

## Doing Chemistry in the Round

*Why buckminsterfullerene and its kindred carbon-cage molecules have topped the pop chemical charts—and what might burst the buckyball bubble*

WHEN ASKED WHAT 60 CARBON ATOMS bonded into a soccerball-shaped molecule called buckminsterfullerene—alias buckyball, alias  $C_{60}$ —ultimately will bring to chemistry, most chemists start out by saying, “It’s too early to speculate.” Then they speculate, often at length and sometimes with reckless abandon.

Truth be told, it is too early for anybody to argue convincingly whether the fullerenes—a growing class of carbon spheres including buckminsterfullerene, the most abundant and most studied of the lot—will give birth to a flourishing area of industrial chemistry or remain laboratory curiosities. But chemists do agree that, whether or not any buckyball derivatives ever reach the market, chemistry has changed for good in the single year since physicists in Heidelberg and Tucson described a ready way to synthesize gram quantities of buckyballs, making them widely available to chemists and anybody else who wants them.

The changes have touched both the sociology and the substance of chemistry. By straddling the division between organic and inorganic chemistry,  $C_{60}$  is breaking down disciplinary barriers. Chemists of all stripes are flocking to study it, entranced by its unorthodox bonding behavior—a reflection of the way electrons are shared among the molecule’s carbon atoms—and its uncanny geometry: its symmetry, its hollowness, the almost boundless structural permutations it promises.

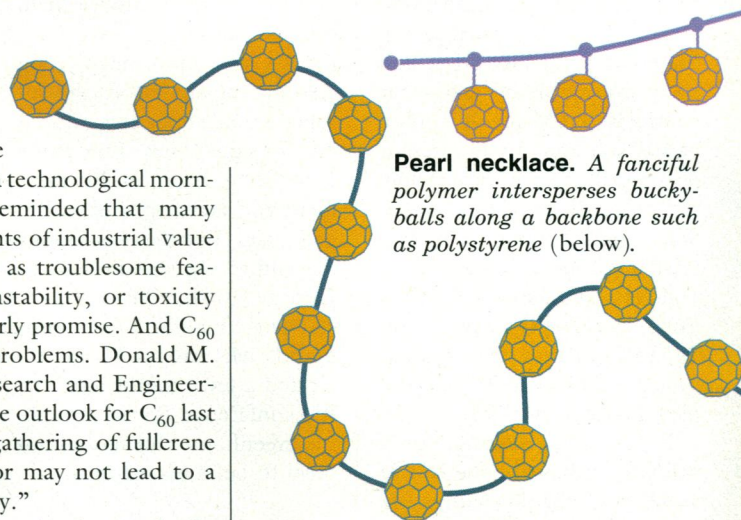
The past year’s work has sent fanciful visions of buckyball products bouncing around like balloons at a rock concert—ranging from superconductors to building blocks for polymers, from catalysts and nonlinear optical materials to computer

memories, rocket fuels and metal-free organic magnets. But already some fullerene scientists worry about a technological morning-after. They are reminded that many molecules showing hints of industrial value have come to naught as troublesome features such as cost, instability, or toxicity came to offset their early promise. And  $C_{60}$  has its share of such problems. Donald M. Cox of the Exxon Research and Engineering Co. summed up the outlook for  $C_{60}$  last month at an August gathering of fullerene researchers: “It may or may not lead to a revolution in chemistry.”

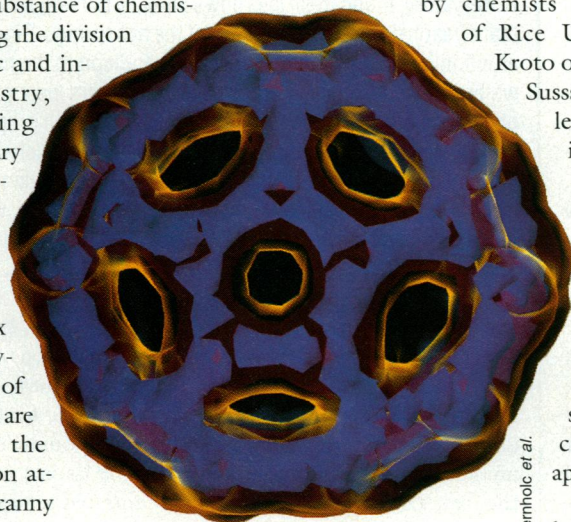
The outcome may soon be clearer, thanks to the zeal with which scientists are probing buckyballs. “Just look at how many people dropped what they were doing,” exults Orville Chapman of the University of California at Los Angeles, credited with discussing the possibility of such molecules years before they were actually discovered in 1985

by chemists Richard Smalley of Rice University, Harry Kroto of the University of Sussex, and their colleagues. The ongoing research wildfire, which places several papers a week in major journals and has researchers scurrying to fullerene conferences every month or so, is stoked by the cross-disciplinary appeal of fullerenes.

As a discrete carbon-containing molecule,  $C_{60}$  might seem to be a creature of organic chemistry, yet in raw form it lacks the hydrogen or oxygen atoms traditionally present in organic molecules. But chemists are quick to stress that fullerene chemistry is more than a hybrid of familiar subfields. After all, its basic motif—the soccerball structure Smalley and his col-



**Pearl necklace.** A fanciful polymer intersperses buckyballs along a backbone such as polystyrene (below).



**Electronic beauty.** Supercomputer calculations suggest regions of highest (dark blue) and lowest (yellow) electron density on the  $C_{60}$  sphere.

Bernholc et al.

leagues discovered in 1985—is a fundamentally new form of carbon: the third pure form of the element after graphite and diamond.

Some chemists liken the potential transformation to the one wrought by the discovery of benzene in the 19th century. The unexpected stability of the carbon-carbon bonds in benzene’s ring structure ushered in the chemistry of so-called aromatic organic molecules. That molecule gave chemists an entirely new structure and bonding pattern to play with and has served as the basic architecture for countless new molecules, with uses ranging from household paint to flavorings and medicines. Now  $C_{60}$  and its fullerene relatives, by adding a spherical scaffold to chemists’ geometric repertory, might have much the same effect. “There’s going to be a whole new chemistry coming out of the fullerenes,” predicts chemistry Nobel Prize-winner Donald Cram of UCLA.

Hints of what kind of chemistry might be possible in that round world are beginning to emerge.  $C_{60}$ ’s spherical shape, for example, gives it an unusual electronic structure—and thus the potential for surprising reactions and products. In benzene, polyacetylene, and other familiar molecules that, like  $C_{60}$ , have multiple sets of nearby double bonds, the electrons in these bonds are especially mobile because of the way their orbitals overlap. But because of  $C_{60}$ ’s curvature, these so-called pi-electrons overlap more than they do in other molecules.



Jerzy Bernholc and co-workers at North Carolina State University have carried out detailed quantum mechanical computations to help understand and visualize  $C_{60}$ 's novel spherical distribution of electrons (see figure on opposite page).

"This is where  $C_{60}$  breaks the rules," says Robert C. Haddon of AT&T Bell Laboratories in Murray Hill, New Jersey.

Haddon was one of the first to report that mixing  $C_{60}$  with electron-donating ions such as potassium leads to fullerene materials that are conductive or even superconductive—properties based in  $C_{60}$ 's electronic structure, which can provide conductive pathways in and between buckyballs. Fred Wudl of the University of California

has even exploited that structure to create a magnetic fullerene material, by mixing  $C_{60}$  with an organic electron-donating compound.

Devising reactions that preserve the pi-electron system will be a key goal of buckyball chemistry, Wudl remarks. One of the main forwards sprinting with buckyballs toward chemistry goals, Wudl has been studying ways to do just that. One trick, he says, is to rely on reactants that provide replacement pi-electrons even as they link to  $C_{60}$  and initially disrupt the carbon sphere's native pi-system.

Once the fundamental rules of fullerene chemistry are laid down, Wudl thinks, the fun will begin. By linking buckyballs serially, for example, he expects to build "pearl necklace" polymers. Hung periodically from another polymer chain, buckyballs could become the ornaments in "charm-bracelet polymers," he speculates. Would such polymers be fragile, point-less curiosities, new superstrong aerospace materials, or something else entirely? There's no way to know until they are synthesized.

Besides decorating and expanding fullerene spheres and stringing them together, chemists are peering inside them for new possibilities. By locking atoms, molecules, or even other fullerenes inside the carbon spheres like little ships in bottles, scientists think they might create the building blocks for another brand new arena of chemistry and materials. At a New York City

chemistry meeting last month, for example, Smalley reported strong evidence that he and colleagues had locked lanthanum atoms inside fullerene molecules. And he says he has evidence from mass spectrometry for fullerenes with as many as 600 carbon atoms, a number suggestive of a 540-carbon superfullerene enclosing a 60-carbon buckminsterfullerene.

What might scientists do with such bizarre building blocks? Speculations abound. For example, by locking sodium and chloride ions inside buckyballs and then crystallizing them,

chemists might be able to make a strange version of sodium chloride in which the distances between the ions are larger than in table salt. This kind of crystal engineering could enable materials scientists to tailor the solubility, conductivity, hardness, and other properties of crystals. Or they might cage a molecular prisoner that could be reversibly altered with light or voltage, thereby creating a tiny medium for storing information.

But the more chemists talk about such possibilities, the more often they're brought up short by thoughts of potential technical snags. Take the stability problem that some scientists are running into, remarks organic chemist Philip Magnus of the University of Texas at Austin. "If you have them [fullerenes] in solution exposed to air, they're gone in about an hour" as a result of unknown chemical reactions, Magnus says. Besides threatening the utility of new fullerene compounds, this instability might also explain why nobody has found  $C_{60}$  occurring naturally in sooty places like chimneys, as Kroto and his co-workers have noted.

And what about suggestions that  $C_{60}$  could be toxic? Earlier this year, Magnus points out, a team led by François Diederich of UCLA found that as a result of  $C_{60}$ 's ability to wrest electrons from other compounds, it readily generates so-called singlet oxygen, which the researchers suggested could damage living tissue. One other problem: If you don't make it yourself

$C_{60}$  costs about \$100,000 a kilogram, and that's in its cheapest unpurified form. That price will have to come down if the fullerenes are ever to find widespread use, adds Magnus.

But  $C_{60}$ 's fascination has proved irresistible even to Magnus. He's doing his best to overcome the last of the drawbacks he lists by finding a more efficient way of synthesizing  $C_{60}$ , now made largely by burning graphite and collecting and purifying the fullerene-containing soot. Magnus and others are now racing to replace that technique with some means of chemically synthesizing the molecules from smaller chemical building blocks—indanes, in Magnus' case. These molecules host five- and six-member carbon rings that could serve as the facets of a complete buckyball, if Magnus and his colleagues can find a way of putting them together.

The fact that Magnus and other chemists are still struggling to synthesize

the basic molecule makes it clear how new the fullerene story is. As chemist Ed Wasserman of E.I.

Du Pont de Nemours and

Co. notes, "We're still dealing with a baby in the maternity ward."  $C_{60}$  could go down in history as a luminary or an environmental or toxic villain in disguise, a little like chlorofluorocarbons—wonder materials that went bad. Or it could fade into obscurity as making research contributions gets tougher and hope for technological payoff wanes.

If the fullerene boom does go bust, in spite of the efforts of Magnus and all the other chemists now seized by fullerene fever, at least one consumer product will remain alive, at least in science fiction circles. In Poul Anderson's contribution to the 1988 collection of stories titled "The Man-Kzin Wars," (a series

created by Larry Niven), protagonist Robert Saxtorph finds himself on a perilous slope in a planetary basin filled with a superslippery dust made of buckyballs. "In fact, it's virtually a perfect lubricant, and if we didn't have things easier to use you'd see synthetic buckyballs on sale everywhere," rescuer Laurinda Brozik explains to a humbled Saxtorph. At the moment that fictional conclusion about buckyballs is about as reliable as any of today's speculations.

■ IVAN AMATO

#### Charm bracelet.

Buckyballs dangle from the backbone of another hypothetical polymer.

J. Cherry