

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 11-01-2006		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Energetic Ionic Liquids as TNT Replacements (Preprint)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) A. Brand, T.W. Hawkins & G. Drake (AFRL/PRSP); I. Ismail, L. Hudgens & G. Warmoth (ERC)				5d. PROJECT NUMBER 50260541	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-TP-2006-008	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-TP-2006-008	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (AFRL-ERS-PAS-2006-016)					
13. SUPPLEMENTARY NOTES Presented at the JANNAF 33 rd Propellant & Explosives Development & Characterization Subcommittee (PEDCS) / 22 nd Safety & Environmental Protection Subcommittee (SEPS) Joint Meeting, Sandestin Beach, FL, 6-10 Mar 2006.					
14. ABSTRACT The US munitions community is searching for advanced replacements for 2,4,6-trinitrotoluene (TNT) for use in melt castable explosives. The identification of such a replacement is constrained by many requirements such as: (1) The replacement must afford identical (preferably improved) performance over TNT; (2) The melting point of the replacement should fall into a temperature regime that is useful for cast operations; (3) The replacement must possess safety/sensitivity properties that are as good or better than TNT; (4) The replacement must have sufficient thermal stability to undergo casting at elevated temperature; and (5) Adequate compatibility must exist between the replacement and other compounds present in the explosive composition. The Air Force Research Laboratory (AFRL) has recently investigated the feasibility of replacing TNT with an ionic liquid (m.p.<100°C) for use in melt castable explosives. The approach focuses on synthesizing triazolium-based salts that have the appropriate physical and safety properties, thermal stability, and theoretical performance to potentially replace TNT. Individual salts selected from several families of energetic triazolium salts recently synthesized at AFRL possess high densities, relatively high heats of formation, and pass accepted thermal stability tests. The results and suitability of the explosive salts' physical properties, processing, hazards, compatibility, and ultimately their performance are presented.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT A	18. NUMBER OF PAGES 15	19a. NAME OF RESPONSIBLE PERSON Dr. Tommy W. Hawkins
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5449

Energetic Ionic Liquids as TNT Replacements (Preprint)

A. Brand, T. Hawkins, and G. Drake
Air Force Research Laboratory
Edwards AFB, CA

I.M.K. Ismail, G. Warmoth, and L. Hudgens
ERC, Inc.
Edwards AFB, CA

ABSTRACT

The US munitions community is searching for advanced replacements for 2,4,6-trinitrotoluene (TNT) for use in melt castable explosives. The identification of such a replacement is constrained by many requirements such as: (1) The replacement must afford identical (preferably improved) performance over TNT; (2) The melting point of the replacement should fall into a temperature regime that is useful for cast operations; (3) The replacement must possess safety/sensitivity properties that are as good or better than TNT; (4) The replacement must have sufficient thermal stability to undergo casting at elevated temperature; and (5) Adequate compatibility must exist between the replacement and other compounds present in the explosive composition.

The Air Force Research Laboratory (AFRL) has recently investigated the feasibility of replacing TNT with an ionic liquid (m.p. < 100°C) for use in melt castable explosives. The approach focuses on synthesizing triazolium-based salts that have the appropriate physical and safety properties, thermal stability, and theoretical performance to potentially replace TNT. Individual salts selected from several families of energetic triazolium salts recently synthesized at AFRL possess high densities, relatively high heats of formation, and pass accepted thermal stability tests. The results and suitability of the explosive salts' physical properties, processing, hazards, compatibility, and ultimately their performance are presented.

INTRODUCTION

For over ten years the USAF has been active in the research and development of ionic liquid (IL) materials for energetic applications. Ionic Liquids are defined as a pure salt that exists in the liquid state below the boiling point of water.^{1,2} AFRL has produced such materials with very low melting points (significantly below that of hydrazine). In fact over the last five years, ionic liquids have emerged within the international chemical industry as preferred materials for toxic solvents in many commercial processes.^{3,4}

ILs can differ markedly from TNT, both in thermochemical and in physicochemical properties:

- ILs can have both higher densities and energy densities. Some ILs have exhibited densities greater than 1.8 g/cc (TNT is 1.65 g/cc). Also, calculated theoretical formation enthalpies of ILs can reach positive (or near positive values) compared to the negative value of TNT. Such differences can lead to significant performance advantages of ILs over TNT.
- ILs have essentially no toxic vapor in the liquid state. As a lower toxicity replacement for TNT, operational costs and risks may be lowered.
- ILs have passed safety/sensitivity tests required to qualify for handling and use in formulating energetic materials.

The Air Force approach has been to focus on first identifying recently synthesized triazolium-based salts that have the appropriate physical and safety properties, thermal stability, and theoretical performance to potentially replace TNT. Individual salts selected from several families of energetic triazolium salts recently synthesized at AFRL possess high densities, relatively high heats of formation, and pass accepted thermal stability tests. In this effort, preliminary Cheetah calculations were performed with both the pure triazolium-based compounds and with binary salt mixtures potentially capable of forming eutectics with melt temperatures in a desirable range (70-100°C). These theoretical calculations indicated whether the explosive performance of many candidates may be comparable if not superior to TNT. The synthesis of down-selected salts was subsequently scaled-up to the 50 gram level for further characterization. Eutectic mixtures of these salts were also investigated in the hopes they could provide improved explosive performance and/or improved safety properties. Salt mixtures were melted in the lab to assess solubility and processability prior to being analyzed to determine the resulting compatibility, melt point, exotherm onset, and thermal stability. Small-scale hazard testing such as impact and friction testing were also carried out on all promising candidates. Finally, the shock velocity of down-selected systems were experimentally measured and compared to theoretical predictions.

RESULTS

Initial Candidate Salt Survey and Down-selection

AFRL has expended a significant amount of synthesis effort to produce a range of ILs based on several families of triazolium salts.⁶ Types of triazoles that have been examined include 4-amino-1,2,4 triazole, 1-H-1,2,4 triazole, 3,4,5-triamino-1,2,4 triazole, 1-H-1,2,3 triazole, and recently 1-amino-3-alkyl-1,2,3 triazole (Figure 1). Such triazole salts have had little previous disclosure in the open literature.

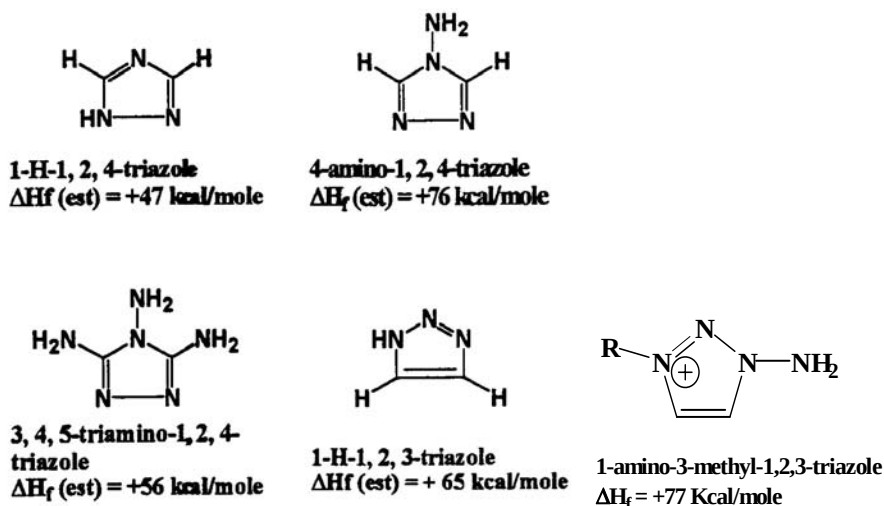


Figure 1. Examples of Triazoles Evaluated

Based on properties such as thermal stability, impact/friction sensitivity, and melt point, a list of the most viable triazolium salts from Table 1 were selected for further investigation as TNT replacements. Desirable properties chosen for initial screening include an impact sensitivity value greater than 20 kg-cm, thermal stability of less than 1% weight loss per day when isothermally heated at 75°C, and a DSC exotherm onset greater than 140°C. Based on these criteria, the 1,2,3-triazolium family of salts was eliminated from further investigation due to either unacceptable thermal stability or impact sensitivity values. In addition, for safety reasons, dinitramide salts were removed as potential candidates. Although 3,4,5-triamino-1,2,4-triazolium dinitramide is quite stable, its melt point of 145°C precludes it from being used in a single component system, and it was felt that intimate liquid phase mixtures with other salts capable of depressing

the melt point could pose a safety concern. Furthermore, the cost of producing a dinitramide salt would also be prohibitively high in comparison with other commercial explosives.

A new family of energetic ionic liquids based on the 1-amino-3-alkyl-1,2,3-triazolium heterocycle was synthesized at AFRL late in the program. One of the salts with a short alkyl group, 1-amino-3-methyl-1,2,3-triazole nitrate (1-AMTN), was identified as a viable candidate as a TNT replacement due to its relatively high melt point of 88⁰C. The ensuing chemical and physical properties characterization of 1-AMTN under this program has yielded encouraging results, and is thus included in the list of triazolium salts investigated to date. The properties listed for 1-AMTN far exceed the desired threshold values chosen for initial screening in contrast to the 1,2,3-triazolium family of salts which was eliminated from further investigation due to either unacceptable thermal stability or impact sensitivity values. The amino and alkyl group addition to the heterocycle appear to offer significant improvement in the molecular stability.

Table1. Properties of Recently Synthesized Triazolium Salts⁶

Molecule	Melt Point °C	Decomposition Onset (°C)	Thermal Stability @ 75°C (% Wt. loss/day)	Impact Sensitivity* (kg-cm)
1,2,4-T Nitrate	137	182	0.88	>200
1,2,4-T Perchlorate	>250	285	0.02	114
1,2,4-T Dinitramide	75	120	0.29	98
4-AT Nitrate	70	180	0.58	>200
4-AT Perchlorate	83	242	0.02	30
4-AT Dinitramide	20	146	0.29	<5
TT Nitrate	206	245	0.20	>200
TT Perchlorate	194	275	<0.01	50
TT Dinitramide	145	160	0.13	196
1,2,3-T Nitrate	110	125	73.5	>200
1,2,3-T Perchlorate	73	200	0.05	<15
1,2,3-T Dinitramide	61	80	---	---
1-Amino-3-Methyl-1,2,3-T Nitrate	88	257	<0.01	>200

* Threshold initiation values where 5 consecutive “no go” results were obtained

Synthesis of Triazolium Salts and Their Physical Properties

All of the downselected salts listed in Table 2 were synthesized under this program to allow for further characterization. The 4-ATN, 4-ATP, and the 1-AMTN all possess melt points in an appropriate range for melt castable explosives. The remaining salts were prepared for their potential use in binary eutectic mixtures.

From a performance perspective, both the 4-amino-1,2,4-triazolium perchlorate (4-ATP) and the 1,2,4-triazolium perchlorate (TP) are the most attractive salts for the replacement of TNT because they are the most balanced molecules with high densities and high heats of formation. Although 1,2,4-triazolium perchlorate does not melt before it exotherms (285°C), solutions/eutectics with other energetic salts offer high theoretical explosive performance potential as discussed later in the report. Density measurements, X-ray crystallography, DSC, and heats of combustion were performed on these salts to confirm previous estimated and experimental values⁶. The densities obtained by helium pycnometer at 25°C for 1,2,4-TP and 4-ATP were 1.85 and 1.81 respectively. The x-ray single crystal structures of 1,2,4-triazolium perchlorate and 4-amino-1,2,4-triazolium perchlorate are shown below (Figure 2 and 3). The densities of the salts measured by helium pycnometer were approximately 95% of those obtained from the single crystal. X-ray crystallography studies were conducted at -176°C. Nonetheless, both are still significantly higher than that of TNT (1.65) and even slightly higher than RDX (1.80).

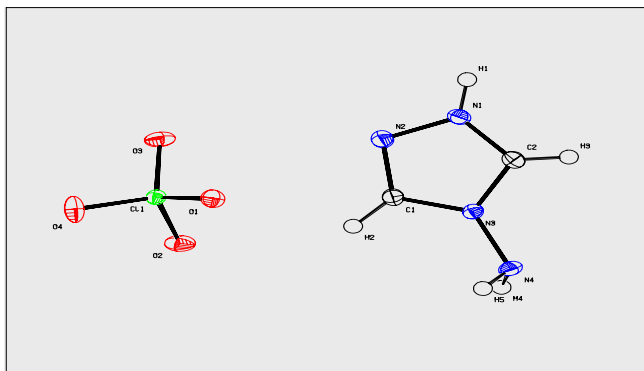


Figure 2. X-ray Crystal Structure of 4-Amino-1,2,4-Triazolium Perchlorate.
 $\rho = 1.91 \text{ g/cm}^3$ @ -176°C

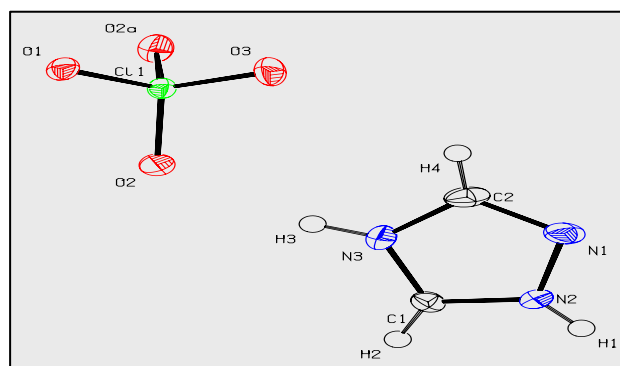


Figure 3. X-ray Crystal Structure of 1-H-1,2,4-Triazolium Perchlorate.
 $\rho = 1.96 \text{ g/cm}^3$ @ -176°C

Another candidate single salt with the potential to meet the program objective is 1-AMTN. Density measurements, X-ray crystallography, DSCs, and heat of combustion tests were also performed to characterize the physical properties of 1-AMTN. The density obtained by helium pycnometer at 25°C for 1-AMTN was 1.63 g/cc and the heat of formation was calculated to be $+20 \text{ kcal/mol}$ (Table 2) based on the measured value obtained for 1-amino-1,2,3-triazole ($+82 \text{ kcal/mol}$). Although the density of 1-AMTN is slightly lower than that of TNT (1.65), its superior heat of formation allows the performance to be competitive. The x-ray single crystal structure of 1-amino-3-methyl-1,2,3-triazolium nitrate is shown below (Figure 4).

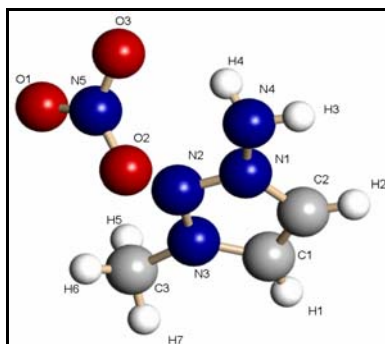


Figure 4. X-ray Crystal Structure of 1-Amino-3-Methyl-1,2,3-Triazolium Nitrate

DSC's were performed on the salts to confirm their melt points and exotherm onsets and give an indication of their purity. Accurate melt point data of the pure compounds was also desired before initiating the identification of eutectic compositions. The melt points, phase changes, and exotherms were very similar

to what has been previously reported⁷. The DSC plots in Figure 5 show the similarity in the melt point between 4-ATP, 1-AMTN, and TNT. The exotherm onset for 4-ATP and 1-AMTN did not take place until 242 and 257°C respectively.

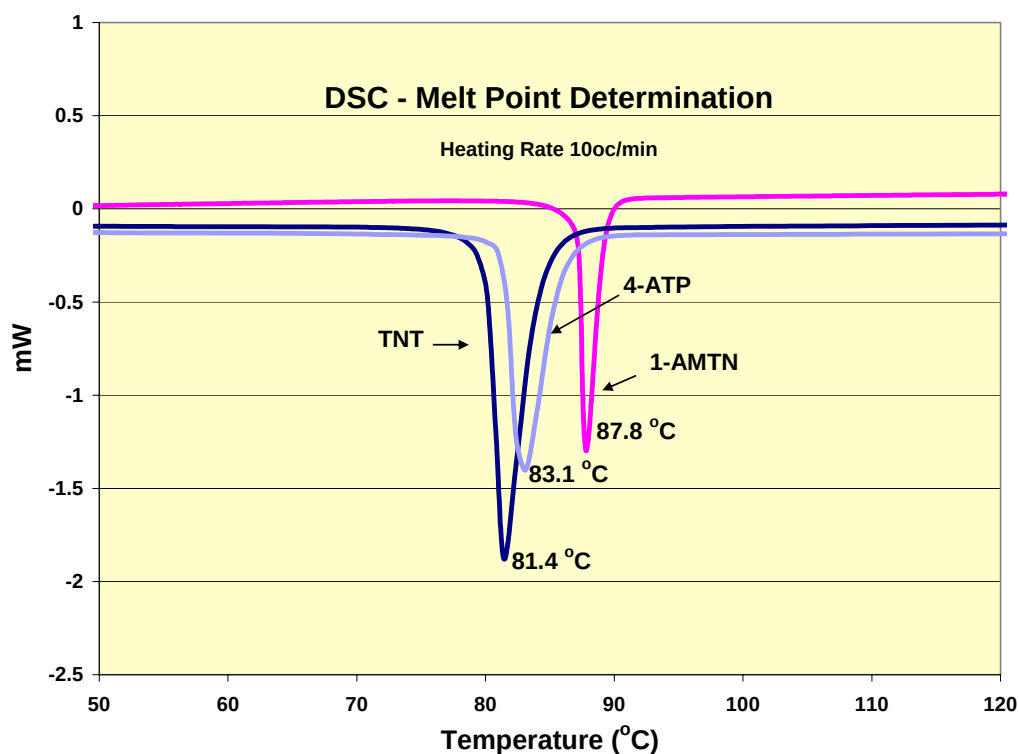


Figure 5. DSC Endotherms of TNT, 4-ATP, and 1-AMTN

The heats of formation of the parent heterocycles 1,2,4-triazole and 4-amino-1,2,4-triazole were measured by bomb calorimeter and were found to be lower than originally anticipated, but more than sufficient to attain the program objective. The more accurate estimated heats of formation of the subsequent salts and their measured physical properties are listed in Table 2.

The heat of formation 1-AMTN was conservatively estimated by using the value obtained for the 1-amino-1,2,3-triazole heterocycle, +82 kcal/mol. Typically, a decrease of 50 - 60 kcal/mol occurs when converting the heterocycles to the nitrate salts. A slight decrease in the heat of formation (-5 kcal/mol) was estimated for the addition of the methyl group. The estimated heat of formation of 1-AMTN and its measured physical properties are listed in Table 2. The measured density and impact sensitivity values for TNT were obtained and have been included for comparison in Table 2 and Table 5 respectively.

Table 2. Measured Physical Properties of Down-Selected Salts

Molecule	Melt Point °C	Density (g/cc)	Heat of Formation (kcal/mol)
TNT	81	1.65	-15*
1,2,4-T Nitrate	137	1.64	-34
1,2,4-T Perchlorate	>250	1.85 (1.96**)	-17
4-AT Nitrate	70	1.62	-10

4-AT Perchlorate	86	1.82 (1.91**)	5
TT Nitrate	206	1.52 est.	-63
TT Perchlorate	194	1.72 est.	-48
1-A-3-M-1,2,3 T Nitrate	88	1.63	20 est.

* Literature values⁷

** From single crystal x-ray crystallography at -176°C

The synthesis of several of the down-selected salts (4-ATP, 4-ATN, and TP) was scaled-up to the 50 gram level to allow for more in-depth evaluation. Synthesis was carried out by neutralization of commercially available triazoles dissolved in methanol with concentrated nitric and perchloric acids. The salts were crystallized out of solution with ether and dried under vacuum. Ultimately, the syntheses of several 50 gram batches were required to perform a rate stick test and to support the eutectic mixture task.

A great deal of effort was dedicated to the synthesis of 1-AMTN due to the fact that the starting heterocycle is not commercially available. The making of the 1-amino-3-methy-1,2,3-triazole cation is a two step process involving the cyclization of glyoxal bishydrazone. The addition of the alkyl group was accomplished by reacting the 1-amino-1,2,3-triazole with excess methyl iodide in acetonitrile. The resulting iodide salt was then converted to the nitrate salt by adding silver nitrate. Currently, this 4 step process is being scaled up to the 100 gram level.

Theoretical Performance Calculations

At the outset of the program, predictive explosive performance calculations were performed using Cheetah Code 2.0. This tool was used to screen for materials and mixtures capable of matching the performance of TNT. There are several explosive properties that may be employed to assess explosive performance (detonation pressure, detonation velocity, detonation energy, etc.). In many instances computed values were obtained where one performance property exceeded the performance of TNT while another was deficient. For this study, emphasis was placed on compounds or mixtures of compounds that were equivalent to TNT in total detonation energy.

One of the more attractive ingredients down-selected for further study, 4-ATP, has a theoretical performance that exceeds that of TNT and has an appropriate melt point for processing. Although seemingly sufficient, there is room for improvement in two areas. First, 4-ATP is slightly under-oxidized, and second it is moderately sensitive to impact (30 kg-cm). Several attempts were made to incorporate an oxidizer that would not depress the melt point, but would in fact improve the performance and lower the impact sensitivity. Three candidate oxidizers were selected; ammonium nitrate (AN), ammonium perchlorate (AP), and lithium nitrate (LN). All three are net oxidizers with densities greater than TNT and have low impact sensitivities. Cheetah calculations of 4-ATP with small amounts (20-30%) of AP or LN exhibit improved theoretical explosive properties that match those of RDX (Figure 6). It is conceivable that these oxidizers, whether soluble or not, could replace melt-cast explosive such as Comp B without the use of RDX. It remains to be seen whether the theoretical performances can be achieved utilizing an oxidizer that is not a completely homogenous system. With respect to AN addition, the theoretical performance of the mixture was lowered slightly compared to 4-ATP, but the mixture maintained theoretical total detonation energies well above that of TNT even at high AN concentrations (approaching 50%).

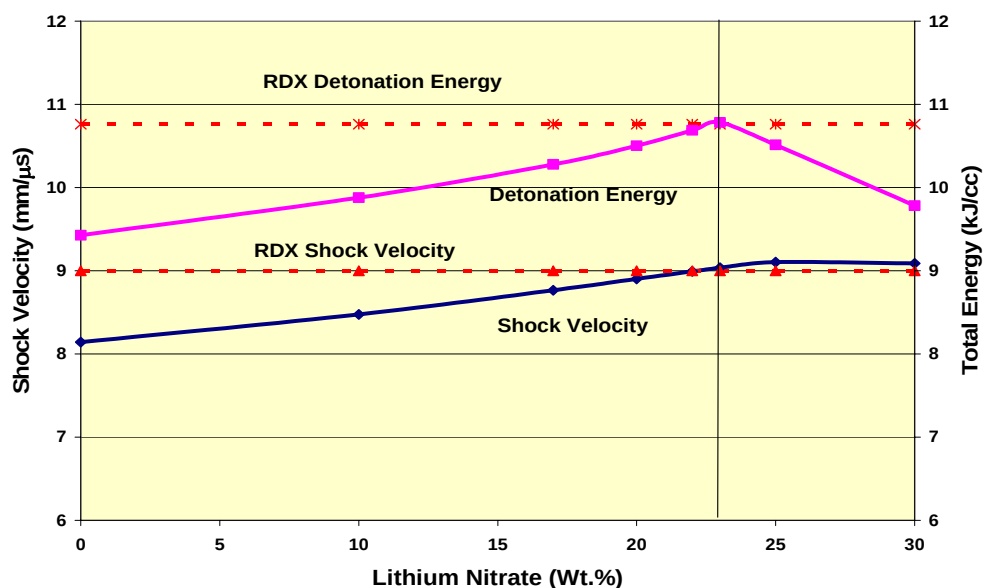


Figure 6. Theoretical Explosive Performance of Lithium Nitrate and 4-ATP

Additional calculations were performed using binary mixtures of compounds with the assumption that eutectics could be formed with melt points in the appropriate range. An example of such an investigated system was a mixture of 4-ATN and 4-ATP. Figure 7 depicts the concentrations of 4-ATP mixed with 4-ATN that meet or exceed the theoretical performance of TNT (highlighted triangular region). This type of plot was made for all the possible combinations of the down-selected triazolium salts before the experimental work in identifying eutectics was conducted.

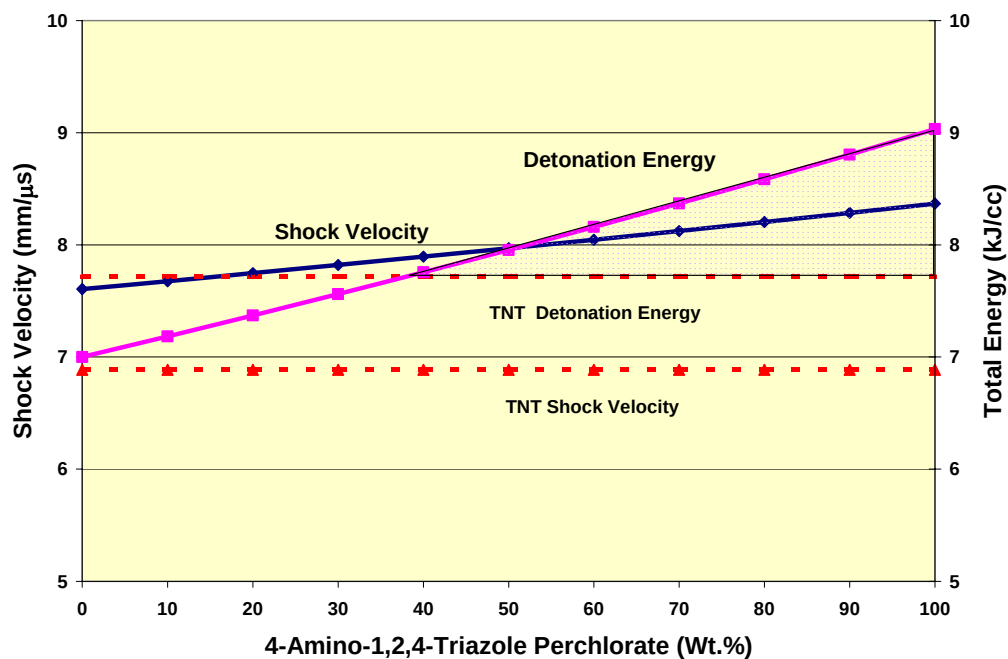


Figure 7. Theoretical Explosive Performance of Mixtures of 4-ATN and 4-ATP

The 1,2,4-triazolium perchlorate offers a theoretical performance exceeding that of 4-ATP partially due to its superior density and better oxygen balance. A number of calculations were made with this candidate and the other triazolium-based salts. The addition of oxidizers was also shown to improve the performance to a level equivalent with RDX. The use of TP as a sole ingredient is unlikely due to the lack of a melt point. Nonetheless, it was found to be quite soluble in some of the 4-AT-based salts. Table 3 lists the ingredients and binary mixtures and their predicted theoretical explosive parameters along with TNT and RDX for comparison.

Table 3. Predicted Detonation Properties using Cheetah 2.0 Code

Ingredients (Composition, Wt/Wt)	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/μs)	C-J Pressure (GPa)
TNT	7.716	6.886	19.57
4-ATP	9.032	8.368	29.94
4-ATP/4-ATN (40/60)	7.756	7.895	24.49
4-ATP/TN (50/50)	7.720	7.915	25.10
4-ATP/TTN (76/24)	7.719	7.947	25.25
4-ATP/TTP (49/51)	7.728	8.027	26.15
TP	8.820	8.306	29.91
TP/4-ATN (45/55)	7.754	7.902	24.86
4-ATP/AN (47/53)	7.753	8.331	26.44
4-ATP/AP (66/34)	10.188	8.590	30.55
TP/AP (71/29)	10.045	8.505	30.23
RDX	10.444 (10.761*)	8.942 (9.000*)	34.74 (33.78*)
4-ATP/LiN (77/23)*	10.783	9.035	34.49
TP/LiN (80/20)*	10.481	8.786	33.70

* Optimized using the BKWS gaseous equation of state

During the latter part of the program, predictive explosive performance calculations were repeated using a recently obtained beta version of Cheetah Code 4.0 from Lawrence Livermore National Laboratories. This version of Cheetah uses enhanced equations of state that allow improved predictions for compounds containing elements other than C,H,O, and N. The software package specifically claims improved results for compounds containing F and Cl. Since several of the salts under investigation under this program are perchlorate salts, this code was utilized to compare the performance of the most viable candidates with respect to TNT. The results of the new code were also compared to the results obtained using Cheetah 2.0, and although there was a slight difference in the numbers, the relative difference between compounds remained similar. The results using Cheetah 4.0 for the downselected candidates are presented in Table 4.

In addition to 4-ATP, the other single promising ingredient that has a theoretical performance that exceeds TNT, and has an appropriate melt point for processing is 1-AMTN. Although 1-AMTN is more fuel rich than 4-ATN, which does not meet the performance objectives, its superior heat of formation allows it to be competitive with TNT. The detonation energy is not nearly as high as that calculated for 4-ATP, however, 1-AMTN has the advantage of being significantly less sensitive to drop-weight impact and sliding friction stimuli. All the initial screening tests have been completed and the program is currently focusing on scaling up the production of 1-AMTN.

Additional calculations were also performed for the three eutectic mixtures identified in the next section. All three eutectics fell within the acceptable performance range identified using Cheetah 4.0.

Table 4. Predicted Detonation Properties using Cheetah 4.0 Code*

Ingredients (Composition, Wt/Wt)	Total Detonation Energy (KJ/cc)	Shock Velocity (mm/ μ s)	C-J Pressure (GPa)
TNT	7.389	6.843	17.90
4-ATP	8.911	8.516	31.39
4-ATP/4-ATN (70/30)	8.230	8.324	28.26
4-ATP/4-ATN (30/70)	7.408	8.075	24.74
4-ATP/TP (30/70)	8.784	8.462	31.44
1-AMTN	7.923	8.115	23.58

* Using new CHEETAH 4.0 Beta Version product library exp6.2

Eutectic Identification

To identify additional ionic liquids as TNT replacements, binary eutectic mixtures were explored. Unfortunately, it was not possible to prepare classic eutectic phase diagrams because of the very broad melts observed coupled with the slow solvation of one compound into the other. However, a series of each salt mixture being evaluated was melt-cast and then analyzed by DSC. Several eutectic mixtures were identified, though most exhibited a lower than desirable melt temperature. Even the addition of triazolium and oxidizing salts that have high melt temperatures (or no melt temperature) tended to be quite soluble and depress the melt point of the mixture below the desirable range of 70-100°C.

The first compounds targeted in this study were 4-ATN (m.p. 70°C) and 4-ATP (m.p. 83°C). 4-ATN is fuel rich and requires the addition of an oxidizer to meet the target performance. These salts were processed at 90°C in a heating block and the solubility of the other salts and the melt point of the resulting mixtures were ascertained by DSC. Several mixtures of 4-ATP and 4-ATN were prepared and two eutectics were identified, 4-ATN/4-ATP at (70/30 by weight or 3:1 molar ratio) as well as 4-ATN/4-ATP (30/70 by weight or 1:2 molar ratio). A third high performance eutectic mixture of 4-ATP/TP (70/30 by weight or roughly a 2:1 molar ratio) was also identified and characterized. As was found with the 4-ATP/4-ATN mixtures, the 4-ATP/TP melt points also could not be plotted to make a classic eutectic phase diagram. Very similar results with 4-ATN and 4-ATP mixtures were observed independently by Dr. John Wilkes and his team at the Air Force Academy in Colorado Springs, CO. They reported finding the 4-ATN/4-ATP (70/30) eutectic as well, but had difficulty in completing a phase diagram. Therefore just the melt points of the eutectics discovered at AFRL along with their measured densities and hazard data have been tabulated in Table 5.

The DSC plots of all the eutectics investigated exhibited slightly broader endotherms than a pure material, but showed symmetrical curves indicating that the mixtures are indeed acting as a single material. Unfortunately, all of the eutectic mixtures discovered melted in the 63-68°C range. Although the melt temperatures were close to the target range, the problem was coupled with the inability to reliably reproduce the same melt point using different batches of starting materials. It is believed that the introduction of small amounts of moisture or some other impurity in each case had the effect of significantly depressing the eutectic melt temperature.

It was also attempted to make mixtures of triazolium perchlorate (TP) with thermally stable, high melting ionic oxidizers such as lithium nitrate, AP, and AN. Due to the high melting nature and poor solubility of the TP, this required the use of acetonitrile to break the lattice structure of the salts. The samples were then heated to remove the acetonitrile. It was extremely difficult to remove all of the acetonitrile even when heated above its boiling point, and consequently nearly all of the samples contained both a liquid and a solid phase which made any assessment impossible. The use of an alternative solvent should be investigated.

Table 5. Physical and Hazard Properties of Eutectic Mixtures

Ingredients (Composition, Wt/Wt)	Melt Temperature (°C)	Density of Melt at 25°C (g/cc)	Impact Sensitivity* (Kg- cm)	Friction Sensitivity* (N)
TNT	81	1.64	>200	>371
4-ATP	86	1.82	30	27
4-ATP/4-ATN (70/30)	63	1.63	138	88
4-ATP/4-ATN (30/70)	66	--	>200	>371
4-ATP/TP (70/30)	67	1.80	32	29
4-ATN	70	1.62**	>200	371
1-AMTN	88	1.63**	>200	>371

* Threshold initiation values where 5 consecutive “no go” results were obtained

** Density of the powdered material

Future work with eutectic mixtures containing 1-AMTN may also be worth pursuing. 1-AMTN is fuel rich and the overall performance would benefit from the addition of a more balanced salt. Current efforts are now focused on evaluating the pure material before making any blends due to a short supply of material.

Safety/Sensitivity Assessment

Initial small-scale hazard tests have been completed on all of the candidate individual salts and promising eutectic compositions, as well as a TNT baseline (Table 5). It was interesting to note the effects of eutectic mixtures employing 4-ATP. The addition of TP had no significant effect on the hazards of 4-ATP even at a 30% by weight concentration. In contrast, the addition of 4-ATN to 4-ATP immensely improved the sensitivity of the mixture. Consequently, the 4-ATN/4-ATP (70/30) eutectic mixture appeared to be the most promising candidate for continued investigation. Unfortunately, the fact that the melt point of the mixture fell below the 70°C threshold precluded it from further testing. The relative insensitivity of 1-AMTN was very encouraging. 1-AMTN passed all the initial screening tests and proved attractive enough to warrant VTS testing.

Since TNT is such an ideal compound with respect to compatibility with metals and other energetics such as nitramines and oxidizers, it is important to evaluate the thermal stability of candidate ingredients with these materials by both DSC and VTS. Crude baseline screening has been performed with 4-ATP and contaminate materials such as steel, iron oxide, and copper before casting is to take place. No reaction was observed when these materials were added to 4-ATP at 90°C for 15 minutes. More quantitative testing is recommended in future work.

VTS tests were performed on 4-ATP and 1-AMTN and compared to a TNT baseline. The VTS apparatus is shown below in Figure 8. A 1 gram sample of each material was dried under vacuum at 50°C for 24 hours and analyzed by TGA prior to being tested. The VTS Test was performed at 100°C for 48 hours (Table 6). TNT showed no significant weight loss which corresponds to the literature value of 0.005 cc gas/g @ STP.⁷ Under the same conditions, 4-ATP evolved ~0.10 cc gas/g @ STP and 1-AMTN evolved ~0.04 cc gas/g @ STP which is well below the pass/fail criteria of 2 cc gas/g cited in Mil STD 1751A. Slight fluctuations in the pressure profiles were observed with all the runs because the decomposition rates were so low that the pressure changes were well below the recommended range of the pressure transducers.

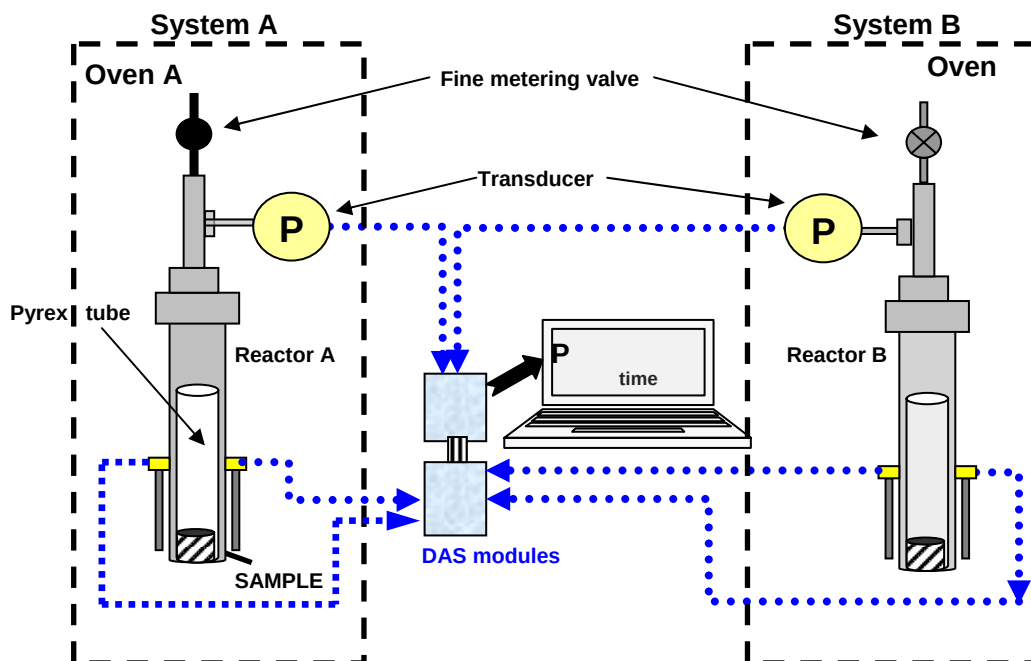


Figure 8. Diagram of the Vacuum Thermal Stability Test Apparatus

Both the 4-ATP and 1-AMTN test runs started at a measured pressure of 10 – 30 torr. These pressure readings were attributed to a small amount of volatiles (residual moisture or free base) not completely removed during the drying process. This initial rise in pressure only occurred while ramping the heat to the run temperature. The values obtained for both materials represent the most conservative estimates of the decomposition that took place once the run temperature was achieved.

Table 6. Vacuum Thermal Stability Test Results

Ingredients	VTS at 100°C for 48 hrs (cc gas/g @ STP)
TNT	0.00
4-ATP	~0.10
1-AMTN	~0.04

Shock Velocity Measurements

For this task a 0.75 inch confined critical diameter test was conducted to measure detonation velocities as a verification tool of the theoretical performance predictions. The AFRL modified “rate stick” test (Figure 9) was initially developed as a small-scale hazard test that requires less than a third of the material of a standard NOL Card-Gap test. It consists of a 0.75 inch I.D., 6.0 inch long steel pipe (L/D =8) with 0.125 inch thick walls. A 0.25 inch steel witness plate is used, and the pipe is instrumented with 6 piezoelectric crystal pins connected to a LeCroy oscilloscope to measure the shock front arrival times. The shock input is supplied by a C-4 donor with an L/D of 1. In previous efforts this test has been used successfully for screening salt-based monopropellants, and has shown a good correlation with the theoretical predictions of standards such as 1,1,1-trimethylolethane trinitrate (TMETN).



Figure 9. AFRL Modified Rate Stick Test Configuration

For this effort, TNT was provided by Dr. May Chan (NAWC/China Lake) and was tested as the baseline material. The subsequent test was performed using 4-ATP. Both test articles were prepared by a melt-cast process. The resulting shock velocity measurements were then plotted as a function of pipe distance in diameters (Figure 10). The average shock velocity of 4-ATP (8.3 mm/ms) is significantly faster than that of the TNT (6.3mm/ms), thus confirming the theoretical predictions. The 4-ATP results closely matched the Cheetah 4.0 theoretical prediction of 8.52 mm/ms @ TMD. Although the shock velocity for TNT was slightly lower than the prediction (6.9 mm/ms @ TMD), the result corresponds to the value one might expect at 90% TMD which is in the range of what has been reported for TNT melt-cast densities.⁷

Shock Velocity in 3/4" Confined Test

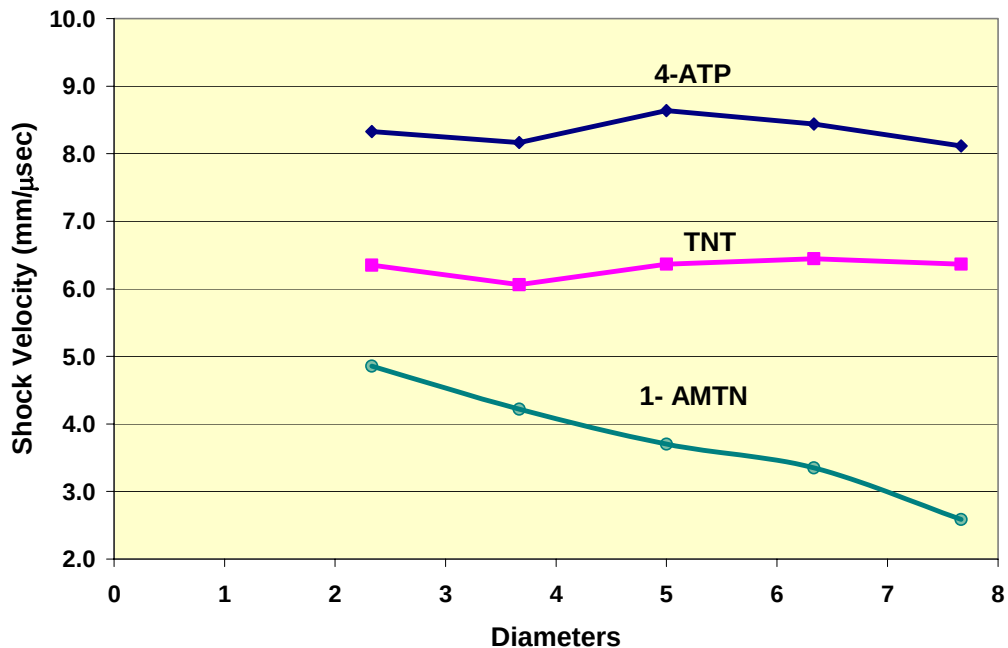


Figure 10. Shock Velocity Profiles of 4-ATP, 1-AMTN, and TNT in AFRL Modified Rate Stick Test

The rate stick test containing 1-AMTN surprisingly did not sustain a constant shock velocity at 96% TMD (Figure 8). In fact, the velocity profile decayed rapidly to sonic velocity. Barring an unknown error that may have occurred during the test preparation, it appears the critical diameter of 1-AMTN is greater than 0.75 inches. If this is indeed correct, 1-AMTN may be a good candidate material for insensitive munitions applications. Additional quantities are being synthesized to elucidate the properties of this material.

Overall, the ionic liquid, 4-ATP, shows promise for obtaining superior performance to TNT while maintaining desirable stability properties above the lower threshold values targeted at the outset of the program. There is room for improvement with regards to the impact and friction hazards of 4-ATP. To that end, current efforts are focused on preparing several batches of 1-AMTN to validate its theoretical performance.

SUMMARY

Several families of triazolium-based energetic ionic liquids synthesized at AFRL have been assessed as potential TNT replacements in melt cast applications as either a single salt or in a binary eutectic mixture. Two candidate salts, 4-amino-1,2,4-triazolium perchlorate (4-ATP) and 1-amino-3-methyl-1,2,3-triazolium nitrate (1-AMTN), exhibited properties that demonstrated the feasibility of replacing TNT with an ionic liquid. Both salts easily passed accepted thermal stability tests, have appropriate melt points (83-87°C), and have superior calculated performance over TNT. The theoretical performance of 4-ATP was realized in a rate stick test which determined the shock velocity (key indicator of explosive performance) to be 8.3 km/s versus 6.3 km/s achieved with TNT under the same test conditions. This test validated the potential performance advantage afforded by ionic liquids.

With 4-ATP however, there is needed improvement in the small scale hazards. The drop weight impact sensitivity of 4-ATP although sufficient to meet the initial screening criteria of >20 kg-cm, was less than desirable (32kg-cm). The addition of 4-amino-1,2,4-triazolium nitrate (4-ATN) was found to have a stabilizing effect and significantly reduced the impact and friction sensitivity of 4-ATP. Two eutectic mixtures, 70/30 and 30/70 by weight (4-ATP/4-ATN), were identified, but did not solve the situation as their melt points were suppressed to 63-67°C (below the target range of 70-100°C). Unfortunately, all eutectics identified and all mixtures with other triazolium salts and conventional oxidizers during this program had greatly suppressed melt points. The sensitivity issue of 4-ATP was not solved without compromising an adequately high melt point.

Conversely, 1-AMTN did not exhibit sensitivity in small scale hazards testing. In fact, all the test results obtained with 1-AMTN compared favorably to TNT. 1-AMTN has a theoretical explosive performance that is slightly higher than that of TNT. However, since 1-AMTN did not sustain a shock velocity at 0.75 inches in diameter, a larger diameter rate stick test must be performed to confirm its performance. Although the density is slightly lower than TNT (1.63 g/cc) and both materials are fuel rich, it is believed that the superior heat of formation of 1-AMTN more than compensates for the difference.

1-AMTN appears to successfully meet all of the objectives proposed for this program and certainly warrants further investigation. Additional testing to confirm its properties and evaluate properties such as compatibility with other conventional explosive materials, explosive performance, critical temperature, and critical diameter should be performed. Several other novel triazolium-based salts targeted for synthesis at AFRL may also be worth investigation.

ACKNOWLEDGEMENTS

We gratefully acknowledge the support for this program from our ONR sponsors Dr. J. Goldwasser and Dr. C. Bedford. In addition, we thank Dr. Michael Berman of AFOSR for sponsoring our ionic liquid fundamental synthesis effort. We thank Dr. R. Doherty of NSWS-IH for her encouragement and helpful discussions on this work. We also appreciate the effort of Lt. L. Hall for his ingredient synthesis work, and the technical support of Mr. M. McKay and Mr. M. Bowen during the explosive testing and evaluation.

Finally, we want to acknowledge the strong encouragement we have received for this work from Mr. M. Huggins, Dr. R. Corley, Dr. R. Channell, and Mr. W. Kalliomaa.

REFERENCES

1. Wilkes, J.S., "A Short History of Ionic Liquids – From Molten Salts to Neoteric Solvents", *Green Chemistry*, Vol 4, 2002.
2. Welton, T., "Room Temperature Ionic Liquids", *Chem. Rev.*, Vol 99, 1999.
3. Wasserscheid, P. and Keim, W., "Ionic Liquids – New 'Solutions' for Transition Metal Catalysis", *Angew. Chem. Int. Ed. Engl.*, Vol 39, 2000.
4. Seddon, K.R., "Room Temperature Ionic Liquids: Neoteric Solvents for Clean Catalysis", *Kinet. Catal.*, Vol 37, 1996.
5. Doherty, R.M., Communication to the authors, OUSD (S&T)/WS, Arlington VA, 3 December 2002.
6. Drake, G., Hawkins, T., Brand, A., Hall, L., McKay, M., Vij, A., and Ismail, I., "Energetic, Low-Melting Salts of Simple Heterocycles", *Propellants, Explosives, Pyrotechnics*, Vol 28, No. 4, 2003.
7. Dobratz, B.M., "LLNL Explosives Handbook, Properties of Chemical Explosives and Explosive Simulants", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-52997, March 16, 1981.