Versatile EXPLOSIVES

“Playing” with Fire

by Vin LoPresti

Fireworks propelled by high-nitrogen energetic materials display vibrant colors and patterns in a virtually smoke-free environment. These vivid pyrotechnics eliminate sulfurous fumes and minimize the use of toxic colorants.

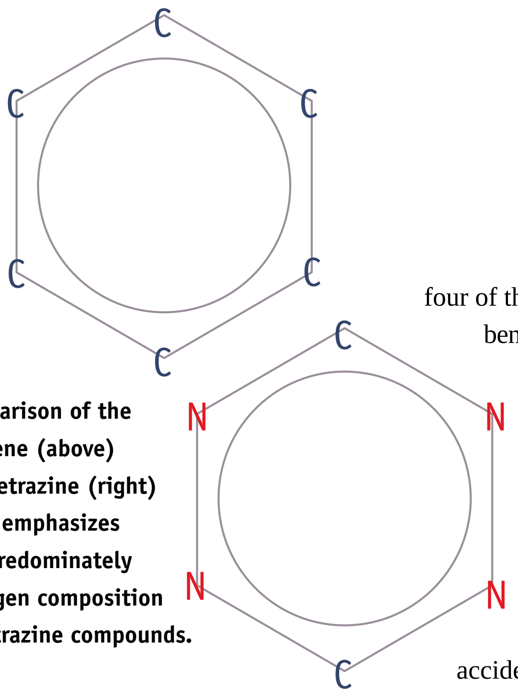
John Flower

Smokeless, odorless, and delayed response—these are not characteristics typically associated with explosives. But Laboratory researchers have been focusing on a group of compounds—high-nitrogen energetic materials—that are challenging stereotypical notions of how explosives behave. In addition to their use in weaponry, these compounds have applications in fire suppression, entertainment, and automobile safety.

Traditionally, explosives have been substances rich in carbon—for example, the charcoal in gunpowder. Combustion of a carbon-rich explosive in air results in the formation of carbon dioxide and carbon monoxide, together with water vapor and soot (unburned carbon particulates). Energy is rapidly liberated, accompanied by high temperatures (see the combustion primer on page 7). When combustion occurs within a gun barrel, the hot gases expand and propel a bullet or other projectile toward its target.

High-nitrogen energetic materials contain more nitrogen than carbon by weight, and their combustion products therefore differ from those that result from carbon-rich compounds. Nitrogen gas (N_2, which makes up 78 percent of Earth's atmosphere) is a main combustion product. Additionally, the high nitrogen content of these materials often leads to high densities; that is, individual molecules of the material pack closely together, so that a small quantity of the compound contains more combustible material than would a less dense compound. This high density is desirable in an explosive, in that large amounts of energy can be liberated from a relatively small amount of material.

The high-nitrogen compounds occupying the attention of a Los Alamos team in DX-2 (Materials Dynamics Group) are derivatives of the 1,2,4,5 tetrazine ring, a benzenelike, or aromatic, chemical structure in which



Comparison of the benzene (above) and tetrazine (right) rings emphasizes the predominately nitrogen composition of tetrazine compounds.

four of the six carbon atoms in the benzene ring are replaced by nitrogen. Many of the tetrazine-derived compounds studied to date share the quality of "insensitivity"; that is, they will detonate only upon reaching a target but not when subjected to high temperature, friction, or accidental impact.


John Flower

(Top) Combustion of a conventional explosive pellet is accompanied by flame, smoke, and residue. (Bottom) By comparison, combustion of a DHT pellet is nearly smokeless and flameless. The DHT pellet is encased by epoxy resin (arrow) to control combustion conditions; this was unnecessary for the conventional explosive because of its relatively slow combustion rate.

Empirical Chemistry

Because the tetrazine ring does not exist in nature, its similarity to benzene can be misleading. The synthesis of tetrazine compounds does not proceed directly from benzene and can require a long series of reaction steps. As many organic chemists would attest, chemical syntheses are part understanding, part experience, and part trial and error, sometimes with a healthy dollop of luck stirred in.

By modifying the molecular groups bonded to tetrazine rings, the DX-2 team of Mike Hiskey, Darren Naud, David Chavez, and My Hang Huynh has synthesized a host of compounds that differ in the rate and the temperature at which they burn. "You never know exactly quite what you'll get. You set out to make one thing and then find other applications," comments Hiskey, alluding to the fact that it is often difficult to predict a compound's properties before synthesizing it.

One compound the team has synthesized is DHT (dihydrazino-tetrazine). Because it is both a high-nitrogen and a high-hydrogen compound, it tends to burn hotter in air, forming both nitrogen gas and water. These characteristics make it a candidate for so-called thermobaric bombs. First used in Afghanistan during the March 2002 attacks on Al Qaeda caves, these bombs use a primary explosion to propel a solid-fuel explosive into a tunnel, bunker, or cave. The secondary explosive then detonates via a delayed fuse to generate both high heat (*therme*) and high pressure (*baros*) within the enclosed space. Finely divided fragments of aluminum metal are often included in the solid explosive, because in the high-energy environment of the explosion, aluminum oxidizes in air. Forming aluminum oxide, this reaction both consumes significant oxygen and generates additional heat (it is highly exothermic).

Chemical syntheses are part understanding, part experience, and part trial and error.

The army and navy are testing DHT-aluminum as a candidate explosive because, in addition to its high density, its detonation also generates significant volumes of nitrogen gas. When the gas replaces the oxygen consumed by the burning aluminum, a nitrogen-rich atmosphere is created that leads to nitrogen narcosis in anyone exposed to it. This physiological phenomenon was originally described in deep-sea divers. As the total gas pressure increases with increasing dive depth, the partial pressure of nitrogen increases, and more nitrogen becomes dissolved in the blood—and therefore in the brain. Dubbed “rapture of the deep,” this misnomer alludes to the fact that nitrogen’s intoxicant and soporific effects are equivalent to those of one martini on an empty stomach for each 50 feet beyond a 100-foot dive. Since nitrogen impairs the conduction of nerve impulses, at very high brain concentrations, nitrogen narcosis is fatal.

Cleaner Pyrotechnics

Ironically, the same compound that can be weaponized can also entertain. The hot flame and carbon-free combustion of DHT have made it ideal for a new generation of reduced-toxicity fireworks. Traditional carbon-based fireworks generate large quantities of sooty, sulfurous smoke that interferes with viewing and can also cause respiratory discomfort or asthmatic reactions in audiences. Remaining unseen are constituents that are even more toxic: carbon monoxide and the heavy metals (for example, barium) used as colorants.

The odorless, colorless nitrogen gas released in the combustion of DHT enables brighter, more deeply saturated display colors with only one-tenth the conventional amount of metal-ion colorants. DHT’s hot flame also allows the use of safer substitutes for traditional colorants, for example, boric acid instead of barium. Moreover, the absence of carbon monoxide, soot, and sulfurous fumes makes DHT-powered fireworks much safer for indoor use.

Hiskey’s interest in fireworks and high-energy chemistry dates back to his teens, and that curiosity provided him

Cannons to Carbohydrates: A Combustion Primer

Explosives are compounds that rapidly liberate energy when chemically rearranged through combustion. Energy (typically in the form of a flame or an electrical discharge) ignites the explosive and breaks weaker chemical bonds in the explosive molecule, rearranging its atoms to form new, stronger chemical bonds. This new bond formation liberates energy that makes the reaction self-sustaining. Overall, forming new bonds liberates much more energy than what is needed to break the original bonds, resulting in a net release of energy, including heat—a so-called exothermic reaction (*exo* meaning out; *therme* meaning heat).

For example, in the combustion of gasoline (C_7H_{16}) in air, carbon-carbon and carbon-hydrogen bonds are broken, and carbon-oxygen and hydrogen-oxygen bonds are formed, producing carbon dioxide, carbon monoxide, and water vapor. Combustion is rapid, and energy is liberated as an explosion within a car engine’s cylinders, with the heated gases expanding and exerting a force on the pistons.

When your body cells burn food for energy, fundamentally the same exothermic chemistry occurs with the bonded atoms in food molecules such as fat, which is mostly carbon and hydrogen. The oxygen that we breathe and that is distributed by the bloodstream to all our body cells ultimately supplies the oxygen atoms to create carbon dioxide and water. But the bonds are broken and formed gradually, in many carefully controlled steps, so that energy is liberated slowly rather than explosively. Nonetheless, we correctly speak of “burning fat,” a nonexplosive form of combustion known as cellular respiration. That this is an exothermic process is demonstrated by body heat. The faster we “run” our metabolism (such as when we burn more fats or carbohydrates during exercise), the warmer our bodies get. Sweating dissipates the heat and regulates body temperature.

Powered by sunlight, trees perform this metabolic process in reverse (thermodynamically, but not in terms of the details) in photosynthesis. The resulting carbohydrate, cellulose, is burned as wood to form the charcoal used to make gunpowder—first documented in the Middle East in 1200. It has taken 800 years for chemists to discover viable gunpowder alternatives in the form of high-nitrogen energetic compounds.

U.S. Navy

U.S. Navy

Naval gun propellants, past and present. Sixteen-inch guns on the battleship New Jersey spew the smoke and flame characteristic of carbon-rich propellants (Persian Gulf, 1989). (Inset) Today's naval guns, like this five-inch gun on a destroyer, may undergo less wear through the addition of high-nitrogen energetic materials to propellants.

with both a practice-based learning environment and a career path. Teaming with Naud and Chavez, Hiskey developed a cost-effective synthesis of DHT, which led to "smokeless" fireworks. Their invention won an R&D 100 Award in 1998 and has drawn the interest of at least one major theme park.

Better Big-Gun Propellants

As most gun owners know, the high gas temperatures and sooty residues produced by the combustion of gunpowder mandate frequent cleaning of gun barrels. Less appreciated is the wear and tear on a gun barrel produced by carbon-based propellants. This wear is of particular concern for military guns, whose powerful blast charges propel projectiles to targets miles away. Another tetrazine relative, known as GUZT (guanidinium azotetrazolate), may help reduce such wear when added to gun propellants.

In gun barrels, the propellant is burned behind a projectile, and—in accord with gas laws—the expanding gases from that combustion exert pressure on the projectile, accelerating it toward a target. During this process, two major sources of wear contribute to reducing gun barrel life. First, the combustion's very high temperature deforms metal alloys in the barrel. Second, carbon-based propellants generate significant carbon monoxide, which at elevated temperatures, reacts to form metal carbides that embrittle the barrel's interior, resulting in increased wear.

A high-nitrogen propellant additive like GUZT addresses both issues. Its lower-temperature combustion moderates temperature deformation, while its generation of nitrogen gas helps mitigate reactivity. In sufficient concentration, nitrogen gas can inhibit the carbon monoxide–gun barrel reaction, thereby reducing the extent of metal carbide formation.

For barrels as large and as expensive as those on naval warships, this reduced wear could represent significant cost savings. Barrels are currently replaced after every eight thousand rounds fired, and the navy expects the replacement frequency to rise as more-energetic propellants come into use. But the cost of the barrel is overshadowed by two other factors. Since barrels cannot be replaced at sea, there is the expense of bringing a ship back to port for the work. More important from a strategic standpoint is the impact of this return to port on fleet readiness.

Fighting Fire with Fire

A compound known as BTATz (bistetrazolylaminotetrazine) has shown considerable promise as a fire suppressant. The current suppressant of choice is Halon-1301 (bromotriflouromethane). Halon works by evaporating within a fire and displacing the oxygen that would sustain the blaze. It has several drawbacks, however. First, it destroys Earth's ozone layer (its production was thus halted in 1994). Second, as a gas, it is stored in pressurized bottles for application as a liquid. Particularly for use in an airplane, these bottles add undesirable weight.

For several years, the U.S. military has been evaluating solid and hybrid (solid/liquid, solid/gas) fire suppressants, and the properties of BTATz rank it among the more promising agents now undergoing evaluation. Almost 80 percent nitrogen by weight, BTATz burns very rapidly to form 0.7 liter of nitrogen gas per gram of solid combusted. Because of its low carbon content, it burns cleanly, without smoke, leaving a minimal residue. And like GUZT, it burns at a temperature hundreds of degrees lower than do carbon-rich compounds of similar molecular weight.

The large volume of inert nitrogen gas rapidly generated by BTATz is precisely what is needed to displace

Interagency Partnering

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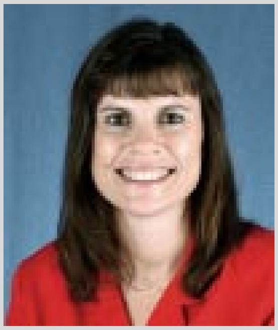

U.S. Navy

Decreasing federal budgets have put a premium on teaming between governmental agencies to provide innovative, cost-effective solutions to the military's needs. For example, a memorandum of understanding between the Departments of Defense and Energy specifies that the Department of Energy will develop and transition technologies that are of interest to the Department of Defense.

Under this agreement, I am collaborating with a team led by Mike Hiskey at Los Alamos National Laboratory. His team is developing novel energetic ingredients that can be used as additives in explosives and propellant formulations. These ingredients help solve some of the technical issues associated with improving weapons technology, allowing the navy to provide military forces with better-performing weapons.

As the lead for gun propellant development for the Naval Surface Warfare Center at Indian Head, I am responsible for the development of novel gun propellants for the navy. These propellants are designed to provide better protection for sailors and soldiers by increasing ship-to-shore stand-off distances—allowing ships to stay out of harm's way—and by increasing fire support for land-based troops, such as the marines. This Los Alamos–U.S. Navy collaboration allows both organizations to leverage each other's technology and scientific expertise to provide mutually beneficial solutions to real-world needs. It exemplifies a partnership demonstrating that the whole is greater than the sum of its parts.

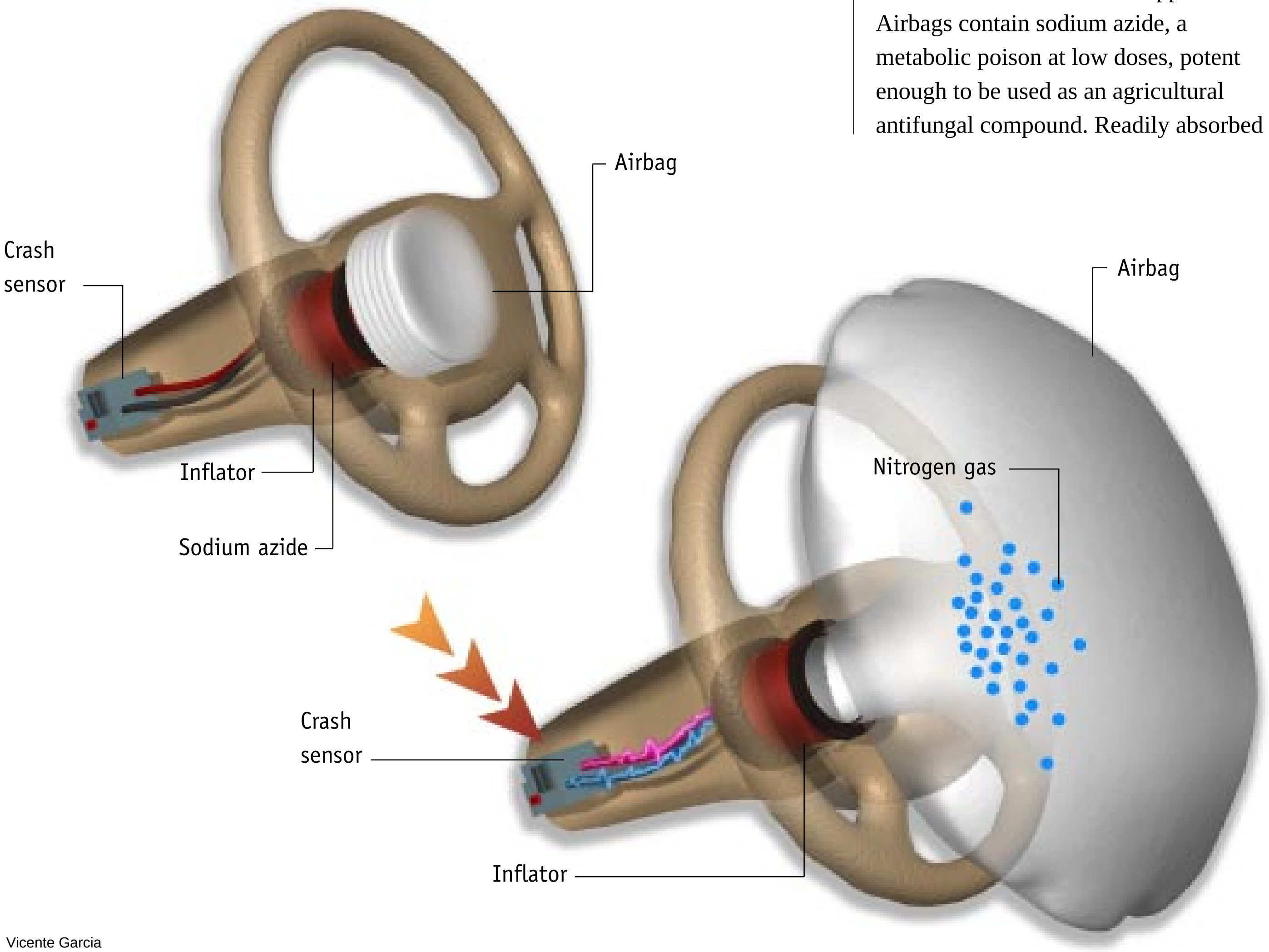
oxygen from the vicinity of a fire. Nitrogen gas is composed of smaller, less-massive molecules than vaporized halon, and nitrogen's more rapid rate of expansion helps cool its surroundings (all gases absorb heat from their environments as they expand). BTATz thus addresses a problem encountered with other fire suppressants, namely, effluent gases that are too hot.

As a solid, BTATz can be formed into a paint that, when applied to a surface (such as the wheel well of a carrier-based aircraft), will remain chemically stable until it ignites. Requiring no heavy storage containers, it is also lighter than halon. BTATz now costs $75 per pound to manufacture, but the navy's Air Warfare Weapons Division at China Lake, California, is seeking to scale up its synthesis, thus further reducing its cost. The navy is also experimenting with combining BTATz with flame inhibitors. Since halon is also the civilian fire suppressant of choice, this research may ultimately produce a widely used, environmentally friendly fire suppressant.

Airbags

Gas-generating solids are used in automobile airbags, and BTATz is also a candidate for this civilian application. Airbags contain sodium azide, a metabolic poison at low doses, potent enough to be used as an agricultural antifungal compound. Readily absorbed

The basics of airbag inflation. (Top) An undeployed airbag is folded within a car's steering wheel, its sodium azide–containing inflator attached to the crash sensor in the steering column. (Bottom) Activated by a crash (arrows), the sensor triggers the inflator to produce an electric spark that ignites the sodium azide, which rapidly produces nitrogen gas that inflates the airbag.



Vicente Garcia

through the skin and lungs, it can cause cardiovascular abnormalities, convulsions, and upon prolonged exposure, even death. Although airbags contain very small quantities of the chemical, eliminating it from automobiles is clearly desirable, particularly since it also accumulates in landfills where undeployed airbags are discarded.

In an automobile accident, a crash sensor activates a circuit that sends an electrical discharge into the sodium azide, causing it to ignite and decompose into sodium metal and nitrogen gas, which rapidly expands to inflate the airbag (see sidebar on airbag chemistry). Although currently more expensive than sodium azide, BTATz efficiently generates nitrogen gas, and it may well find an application in this area if its synthesis cost can be lowered.

Small-Scale Rocket Propellants

From GPS data to live transoceanic newscasts, satellite communications have become central to our way of life. Despite satellites' generally stable orbits, their orientations must occasionally be fine-tuned by tiny


NASA

Microthrusters on the Jason-1 satellite maintain a precision orbit for its mission: to accurately determine ocean height and monitor global ocean circulation.

Airbag Chemistry

Folded (undeployed) airbags—in the steering-wheel assembly and passenger-side dashboard of all new vehicles—contain sodium azide (NaN_3), a potent metabolic poison. Although the precise formulations used are guarded as trade secrets, a well-known one includes potassium nitrate (KNO_3) and silicon dioxide (SiO_2) as secondary reactants. In the gas generator, a mixture of sodium azide, potassium nitrate, and silicon dioxide is ignited by an electrical impulse. This liberates a volume of nitrogen gas (N_2), which rapidly fills the airbag:

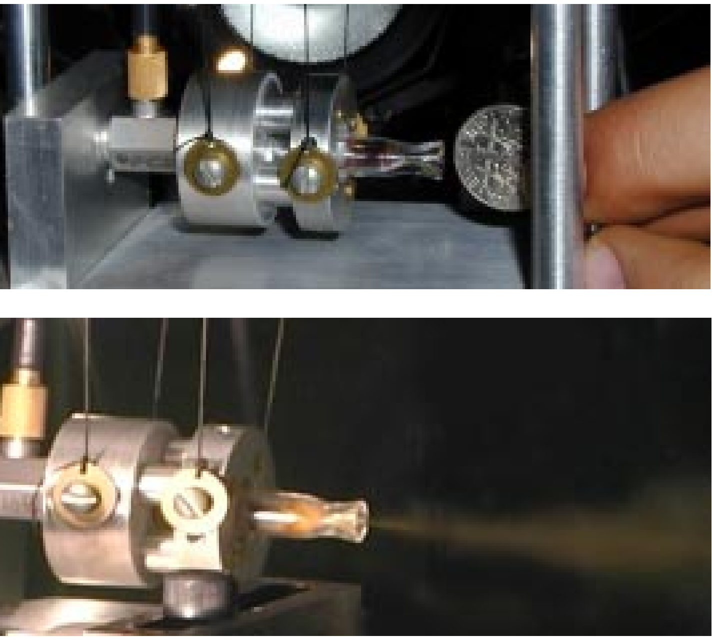
$$2NaN_3 \rightarrow 2Na + 3N_2 \ .$$

Sodium metal (Na), the other byproduct of this reaction, is an unstable substance that can undergo an explosive reaction with water at room temperature (a common demonstration in college chemistry classes). This sodium reacts with the potassium nitrate to generate additional nitrogen for the airbag in a second reaction:

$$10Na + 2KNO_3 \rightarrow K_2O + 5Na_2O + N_2 \ .$$

The other products of the reaction—potassium oxide (K_2O) and sodium oxide (Na_2O)— react with the third compound of the original airbag mixture, silicon dioxide (SiO_2), to form alkaline silicate, or glass, a stable (unreactive) substance that is harmlessly discarded in a deployed airbag.

The use of BTATz, which produces only water, carbon dioxide, and a large amount of cool, inert nitrogen gas upon ignition, would eliminate the need for the supplementary chemicals and secondary reactions, and more important, would eliminate the need to dispose of the toxic sodium azide from undeployed airbags.



John Flower

A satellite microthruster is shown next to a dime for size comparison (top) and in the process of combusting the solid propellant DAAT-N-Ox (bottom). With a diameter of about 1 millimeter, the thruster's nozzle would be rapidly clogged with deposits from combustion of a carbon-based fuel.

rocket motors (microthrusters). Inspection satellites, launched to inspect other orbiting equipment, also use these thrusters.

Yet another tetrazine derivative, dubbed DAAT-N-Ox, shows promise as a solid fuel for such rocket motors. Like BTATz, DAAT-N-Ox burns at a lower temperature than do conventional solid propellants. These lower temperatures allow the use of materials for rocket nozzles that would otherwise melt during combustion. Such nozzles are frequently only about a millimeter wide at their narrowest point, so they would also rapidly become clogged with the residues deposited by hotter-burning carbon-based fuels. However, DAAT-N-Ox burns very cleanly, thus avoiding nozzle clogging. It also burns much more rapidly than any carbon-rich energetic material, perfectly suiting it for the very short propulsive bursts needed to make minor changes in satellite orientation and orbits. With the fastest combustion rate of any solid rocket fuel, DAAT-N-Ox may well be the best solid propellant available.

DAAT-N-Ox may well be the best solid propellant available.

Variations on a Theme

From microthrusters to naval gun propellants, from thermobaric bombs to smokeless fireworks, from fire suppression to airbag inflation, high-nitrogen compounds promise unique versatility as energetic materials. Their insensitivity, high density, and lower combustion temperatures are attractive characteristics for explosives and rocket motors. Their rapid generation of inert nitrogen in large volumes is ideal for both existing and future applications that require an environmentally friendly gas generator. Although not quite a case of "one compound fits all," these tetrazine derivatives represent variations on a theme, and it appears likely that current and future compounds will find useful niches in both military and civilian life. ■

The Researcher

John Flower

Michael Hiskey received a Ph.D. in explosives chemistry from New Mexico Institute of Mining and Technology in 1990. He then joined the Laboratory as a postdoctoral researcher and became a technical staff member at DX-2 in 1992. He holds patents in the areas of explosives, propellants, pyrotechnics, and gas generants.