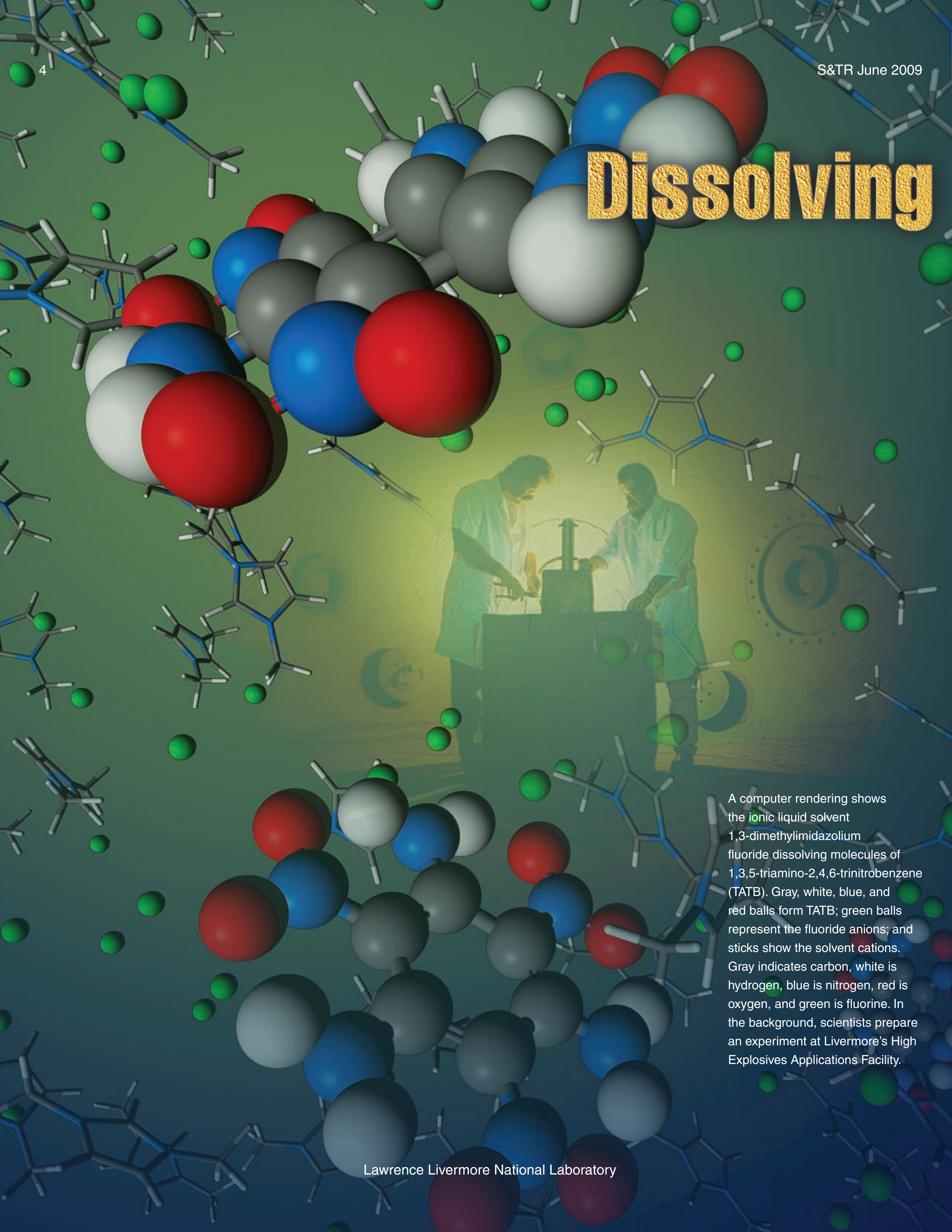
Dissolving

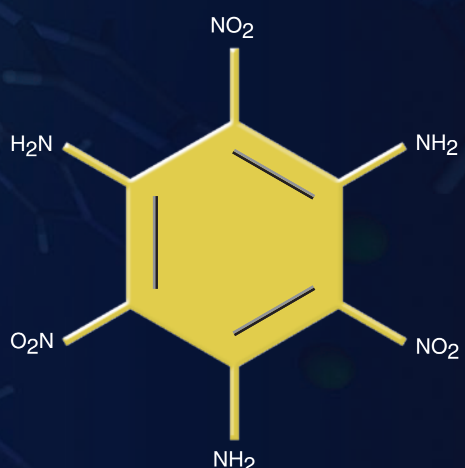


A computer rendering shows the ionic liquid solvent 1,3-dimethylimidazolium fluoride dissolving molecules of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Gray, white, blue, and red balls form TATB; green balls represent the fluoride anions; and sticks show the solvent cations. Gray indicates carbon, white is hydrogen, blue is nitrogen, red is oxygen, and green is fluorine. In the background, scientists prepare an experiment at Livermore's High Explosives Applications Facility.

Molecules to Improve Their Performance

Combining computer modeling and laboratory synthesis, researchers have developed a green method to recycle a valuable and scarce explosive.

FROM space dust to rare isotopes, Lawrence Livermore researchers work with many unusual and exotic materials. Among the most remarkable is a molecule called 1,3,5-triamino-2,4,6-trinitrobenzene, or TATB. Used as a high explosive, TATB is nearly invulnerable to significant energy release from plane crashes, fires, and explosions or to deliberate attack with a small firearm. TATB's extreme insensitivity to impact, shock, and heat make it a valuable component in about one-third of the nation's nuclear weapons, in some Department of Defense (DoD) munitions, and in explosives used by mining and oil production companies. (See the box on p. 6.)



In the six-sided ring structure of TATB, nitro compounds (NO_2 and O_2N) alternate with amine compounds (H_2N and NH_2).

TATB has not been produced for more than two decades primarily because of environmental regulations. As a result, DoD has been purchasing old TATB from Department of Energy (DOE) stockpiles while new, greener manufacturing methods are being developed.

The scarcity of TATB makes recycling the material from old nuclear warheads an attractive option. In any recycling process, TATB molecules must be separated from the polymer binder (the plastic "glue" binding the crystals), dissolved, and then recrystallized to the correct microscopic crystal size and shape. These steps are necessary to produce a recycled material with the same performance characteristics as new material. Until recently, a TATB recycling process was not available because effective solvents did not exist.

In response to urgent needs for replenished supplies of high-quality TATB, Livermore scientists have developed 3-ethyl-1-methylimidazolium acetate–dimethyl sulfoxide, a solvent system that belongs to a class of powerful but environmentally benign compounds called ionic liquids. This system has produced TATB with better crystal quality, size, shape, and purity than previous manufacturing techniques have produced. What's more, the crystals have a uniform size that can be controlled when TATB molecules are recrystallized out of solution. The new system may also have applications for efficiently converting cellulose and other difficult-to-dissolve organic compounds, such as cornstalks, into biofuels.

Focus on Advanced Materials

The TATB development effort was supported under the Transformational Materials Initiative (TMI), which was funded by Livermore's Laboratory Directed Research and Development Program. Begun in 2006, TMI focused on advanced materials for the nation's future nuclear stockpile. Its charter includes addressing critical issues such as the dwindling supply of high-quality TATB. The TMI-sponsored research on TATB was featured on the covers of the January 2009 issue of *New Journal of Chemistry* and the September 1, 2008, issue of *Physical Chemistry Chemical Physics*.

"TATB is a precious resource," says TMI leader Robert Maxwell. "If we could recycle it when we disassemble warheads, we could save the nation many millions of dollars. However, we need exactly the right purity, particle size, and shape of TATB crystals to ensure the highest safety and performance standards."

Under the microscope, TATB particles taken from old warheads appear disorganized, with varying shapes and sizes—not the well-faceted crystals chemists require to confidently predict performance and safety. Chemist George Overturf, high explosives subject-matter expert for the Laboratory's weapons program, notes, "We need TATB to be reconstituted back to the original particle specifications."

Some experts are concerned that in its current formulation, recycled TATB could harbor an excessive number of "hot spots," microscopic voids located within crystals or at the interfaces with particles of binder. Voids tend to heat up, which could reduce TATB's insensitivity to shock. "Keeping the molecules tightly packed means greater insensitivity to shocks," says chemist Yong Han, lead author of the *New Journal of Chemistry* article.

The Livermore team, drawn from the Weapons and Complex Integration Principal Directorate and the Physical and Life Sciences Directorate, focused on developing a method that controls the size and shape of crystals as they are reconstituted from old TATB. The effort included work at the Laboratory's High Explosives Applications Facility and Site 300, the experimental test site about 24 kilometers east of Livermore's main site. Computer modeling also helped guide the chemists' synthesis efforts. The result is a patented process that improves the quality of recycled TATB and can be

Simulations to Measure Sensitivity

Some high explosives such as trinitrotoluene (TNT) are easily detonated. Others such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which is used in some of the nation's nuclear weapons, are insensitive to shock, heat, or impact and thus are difficult to detonate accidentally. High explosives have held tight to their secrets about why some are insensitive and safe and others very sensitive. "Despite the extensive production and use of explosives for more than a century, their basic microscopic properties during detonation have yet to be unraveled," says Laboratory physicist Evan Reed.

Two years ago, Reed led a team that performed the first-ever quantum molecular dynamics (QMD) simulations of a high explosive's detonation front. This first test case studied nitromethane, a fairly simple molecule and a high explosive of moderate sensitivity. Almost as energetic as TNT, nitromethane is oxygen poor. However, when mixed with ammonium nitrate, as it was in the 1995 bombing of the Alfred P. Murrah Federal Building in Oklahoma City, it can be extremely lethal.

A QMD simulation of only 0.2 nanoseconds revealed that nitromethane undergoes a totally unexpected change during detonation. First, it decomposes chemically and then transforms into a semimetallic state for a short distance behind the detonation front. Nitromethane is an optically transparent, electrically insulating material. Yet, for a brief moment, it turns into an optically reflecting conductor before returning to its transparent, insulating state. New experiments based on this simulation are designed to send shock waves into nitromethane to measure changes at the detonation front. "The challenge at the moment," says Reed, "is matching the shock pressure of the experiment to the pressure used during the QMD simulation."

A more recent set of QMD simulations by Reed and Riad Manaa examined TATB. "We were looking for a possible explanation for its lack of sensitivity," says Reed. The simulations show for the first time that, during detonation, TATB's numerous carbon and nitrogen atoms form big, viscous globs, known as heterocycles. Atoms of nitrogen, the ingredient in explosives that makes them boom, must diffuse out of the carbon globs before they can release their energy to power the detonation process. In contrast, nitromethane breaks down quickly into small molecules rather than viscous globs. The discovery of these globs may explain TATB's long reaction time.

used as a last step in any new production method to ensure that quality standards are met.

Molecular Crystals Tightly Packed

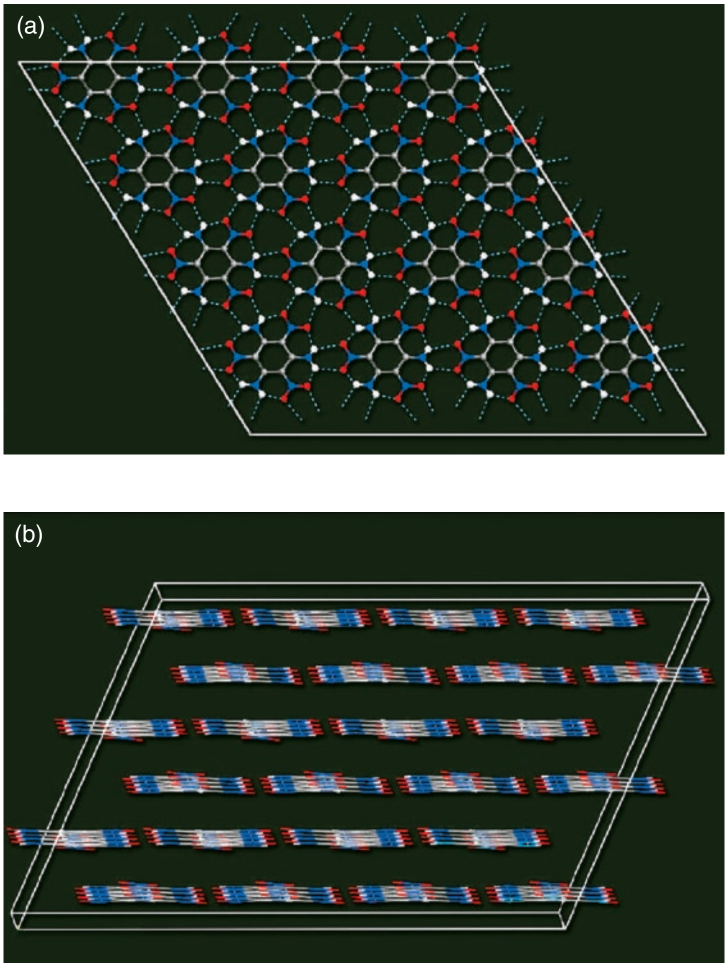
Like most high explosives, TATB belongs to a class of materials called molecular crystals, which are made of electrically neutral molecules that are tightly packed together. Materials made from molecular crystals include drugs, pigments, agricultural chemicals, and active components in optoelectronics.

Molecular crystals are often bound together by a strong network of hydrogen bonds in which an electronegative atom is attracted to a positively charged hydrogen atom bonded to another electronegative atom. Hydrogen bonds also link TATB molecules together in well-defined layers. (See the figures at right.)

TATB is one of the most strongly hydrogen-bonded solids known. As a result, it is extremely insoluble in common solvents, even at high temperatures. Dimethyl sulfoxide (DMSO), the best conventional organic solvent for TATB, dissolves only 70 parts per million and is difficult to remove from solution. "Super" acids, such as concentrated sulfuric acid, can dissolve much more TATB at room temperature than DMSO, but they are dangerous to work with. They also can degrade the TATB molecular structure and thus weaken insensitivity to shock.

Keeping in mind that TATB's hydrogen bonds must be broken in a chemically benign manner, the Livermore team focused on ionic liquids. Ionic liquids have proved useful for dissolving hydrogen-bonded solids such as natural fibers. One example is cellulose, a biorenewable material with applications to the paper, fiber, membrane, polymer, and paint industries. Ionic liquids had not previously been considered as candidates for dissolving high explosives, although they are known to be powerful breakers of hydrogen bonds.

"Researchers are excited about ionic liquids," says Larry Fried, who leads Livermore's extreme chemistry group. "It's one of the most rapidly growing areas in chemistry. More than 1,000 papers are published on this topic every year."



(a) Hydrogen bonds (dotted lines) tightly link TATB molecules to each other within a single layer.
(b) These bonds are also responsible for connecting TATB's well-defined layers.

Ionic liquids are a kind of salt, compounds that combine a cation (positively charged ion) with an anion (negatively charged ion). Because so many combinations of cations and anions are possible, the number of different ionic liquids is nearly infinite. Many of them feature a cation based on a molecule called imidazolium, which forms part of many biological molecules, and an anion with a halogen atom such as fluorine, chlorine, or bromine.

Scientists believe the ionic liquid anion breaks TATB hydrogen bonds by pulling individual molecules away from the molecular crystal. In contrast, the ionic liquid's cation has more subtle effects. "It's more like a spectator," says Fried.

Ionic liquids are also attractive because they offer reduced environmental and safety concerns compared to other solvents. As a result, they are sometimes called green solvents. The ionic liquids considered for use as solvents melt at 100°C or below, and many of them are liquid at room temperature. In addition, they have no vapor pressure—that is, they do not evaporate if left out and thus do not contribute to air pollution. Another advantage is that they are recyclable. Finally, their stability at high temperatures provides an added measure of safety.

Modeling Finds a Good Match

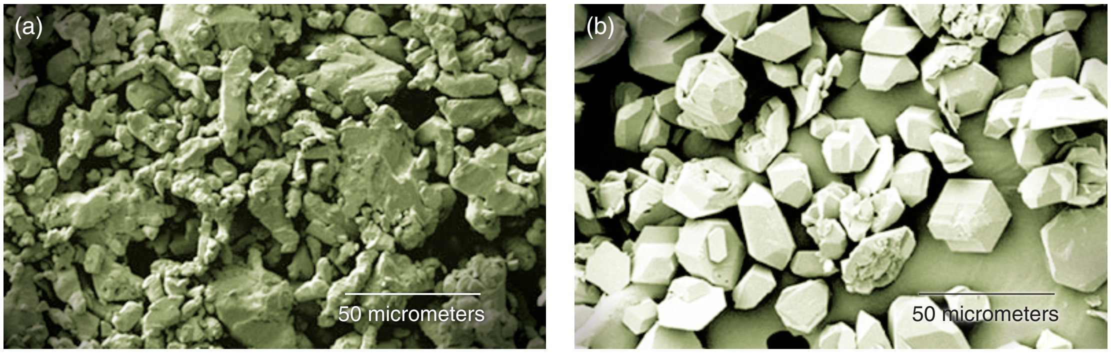
Because ionic liquids containing chloride anions are effective solvents, the team first considered these compounds as candidates for dissolving TATB. In particular, the team investigated 3-butyl-1-methylimidazolium chloride, known to dissolve cellulose and silk and wool fibers. However, it proved ineffective at dissolving TATB. Similar results were observed for other ionic liquids containing chloride anions.

To narrow the possible solvent choices, computational physicist Amitesh Maiti used advanced quantum mechanical simulations. "Synthesizing new ionic liquids and then accurately measuring their solubility are time-consuming and expensive," says Maiti. "Computer simulations can be a much faster and cheaper alternative for screening potentially efficient solvents."

For this effort, Maiti adopted a two-step procedure. The first step applies a quantum mechanical density functional theory approach to compute the electronic charge density of individual solute and solvent molecules—in this case, a TATB molecule and the constituent ions of the candidate ionic liquid. In the second step, a realistic solvation model called COSMO-RS simulates TATB in different ionic liquid environments and uses the results to estimate the extent to which TATB is likely to be dissolved. "We realistically mimic the solvent environment without needing thousands of molecules," he says. "In this way, we can efficiently screen a large number of solvents in a reasonable amount of time."

The modeling effort identified a class of ionic liquids containing fluoride anions that theoretically seemed excellent at dissolving hydrogen bonds, with predicted TATB solubility more than

Chemists (a) Phil Pagoria and (b) Yong Han (front) and Pat Gallagher work at Site 300, the Laboratory's remote experimental test site, to produce TATB solvents for testing.



Images taken with a scanning electron microscope reveal the shape of TATB crystals (a) before and (b) after recrystallization with the ionic liquid 3-ethyl-1-methylimidazolium acetate.

100 times better than the best conventional solvents. Experiments using some of these combinations soon followed, and the measured solubilities compared well with the theoretically computed values, with differences ranging from a factor of 2 to within just a few percent. “We were encouraged to see the excellent agreement between theory and experiment over a broad range of temperatures and solubility values,” says Maiti.

With fluoride established as the most efficient anion, the researchers looked for a matching cation to maximize solubility. Calculations pointed to 1,3-dimethylimidazolium as the best match. However, because that molecule has a high melting temperature, the team worked with a related, but slightly larger cation: 1-butyl-3-methylimidazolium. When synthesized, this ionic liquid successfully dissolved TATB, producing large, defect-free crystallites. The solubility of the new material proved roughly 200 times greater than that achieved with DMSO.

The team compared scanning electron microscope images of available TATB with material recrystallized using the ionic liquid. The superior quality of the newly recrystallized TATB was clearly evident in the uniform, well-faceted crystals.

Using x-ray diffraction and nuclear magnetic resonance, the researchers extensively characterized solid TATB and the TATB–ionic liquid solution to decipher how 1-butyl-3-methylimidazolium fluoride works as a solvent. Experimental images and computer calculations showed that the individual fluoride ions are stabilized (that is, they remain as distinct, chemically unreacted ions) in the presence of coordinating water molecules. Such anions, being strong hydrogen-bond acceptors, disrupt the network of TATB molecules in its crystalline phase and lead to efficient dissolution. In contrast, ionic liquids using chlorine are weaker at breaking hydrogen bonds and are ineffective in the presence of even a small amount of water.

An Even Better Solvent

Although 1-butyl-3-methylimidazolium fluoride was an effective TATB solvent, it proved unstable and difficult to work with, and its solubility decreased when it was exposed to water from air. Also, it is not readily available commercially, thereby increasing costs.

The chemists turned to ionic liquids with anions that contain acetate, while retaining the imidazolium family of cations. Acetate is a cheap chemical, less toxic than fluoride and known for breaking hydrogen bonds. It is also easy to work with because it does not absorb water. Guided by Maiti’s modeling results, chemists tested several formulations, using both commercially available and custom-synthesized ionic solvents.

Three-ethyl-1-methylimidazolium acetate (EMImOAc) showed a surprisingly good solubility of TATB, almost as good as 1-butyl-3-methylimidazolium fluoride. In experiments performed by Phil Pagoria, leader of advanced materials synthesis, an EMImOAc–TATB mixture was heated to 100°C and maintained at this temperature until all of the particles dissolved. Over time, single TATB crystals appeared and grew larger as they slowly cooled to room temperature. These crystals were far more uniform in size and shape than the starting TATB crystals. (See the figures above.)

However, the viscosity of EMImOAc at room temperature made the recrystallized TATB difficult to filter. “Ionic liquids can be very viscous, like honey or molasses,” says Fried. To reduce the viscosity, the research team added DMSO, the long-standing (but not particularly effective) solvent for TATB. As expected, mixing DMSO with EMImOAc lowered the solubility of TATB proportionate to the concentration of DMSO. However, a solution with as much as 80 percent (by weight) of DMSO dissolved a significant amount of TATB and reduced material costs appreciably.

Controlling Crystallization

Electron micrographs of the recrystallized TATB crystals showed good morphology compared to the starting material, with sizes ranging from 10 to 50 micrometers in diameter. However, at room temperature, some of the TATB remained in solution. As a result, the chemists investigated using acetic acid (purified vinegar) as an “antisolvent.” Experiments showed that by varying the concentration of acetic acid and the rate at which it is added, they could control the size of the recrystallized crystals. Adding acetic acid slowly resulted in larger (100-micrometer-diameter) crystals, while adding it faster produced smaller (10-micrometer-diameter) crystals. “We want both sizes—larger crystals to take up most of the volume, and smaller crystals to fill in the gaps between the larger ones,” says Han. “This combination produces the highest density material when TATB is pressed into parts with the plastic binder.”

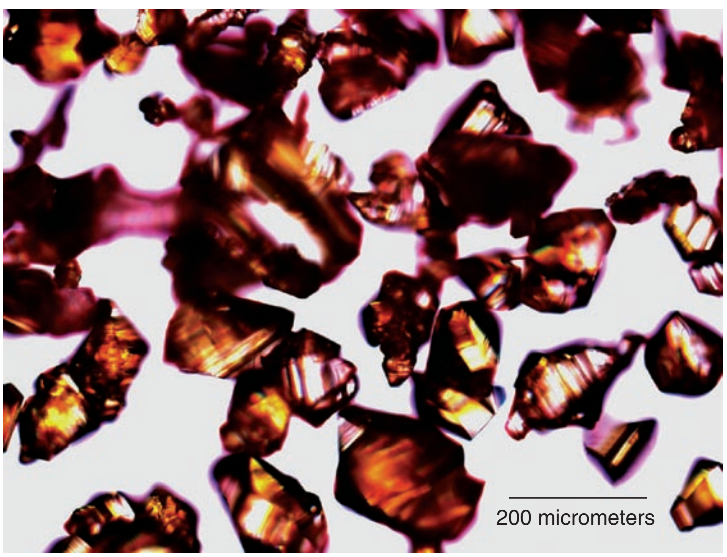
The chemists have subjected the recrystallized TATB to a battery of tests, with excellent results. They have also used nuclear magnetic resonance and Raman spectroscopy to investigate exactly how EMImOAc dissolves TATB.

“We now have a process where we can control the size and morphology of TATB crystals,” says Fried. “Before, they looked like misshapen crystals. Now, they look like well-faceted jewels with far fewer defects.” (See the figure below.) With the Livermore technique, TATB from any source and of unknown quality can be purified and standardized.

Randy Simpson, a high-explosives expert, underscores the significance of the Livermore research effort. “Rarely do scientists achieve this degree of improvement so quickly in any field of research,” he says.

Other Applications

The TMI researchers have presented their findings at scientific conferences and are optimizing how to transfer the process to DOE and DoD materials experts, who are working to restart TATB production lines. In the meantime, the research team is studying whether the quality of other insensitive high explosives, such as LLM-105, could be improved by the same dissolution–recrystallization process.



This optical micrograph shows recrystallized TATB molecules.

Maxwell notes that many industries using hard-to-dissolve materials, especially hydrogen-bonded materials, might benefit from the Livermore research results. For example, in tests of the EMImOAc–DMSO solvent combination on cellulose, the team obtained solubilities comparable with those reported using chloride-based ionic liquids. Simpson points out that the ethanol industry uses ears of corn as feedstock, leaving behind much of the cornstalk. With the right solvent, cornstalks could be added to the mixture, markedly increasing the amount of ethanol in the marketplace and reducing production costs. Other potential applications include producing plastics, pharmaceuticals, paints, and propellants.

For his part, Maiti is applying his computer modeling experience to designing ionic liquids for carbon sequestration research. One day, carbon dioxide generated by fossil fuel power plants could be trapped at the smokestack, dissolved in an ionic liquid, filtered, pressurized into a dense stream, and then stored in a repository.

Maxwell says that an important result of the ionic liquid research effort was demonstrating the utility of combining computer modeling with traditional “benchtop” chemistry. Clearly, such a marriage has a long and profitable future.

—Arnie Heller

Key Words: high explosive, High Explosives Applications Facility, hydrogen bond, ionic liquid, molecular crystal, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), quantum molecular dynamics (QMD), Site 300, Transformational Materials Initiative (TMI).

For further information contact Robert Maxwell (925) 423-4991 (maxwell7@llnl.gov).