Tracking an Elusive Carbon

By CHRISTOPHER VAUGHAN

Scientists suspect a 'Third Man' molecule will help solve galactic mysteries

Light a candle. A liquid pool blossoms at the wick's base as solid wax melts, then travels up the wick to burn and vaporize. It is a fascinating process to watch, but the wax's most intriguing transformation may take place at the other end of the flame. There, among the carbon soot, the candle may be producing an exotic collection of huge "fullerene" carbon molecules, all spherically shaped and having the geometric facets of gems.

In theory, the fullerenes are symmetric molecules made of hexagonal and pentagonal arrays of anywhere from 28 to 540 or more carbon atoms. If the fullerenes do in fact exist – which scientists say they are close to proving – they could be the source of a whole new class of chemical compounds. In interstellar space, these molecules could play a critical role in planet formation, and they may be the source of mysterious spectral lines emanating from stars, an observation that has puzzled astrophysicists for decades.

The story starts with a less grandiose mystery: Why does carbon prefer to form even-numbered clumps after a laser vaporizes graphite? Exxon scientists discovered this phenomenon in 1984, and Harold Kroto of the University of Sussex in Brighton, England, became so intrigued by it that he convinced scientists at Rice University in Houston to stick carbon in a new machine they were using to investigate silicone chemistry.

"It seemed like a stupid idea at the time," says Rice chemist Richard E. Smalley. "After all, we know the chemistry of carbon better than that of any other element."

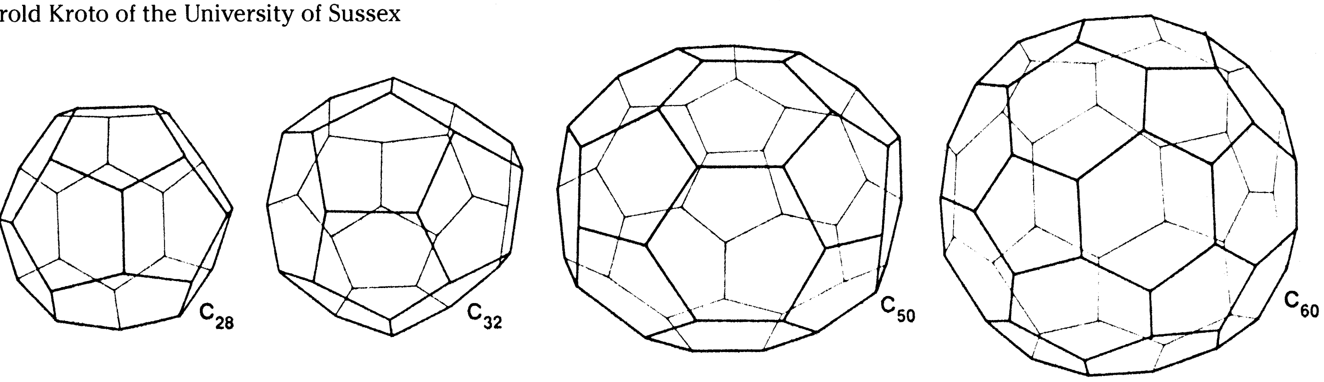
Kroto wanted to see if the large carbon clusters were actually carbon chains, but the experimental results at Rice got the scientists thinking otherwise. A scientist in Smalley's lab showed not only that carbon tends to form groups with an even number of members, but also that groups with certain numbers of carbon atoms become particularly abundant when the experimental machinery is adjusted. The predominant clusters were 30-carbon, 70-carbon and especially 60-carbon groups. Under some conditions the graph showing C_{60}'s abundance "shot up like a flagpole," showing that clusters containing other numbers of carbon atoms were much rarer. What, the researchers wondered, was special about these groups?

They knew that carbon tends to form hexagons, but it was Smalley who had a "eureka experience" in his office one day as he realized that 60 carbon atoms, arrayed in a sphere of interlocking hexagon and pentagon patterns, would form a very stable structure. Kroto and Smalley gave the large molecule a suitably large name, buckminsterfullerene (because the molecule was reminiscent of the geodesic domes designed by R. Buckminster Fuller), and promptly began work on a paper for NATURE (SN: 11/23/85, p.325).

The two journeyed over to the Rice math department with a drawing of the molecule to ask if there was a geometric name for this type of structure. There, Smalley recalls, they ran into a student who told them: "I could explain it to you a number of ways, but what you've got there, boys, is a soccer ball." And it was true – a soccer ball is exactly what the molecule's shape resembles. Since then, the proposed structure for C_{60}, officially called a truncated icosahedron, has been joined by proposed structures for a slew of fullerenes with different numbers of carbon atoms.

Of all the possible fullerenes, none with an odd number of carbon atoms could physically fit together in a closed shape, and the predicted fullerenes with the most stable structures tended to show up most often in the laser vaporization experiments, Smalley says.

Since proposing the structure three years ago, Smalley and Kroto have puzzled over how such a complex molecule could condense out of a chaotic gas of vaporized carbon. They now suggest that the fullerenes begin with a small collection of carbon atoms bonded to each other in a network of adjoining hexagons. The sheet has quite a few possible bonds along the edges dangling in space, and it is thermodynamically advantageous to eliminate those dangling bonds, Smalley says. One element of the sheet forms a pentagon instead of a hexagon, and the sheet curves to allow



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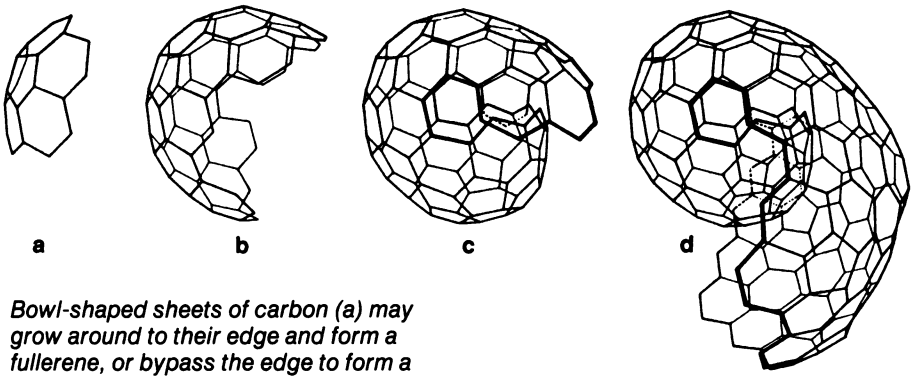
Some possible structures for fullerenes show that the molecules get less spherical as they grow large. Molecular strain increases as the fullerenes get smaller than C_{60}. C_{60} is the only fullerene in which the strain is evenly distributed among all carbon atoms.



Bowl-shaped sheets of carbon (a) may grow around to their edge and form a fullerene, or bypass the edge to form a nautilus-shaped "icospiral" (d).

two of the dangling bonds to attach to each other (see illustration). Curving the sheet eliminates two open bonding sites, but the price is an increase in strain within the molecule's structure as carbon bonds "bend" slightly.

As more carbon atoms attach themselves to the growing edge of the molecule, the sheet keeps curving. When it reaches its own edge, Kroto and Smalley say, either it closes up to form a fullerene, or new carbons keep adding on so fast that the growing sphere bypasses its own edge and spirals around itself like a nautilus shell.

All of this remains conjecture, because there is no way to put a fullerene together piece by piece in the laboratory. In fact, scientists had envisioned 60-carbon, soccer-ball-shaped molecules long before Smalley and Kroto came across them, but the inability to synthesize them using classical chemical methods led to doubt about C_{60}'s existence.

Now two good pieces of evidence argue that the molecules really do exist, Smalley and Kroto say. First, when the scientists shine a very powerful laser on C_{60}, carbon atoms break off the cluster. What C_{60} expels, though, is not the three-carbon groups that are most stable and therefore the most likely to come off. Instead, C_{60} loses a two-carbon group, suggesting the molecule is shrinking to become the next-largest fullerene down the chain, C_{58}.

As the fullerenes keep losing two carbon units and shrinking, the bond strain should increase. At some minimum size, the bond strain becomes so great that the molecule shatters instead of losing two carbons, Smalley says. This is exactly the behavior he sees at C_{32}.

The second major piece of evidence comes when Smalley lets the C_{60} molecules form around a "rock." This is how he describes the large ions that he believes may be inserted into a fullerene cage. With a large ion in the center of the cage, the fullerene should shrink only so far before it tightens around the ion and shatters.

Although he can't tell for sure that the potassium he binds to C_{60} in the lab really sits at the molecule's center, Smalley finds that such a C_{60}-potassium combination will indeed shrink only to C_{44} before shattering. Cesium, an even larger atom, when bound to C_{60} will let the carbon molecule shrink only to C_{48}. This is a near-proof that ions are at the center of a fullerene cage, Smalley says. Such ions, encased in fullerenes, could give chemists an entirely new family of chemicals to explore, he adds.

If a candle or any other sooting flame really makes fullerenes on Earth, then logic suggests that stars make them too, Kroto and Smalley say. Stars, especially red giants during their carbon-burning stage, could create a great number of carbon atoms, Smalley says.

A star's intense radiation would blast apart most large carbon molecules, but fullerenes seem incredibly stable. Each carbon atom is actually held into the structure by three bonds to neighboring carbons and a fourth bond that is "shared" by each carbon. The shared bond makes the fullerenes "aromatic" molecules that are much more stable than they would be with just single bonds. The absence of any edges or open bonds also contributes to stability.

In fact, Smalley says, in the laboratory C_{60} turns out to be the least chemically reactive and most photon-resistant molecule he has ever seen. Getting it to break under bombardment with electromagnetic radiation takes an enormous blast of energy – more than stars usually put out, he says.

"Given the lasers of Star Wars [the Strategic Defense Initiative] we can [break C_{60}], but given photons from the sun you'd have a hard time," Smalley says. The molecule may be so photon-resistant that it couldn't be destroyed by anything other than a laser or a supernova, he suggests. This is because a photon's energy doesn't stay in one place to break bonds, but instead spreads almost immediately over the whole sphere.

The presence of an ion of C_{60} in interstellar space may explain the mysterious spectral lines that astrophysicists find when they split the light coming from stars in our galaxy. When they take the spectrum caused by interstellar material and subtract those lines caused by known molecules, there remain about 15 to 20 lines whose origins have long baffled scientists, Smalley notes.

"The more you think about these lines, the more difficult it is to believe they could possibly exist," Smalley says. "We have learned a lot about the spectra of known molecules in the last 20 years or so, so this may be [caused by] a molecule that hasn't been seen before."

Smalley and Kroto suggest this unknown molecule could be buckminsterfullerene. The characteristic of the diffuse interstellar spectrum is very much what the spectrum for a fullerene cage should be, they say. Of course, the most convincing way to demonstrate the presence of a C_{60} fullerene in interstellar space would be to find the spectrum of buckminsterfullerene and compare that to the spectral lines from outer space. But that's not so easy to do, Smalley reports.

Smalley can't isolate enough C_{60} to just shine a light on it and see what spectrum comes out, so he must resort to other means of finding the spectrum of the molecule. Unfortunately, the [only] technique available requires the destruction of C_{60} molecules. The high energies and the multiple photon bombardments needed to break the molecule's bonds distort the spectrum, Smalley says. He is now working on snatching the spectrum using a few subtle tricks.

Many scientists are withholding judgment on the existence of fullerenes in space until someone obtains a spectrum, but Smalley and Kroto are already thinking of the implications of interstellar C_{60}. The molecule's most striking role may be to enable dust, comets, asteroids and planets to form.

After the Big Bang, the first generation of stars spewed out many species of light molecules. But these molecules never clumped together, because they bounced off each other as they collided, Smalley explains. What was needed was a molecule large enough to absorb some of the collision energy so other molecules could stick. C_{60}, being the largest interstellar molecule, would fit that bill perfectly, Smalley says. Without such a molecule, no really convincing way exists for any macroscopic particles at all to form, he adds.

Smalley and Kroto hope to learn soon if both stars and soot-producing flames create fullerene molecules. If their guesses are confirmed, it will mean those amazing molecules act throughout the universe in what Kroto calls the "mysterious role of the Third Man" – almost never seen but making their presence strongly felt nonetheless. ☐