This Nitrogen Molecule Really Packs Heat

NITROGEN is a critical ingredient in most explosives—think of TNT (trinitrotoluene), the ammonium nitrate used in the Oklahoma City bombing, and the Department of Energy's most sophisticated high explosive in nuclear weapons, TATB (1,3,5-triamino-2,4,6-trinitrobenzene).

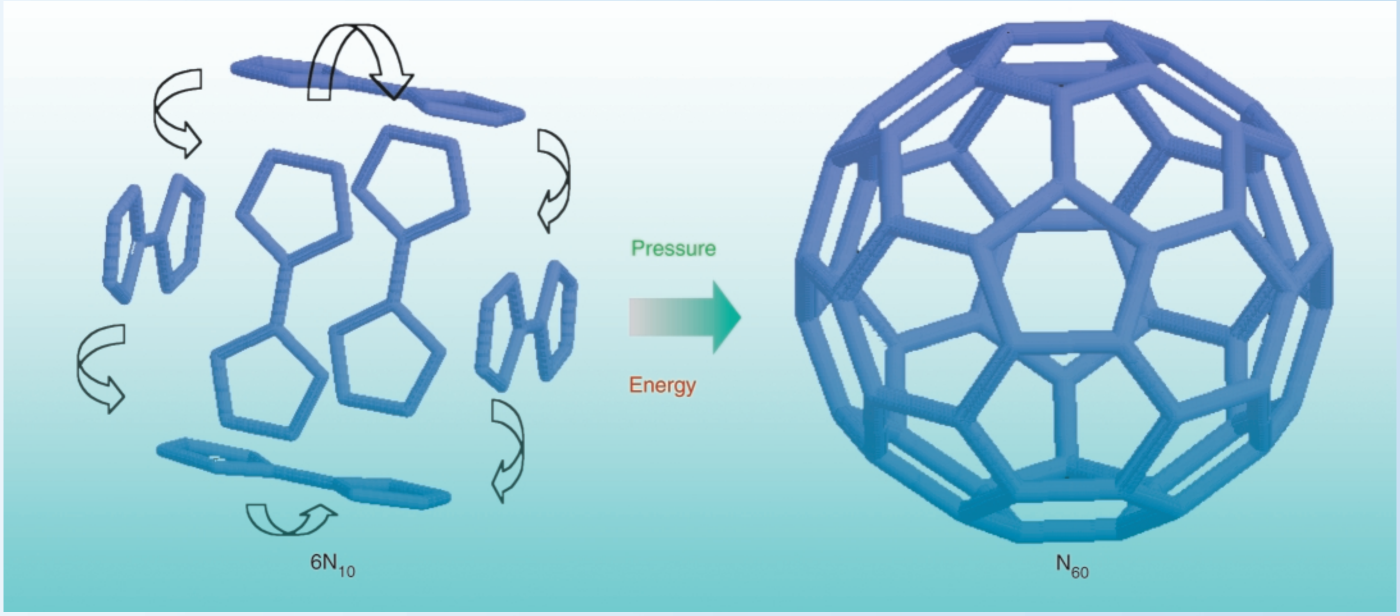
Huge amounts of energy are released when the tight bonds of a typical metastable (readily changed) energetic molecule are broken and the molecule reforms into smaller ones. A molecule composed solely of nitrogen atoms will release even more. For example, the tiny nitrogen anion N_3^- is a propellant used in automobile air bags. Because of the nature of nitrogen bonding, the explosive power of a molecule 20 times larger than N_3^- would be stunning.

Theoretical chemist Riad Manaa of Livermore may have found this unusual nitrogen molecule. His computer simulations show that it might be possible to join six 10-atom nitrogen molecules into a soccer-ball-shaped molecule known as a buckminsterfullerene—fullerene, for short.

Currently, the only fullerenes are large carbon molecules, with from 32 to as many as 600 atoms. A nitrogen fullerene would truly be an oddity, because the only forms of nitrogen known outside the laboratory are N_2, the most abundant element in our atmosphere, and the highly explosive N_3^-. In the laboratory, other forms of N_3^- as well as N_4^+ and N_5^+ have been created successfully. However, of these, all but N_5^+ were short lived.

The first fullerene, a 60-atom carbon molecule, was created in the laboratory in 1985, winning its discoverers a Nobel Prize in 1996. Says Manaa, "With their remarkable, perfect symmetry, fullerenes continue to create enormous excitement among scientists." Fullerenes are named for R. Buckminster Fuller, whose popular geodesic dome is structurally similar to a fullerene molecule. Also known as buckyballs, the closed, hollow carbon fullerenes have been produced in bulk quantities in the laboratory and show promise for use as superconductors and molecular containers. Their cage shape also makes them excellent building blocks for carbon-based nanotechnology.

With their high energy density, large nitrogen molecules would be prime candidates for new high explosives or perhaps for a novel propellant. Supersonic transport vehicles, for example, must achieve extremely high speeds. A new propellant that incorporated nitrogen fullerenes could generate the high thrust (energy release) needed to attain those speeds.



A combination of six molecular units of N_{10} form the nitrogen fullerene, N_{60}.

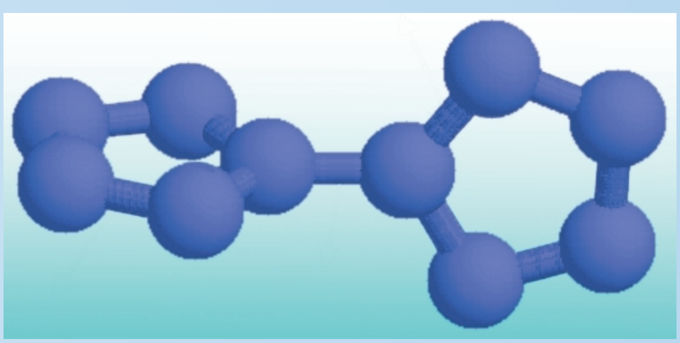
The Search Is On

Both the U.S. Air Force and the Department of Defense's Defense Advanced Research Projects Administration (DARPA) have funded research at Livermore and elsewhere to find a way to destabilize the strong N_2 triple bond, the second strongest covalent bond in all of nature. The goal is to find polymeric forms of nitrogen with single and double bonds, which are significantly weaker. Experiments with a diamond-anvil cell that pressurized N_2 up to almost 200 gigapascals failed to find a polymeric form of nitrogen. Shock compression experiments at high temperatures and pressures were equally unsuccessful. Only by direct synthesis in the laboratory have scientists been able to create any new polynitrogen phases.

Thus far, the N_3^-, N_3^+, and N_4^+ molecules created in the laboratory had a linear structure and were unstable because of their weak bonding. Only the N_5^+ molecule demonstrated long-term stability. Extensive research continues, however, on such exotic species as a tetrahedral N_4 and a cubic N_8. To date, quantum-chemistry-based computational studies predict that they will be at least metastable.

Because nitrogen atoms so clearly like to be triple bonded, no one had previously examined the possibility of creating a nitrogen fullerene. Manaa was thus the first to suggest that a super-high-energy molecule N_{60} was a possibility. He has shown that N_{60} could be formed from six units of bicyclic N_{10} molecules, which are themselves formed from two units of N_5. Using several quantum-chemical methods, he determined the structure and spectroscopy of the N_{10} molecule.

Simulations based on first-principles quantum chemistry accurately predict the chemical properties of atoms and molecules. The technique uses quantum mechanics to determine the distribution of electrons around each atom. From this electron distribution, any chemical property can be determined, including the structures and energies of the molecules.



The two pentazole ions (N_5^+ and N_5^-) that constitute dipentazole (N_{10}) are flat and connected perpendicularly to one another.

Such simulations showed that N_{10}, or dipentazole, would contain a mixture of single and double bonds and would be metastable. Each of its two pentazole ions (N_5^+ and N_5^-) would be flat, long lived, and connected perpendicularly to one another. The bridging bond between the ions appears to be strong and yet flexible enough to allow movement between them.

Bringing six such molecules together into a 60-atom buckyball would be tricky. Says Manaa, "It would likely have to be prepared under extreme conditions, such as high pressure."

The resulting molecule would be purely single bonded. Breaking those bonds—splitting N_{60} into 30 triple-bonded N_2 molecules—would release 50 percent more energy than can be released by CL-20, the best performing explosive currently known.

Manaa now has several studies under way to examine the possibility of creating N_{60} and the stability of the resulting molecule. He has also begun to look at a possible boron fullerene.

This work is part of research on the properties of energetic materials for the Department of Energy's Stockpile Stewardship Program, which uses the supercomputing capabilities of the Accelerated Strategic Computing Initiative (ASCI). Manaa notes that the use of extensive and rigorous computational tools coupled with the relatively large size of these molecules renders the use of massively parallel platforms—such as ASCI Blue—of paramount necessity.

Still a Long and Winding Road Ahead

Manaa's simulated nitrogen fullerene and other polynitrogen molecules currently under study are still a long way from practical use. To create a propellant for supersonic transport vehicles, the material being considered must first have a high energy density. It must also be reactive and must release large amounts of energy while increasing the number of particles—for example, one N_4 molecule reacting and releasing two N_2 molecules. The reaction must be controllable, and the material must be easily synthesized.

Polynitrogens are certainly high-energy-density materials and highly reactive. Of the new ones under study, only N_5 shows stability. N_{60} still exists only in ASCI simulations. So Manaa is quick to note that these new forms of nitrogen are "still strictly hypothetical."

—Katie Walter

Key Words: Accelerated Strategic Computing Initiative (ASCI), fullerenes, high-energy-density materials, nitrogen.

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