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FULLERENES GAIN NOBEL STATURE

Discovery of C_{60} and its relatives in 1985 reshaped chemists' understanding of the fundamental properties of carbon

Rudy Baum

C&EN Washington

Robert F. Curl Jr., Sir Harold W. Kroto, Richard E. Smalley. Three very good, maybe brilliant, chemists who came together for 11 days at Rice University, Houston, in September 1985 to perform a series of experiments that would, at the very least, change chemistry, and, just maybe, change the world.

Within weeks of the experiments and the seminal *Nature* paper describing and interpreting them, the collegial collaboration would begin to unravel; within months, it would be dead. But the controversial hypothesis the collaboration spawned - that another form of pure carbon besides graphite and diamond exists - would thrive over time. The fullerenes, a family of carbon cage molecules epitomized by the exquisitely symmetrical C_{60}, would come, for a time, to occupy center stage in chemistry. Though their cachet has waned somewhat in recent years, fullerenes and related molecules known as carbon nanotubes may well power new technologies now only dreamed of.

Curl, Kroto, and Smalley, and their equally talented but, as it turns out, not quite so lucky collaborators, had the rare privilege of observing a fundamentally new facet of nature for the very first time. This being today, what they saw were the data from a highly sophisticated, essentially one-of-a-kind instrument, in this case a series of mass spectra that unequivocally demonstrated that C_{60} is an extraordinary molecule.

The discovery of C_{60} - fancifully named buckminsterfullerene by the researchers when they gleaned that its bonds had an architecture similar to R. Buckminster Fuller's geodesic domes - and the family of molecules for which C_{60} is the prototype earned Curl, Kroto, and Smalley the 1996 Nobel Prize in Chemistry (C&EN, Oct. 14, 1996, page 7). They received the prize on Dec. 10, 1996, the 100th anniversary of Alfred Nobel's death. As C&EN's managing editor and a science writer with a long- standing interest in the fullerenes, I was invited to attend the Nobel festivities.

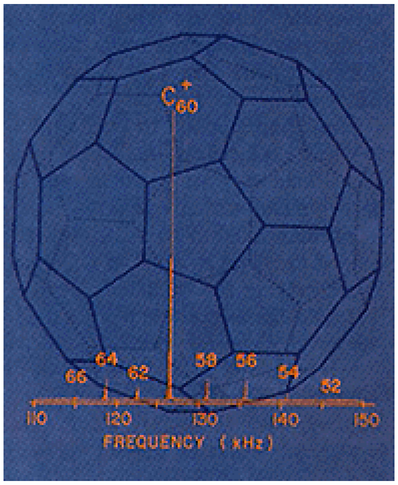
Photo by Rudy Baum

From left, Osheroff, Curl, Kroto, and Smalley at a press conference at the Swedish Royal Academy of Sciences, Stockholm; mass spectrum (right) reveals the special stability of C_{60}, which is explained by its truncated icosahedron structure.

Innumerable prizes and awards for achievement in the sciences and arts exist today, but none rivals the Nobel Prizes. The amount of money involved - about $1.2 million for each 1996 prize - is one not insignificant factor in the distinction of the Nobels. But there also is a remarkable aura surrounding the Nobel Prizes unmatched by any other. The Nobel Prizes simultaneously celebrate excellence across a wide range of human endeavors - physics, chemistry, medicine, literature, economics, and the quest for peace. Five of the six prizes are presented together, in dark, often dreary wintertime Stockholm, and the events surrounding them - the lectures, press conferences, and receptions; the awards ceremony and the splendid banquet that follows - enchant an entire capital city.

And yet, despite the acknowledged preeminence of the Nobel Prizes and the tremendous effort that goes into selecting the prize winners, there is a perhaps unavoidable capriciousness to them. Some winners of the literature prize have been remarkably obscure writers. There seem to be a finite number of economic theorists prominent enough to merit the economics prize who haven't already won it.

The limit of three recipients per prize (imposed by the statutes of the Nobel Foundation) inevitably means that important collaborators sometimes do not share in a prize they and others might otherwise believe they are due. This year's prizes in chemistry and physics dramatically illustrate the problem. In physics, two Cornell University physics professors, David M. Lee and Robert C. Richardson, and their then-graduate student, Douglas D. Osheroff (now a physics professor at Stanford University), shared the prize for the discovery of the superfluidity of liquid helium-3. In chemistry, two graduate students who were key in discovering the fullerenes - James R. Heath (now a chemistry professor at the University of California, Los Angeles) and Sean C. O'Brien (now a scientist with Texas Instruments, Dallas) - were passed by. For Heath and O'Brien, who not only participated in the experiments that revealed the existence of the fullerenes but also carried out seminal work in establishing the validity of the fullerene hypothesis, the selection of this year's prize appeared particularly fickle.



And while most chemists expected Smalley and Kroto eventually to share a Nobel Prize in Chemistry for the discovery of the fullerenes, many were at least mildly surprised by the selection of Curl to share the prize with them. Although Curl introduced Smalley and Kroto, participated in the experiments that led to the discovery of the fullerenes, and conducted research on them for several years following the discovery, he was not generally perceived to be as central a figure in the fullerene saga as were Smalley and Kroto. Curl also stopped research on fullerenes in his lab in 1992, after a method for production of macroscopic amounts of C_{60} and C_{70} was discovered elsewhere.

I recently talked with Curl when he came to Washington, D.C., with Nobel Prize winners Smalley, Lee, Osheroff, and Richardson for a reception with Vice President Al Gore at the White House and a formal dinner at the Swedish Embassy. Curl discussed discovering the fullerenes, dropping out of fullerene research, and winning the Nobel Prize.

Curl, 63, a native of Alice, Texas, is the son of a Methodist minister. He is a self-effacing man, given to downplaying his considerable intellectual acumen and scientific accomplishments. When asked how winning the Nobel Prize might affect him, Curl responded, typically, "I just hope I can resist the urge to pontificate."

Curl's introduction to chemistry was Norman Rockwellian - his father bought him a chemistry set when he was nine years old and, within a week, he says, he knew he wanted to be a chemist. He attended Rice University as an undergraduate, receiving his bachelor's degree in 1954. He did his graduate work at the University of California, Berkeley, receiving his Ph.D. degree in 1957. He also met his wife, Jonel, in Berkeley. After a postdoctoral fellowship in Edgar B. Wilson's group at Harvard, where he learned microwave spectroscopy, he accepted a faculty position back at Rice in 1958, where he has remained ever since.

Photo above, taken at the conclusion of 1985 experiments at Rice University, includes Curl (standing) and (from left) O'Brien, Smalley, Kroto, and Heath; that photo was restaged (above) just prior to the 1996 Nobel Prize presentation in Stockholm.

At Rice, Curl settled in as a microwave and infrared spectroscopist, applying the techniques to a variety of chemical systems. By the early 1980s, he was doing infrared spectroscopy of reactive free radicals, in particular C_2H, collaborating with electrical engineering professor Frank K. Tittel. He was also collaborating with chemistry professor Philip R. Brooks on what they called reaction complex spectroscopy, looking at relatively long-lived species in the process of reacting.

Smalley arrived at Rice from a postdoctoral fellowship at the University of Chicago in 1976. "Rick and I always wanted to collaborate," Curl said. By the early 1980s, Smalley had been promoted to full professor and had begun making a name for himself in the physical chemistry community because of the laser vaporization, supersonic jet technique he had invented for studying refractory materials. By 1983, Curl and Tittel had begun a collaboration with Smalley studying semiconductor clusters.

Curl is generally credited with being the catalyst that led to the discovery of the fullerenes through his introduction of Smalley and Kroto. Curl had met Kroto, a chemistry professor at the University of Sussex, Brighton, England, at a theoretical chemistry meeting in 1977, and subsequently Kroto had invited Curl to visit him at Sussex. In 1984, at a meeting in Austin, Texas, on gas-phase molecular structure, Curl reciprocated by inviting Kroto to visit Rice. There, Kroto was introduced to Smalley and his revolutionary laser vaporization technique.

Kroto saw in Smalley's device an opportunity to test ideas he had been developing about the formation and chemistry of long-chain polyyne species formed near carbon-rich stars. The following year, an updated version of Smalley's instrument was used to vaporize carbon and produce the first fullerenes.

Since then, many talks, especially by Kroto and Smalley, and articles (including several by me) and books have explored the intense intellectual ferment at Rice among Curl, Smalley, Kroto, Heath, O'Brien, and coworkers that went into devising an explanation for the unique mass spectral signature of C_{60}. Certainly, it was an exhilarating several days, with Heath and his wife, Carmen, one night trying to build C_{60} models with candy and toothpicks; with Kroto trying to recall the precise geometry of a "star sphere" he had once built for his children; and with Smalley, after a few latenight beers, succeeding with a crude paper and Scotch tape polygon that contained the required 60 vertices in a highly symmetrical closed shell.

But Curl today has an interesting take on the fullerene discovery and what primarily contributed to it. "Rick would maintain," Curl said, "and I tend to agree, that, 'It's the machine, stupid,'" borrowing and modifying a phrase made famous by the 1992 Clinton presidential campaign. That is, without the laser vaporization device invented by Smalley, the fullerenes would have remained undiscovered, at least for a few more years.

Curl elaborated: "If we had published the first *Nature* paper without a structure - just said, look, we found this interesting mass spectrum - it wouldn't have been two weeks before someone had said,' You dolts, soccer-ball C_{60} is a rational explanation for it.' Look, Orville L. Chapman[a chemistry professor at UCLA] had four graduate students trying to make C_{60} at that time. So I don't think that there's any question that people would have said this was a reasonable explanation."

As Curl and Smalley pointed out in their Nobel lectures in Stockholm, unbeknownst to the researchers at Rice in 1985, the idea for icosahedral (that is, soccer-ball) C_{60} was not new. David E. H. Jones, writing as the columnist Daedelus in the Nov. 3, 1966,*New Scientist,* speculated on a hollow, closed-shell carbon molecule derived from a graphitic sheet in which incorporated pentagons caused the flat graphite to curve around on itself. The Japanese synthetic organic chemist Eiji Osawa in 1970 published a paper in the Japanese-language journal *Kagaku*[**25,** 843 (1970)] that contained the structure of the now-familiar truncated icosahedron C_{60}. Russian chemists also speculated on the compound [*Proc. Acad. Sci. U.S.S.R.,* **209,** 239 (1973)]. And UCLA's Chapman, legendary for his innovative ideas about molecular structure, was attempting a classical synthesis of C_{60}.

But as Curl noted in Stockholm, "If Orville Chapman had succeeded in synthesizing C_{60}, it would have been like dodecahedrane, a tour de force of synthetic organic chemistry. But it would not have been the same as the fullerene hypothesis. It would not have revealed a fundamental property of condensing carbon vapor."

That fundamental property of condensing carbon vapor - the tendency of carbon atoms to form a variety of closed structures heretofore unknown in chemistry - is what earned Curl, Kroto, and Smalley the Nobel Prize. But after Wolfgang Krätschmer, of the Max Planck Institute for Nuclear Physics, Heidelberg, Germany, and Donald R. Huffman, a physics professor at the University of Arizona, Tucson, developed a method for producing macroscopic amounts of the fullerenes, Curl decided to abandon the field of fullerene research. "Why?" I asked him in our interview in Washington, D.C.

"Once the Huffman-Krätschmer technique was developed, it became an area of organic chemistry and materials science," Curl said. "Essentially, I was faced with the issue of having to redefine myself if I wanted to continue in the fullerenes. As a physical chemist, I could have gotten into the issue of fullerene formation. I did do a fair amount of thinking about that, but I really couldn't think of a definitive experiment that would settle the question. I didn't want to do materials science and I didn't want to do organic chemistry, and I didn't want to work in a field where there were papers coming out every week. Rick has these three-ring binders with 3- or 4-inch rings, and he was putting fullerene papers in them. And when he got up to the seventh binder, I knew it was time for me to do something else."

Today, Curl is being drawn in a new research direction through his collaboration with Tittel. The infrared lasers they have developed to study free radicals appear to be suitable for use in small, portable monitoring devices that could be used to detect, for example, trace atmospheric gases such as methane. "We're having a good time," Curl said, "because the work involves questions of engineering that I had never thought of before."

No one who knows them would use the phrase "self-effacing" to describe either Harry Kroto or Rick Smalley. Both are brilliant, creative, articulate, and ambitious. Perhaps it was inevitable that a collaboration between them would be both extraordinarily successful and exceedingly short-lived. Kroto's interests range from chemical physics to technical drafting and design to filmmaking. His career as a chemist has been marked by innovative ideas on a range of subjects, one leading to the next, and numerous successful collaborations, not all of which ended cordially. He is charming and gregarious, a natural showman.

Smalley combines what many people who know him well describe as true genius with dogged determination, a passion for perfection, and an incredible ability to design innovative approaches to intractable experimental problems. "I've never met anybody like Rick," O'Brien told me in Stockholm. "He's never wrong." Smalley challenges everyone around him - colleagues, collaborators, graduate students and postdocs, and the occasional science writer who wanders into his sphere. And he does it with what is a quiet, but sometimes biting, wit.

Kroto, 57, was born in Wisbech, Cambridgeshire, England. He obtained his Ph.D. degree in chemistry in 1964 at the University of Sheffield, England. But, as he told me in an interview in Stockholm, chemistry never dominated his life - graphic design was at least as great a passion. "I was the art director of the student magazine," he said. "The first prize I ever won was for a book jacket." But chemistry was his calling, and he took a faculty position in the department of chemistry and molecular sciences at Sussex in 1967.

Like Smalley and Curl, Kroto has to his credit a variety of significant accomplishments in chemistry besides the discovery of the fullerenes. As he pointed out in his Nobel lecture in Stockholm, one of the first, of which he is quite proud, was the synthesis of the first compound containing a carbon-phosphorus double bond. "When we discovered the carbon-phosphorus double bond, that was a fantastic day," Kroto recalled. "Because people had said in the literature that you can't make a carbon-phosphorus double bond."

In his Nobel lecture, Kroto traced his evolution as a chemist - from the early work on carbon-phosphorus double bonds, to carbon species in interstellar space, to the discovery of the fullerenes, to current work on nanoscale carbon structures and nanotechnology. Throughout his talk, Kroto emphasized the idiosyncratic way he approaches chemical research.

In the 1970s, Kroto began the work that would lead, in a roundabout way, to the discovery of the fullerenes. Working in collaboration with Sussex colleague David Walton and physical chemist Takeshi Oka and astronomers at Canada's National Research Council, Kroto began a search for long-chain carbon species in interstellar space. Kroto's idea was that carbon-rich red giant stars were throwing off complex carbon species and that radioastronomy could detect them. The collaboration involved determining the spectral signatures of various polyynes and searching for those signatures in the infrared and microwave absorption spectra of interstellar clouds. The team definitively detected linear polyyne species including HC_5N, HC_7N, and HC_9N.

But spectroscopy and radioastronomy can only take you so far in understanding the chemistry of species light-years away from where you are standing, and Kroto longed to know more about how such species might form in the circumstellar shells of red giant stars.

"On the discovery of C_{60}, I was interested in carbon stars," Kroto told me in Stockholm. "I was interested in proving this hypothesis I had that the material was coming out of a carbon star - which at the time was not accepted by most people because there were some very good ideas about the formation of molecules in the interstellar medium that did not fit with that. Those ideas are right, but they didn't seem to work for carbon. I think we proved conclusively that carbon chains are coming from carbon stars. We discovered C_{60} as serendipity."

About his research on nanoscale structures, Kroto said, "Let's just let carbon do what it wants. Let's probe these things and use metal clusters to catalyze their formation. Let's see what happens and build on that. It's sort of a different way, a more fundamental approach to strategic science. I'm not saying, 'I want to produce material of a given nature.' I work in a different way. I go down a street and I find a stone and turn it over, and I say, 'That's an interesting fossil.' What I do is more like fossil hunting the way that nature operates. Just probing the way it works rather than trying to force it into submission. I can't do it the other way. It doesn't seem to work. Rick is doing it with a laser, trying to produce, say, long tubes, and he's getting there. My approach is, I can see this particular thing we've achieved, and just by playing around, doing it a different way, let's see if we can do something useful."

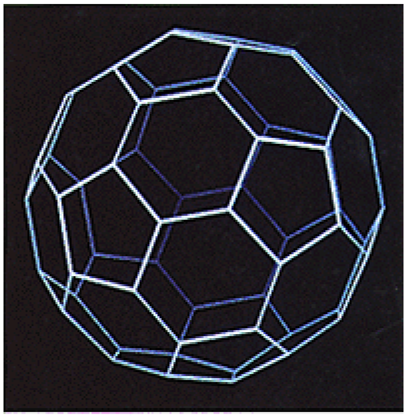
Kroto is eloquent in his defense of basic research in the face of budget cutters in the U.K. and the U.S. "Fundamental science is difficult to directly support because, at the present moment, people want direct applications and direct goals. But there are a group of people out there, such as myself and others doing fundamental science, we're on the edge of extinction if we're not careful, and that's sad, because those people can't work in any other way. And they have historically produced, I think, some of the most important discoveries. C_{60} is one of them."

Smalley, 53, was born in Akron, Ohio, and grew up in Kansas City, Mo. He attended Hope College, Holland, Mich., from 1961 to 1963, and received his bachelor's degree in chemistry from the University of Michigan in 1965. From there, he went to Shell Chemical Co. as a research chemist from 1965 to 1969, where he came to realize that he would not be able to do the kind of chemistry he wanted to do without an advanced degree. That realization led him to Princeton University, where he received a Ph.D. degree in chemistry in 1973.

Smalley is a gifted technician, using the word in its most fundamental sense. He invented machines that change the way we look at the chemical world. In his Nobel lecture, Smalley flatly stated: "The apparatus discovered the fullerenes." While Kroto and others may disagree, the argument has the ring of truth to it. Since the time of Galileo and his telescope, new devices, new instrumentation in the hands of the prepared observer, have generated new insights into nature that simply would not have been possible in the absence of the technology. To disparage development of new instrumentation as somehow "applied" science rather than" basic" science is to condemn science to perpetual ignorance.

Nanotechnology almost certainly won't come into existence through the efforts of basic researchers alone. The word itself gives the game away - nanotechnology. By definition, this is now applied or directed research. Smalley, perhaps for the first time in his career as a chemist, knows exactly what he wants to achieve - synthesis of essentially infinitely long, single-walled nanotubes of a particular symmetry. That's his goal because he sees in such nanotubes almost unlimited potential to change technology, a worthy enough goal to switch from basic to applied research. We don't need to noodle along to discover what carbon can do anymore, Smalley seems to be saying; that's what the 1996 Chemistry Nobel Prize was awarded for.

Smalley has been fascinated by carbon nanotubes since they were discovered in 1991 on the cathode of a carbon arc by Sumio Iijima at NEC Fundamental Research Laboratories in Tsukuba, Japan. Iijima's high-resolution electron micrographs of multiwalled nanotubes and their hemispherical end caps clearly showed that these carbon species are extended members of the fullerene family. Subsequent patented work by inventor Howard G. Tennent showed that finer and more perfect tubes could be produced by flowing a hydrocarbon such as ethylene mixed with hydrogen and an inert buffer gas over nanometer-sized catalytic metal particles dispersed onto a support. Smalley believes that the mechanism of this catalytic process is now well understood. But while multiwalled nanotubes are clearly related to fullerenes, they are not molecularly perfect; they are not fullerenes.

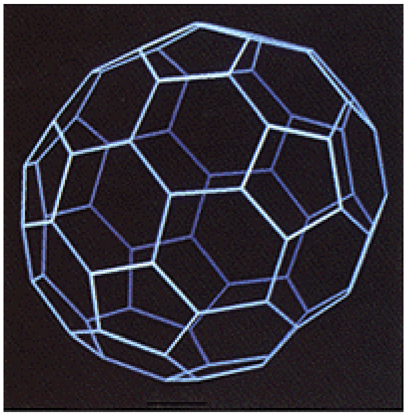


C_{60}

That's not the case with the single-walled nanotubes discovered in 1993 simultaneously by Iijima and Toshinari Ichihashi at NEC in Japan and Donald S. Bethune and coworkers at IBM Almaden Research Center in San Jose, Calif. The two groups showed that if certain metals are inserted into the anode of a carbon arc operated in a way expected to produce C_{60}, the soot collected on the walls of the chamber has a rubbery texture. Transmission electron microscopy images of this soot showed that it contained many single-walled nanotubes with a narrow distribution of diameters, about 1.2 nm. The soot contained no multiwalled nanotubes.

The results from the NEC and IBM groups suggest that the mechanism for formation of the single-walled nanotubes must be very different from that of the multiwalled nanotubes, Smalley told me when he was in Washington. "The fact that the single-walled nanotube diameters are so small and have such a narrow distribution indicates that there must be some other process at work here," Smalley said. "We believe it is intimately associated with the self-assembly process of C_{60} and the other fullerenes.

"While the diameters of catalyzed arc-grown single-wall nanotubes are fairly uniform," Smalley added, "those produced by another method recently discovered in our laboratory are stunningly so." The Rice chemists used a laser to vaporize a target rod composed of 98.8% carbon, 0.6% nickel, and 0.6% cobalt to produce soot that contained 70 to 90% single-walled nanotubes, of which 50% are of a particular geometry, dubbed the 10,10 tube (C&EN, July 29, 1996, page 5). The tubes are bundled together in "ropes" 5 to 10 nm in diameter. Ropes as long as 100 &mgr;m have been observed.



C_{70}

In his Nobel lecture in Stockholm, Smalley said: "My main message is that the process of discovering the fullerenes is ongoing. We weren't the first to conceive of the truncated icosahedron. Nor were we the first to think of C_{60}. Carbon has the genius wired into it to self-assemble into this structure, and we were lucky enough to discover that fact. In addition to making fullerenes, we can use cobalt or nickel to trick carbon into making its next favorite structure, nanotubes, of which the 10,10 tube is to tubes as C_{60} is to the fullerenes."

The 10,10 nanotube, Smalley continued, "is one of the most important species in the future of chemistry." Although it contains literally millions of carbon atoms, the 10,10 tube is truly molecular. By symmetry, the 10,10 tube is metallic, comparable to copper. The 10,10 nanotubes" have the potential to revolutionize every technology in which an electron moves from one location to another," Smalley said. The ends of the tubes conceivably can be opened to allow the carbon atoms to make covalent bonds to other atoms. Heat an opened tube to 1,000 °C, and it will spontaneously close. They will also be the strongest fiber ever made, "perhaps the strongest fiber that ever can be made," Smalley said, about 100 times stronger than steel while having only one-sixth the weight.

In November, my wife Jan and I took Bob and Jonel Curl and Smalley to dinner when they were in Washington, D.C. We spent a long time together that night talking about a variety of subjects. John Horgan's book "The End of Science" came up (C&EN, Dec. 2, 1996, page 27). Smalley had read it. Curl had not, but knew of its premise, which holds, essentially, that there's not much left to discover in science. Curl's typically succinct comment on Horgan's thesis was: "What that's fundamentally saying is that there is no virtue in understanding complex systems. I think that that's obviously lunacy. People would like to understand, for example, living organisms."

Smalley dismissed the book entirely." I doubt very much that 2% of what's important in science is now known," he said. "Maybe that's a bit extreme. But I'm quite certain that the universe holds important surprises yet for us. Easily 80% of what we need to know remains to be discovered."

But in Washington, Smalley was more interested in nanotubes than he was in arguments about what's left to be discovered in science or about meeting with Vice President Gore. No fullerene research is currently being done in Smalley's lab at Rice - his entire effort now focuses on nanotubes, which he believes hold the potential for revolutionizing human existence. And as such, he wants other chemists to investigate the chemistry and properties of 10,10 nanotubes.

"The more we've gotten into this," Smalley told me, "the more I am convinced that if this stuff is anywhere near as cool as I think it is, this is a lot bigger than anything I've ever done before. It really contains the seeds of many new major technologies. Here we have a molecule that's tubular made out of our favorite element. The ends can be derivatized. For the first time, we have a molecule the two ends of which are communicating with each other by metallic transport. We've never had that before. We've had conducting molecules, but they are not really very good conductors. Those cases where they are good conductors, they are not very good molecules.

"The reason I'm trying to get this out is that I would like many of the best organic and organometallic chemistry groups in this country seduced into working with this material. That's not going to happen unless either a lot of time passes and they get bored with what they are now doing or, if you want it to happen quicker, and I think that's important, the federal government needs to establish some sort of national initiative to develop this area. The best groups have plenty of ideas - they are the least likely to drop what they are doing and start in a completely different area. And I want to attract them into it."

According to Alfred Nobel's will, the Nobel Prizes honor achievements of the preceding year that benefit humanity. By necessity, the "preceding year" part of the bequest has fallen by the wayside - the world is much too complicated as the millennium draws to a close to be able to judge achievement that rapidly.

The Nobel Prize in Chemistry in recent years has recognized a variety of types of achievement. In some years, the Nobel Chemistry Committee has selected chemists for what appeared to be a lifetime of outstanding work - Rudy Marcus and George Olah come to mind. In other years, the committee has anointed chemists for a single essential insight, the clarity of which redirected a whole field of research - last year's award to Sherry Rowland, Mario Molina, and Paul Crutzen is a prime example.

The 1996 Nobel Prize in Chemistry went to three men for a single set of experiments conceived by one, facilitated by another, on a revolutionary instrument invented by the third that, it has now become clear, changed the face of chemistry. The prize, almost everyone involved agrees, should have gone to five scientists, for Jim Heath and Sean O'Brien played essential roles in the discovery of the fullerenes.

Perhaps I am prejudiced, because I have been writing about the fullerenes since the first paper on them was published in *Nature,*but the 1996 Nobel Prize in Chemistry seems to me to be an especially fitting one. As Rick Smalley emphasized in Stockholm, the fullerenes are still being discovered. But already, it seems clear, their discovery and what it revealed about the fundamental properties of carbon will be benefiting humanity for many, many years to come.

And like the vast majority of Nobel Laureates in Chemistry, Curl, Kroto, and Smalley, each in his own way, continue to make vital contributions to chemistry.