



The Disputed Birth of Buckyballs

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The Disputed Birth of Buckyballs

Who was the first to picture a carbon molecule shaped like a geodesic dome? That's one chemical mystery Harry Kroto and Richard Smalley can't resolve

IT HAD THE MAKINGS OF A CLASSIC SCIENTIFIC collaboration. Harry Kroto, a spectroscopist at the University of Sussex in Brighton, England, was the driving force behind the experiment. Richard Smalley, a chemist at Rice University in Houston, created the machine on which to try it. And the surprising result—the discovery of a 60-atom carbon molecule in the shape of a soccerball—has been hailed as one of the key scientific developments of the 1980s. Called buckminsterfullerene after the creator of the geodesic dome, the molecule and its relatives represent the third known form of carbon in the universe, after graphite and diamond. The molecules have opened up new avenues in superconductivity research and an entirely new area of carbon chemistry. There's more than enough acclaim to go around, and a lot of work left to be done. And yet the collaboration is in tatters, offering a cautionary tale in how a partnership can go wrong.

It fell apart despite Smalley and Kroto's best intentions. Each of the two chemists is careful to credit the other with a key role in the research. Smalley says he feels sheepish about their quarrel, calling it a "silly issue." Kroto feels that he has been drawn into it against his will. Yet the discovery was and likely will remain the most profound scientific contribution of both men's lives. Each is certain the other has overstated his own role at the key juncture: the moment of creation when Smalley, Kroto, and their collaborators realized that they had in their hands a totally new molecular form—a closed cage of carbon atoms in the shape of a geodesic dome.

Underlying the animosity that has torn apart the collaboration are two seemingly irreconcilable claims about the critical revelation. Smalley, in his account of the discovery in the March/April 1991 issue of *The Sciences*, stresses what he calls his "eureka experience" on Monday, 9 September 1985. That was when he sat up all night with scissors, a pad of paper, and tape and found he could build a

closed, spherical structure that had 60 vertices, obeyed all the rules of carbon bonding, and had the form of a geodesic dome. Kroto, in journal articles and in letters responding to popular accounts that he feels overstate Smalley's role, has emphasized his lifelong fascination with the work of Buckminster Fuller. He was, he says, primed to recognize the correct structure and propose it to Smalley and their co-workers before Smalley went home and actually built it.

It may be simply in the nature of discovery that given more than one participant at the moment of creation, the result will be more than one version of how that moment came about. Call it the *Rashomon* factor, after the renowned Japanese story in which every witness to a crime remembers a different perpetrator. In the case of buckminsterfullerene, it's not just Smalley and Kroto who can't agree about the genesis of the critical insight. Neither can Smalley's graduate students Jim Heath and Sean O'Brien and his colleague Bob Curl, who were all vital participants in the hectic days in the laboratory and the late nights of discussion. The story forms an object lesson in the fallibility of long-term memory and the irrevocable difficulty of apportioning credit in intensely collaborative work.

One thing is certain: The collaboration

would never have come about if it had not been for Kroto's enthusiasm and persistence. The groundwork was laid in the spring of 1984, when Kroto met Curl, a long-time friend, at a conference on molecular structure in Austin, Texas. Kroto was pursuing a 10-year fascination with molecules in interstellar space that consist of long chains of carbons. Curl, a spectroscopist at Rice, had recently begun collaborating with Smalley in making and studying small clusters of atoms. Curl told Kroto about their apparatus, a machine designed by Smalley and his students. To Kroto, it sounded like a dream come true.

Kroto went back to Houston with Curl, who introduced him to Smalley and showed him around the lab. Kroto's excitement grew. Smalley's machine was called a laser-supersonic cluster beam apparatus. As the name suggests, its key working parts include a laser that can be trained on virtually any target material and a supersonic jet of inert gas that sweeps up the vapor and allows the atoms to clump together into energetically favored clusters. Smalley and Curl had been making atomic clusters from semiconducting elements like silicon, but Kroto saw the machine as a way to explore the possibility that carbon chains might be forming in the dense, carbon-rich winds blowing from giant stars. As Curl recalled it, "[Kroto] was very keen to start a collaboration."

Smalley was less keen, mainly because he and Curl were deeply involved in their semiconductor work. Says Curl, who favored the collaboration, "It simply didn't fit in with our research priorities for a long time." In August 1985, Smalley finally agreed to give Kroto's idea time on his machine. He was still reluctant: Researchers at Exxon, using a machine built by Smalley, had just published an investigation of carbon clusters, and Smalley was hesitant, he says, "to horn in on the carbon act." Nonetheless, Curl telephoned an invitation to Kroto, who packed his bags and caught

Buckyball squad. Bob Curl (standing) and, from left to right, Sean O'Brien, Richard Smalley, Harry Kroto, and Jim Heath.



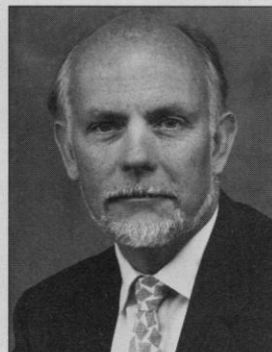
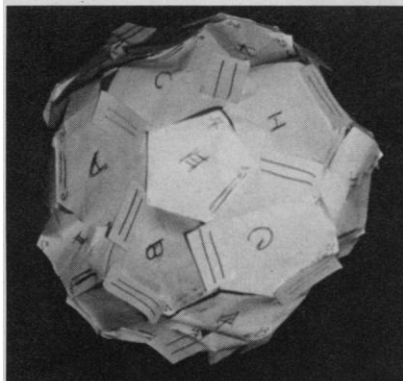
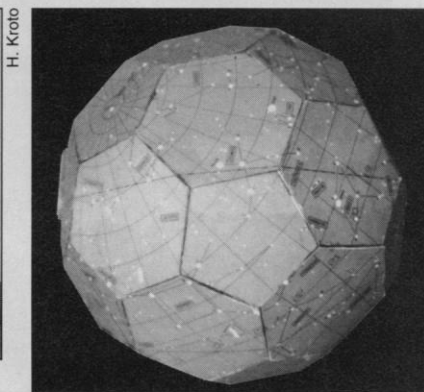
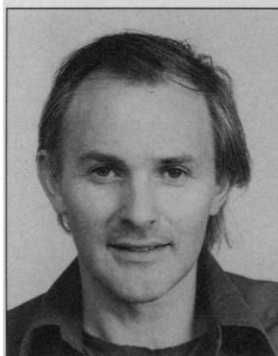
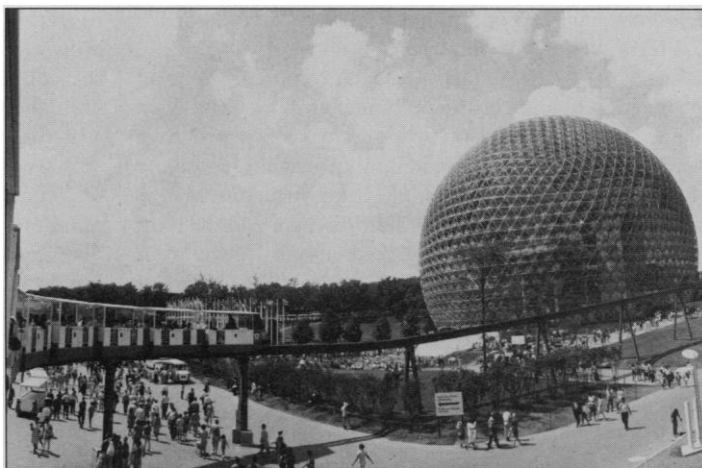
the next flight out.

On Sunday, 1 September, 4 days after Kroto arrived in Houston, the carbon experiments began. Heath and O'Brien ran the machine, while Kroto suggested the direction of the experiments. To re-create conditions near red giant stars, the workers vaporized carbon in an atmosphere heavy with hydrogen, nitrogen, and other elements. In just a week, they had gathered a full set of data on the small (12 atoms or less) carbon molecules formed in the vapor—among which they found Kroto's carbon chains. Heath describes Kroto as ecstatic: "We were just pulling out reams of data and it all looked pretty significant."

In retrospect, the most significant finding was an odd peak in the mass spectroscopy readings, which registered the mass of the molecules that formed in the vapor. The peak, which the researchers first noticed on Wednesday, 4 September, fell at a molecular weight of 720, corresponding to an aggregate of exactly 60 carbon atoms. A smaller peak also kept popping up at a higher mass, corresponding to 70 carbons. An entry in the lab book for that day reads, "C₆₀ and C₇₀ are very strong!" Here was a puzzle quite different from the one Kroto had set out to solve.

At this point, when the researchers began to recognize the unique properties of C₆₀, consensus about the sequence of events starts breaking down. Smalley credits Heath with noticing that C₆₀ could be made "preeminently stable"—no matter how the researchers varied the conditions of the experiment, up popped the C₆₀ peak. Heath, however, says Kroto's role was pivotal. "This lab," says Heath, "is like being in an Army helicopter or something: You have five lasers going over your head; it's noisy; all kinds of pumps are going and data coming on screen. But Harry, whenever he saw anything a little bit unusual, he would really key in on it. Almost all the time it would be nothing—some artifact or something. But this C₆₀ was such a thing, and he really keyed in on it."

Throughout the week, Kroto, Smalley, and occasionally Curl would meet in Smalley's office to discuss the experiments



Two men and their domes. Smalley and his model (bottom), Kroto and his stardome (center), and the dome Kroto says he remembered from Expo 67 (top).

and the data. Now the discussions became a concerted effort to get to the bottom of the C₆₀ mystery. "We were imagining some kind of graphitic sheets being lifted off the [sample] surface and blown into the machine," Smalley recalls. There, the sheets had to be clumping together somehow. The group first called them wadges, a "peculiarly British expression," says Kroto, "for a featureless heap of junk." In deference to C₆₀'s ubiquity, Smalley took to calling it "mother wadge"; Kroto preferred "godwadge."

Because Kroto was scheduled to fly back to England on Tuesday, Heath and O'Brien, the graduate students, worked over the weekend to probe C₆₀'s properties. On Monday

morning, the two reported new evidence of the molecule's extraordinary stability: In one case, Smalley's machine had produced 40 times as much C₆₀ as any other carbon cluster. That the C₆₀ peak was so prominent also meant that the molecule was chemically inert.

The constraints of the riddle had been set: Imagine a structure for a stable, 60-carbon molecule that would not react with other molecules, which meant it had no dangling bonds. "Any concept of carbon you can imagine," Heath says, "is going to have some edge. Even benzene, which is a ring of carbon atoms, has some edges, but they're all terminated with hydrogen. But we could quite clearly say that the mass of the molecule was exactly that of 60 carbon atoms, and not 60 carbon atoms plus one hydrogen or two hydrogens....[So] if it was chemically inert, it must have managed to tie up its own bonds without the help of hydrogen."

Now the discussions grew feverish. They centered on two candidates for the structure of C₆₀, both of which had been raised the week before. One the group called the flatlander model: The wadges were stacks of hexagonal carbon sheets—similar to graphite—but with the dangling bonds somehow tied up. The other was the spherical model: flakes of carbon were curled up into a closed cage—again nobody knew how.

Neither Smalley nor Kroto lays exclusive claim to the first suggestion of a spherical, caged structure. Smalley credits it to "all the authors"; Kroto to "in-

tense discussions in which we all participated." But Smalley insists that Kroto leaned away from it. He remembers Kroto as "somewhat of a flatlander" right up until Tuesday morning, when Smalley produced his paper model of the full-fledged structure.

Not so, says Kroto. He acknowledges that he suggested one flatlander model—which he still finds quite elegant—but he also saw the appeal of a closed cage. Everyone did, he says. The claim that he was won over only after he saw the paper model he calls "patently false." As for the other members of the team, Heath agrees with Smalley in saying that Kroto at one time or another suggested a flatlander model but says they were all

Photo Researchers

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Rice University

trying to think of everything. “He definitely did at one time mention this ball,” Heath adds, “which turns out is the crux shape.” O’Brien, too, says that Kroto emphasized that the “only way possible to make an unreactive piece of carbon with 60 atoms is a closed-up ball without any dangling bonds.”

The focus of Smalley and Kroto’s disagreement comes at the next step, when the general idea of a closed cage crystallized into the complete buckminsterfullerene structure. The group had already realized that a flat sheet of the hexagonal carbon molecules—a graphite sheet—would not curl. It remained for them to rediscover a mathematical truth Fuller had exploited in his domes: that a sheet of regular hexagons can be made to curl by adding pentagons.

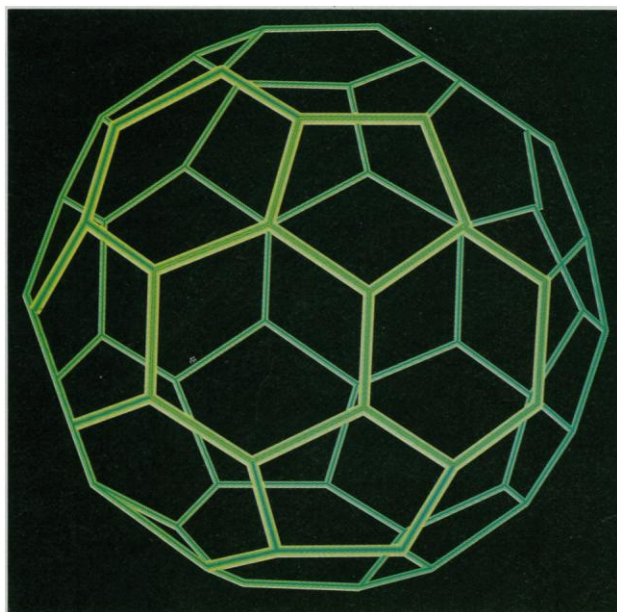
Kroto says he introduced Buckminster Fuller’s domes into the discussion. He was the natural one to do so, he says: He’s a graphic artist in his spare time, and he was steeped in Fuller’s work. As a student, Kroto once wanted to study with Buckminster Fuller, and at least one of Fuller’s domes had left a powerful impression on him—the geodesic dome at Expo 67 in Montreal. “I had actually been inside this remarkable structure 18 years before,” he writes, “and remembered pushing my small son, in his pram, along the ramps and up the escalators, high up among the exhibition stands and close to the delicate network of struts from which the edifice was constructed. This experience left an image, which could not be erased, in my mind.”

When the concept of a closed cage came up in the discussions at Rice, Kroto says, it “brought back vivid memories of Buckminster Fuller’s geodesic domes....” Among others, Kroto recalled a toy geodesic dome he had at home in Brighton—a cardboard polyhedral sphere with a map of the night sky printed on it, which he called the stardome. Around noon on Monday, he says, he described it to the group as best he could. He says he remembered that it was made of pentagons and hexagons, and he thought it might have 60 vertices.

Smalley, in his written account, recalls nothing so definite. There was casual talk of geodesic domes as early as Thursday of the previous week, he says, and at some point, Kroto brought up the stardome: “Kroto had once built a cardboard dome for his children that was, he thought, something like a geodesic sphere, and he seemed to remember it somehow included pentagons as well as hexagons. But his memory was vague.” Curl, for his part, says he may or may not have been present when the subject of geodesic domes

was raised. “But I sure as heck couldn’t tell you who thought of the idea first.”

That night, everyone except Curl went off to a Mexican restaurant. The talk once again converged on ways to make a closed cage work, accommodating 60 carbons and tying up all the bonds, and Kroto maintains that he once again nudged the discussion in the right direction. “We talked about Buckminster Fuller’s domes,” says Kroto. “Smalley mentioned chicken-wire cages [consisting only of hexagons]. I reiterated the essentials of the stardome: its spheroidal shape, hexagonal faces, and—in particular—the pentagonal faces. Smalley expressed an interest.”



It takes 12 to tangle. Twelve pentagons scattered among the usual carbon hexagons curl a flat sheet of 60 atoms into a geodesic sphere.

Even if Kroto did suggest the key notion, though, it remained for someone to show that a closed-cage structure really could work. Kroto, who was staying with Curl, returned from dinner hoping to call his wife in England and have her find his stardome and count the vertices. Curl talked him out of it. Curl recalls: “It just didn’t seem to make much sense to call in the middle of the night, and she wouldn’t know where it was.” Heath went home and tried to build a closed cage using gummy bears and toothpicks, but his modeling equipment wasn’t sturdy enough. Smalley also sat down to find a solution by trial and error, and he used his paper, tape, and scissors to better effect. By the wee hours he had found that by interspersing pentagons among the usual carbon hexagons, he could produce a geodesic sphere of 60 vertices. Eureka.

“The next morning,” Smalley writes, “on my long drive to work, I telephoned Curl’s answering machine and excitedly reported that the closed solution worked. I asked him

to gather everyone in my office. When I arrived, I tossed the paper C₆₀ model onto the coffee table in their midst. Kroto was immediately taken with the beauty of the structure.”

But was that because it was the realization of something he had already pictured in his mind’s eye, or because it was a complete revelation? To Kroto, that’s the key issue in the dispute. When he returned to Brighton, he says, he confirmed that his stardome had 60 vertices. It was exactly what Smalley had built, and what Kroto says he had described in detail. But to Heath, whether Kroto had already pictured the correct structure may be beside the point. “Whether Harry believed it or not,” he says, “he didn’t believe it enough to stay up all night working on it. And Rick did.”

In any case, it took Smalley’s model to make converts of the entire group—especially Curl, whom Smalley calls their devil’s advocate. He insisted that they check the bonds on the structure to make sure it obeyed the rules of carbon bonding. He and Kroto set to work with a magic marker and succeeded within minutes. “When we saw that Bob Curl was a believer,” says Heath, “everyone was a believer.”

Then came the genesis of the name buckminsterfullerene, which has done so much to convey the wonder of the molecule. This too has generated its share of disagreement. Kroto says he proposed the name on the spur of the moment on Tuesday as the group was writing the title of the paper claiming the

discovery, and that it took some work to talk Smalley and Curl into accepting it. Curl agrees that Kroto had to convince him. Smalley, whom the popular press has often credited with coining the name, says he can’t remember who first suggested buckminsterfullerene, but he admits that he was less fond of it than Kroto.

Over the years, Kroto and Smalley have tried to play down these disagreements, doing their best to present the genesis of buckminsterfullerene as simply a group effort. As Kroto puts it, “The discovery itself and the fact that *we* got the correct solution are what really matter.” Still, it was Kroto and Smalley’s divergent views of the discovery that began fraying the collaboration, starting the very next day after the group agreed it had the solution.

Kroto had rescheduled his flight back to England for Wednesday in order to write up the paper. The extra day also gave the group time to discuss the next step: proving that C₆₀ had a cage structure. Kroto says he

Source: R. Smalley. Illustration: D. DeFrancesco

suggested the strategy of trying to trap metal ions inside the molecule. Heath says the idea was obvious—any chemist would have thought of it. In any case, Kroto had suggested iron, which didn't work; Heath then tried lanthanum ions, which did. The experiments took place after Kroto left, and the draft reporting them, instead of listing Kroto as an author, only acknowledged him for "stimulating discussions."

When Kroto saw the draft, says Smalley: "Harry was really steamed. He felt that we were trying to ride him out of this." Kroto believes he was entitled to authorship by virtue of his role in the original discovery. "I felt I had earned an inalienable right to be an equal partner in bringing up the baby. No one had made a greater contribution to its birth," he says, pointing out that he was first author on the original paper.

After a day's reflection, Smalley agreed to write him in as an author. Smalley stipulated, however, that he would include Kroto in future papers only if he were an active collaborator. That put Kroto in what Curl calls the "terrible position" of having to commute from England if he wanted to share credit for the continuing C₆₀ work. As a result, Kroto recalls, he went back and forth between Houston and Brighton "like a yo-yo."

The resentment between Kroto and Smalley finally crystallized in March 1986, when Kroto lectured to the space physics group at Rice. Smalley heard the presentation and bristled. He felt that Kroto had portrayed himself as the idea man and the Rice contingent as the technical help. Heath, Curl, and O'Brien saw no reason to object initially, although Heath says he later acknowledged Smalley's point. Smalley then discussed his objection with Kroto, and their relationship "deteriorated overnight," according to Kroto. To Smalley, too, it became "increasingly unpleasant."

Finally, in April, 1987, after Kroto had made eight fruitful trips to Rice, the collaboration died. It had produced some of the best science of his and Smalley's careers—at the price of an intensity that, for a few hours at least, dissolved the clear boundaries separating the two men's intellectual claims. "There is still a question of what really happened," says Smalley, "and we'll never know." Kroto, not surprisingly, disagrees. It's unfortunate, he says, that individual contributions were ever singled out, but once they were, it's never too late to get them right.

C₆₀, the molecule that is an emblem of technical possibilities to so many chemists, is also a monument to the power and perils of collaboration. ■ GARY TAUBES

Gary Taubes is still working on a book on cold fusion for Random House.

France Set to Reopen AIDS Pact?

Paris—Even though the investigation by the U.S. National Institutes of Health into the early AIDS work of National Cancer Institute virologist Robert C. Gallo is not yet completed, some French government officials and researchers have apparently seen enough. Last week, *The Chicago Tribune* published parts of a draft report of the investigation indicating that NIH investigators had determined that a landmark paper published by Gallo in *Science* in 1984 contained inaccurate and misleading statements (*Science*, 20 September, p. 1347). This week, a senior official at the French Ministry for Research and Technology, who asked not to be identified, told *Science* that French diplomats have been instructed to "lean harder" on Washington to tear up a 1987 Franco-American agreement over patent rights to the blood test for the AIDS virus.

The agreement, signed by former President Ronald Reagan and then French Prime Minister Jacques Chirac, gives Gallo and Pasteur Institute virologist Luc Montagnier equal credit for discovering the AIDS virus, and splits royalties from the patent on the blood test equally between the United States and France. Gallo's 1984 paper was central to the agreement. Gallo and cell biologist Mikulas Popovic reported in that paper that they had grown the AIDS virus in a permanent cell line for the first time—a key step in developing the blood test.

The draft report of the NIH investigation says that Gallo edited out of early draft versions of the paper references to the fact that Popovic had infected cells with samples of the AIDS virus Montagnier sent him in 1983. Those references, which Popovic had put in the draft, would have made it clear that the Gallo lab did more with Montagnier's virus than Gallo publicly acknowledged at the time. The report, which is currently being rewritten, also accuses Popovic of making false statements in the paper, although it says these alleged misstatements "did not negate the central findings of the paper."

"As far as we are concerned there is now little doubt that the agreement is null and void and should be renegotiated," the research ministry official told *Science*. "We are getting very impatient," he added. This impatience is news: It is the first time since the dispute over patent rights first arose that the French government has broken diplomatic silence over the affair, even off the record.

Gallo and Popovic, in a statement released by their lawyers, say that references to their work with Montagnier's virus were omitted from the *Science* paper because they intended to publish a joint paper with the Pasteur Institute scientists on this work. Montagnier was informed that "we had successfully cultured the 'French virus' in a cell line," they state, adding that "we did so only transiently." "Publication of the *Science* article (with or without reference to the work of the Institut Pasteur) does not change the conclusion that we and Dr. Montagnier, together with his former colleagues Drs. [Jean-Claude] Chermann and [Françoise] Barré Sinoussi, are co-discoverers of the AIDS virus," the statement says.

Montagnier, who is head of the viral oncology department at the Pasteur Institute and co-owner of the patent on the AIDS blood test, is not satisfied, however. "If Popovic had said at the outset what he has said now, it could have saved a lot of time," Montagnier told *Science*. "And, more important, the outcome of the 1987 agreement would have been different." If all the facts had been known at the time, Montagnier claims, "the agreement would not have been 50:50, but it would not have been 100:0 either. Of course there is still a contribution from Gallo's laboratory. We could grow the virus in continuous cell lines in 1984, but they did it better. They carried out a Western blot and confirmed it with serological findings."

Montagnier also argues that the *Science* paper—and some later papers—should be retracted. And, 7 years after Gallo says he first proposed it, Montagnier says: "We should perhaps write a joint paper" about the work the two labs did with the virus Montagnier isolated. He adds: "I am not aggressive about this, but it is important to clarify what happened. The scientific debate is closed now. Gallo has recognized that HTLV-IIIB [Gallo's virus] was contaminated by LAV [Montagnier's virus]. The only remaining problem is scientific history, which is important, but only affects a few people. It will not affect the problem of AIDS as an illness." ■ PETER COLES

Peter Coles is a free-lance science writer based in Paris.