a means to tell all sides of the story.

REFERENCES

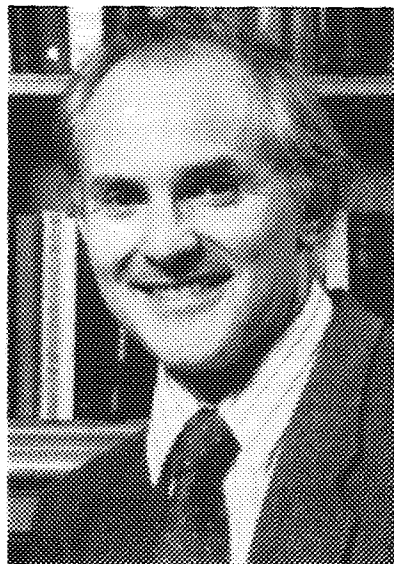
1. Kroto H W. C₆₀—the third man. *Citation Classic*[®] commentary on *Nature* 318:162-3, 1985. *Current Contents/Engineering, Technology & Applied Sciences* 24(36):8-9, 6 September 1993 and *Current Contents/Physical, Chemical & Earth Sciences* 33(36):8-9, 6 September 1993.
2. Kroto H W, Heath J R, O'Brien S C, Curl R F & Smalley R E. C₆₀: buckminsterfullerene. *Nature* 318:162-3, 1985.
3. Browne M W. 'Buckyball' may block AIDS step. *NY Times* 3 August 1993, p. C8.
4. Friedman S H, DeCamp D L, Sijbesma R P, Srdanov G, Wudl F & Kenyon G L. Inhibition of the HIV-1 protease by fullerene derivatives: model building studies and experimental verification. *J. Amer. Chem. Soc.* 115(15):6506-9, 28 July 1993.
5. Sijbesma R, Srdanov G, Wudl F, Castoro J A, Wilkins C, Friedman S H, DeCamp D L & Kenyon G L. Synthesis of a fullerene derivative for the inhibition of HIV enzymes. *J. Amer. Chem. Soc.* 115(15):6510-2, 28 July 1993.
6. Culotta E & Koshland D E. Molecule of the year. Buckyballs: wide open playing field for chemists. *Science* 254:1706-9, 1991.
7. The renaissance molecule. *Economist* 323(7760):91-3, 23 May 1992.
8. Garfield E. The 1985 chemistry articles most cited in 1985-1987: quantum mechanics, superconductivity, and...Buckminster Fuller?! *Current Contents* (48):3-13, 28 November 1988. (Reprinted in: *Garfield E. Essays of an information scientist: science literacy, policy, evaluation, and other essays.* Philadelphia: ISI Press[®], 1990. Vol. 11. p. 383-93.
9. The search for carbon in space and the fullerene fallout. *Science Watch*[®] 3(1):3-4, January 1992.
10. Smalley R E. Great balls of carbon—the story of buckminsterfullerene. *The Sciences* 31(3):22-8, March/April 1991.
11. Taubes G. The disputed birth of buckyballs. *Science* 253:1476-9, 27 September 1991.

The Search for Carbon in Space and the Fullerene Fallout

Few stories in the annals of contemporary science provide a stronger argument for pursuing fundamental research than the discovery of C₆₀.

In the early 1970s, British chemist and microwave spectroscopist Harry Kroto hatched a research program at the University of Sussex, in Brighton, U.K., to seek long chains of carbon in interstellar space. This effort, with David Walton at Sussex and with Takeshi Oka and astronomers at the Canadian National Research Council, in Ottawa, eventually led, during 1975-78, to the detection of several different carbon chains, including HC₅N, HC₇N, and HC₉N. Kroto surmised that these chains were the product of carbon-rich, red-giant stars. "But how did the chains form?," he wondered.

A few years later, in 1984, Kroto encountered a unique instrument—a laser vaporization cluster beam apparatus—in the laboratory of Richard Smalley at Rice University, in Houston. Smalley and his group had developed this instrument and were using it for semiconductor research on silicon and germanium clusters, but Kroto im-



Harold W. Kroto

mediately realized that it could be used to simulate the high-temperature conditions under which the carbon chains might form in stars. In September 1985, Kroto, together with Smalley's group and Robert Curl at

Rice, tried to create such conditions and found much more than they had bargained for: a stable molecule consisting of exactly 60 carbon atoms. They suggested that C_{60} took the form of a closed cage resembling a soccer ball and called the molecule "buckminsterfullerene," in honor of the architect R. Buckminster Fuller and the geodesic structures he had designed which exhibit the same form (see *Nature*, 318:162, 1985; cited 485 times by the end of 1991, thus easily qualifying as a citation classic).

The suggestion of a new and third form of carbon (besides graphite and diamond) was both intriguing and controversial. But it was not a subject of widespread investigation until late 1990 when a team of scientists at the University of Arizona, in Tucson, and at the Max-Planck-Institut für Kernphysik in Heidelberg discovered a method for making C_{60} in bulk quantities (see box). Close on the heels of the Arizona/Heidelberg group was Kroto's team at the University of Sussex, which chromatographically purified C_{60} for the first time and confirmed its structure in the form of a single, elegant ^{13}C NMR line (see box).

As soon as the chemistry community could obtain enough C_{60} to explore its properties, fullerene fever spread like wildfire. In short order, physicists found high-temperature superconductivity in alkali-doped "buckyballs." The study of C_{60} and other fullerenes is the hottest area of science today: It accounts for nine of the 23 hottest papers of 1991. All this from a fundamental question about the chemistry of stars!

Harold W. Kroto earned his B.Sc. in chemistry, with first class honors, in 1961 and his Ph.D. in 1964, both from the University of Sheffield, U.K. After two years as a postdoctoral fellow at the NRC, in Ottawa, Kroto spent a year at the (then) Bell Telephone Laboratories in Murray Hill, New Jersey. In 1967, he returned to England and joined the faculty of the University of Sussex, where he has since remained. At Sussex he advanced from Lecturer to, in 1985, Professor in the School of Chemistry

and Molecular Sciences. Kroto was named a Fellow of the Royal Society in 1990, and last year he was appointed a Royal Society Research Professor.

Science Watch recently reached Prof. Kroto in the Italian Alps, where he was attending a conference focusing on cluster chemistry.

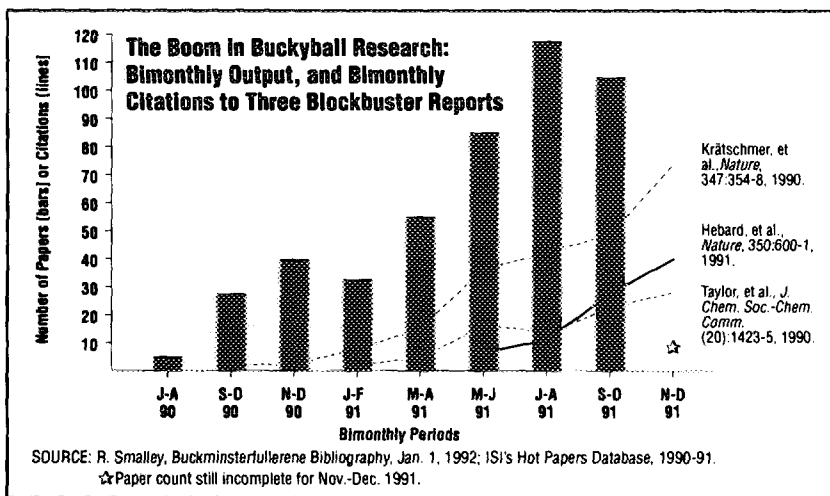
SW: It's an inevitable question, but what do you see as the most promising uses for fullerenes?

Kroto: Well, it's true. Most people do ask, "What can C_{60} be used for?" In fact, there was a question in the House of Lords about its potential applications. The answer has to be, at the moment, that it may have many uses, and then again it may turn out to have none at all. I suspect that the latter is highly unlikely, however. It seems to me that the C_{60} field will find and develop its own applications. The situation appears to be analogous to the discovery of lasers: it was at least a decade before applications of lasers came along. I think that C_{60} is or will be similar. The chemistry itself is quite novel, and it presents major challenges. For example, with benzene there are six possible positions, but with buckminsterfullerene there are 60. So, it's difficult to foresee all the potential of the fullerenes.

I guess I should also say that fundamental scientists are not necessarily the best people to ask about applications. People like myself have, in a sense, spent a lifetime avoiding applications.

We're puzzled about interesting things for their own sake, and we follow up on them. However, having said that, I do see some possibilities.

SW: Not so long ago, *Science Watch* spoke to Donald Cram at UCLA about his work on carceplexes and their potential application in drug-delivery systems. Many have talked about using fullerenes for the same purpose.



Kroto: Yes. The work of Cram and others in producing these cages or carcerands is one route. Perhaps C_{60} and the other fullerenes represent the ultimate way to encage an atom. I think it will take some time before we have the requisite chemical technology to incarcerate anything we want. Whether we can do it efficiently in the near future remains to be seen. Certainly we know it can be done with certain metal species.

As for drug delivery, the idea is to encage an atom or a molecule, move it to a specific site in the body, and then open up the cage to release the agent. As I mentioned, at this stage we don't yet know exactly how to encage atoms efficiently. We can certainly do it by brute force, vigorous methods. C_{60} itself is formed in a very crude manner; rational synthesis is a non-trivial matter. But since we have learned to encage certain metal atoms, one can see a way to trapping a radioactive species and taking it somewhere in the body. For a radioactive atom, cage opening is not necessary. As long as the cage surface is non-toxic and stable, it can be left there or, if not, excreted.

SW: What are some other potential applications?

Kroto: Well, C_{60} is a three-dimensional compound on which one can add many different groups. Therefore, we can consider these as nucleation centers. Linking up C_{60} into polymeric matrices with encapsulated species is, in principle, a possibility. One would hope that this might be a way of designing computer memories at the molecular level.

Applications involving the superconducting and ferromagnetic properties of certain types of fullerenes represent another area which people are looking at very carefully. With endohedral complexes, one can choose not only the physical properties but also the electrical or magnetic properties of the cage. We know the behavior of C_{60} crystals depends on how close atoms are together, and other aspects, and if one can put atoms inside them, then it may be possible to tune the electrical properties to produce very high-temperature superconductivity.

SW: You mentioned that the fullerenes present chemists with many challenges.

Kroto: I think, in fact, fullerenes present massive problems for chemists. Fullerene research is expanding chemists' horizons.

It's a demanding field analytically and technically, and it's taking chemists and others into areas where they've never gone before. Physicists have already put a lot of effort into understanding the properties of fullerenes. High-temperature superconductivity was one drive, but there will be many others. For example, C_{60} exhibits strange phases. That's an area for exploration, too.

SW: Do you anticipate biologists will get in the game as well?

Kroto: I do. One can think of taking these molecules and modifying their overall hydrophobic or hydrophilic properties in order to make a palatable biochemical system. In particular, if one thinks of the larger fullerenes, one imagines that it should be possible to manipulate their shape, and we know, of course, that shape is rather important in biological systems.

SW: Has the discovery of the fullerenes pointed to other areas worth pursuing?

Kroto: There have been many, many exciting and interesting molecules made in small quantities over the years. One thinks of dodecahedrane, $C_{20}H_{20}$, which is effectively a hydrogenated fullerene. Its exploitation hasn't gone very far because it's so difficult to make. That was the case with C_{60} before we could make it in reasonable amounts, or enough so that everyone could start working on some aspect of it. So, I think that there may be many other compounds, ones that we already know about, whose exploitation is inhibited because we don't have a good way of making sufficient material. Probably more effort should be directed at compounds that we already have.

SW: What are you and your colleagues at Sussex focusing on now?

Kroto: We, which is to say myself, Roger Taylor, David Walton, and others, are de-

veloping a Sussex Fullerene Program, which will include topics in transition-metal, organic, and polymer chemistry.

One of my own aims at present is to show that C_{60} is, in fact, in space, but it's still early days. First, we have to decide how to detect it in space. As I've said before, it's a celestial sphere that fell to earth, and now I'm wondering whether it will bounce back into space. I do believe it is there. It was discovered by simulating certain astrophysical conditions, after all. The question is whether it is stable in space. I think it is. I believe that it would be very surprising if C_{60} , in some form, is not responsible for the diffuse interstellar bands that have puzzled astronomers for so long. That's my gut reaction, the feeling in my heart. But if it's not there, then there's something else out there that may be even more exciting.

My other main interest right now concerns how C_{60} forms. It forms under the same sort of conditions that graphite forms. In fact, C_{60} is really a small round form of graphite. On a large scale, such as in large slabs, it is flat. But that's not the most stable form at the microscopic level. The most stable form would be a giant fullerene of some sort. What this means is that, unbelievably, we have overlooked something fundamental from the very beginnings of organic chemistry. The discovery of the fullerenes has changed our picture of how graphite forms and what are the factors controlling its structure. We're starting to recognize that graphite doesn't just happen, and it doesn't want to be flat unless it's in a very large piece. And it doesn't get to be a large piece unless it was in a smaller form beforehand. We now need to focus on why carbon networks are flat on a large scale and why they are round on a small scale. So, my aim is to rewrite the textbook picture of what the most stable form of carbon is and why it takes the different forms it does. ■