CARBON ALLOTROPES

And Then There Were Three

by Edward Edelson
Historically, chemists have known only two allotropes, pure forms of carbon: graphite, a greasy, electrically conducting black substance, and diamond, crystal clear, electrically insulating, and harder than any other solid. But they have constantly theorized about other possible carbon allotropes.

In 1970, for example, a Japanese chemist named Osawa wrote of a molecule that would be made of 60 carbon atoms. It would be, he predicted, a stable, spherical molecule in the shape of a soccer ball. About a decade later, the same idea of a soccer ball-shaped carbon 60 molecule occurred to Orville L. Chapman, an organic chemist at the University of California at Los Angeles. "I spent the summer in Germany on a Humboldt fellowship," he says, "and went there with one question in mind: If I could make one molecule, what would that molecule be? I came to the conclusion that what was needed was a new form of carbon. Carbon 60 was a rational compromise between the larger carbon spheres and smaller molecules."

Chapman then initiated an effort to synthesize this odd molecule. It failed. "At this point no one has a rational synthesis," he says. "That problem is alive and well."

That was, of course, the molecule that has become famous as the buckyball, more formally known as buckminsterfullerene, the third allotrope of carbon, which has become the focus of research in chemistry laboratories everywhere. Chapman notes that chemists can produce buckyballs by the bucketful, but they still are unable to synthesize it, atom by atom, in his rational, controlled way. The buckyball story is one of remarkable coincidences and serendipitous discoveries. It also has a deep significance for the continuing hunt for new carbon allotropes.

While Chapman and his colleagues, including Robert L. Whetten and Francois Diederich, were working at UCLA to synthesize carbon 60, Richard Smalley and his team at Rice University were busy with a totally unrelated subject, the study of atomic clusters. They used a device of their own invention in which laser energy was used to vaporize a sample of an element, which was then blown into a mass spectrometer by a stream of helium for analysis.

The Rice researchers had no interest in carbon until a visitor, Harry Kroto from the University of Sussex in England, suggested that their device could cast light on the nature of the carbon clusters detected in interstellar space. When they ran the experiment, they saw an unusual concentration of large, even-numbered carbon clusters, with an unusual abundance of carbon 60. It is now widely known that the researchers at Rice independently reinvented the idea of a spherical carbon allotrope, gave it a name (buckminsterfullerene, after Buckminster Fuller, inventor of the geodesic dome), and published their idea prominently—something that Chapman had not done.

Smalley and others followed up with papers reporting on the predicted properties of the carbon 60 molecule, but they were unable to make any substantial amounts of it to verify that it was more than a microscopic laboratory curiosity. Those reports, however, eventually caught the attention of two physicists, Donald Huffman of the University of Arizona and Wolfgang Kraetschmer of the Max Planck Institute for Nuclear Physics in Germany, who had been puzzling over some strange features of the carbon clusters they were making in a device for studying interstellar carbon.

Huffman and Kraetschmer had been making the clusters by passing an electric current through a graphite electrode in a low-pressure helium atmosphere. Comparison of the properties of the carbon 60 they were making and those predicted for buckminsterfullerene convinced Huffman and Kraetschmer that they had fortuitously achieved gram-amount production of buckyballs. Their publication of their method and results—including the production of carbon 70 and larger fullerenes—opened the era of research on fullerenes, the family of ball-shaped carbon allotropes frequently called buckyballs.

The discovery of the fullerenes has stimulated a burst of activity among organic and physical chemists, who are exploring an infinite variety of possibilities for this new family of molecules. It also has raised hopes that other hypothesized carbon allotropes can be brought into existence. "It was more than a single result, it was an eye-opener," says Diederich. "We are at a fortunate moment when we have new tools and ana-
lytic methods that make it possible to think about producing more allotropes of carbon."

These carbon allotropes exist in theory, and there is good reason to believe that they could eventually become reality. There's also good reason to believe that, when they are made, they will have properties as interesting and potentially valuable as those of the fullerenes, because of the nature of the carbon atom.

A chemical cornerstone

Carbon is unusual in that it is the cornerstone of a major field of chemistry: organic chemistry, which is defined as the study of carbon-containing molecules and polymers with carbon backbones. Organic chemistry thus includes not only many of the chemicals of living things but also most of the chemicals that have made the modern world possible, polymers, or plastics, to give only one example.

The reason that carbon is so many molecules of interest to scientists lies in its electronic structure. The carbon atom forms covalent bonds, in which electrons are shared between the bonding atoms. The valence electron configuration of carbon is described as 2p2 2p2, which shows that the carbon atom shares more electrons to achieve the stable noble gas configuration than any other nonmetal. (One principle of chemical combination, in oversimplified form, is that atoms form bonds in which they are surrounded by enough electrons to form a noble gas configuration; s and p refer to the shape and location of electron orbitals.)

To achieve that stable configuration, a carbon atom has to gain four electrons. It does so by forming strong covalent bonds, especially with other carbon atoms but also with most of the common metals. In particular, carbon atoms easily form long chains, often with many hydrogen atoms attached, a unique ability that helps to account for the importance of carbon in living things.

Known ways

There is a limited number of ways in which carbon atoms can combine in molecules that do not contain other elements. One way is to form graphite, which chemically is the most stable allotrope of carbon. Graphite consists of flat planes of six-membered rings of carbon. The planes slip easily over each other, making graphite an excellent lubricant. Each carbon atom in the planes of the graphite structure is bonded to three other carbon atoms that lie at the corners of an equilateral triangle; the structure consists of a resonance average of single and double bonds, in which two electrons are shared, and double bonds, in which four electrons are shared. All the bond angles in a graphite molecule measure 120 degrees. Chemists say that the bond exists because the electrons in adjacent carbon atoms form hybrid sp2 orbitals.

In diamond, by contrast, each carbon atom is bonded to four other carbon atoms that are at the corners of a regular tetrahedron. Carbon atoms in diamond form only single bonds, the bond angles are all the same—109°28', and the electrons in the bonds form what are called sp3 hybrid orbitals. The high density of strong carbon-carbon bonds in diamond and the three-dimensional arrangement of such bonds account for the hardness of diamond.

Thermodynamically, however, diamond is less stable than graphite under ordinary conditions. Diamond is more stable than graphite only at very high pressures. Theoretically, diamond should spontaneously decompose to graphite at room temperature, giving up some energy to form the more stable allotrope. That does not happen because diamond is kinetically stable: It takes an input of energy to start the process of decomposition, and the environment ordinarily does not supply that energy. If energy is provided in the form of heat, however, diamond transforms into graphite without air. If air is present, it burns to produce carbon dioxide.

The bonding in the fullerenes, the new allotropes of carbon, is similar to that in graphite. All the carbon atoms in a fullerene are sp2 bonded. There are two notable differences, however: All carbon atoms are shared by two six-membered rings and one five-membered ring, and this ring structure enables the fullerenes to form spherical structures. Therefore, whereas graphite sheets in theory can be infinitely large, fullerenes are closed structures.

Variant themes

Nature has some variations on these carbon allotrope themes. One is a form of diamond called Lonsdaleite, named...
for Kathleen Lonsdale, a British crystallographer. The bonding in both ordinary diamond and Lonsdaleite is the same, but ordinary diamond can be viewed as being composed of an interconnected array of cubic unit cells, with Lonsdaleite being composed of an array of hexagonal unit cells. Similarly, in ordinary hexagonal graphite, the layers are stacked so that every second layer repeats (ABAB), whereas in the alternate rhombohedral form, every third layer repeats, (ABCABC). The study of the higher fullerenes—those molecules with many more than 60 carbon atoms in their spherical structures—is turning up many variations. For example, carbon 76 and other larger fullerenes can be viewed as helical structures.

There are chemists who say that many other allotropes of carbon are possible. Back in the early 1980s, for example, Cornell University's Roald Hoffmann, who won the Nobel Prize in Chemistry for his work with the application of quantum theory to organic molecules, was envisioning alternative carbon allotropes. "I have been fascinated by hypothetical allotropes of carbon for some time," Hoffmann says. "I have concentrated on extended three-dimensional structures, not on discrete molecules. I have found many structures—
hundreds or thousands—but have only published four or five of them.”

Hoffmann has calculated the properties of other possible allotropes. “The most interesting one came about because I was looking for structures more dense than graphite or diamond,” he says. “I have not found a good form of carbon that retains normal bonding that is more dense than diamond. But I have found one that is less dense than diamond but more dense than graphite. So it’s conceivable that by squeezing graphite, instead of making diamond, at some pressure we could make this. It’s a three-dimensional network of \( sp^2 \) carbon atoms. The most interesting thing about it is that it should be metallic, a really good conductor, unlike graphite, which is a mediocre conductor.”

The structure hypothesized by Hoffmann has no six-membered rings. The smallest ring consists of ten carbon atoms. It is metallic because the electrons in the \( p \) orbitals of a set of carbon chains in the hypothetical structure are close to those of other similar chains. It is also unstable for the same reason: The electrons are too close to each other. Nevertheless, Hoffmann believes that such a carbon allotrope would not necessarily decompose to graphite.

**Thermodynamic or kinetic**

His explanation hinges on the difference between thermodynamic stability and kinetic stability. Thermodynamic stability is determined by free-energy differences: An allotrope with higher free energy than another is unstable because of the energy difference. It is predicted, eventually, to give up some energy and decompose to the lower energy form. Free energy is measured in calories per mole of a substance. Kinetic stability is defined by the energy required to cause a material to change from one form to another. This energy is a hypothetical barrier to change.

“Every organic molecule is thermodynamically unstable in the presence of oxygen, but you need a match to set it burning,” says Hoffmann. “Chemists are used to making all sorts of molecules that are thermodynamically unstable.”

Further, Hoffmann’s calculations indicate that most proposed allotropes of carbon are thermodynamically unstable—about 15 kilocalories per mole less stable than graphite or diamond. “But I know that the barrier to rearranging to another form is very high. Once you make them, they will be stable forever,” the Cornell chemist declares.

Hoffmann has collaborated with Alexandru T. Balaban, a Romanian organic chemist at the Polytechnic in Bucharest. In the 1970s, Balaban began describing planar networks of carbon that are alternative allotropes to diamond and graphite. He did calculations on planar networks of carbon atoms built of squares, pentagons, and five- and seven-member rings. Thermodynamically, all are less stable than graphite, but they could be kinetically stable.

Hoffmann has also described three-dimensional networks that are partway between diamond and graphite. Some of the carbon atoms are bonded to four atoms, some to three. “These become interesting when the connection is such that one line of atoms is forced sandwich-like onto the next line,” he says. “The \( p \) orbitals begin to overlap and you could get conductivity.”

**Other schemes**

A Russian group that has done outstanding theoretical work over the years is led by Igor Stankevitch at the Institute of Organometal Compounds in Moscow. Another U.S. scientist who has proposed new allotropes of carbon is Ray H. Baughman of Allied-Signal, Inc. One such allotrope, which he proposed in 1987 and called graphyne, could be constructed by replacing one third of the single carbon-carbon bonds in graphite with triple bonds. “This carbon phase has moderately high density, reasonably low formation energy, and interesting electronic properties,” he says. “Although the formation energy is higher than for graphite, this phase is predicted to have high kinetic stability with respect to graphitization.”

Another possible structure, Baughman said, is cubic graphite, in which all the carbon atoms are \( sp^2 \) bonded but are arranged in a three-dimensional, cubic structure rather than in layers. Calculations he did in collaboration with Changxing Cui of Georgetown Univer-
sity in Washington, D.C., indicate that conversion of cubic graphite to ordinary graphite requires massive disruption of the carbon framework. Cubic graphite thus should be stable to very high temperatures. Although the density of cubic graphite is close to that of ordinary graphite, it would have carbon "cages" that would allow doping with lithium. This doping would transform cubic graphite into a metal, and possibly into a superconductor. The predicted ability to form dopant complexes suggests applications for cubic graphite that would allow doping with lithium.

"Right now we’re just guessing about ways to synthesize it," Baughman says. One possible synthesis method is to use a building-block molecule that could convert to cubic graphite without carbon-carbon bond rupture. High-pressure synthesis methods might cause that conversion. Baughman is collaborating with three others who specialize in high-pressure technology: Kurt Leinenweber at the State University of New York at Stony Brook, Maurice Tathany at the New Mexico Institute of Mining and Technology, and James Wolf at New Mexico State University.

Baughman and W. B. Hammond of Allied-Signal also have described three-dimensional carbon allotropes that are mixtures of sp2 and sp3 carbons and which they call carbophanes. The basic structural motif of the carbophanes is a six-member aromatic ring that is surrounded by six sp3 carbon atoms, a motif seen in well-known organic compounds called phanes. These sp3 carbons in the carbophanes provide bonding between atoms of adjacent layers. Again, high-pressure techniques are being explored for the synthesis of carbophanes.

At UCLA, Diederich, Whetten, and Chapman have described proposed new molecular and polymeric carbon allotropes. Some of the polymeric networks that might be used as precursors are identical to some carbon allotropes described by Baughman. The UCLA group calls its proposed molecular allotropes cyclo[n]carbons.

### Molecules, polymers

A critical issue in the field of carbon allotropes is that of actually making them. Surprisingly little work on the synthesis of carbon allotropes has been done in this country. Probably the most vigorous effort is being made at UCLA, where the allotrope group has taken some steps toward preparation of its cyclo[n]carbon networks. The group has made a monomeric subunit that could be polymerized to form two of the proposed networks, and is working to-
ward that polymerization.

One major achievement of the UCLA group has been preparation of carbon 18, a cyclo[n]carbon with $sp$ bonding.

One way to make this cyclo[18]carbon is first to make a butterfly-shaped molecule consisting of a carbon ring with six anthracenes (polycyclic carbon compounds) attached. A layer of this precursor is placed on a rod and is put into a chamber, where it is exposed to laser light with energy just sufficient to remove the anthracenes, in what is called a retro Diels-Alder reaction. A stream of helium carries the resulting molecules into another chamber, where they are sent into a mass spectrometer. Analysis shows that some of the molecules are carbon 18 rings. It is production "on the level you can compare to the carbon 60 production of Kroto and Smalley in 1985," Diederich says.

The hope is that the buckyball success story will be told again for this and other carbon allotropes. Huffman and Kraetschmer recognized carbon 60 in their samples because of a peculiar feature in the predicted infrared spectrum. Diederich and his colleagues have calculated the infrared spectrum of their molecule and of the polymers it can be expected to form.

In Diederich's view, carbon 18 will not be as stable as carbon 60, and will form beautiful network polymers. He and his colleagues are constructing several apparatuses to see what can be produced.

**Confounding dimensions**

This is a new frontier for organic chemists who, says Diederich, traditionally have "shied away from anything that needs complex machinery." And, Roald Hoffmann notes, the successes of polymer chemists, the foundation of the modern chemical industry, have been made within a self-limited field.

"Organic chemists are clearly the master makers of molecules," says Hoffmann. "They know how to construct all kinds of incredible structures. But in general, they are limited to making molecules only in zero dimensions. If they have an asymmetric center, a carbon with four different substituents, they can use it to attach another asymmetric center, and so slowly elaborate a structure that is a discrete molecule."

Polymer chemists, he observes, have learned how to exercise control in one dimension. "But to make something in two or three dimensions," he says, "it's a wasteland...there is no control. Learning how to control matter in two or three dimensions—that's something for the future of chemistry."

The situation could be changing, however, because of the development of new methods and new instrumentation. The gas-phase instrument used to make carbon 18 was developed only in the 1980s, Diederich notes, and the Fourier transformation nuclear magnetic resonance technique used to analyze molecules such as the chiral fullerene carbon 76 is also a recent development—one for which Richard R. Ernst of the Federal Institute of Technology in Zurich was awarded the 1991 Nobel Prize in Chemistry. The fullerene story has also given impetus to an effort to develop novel methods of synthesis.

"The message is that we organic chemists have not provided the tech-
Ultrahigh pressures. View through diamond anvils at high pressure shows cross-hatch texture at tip of anvils indicating plastic deformation.
niques needed to make new carbon molecules," says Diederich, "so why not look into new extreme plasma-type production processes? This is what we and many other groups are doing."

Fullerene side effects

Surprises about achievable new structures of carbon are emerging constantly from fullerene research. For example, the standard way of producing fullerenes is to gather material from the positive end of the electrode. Sumio Iijima of the NEC Corporation in Japan looked at the material on the negative end of the electrode and found tubular fibers made of hexagonal arrays of carbon atoms, tightly wound to form cylinders. Hollow carbon fibers that appear to be quite similar had been synthesized more than a decade ago in Japan. The existence of hollow "buckytubes" had been predicted by Mildred S. Dresselhaus of the Massachusetts Institute of Technology, and their detection by Iijima was another bit of serendipity. And the UCLA group has found that the carbon-76 fullerene consists of 28 carbon hexagons in two chains of rings that spiral around each other; the carbon-84 fullerene also has been shown to have a spiral structure, and the same is believed to be true of the larger fullerenes.

Both the Iijima and UCLA discoveries are potentially of practical importance. Iijima's tubular fullerenes might be made into high-strength carbon fibers. The helical higher fullerenes studied at UCLA exist in chiral (right-handed and left-handed) isomers, and such chiral materials often have useful optical, electrical, and chemical properties.

Linear carbon

One long-running carbon allotrope story that comes to life periodically concerns the existence of linear chains of pure carbon. In the 1960s, Soviet scientists published papers describing the synthesis of such molecules, which they called karbins, or carbynes, by many different techniques.

Chemists in the United States who studied the Soviet papers and attempted without success to replicate the results concluded that carbynes had not been synthesized. Since then, there have been reports from Japan, Germany, and other countries claiming that synthesis of carbynes has been achieved. However, chemists who have studied these claims and have attempted without suc-
cess to replicate the Soviet results have concluded that carbynes have not been synthesized. Nevertheless, there is a continuing interest in them.

One U.S. chemist, Richard J. Lagow of the University of Texas at Austin, is proposing to undertake a major project to synthesize carbynes. "We have 17 different schemes, and we're working on three or four of them," he says. One technique is to make long carbon chains with atoms or groups of other elements such as lithium and chlorine at each end and then to remove the other atoms. (A comparable technique is being applied at UCLA, where Diederich and his colleagues have made 12-atom carbon chains with silicon groups at each end. They now are trying to join two 12-atom carbon chains to make a 24-atom linear molecule.)

"We believe linear carbon will be stable," says Lagow. "We know after working five years in this area that the model compounds are surprisingly stable. We have large single crystals of a carbon 8 model compound that is surprisingly stable. "(The crystal structure of this compound was done with Robert Bau of the University of Southern California, and nuclear magnetic resonance spectra have been done in collaboration with James Haw of Texas A&M University.)

"I would say high-polymer linear carbon would be stable at about 20 degrees Celsius," says Lagow, "but we can't say for certain whether it's stable until we make the thing."

Ray Baughman, by contrast, believes that if carbynes exist, they are unlikely to consist of linear chains. He cites theoretical predictions and the observed instability—often explosive—of materials containing linear chains of sp carbon atoms. However, there is a method of preserving such unstable molecules, developed by Orville Chapman. The material, in the gas phase, is cooled rapidly to eight degrees Kelvin and is carried into a vacuum chamber by argon gas. The result is a matrix in which 1,000 argon atoms surround each carbon molecule, which can then be studied by spectroscopy and other techniques.

Studying the transient

Some carbon phases that are unstable under ordinary conditions are nonetheless of interest. Many such phases can be made by putting graphite or diamond under extremely high pressure at high temperatures. At Cornell University, William A. Bassett and Maura S. Weathers put diamond chips in a high-pressure apparatus that uses diamond anvils to exert pressure, and they melted the diamond with focused laser light.

At pressures of 300 kilobars (300,000 times atmospheric pressure), the researchers produced a mixture of graphite and diamond. They not only melted diamond but also made an unusual form of graphite in which the layers of carbon atoms were so close together that the researchers concluded that sp3 bonding must exist between carbon atoms in adjacent layers. Ray Baughman is exploring the possibility that one of his theoretically derived cardophane phases might correspond to the new carbon phase found at Cornell.

At the Carnegie Institution of Washington, Russell J. Hemley has put graphite under 500 kilobars of pressure at room temperature. The resulting material resembles Lonsdaleite more than diamond, but does not quite have either structure. "Our current working hypothesis," says Henley, "is that it is a diamond polytype, a phase with intermediate stacking between cubic and hexagonal. The bonding seems to be as strong as, if not stronger than diamond, because our anvils break when we go above 300 or 400 kilobars. It reverts to graphite at about 20 kilobars."

Meanwhile, hypothesizing about new allotropes of carbon and ways of making them goes on. Baughman speculates that cubic graphite or one of his cardophanes might eventually be made as simply as heating a crystal of a suitable building-block molecule. If you are fortunate, you will obtain the new carbon phase," he says. "More likely, from a given experiment, you will make only a disordered carbon or graphite."

"However, these low-energy carbon phases will eventually be made, and they will provide both exciting physics and new applications opportunities. The challenge is to transform these theoretical concepts of today into the new engineering materials of tomorrow. Using theoretical understanding to recognize serendipitously obtained results might be important. Who would have thought that carbon 60 would be so easy to make?"

The National Science Foundation has contributed to the support of the research described in this article through programs in its Division of Chemistry.