

Predicting Stability for the High-Energy Buckyball

WHY do atoms have a propensity to bond in certain configurations? That mystery continues to puzzle the scientists who study molecules and their isomers—molecules that have the same atomic weight as the original but a different structure. A better understanding of the rules governing molecular structure would help them predict which forms of a substance would be most useful.

In 1985, scientists were excited by the discovery of a new form of carbon. This molecule, called a buckyball or a fullerene, contains 60 carbon atoms (C_{60}). Its molecular structure resembles a soccer ball or the geodesic dome designed by architect Buckminster Fuller, for whom the molecule is named.

Building on that discovery, Livermore scientists are developing computer models to study buckyballs that feature other atoms, such as nitrogen and boron, in place of some of the carbon atoms in C_{60} . (See *S&TR*, June 2001, pp. 22–23.) In particular, the research has focused on how to predict the most stable forms of these new compounds and on how other atoms bond to one another to create unique structures.

One team, led by theoretical chemist Riad Manaa, is studying nitrogen fullerenes, especially $C_{48}N_{12}$. Nitrogen-doped fullerenes offer an impressive range of potential applications, from orthopedic implants to new pharmaceuticals to high explosives.

“These fullerenes are interesting to study,” says Manaa, who works for the Chemical Engineering Division in Livermore’s Chemistry and Materials Science Directorate. “Their hollow, cage-like shape and their extreme stability at high temperature and pressure allow them to retain their spherical structure when they interact with other atoms and molecules. By understanding how the carbon and nitrogen bonds come together, we can study

the properties and predict how other atoms will interact with the fullerene to form new compounds.”

The nitrogen fullerene has properties that differ from the more commonly known carbon fullerene. All electron shells in the C_{60} molecule are filled, so C_{60} is inert. However, when some of the carbon atoms are replaced with nitrogen atoms, the new molecule acts as an electron donor. Nitrogen also carries much more energy than carbon, so nitrogen fullerenes might be useful in developing new high-explosive formulations. Computer simulations indicate that other elements could be added to the molecule to form compounds for a range of applications.

Computing the Possibilities

The team’s search to find the most stable forms of nitrogen fullerenes began as a teaching project between Manaa and a group of summer interns. Manaa, who investigates energetic materials and conducts simulations of these materials in extreme conditions, worked with the interns to study various forms of the $C_{48}N_{12}$ molecule, which has a high energy content.

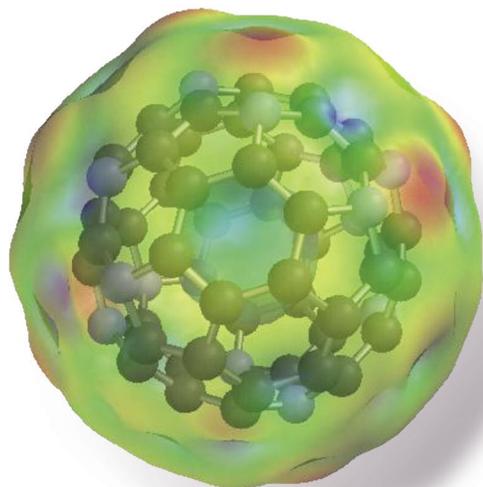
When $C_{48}N_{12}$ was first synthesized several years ago, the electron microscopy and energy-loss spectroscopic analysis showed that its structure corresponds to that of a buckyball. At that time, researchers believed the most stable form of this nitrogen-substituted fullerene had 12 pentagons with evenly spaced nitrogen atoms, one in each pentagon. Nitrogen atoms tend to repel each other and destabilize the structure, so if the molecule is stable, they must be separated.

In the 12-pentagon model, every nitrogen atom is separated by two carbon atoms. The remainder of each pentagon is composed of carbon atoms. That molecule also has two all-carbon hexagons, or benzenelike rings. Benzene rings are very stable, so having two benzene rings and at least two carbon atoms between each nitrogen atom provided the molecule’s stability.

Predicting the most energetically stable structure of a molecule is a formidable task for computational scientists, especially when they must determine the various configurations for as many as 60 atoms. It’s time-consuming work to examine the many possibilities of distributing the 12 nitrogen atoms in $C_{48}N_{12}$ among the 20 hexagons and 12 pentagons of a buckyball structure. Even the Laboratory’s supercomputers, such as ASCI Blue, must process calculations day and night for weeks to model all the configurations.

According to Manaa, the team’s original goal was to find stable molecular structures with subunits of nitrogen–nitrogen

The molecular structure of $C_{48}N_{12}$ with its electronic cloud.



(N–N) bonding, which have high energy content. The team used quantum-chemical methods to predict the stable structures of these fullerenes, which have a radius of 0.35 nanometer. The computer code calculates the distribution of electrons around each atom, which then determines the chemical property of a molecule.

“While we were studying the high-energy, fullerene-analog structures of $C_{48}N_{12}$ with $6N_2$, $4N_3$, and $2N_6$ subunits,” says Manaa, “we also found the energetically most stable structure of this molecule. This finding allows us to predict the chemical and physical properties of the material.”

The new molecule has eight highly stable all-carbon hexagons. Although the nitrogen atoms are separated by only one carbon atom, it has six additional benzenelike rings, which more than make up for any possible repulsion between the nitrogen atoms. Thus, the new $C_{48}N_{12}$ structure is more stable because the molecule’s resonance energy is maximized and the repulsive force from the N–N bonds is minimized. In fact, the team’s calculations showed that this structure is much more stable (as much as 13.1 kilocalories per mole) than the most stable structure reported for the first $C_{48}N_{12}$ molecule.

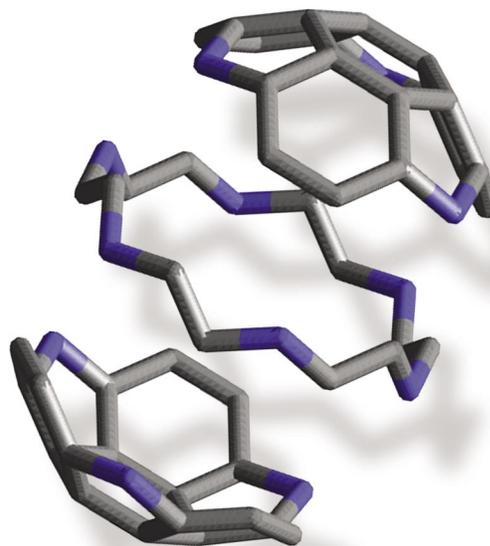
Designing New Molecules

Doping the C_{60} molecule—that is, substituting some of the molecule’s carbon atoms with other atoms—changes the structural, electronic, chemical, and physical properties of the parent fullerene. For example, when some of the carbon atoms on the buckyball cage are replaced with nitrogen, the molecule’s electronic properties change to match those of a semiconductor. Other doped fullerenes are ideal candidates for phototonic devices, such as optical switches, eye protectors, and sensors, and some are being considered as therapeutic agents.

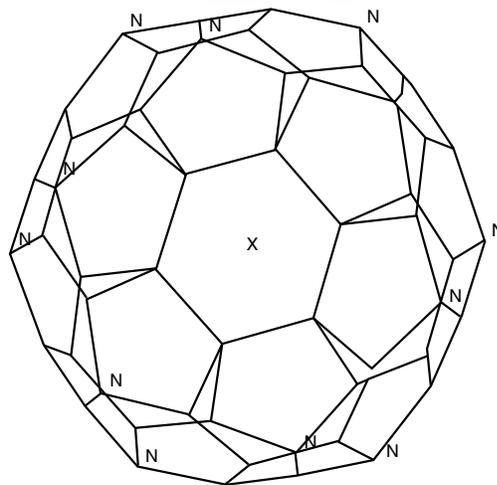
Manaa’s group also examined a fullerene molecule doped with boron. Their results showed that $C_{48}B_{12}$ has the same stability as $C_{48}N_{12}$. This same molecular structure as $C_{48}N_{12}$ decisively confirmed the overall stability of the $C_{48}X_{12}$ molecules (where X can be boron, nitrogen, or silicon). Recent calculations show that, even though $C_{48}N_{12}$ and $C_{48}B_{12}$ have similar structures, they have opposite properties. While $C_{48}N_{12}$ acts as an electron donor, the charge distribution in $C_{48}B_{12}$ makes it an electron acceptor. Thus, when these molecules are combined, $C_{48}N_{12}$ and $C_{48}B_{12}$ become a donor–acceptor pair for molecular electronic building blocks. Potential applications combining the two molecules include circuits for electronic switches and nanocircuits for data exchange.

The team’s efforts are now directed toward building carbon structures with other combinations of nitrogen and boron, such as $C_{48}B_6N_6$. Materials made from this combination would be harder than C_{60} .

Most of the fullerene research to date has been conducted as part of the hardware tests and code development work for the National Nuclear Security Administration’s (NNSA’s) Advanced Simulation and Computing Program, which is an integral



The geometry of the minimum energy (stable) structure of $C_{48}N_{12}$ (nitrogen in blue), indicating the distribution of nitrogen atoms.



Front view of the symmetric $C_{48}N_{12}$ structure, showing the position of the nitrogen atoms. Seven all-carbon hexagons are visible, and the eighth is superimposed on the central ring.

component of the NNSA’s Stockpile Stewardship Program. However, according to Manaa, the team is also interested in collaborating with groups outside the Laboratory to build on Livermore’s expertise in the computational research of fullerenes.

“So much of the progress in synthesizing new forms of nitrogen fullerenes and other molecules requires a thorough understanding of their structure and properties,” he says. “Understanding why molecules take the form they do adds to the predictive possibilities scientists can make about new molecules for all kinds of applications.”

—Gabriele Rennie

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