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Title: High-Nitrogen Explosives

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ABSTRACT

The syntheses and characterization of various tetrazine and furazan compounds offer a different approach to explosives development. Traditional explosives—such as TNT or RDX—rely on the oxidation of the carbon and hydrogen atoms by the oxygen carrying nitro group to produce the explosive energy. High-nitrogen compounds rely instead on large positive heats of formation for that energy. Some of these high-nitrogen compounds have been shown to be less sensitive to initiation (e.g. by impact) when compared to traditional nitro-containing explosives of similar performances.

Using the precursor, 3,6-bis-(3,5-dimethylpyrazol-1-yl)-s-tetrazine (BDT), several useful energetic compounds based on the s-tetrazine system have been synthesized and studied. The compound, 3,3'-azobis(6-amino-s-tetrazine) or DAAT, detonates as a half inch rate stick despite having no oxygen in the molecule. Using perfluoroacetic acid, DAAT can be oxidized to give mixtures of N-oxide isomers (DAATO3.5) with an average oxygen content of about 3.5. This energetic mixture burns at extremely high rates and with low dependency on pressure.

Another tetrazine compound of interest is 3,6-diguanidino-s-tetrazine (DGT) and its dinitrate and diperchlorate salts. DGT is easily synthesized by reacting BDT with guanidine in methanol. Using Caro's acid, DGT can be further oxidized to give 3,6-diguanidino-s-tetrazine-1,4-di-N-oxide (DGT-DO). Like DGT, the di-N-oxide can react with nitric acid or perchloric acid to give the dinitrate and the diperchlorate salts.

The compounds, 4,4'-diamino-3,3'-azoxyfurazan (DAAF) and 4,4'-diamino-3,3'-azofurazan (DAAzF), may have important future roles in insensitive explosive applications. Neither DAAF nor DAAzF can be initiated by laboratory impact drop tests, yet both have in some aspects better explosive performances than 1,3,5-triamino-2,4,6-trinitrobenzene TATB—the standard of insensitive high explosives. The thermal stability of DAAzF is equal to that of hexanitrostilbene (HNS), yet it has a greater CJ pressure and detonation velocity. In an effort to reduce the critical diameter of TATB without sacrificing its insensitivity, we have studied the explosive performances of TATB mixed with DAAzF (X-0561) and TATB mixed with DAAF (X-0563).

Introduction

At Los Alamos National Laboratory, the synthesis of compounds high in nitrogen content has been the focus of our efforts for the past decade. A majority of these compounds derive most of their energy from the heat of formation rather than from the oxidation of the carbon backbone, such as with traditional energetic materials. The increased nitrogen content in the molecular framework typically leads to higher densities and the reduced amounts of hydrogen and carbon allow the oxygen balance to be achieved more easily. Our investigation of the furazan and 1,2,4,5-tetrazine (also known as s-tetrazine) heterocycles has offered a different approach to energetic materials development.

Tetrazine Explosives

Los Alamos has spent considerable effort on energetic tetrazine systems. The tetrazine ring is only exceeded in its nitrogen content by the tetrazoles and yet this ring system has largely been unexplored for use in energetic materials. The precursor for most of the tetrazines that we have synthesized is the useful intermediate, 3,6-bis-(3,5-dimethyl-pyrazol-1-yl)-s-tetrazine (BDT). This compound is easily prepared from triaminoguanidine hydrochloride and 2,4-pentanedione followed by oxidation (Figure 1)[1]. Reaction of BDT with two equivalents of hydrazine yields 3,6-dihydrazino-s-tetrazine (Figure 2, DHT)[2,3], which is a highly energetic fuel having a measured heat of formation of +536 kJ/mol and a H_{50} of 65 cm (2.5 kg, Type 12). DHT detonates unconfined (Dv=7.54 km/s, ρ=1.56) at 0.50 inches and calculates to perform well in both rocket and gun propellant applications, which is partly attributed to its high hydrogen makeup. DHT is an example of a high-nitrogen compound that can sustain a detonation using chemical energy solely derived from its heat of formation rather than combustion-like reactions.

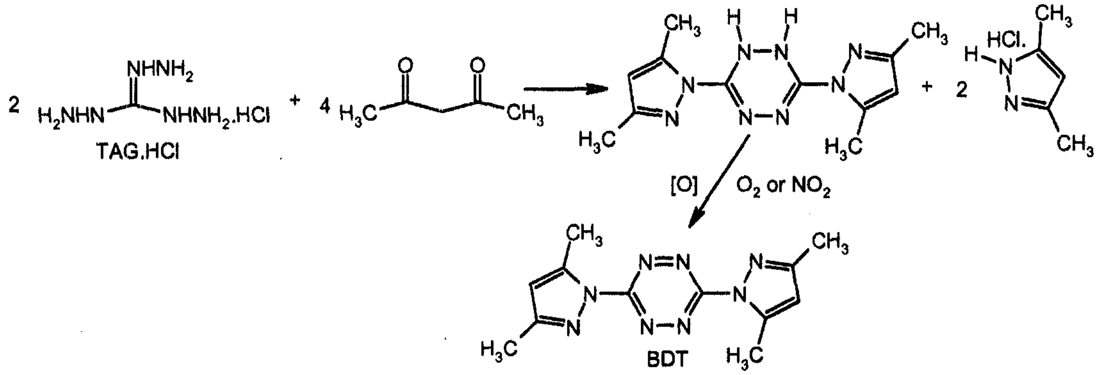

Figure 1. *The important precursor of most tetrazine compounds, BDT, is synthesized from triaminoguanidine hydrochloride and 2,4-pentanedione followed by oxidation by oxygen or nitrogen dioxide.*

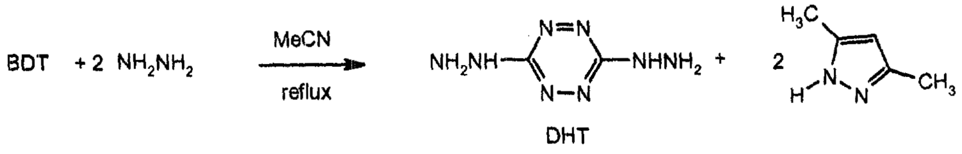

Figure 2. *Synthesis scheme of 3,6-dihydrazino-s-tetrazine (DHT).*

Interest in the synthesis of azo-s-tetrazines came in part from our previous calorimetric studies of compounds containing the hydrazo, azoxy and azo groups. There is a large increase in internal energy in the conversion of the hydrazo group to either the azo or azoxy group. Extrapolating from these data, we speculated that the following target compound containing the azo group, 3,3'-azobis(6-amino-s-tetrazine) (DAAT) would have a very large, positive heat of formation due to the intrinsically energy-rich s-tetrazine ring. Figure 3 gives the synthesis scheme for the formation of DAAT[2]. The precursor, 3,3'-hydrazobis[6-(3,5-dimethylpyrazol-1-yl)-s-tetrazine] (HDPT) is easily generated by treatment of BDT with 0.5 equivalent of hydrazine in isopropyl alcohol. While a variety of oxidizing reagents were tested in the oxidation of the hydrazo group to an azo moiety, none was as effective as *N*-bromosuccinimide (NBS), which also brominated the 3,5-dimethyl-pyrazol-1-yl rings to give the azo compound, 3,3'-azobis[6-(4-bromo-3,5-dimethylpyrazol-1-yl)-s-tetrazine] (ABDPT). Treatment of ABDPT with ammonia in dimethylsulfoxide (DMSO) produces DAAT as a bis-DMSO solvate in about 50% yield. Pure DAAT free of DMSO is obtained by treatment of the solvate with boiling water.

Analysis of the bis-DMSO solvate of DAAT by X-ray crystallography revealed that the molecules are in an *E*-configuration and form planar sheets despite the DMSO molecules present in the crystal. A density of 1.526 g/cm^3 was determined from the X-ray crystal structure of the bis-DMSO solvate, while a density of 1.78 g/cm^3 was measured for the pure material. This is likely to be the most dense C, H, N molecule known and is attributed to the graphite-like structure of DAAT.

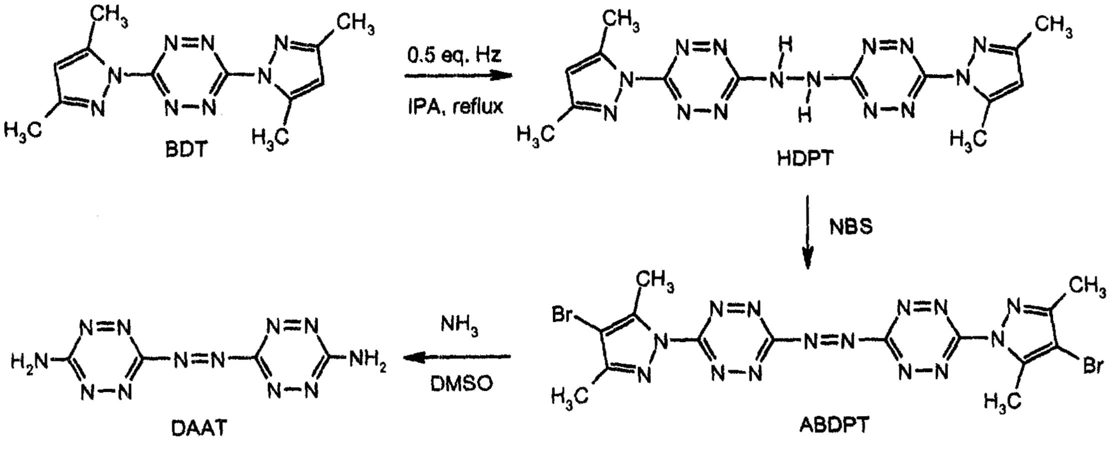

Figure 3. *General synthesis scheme of 3,3'-azobis(6-amino-s-tetrazine) (DAAT).*

The pure material is thermally stable to 252°C by DSC and the ΔH_f was measured to be +862 kJ/mol by combustion calorimetry. This is a very high heat of formation and when normalized on a per atom basis, a value of 43.1 kJ/atom is realized. Some sensitivity properties include a drop weight impact value of 70 cm while the popular high-explosive HMX is 25 cm. The compound is insensitive to initiation by spark (>0.36 J) or friction (BAM, >36 kg).

A poly-rho test was performed on DAAT formulated with 5% Kel-F 800 (Figure 4), which demonstrated the performance of a non-oxygen containing explosive. The poly-rho test can be described as an explosive rate stick composed of pellets with increasing density. Between each pellet is a Mylar® foil switch that can detect the arrival of a detonation front. Typically a booster train of PBX 9407 pellets is used to initiate the rate stick at the low density end, while the times for the detonation front to travel the distance of each pellet are recorded by an oscilloscope. In essence, the poly-rho test is a single shot experiment that yields detonation velocity as a function of explosive density.

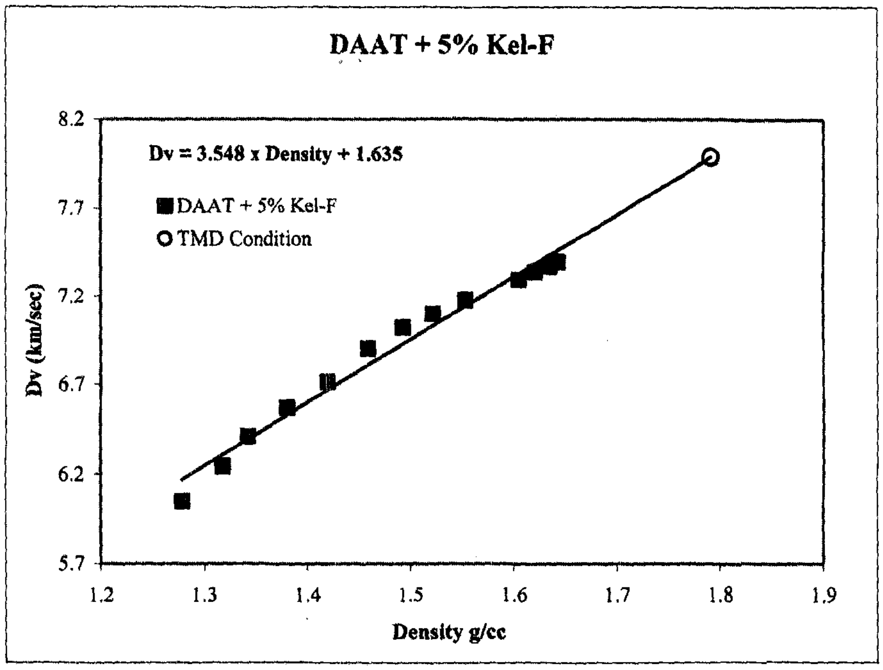

Figure 4. *Poly-rho data for DAAT with 5 weight percent Kel-F 800 binder. The fitted line is extrapolated to the theoretical maximum density (TMD) of the explosive.*

We oxidized DAAT with pertrifluoroacetic acid in methylene chloride in the effort to improve the density and explosive performance of DAAT (Figure 5)[2]. What we obtained was a mixture of various N-oxides of DAAT with an average oxygen content of approximately 3.5 as determined by CHN analysis. We attempted to isolate one or more pure N-oxides from the mixture by recrystallization from DMF solvent, but only 3,3'-azobis(6-amino-5-N-oxide-s-tetrazine) (or more simply the di-N-oxide of DAAT) could be isolated and identified by X-ray crystallography. This mixture of N-oxides, which we name as DAATO3.5, burns at exceptionally high rates and with low dependency on pressure, two attributes that are desirable in high-performance propellant applications. Figure 6 shows the burn rate plot of DAATO3.5 along with that of HMX, a popular propellant ingredient. From the plot the pressure exponent of DAATO3.5 measures at 0.27. Table 1 gives some sensitivity data for the mixture. DAATO3.5 is sensitive to friction and spark; friction testing on the BAM apparatus gave highly varied results with 15 goes out of 25 between 2 and 14 kilograms. However, these sensitivities can be attenuated by the addition of binder. We found the addition of 5% polyvinyl alcohol (PVA) and 1% triethylene glycol plasticizer (TEG) eliminated its sensitivity to spark and reduced friction sensitivity to about 17 kg (BAM); the impact sensitivity (H_{50}) also decreased, changing from 20 to 32 cm (2.5 kg, Type 12). The density of DAATO3.5 was found to be relatively high by gas pycnometry (ca. 1.88), especially so for a mixture of compounds. However, we found that we could not press DAATO3.5 to densities greater than 80% of theoretical maximum density (TMD), which we attribute to its unusual morphology. A scanning electron micrograph (SEM) of DAATO3.5 powder revealed the material to have an extremely porous structure, almost resembling that of coral.

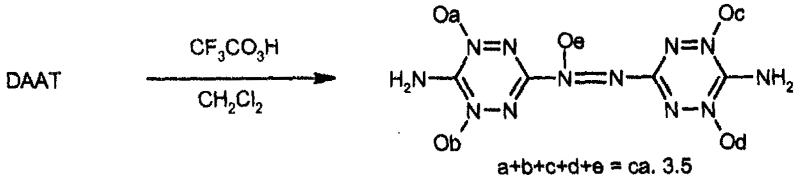

Figure 5. *Synthesis scheme for the oxidation of DAAT.*

Other tetrazine explosives include the nitrate and perchlorate salts of 3,6-diguanidino-s-tetrazine. Similar to the synthesis of DHT (Figure 2), the diguanidino derivative is prepared by reacting BDT with a slight excess of guanidine in methanol solvent (Figure 7). The resulting crude product, which contains the 3-guanidino-6-methoxy-s-tetrazine as an impurity, is recrystallized from dilute perchloric acid to produce in pure form the diperchlorate salt of DGT. The explosive properties of this salt are listed in Table 2. Pure DGT is obtained by treating the diperchlorate salt with aqueous sodium hydroxide to produce a dark red solid, which is filtered and dried. The water-insoluble dinitrate salt of DGT is easily obtained by triturating purified DGT with excess nitric acid in water and filtering. The explosive properties of the dinitrate salt are also listed in Table 2. The poly-rho data of the diperchlorate and dinitrate salts of DGT are shown in Figures 8 and 9 respectively.

	DAATO3.5	DAATO3.5 with 5% PVA + 1% TEG
H_{50} (cm), Type 12	20	32
Onset (°C)	177	169
Spark Sensitivity at 0.36 Joules	13 goes out of 13	0 goes out of 13
Friction (BAM, kg)	between 2-14	> 36

Table 1. *Sensitivity data for DAATO3.5.*

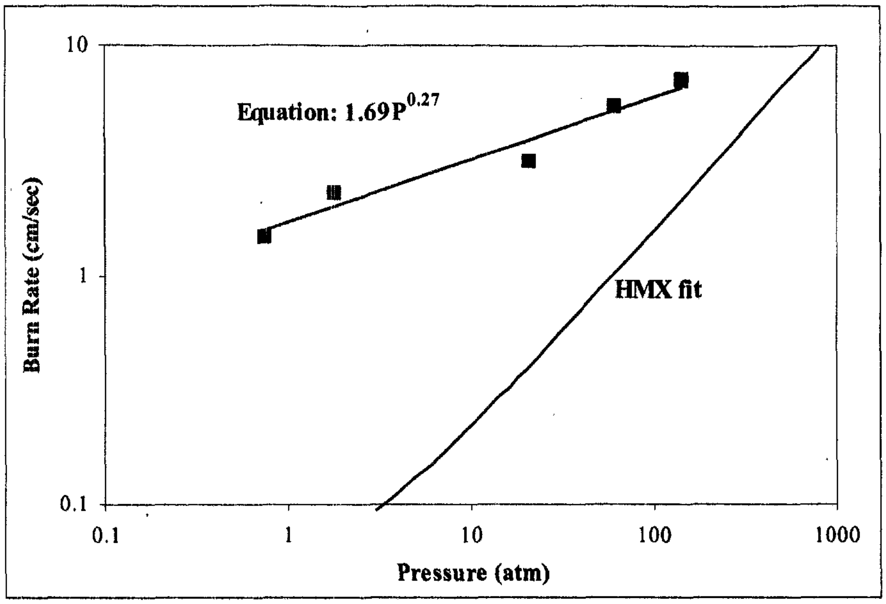

Figure 6. *Burn rate data of DAATO3.5 along with fitted burn rate data of HMX reference. DAATO3.5 is perhaps the fastest burning organic material known.*

Oxidizing DGT with Caro's acid to form the di-N-oxide (DGT-DO, Figure 7) can increase the oxygen balance of DGT. The diperchlorate salt of DGT-DO is nearly CO_2 balanced and has a measured density of 1.94 g/cm^3; the onset of thermal decomposition is 195°C by DSC. The calculated detonation velocity at TMD is 9.1 km/sec with a P_{CJ} of 360 kbar. Unfortunately, this salt has a H_{50} of 10 cm, which is comparable to that of PETN. The dinitrate salt of DGT-DO was also synthesized, but it was found to be an unstable material, having a DSC onset of 115°C.

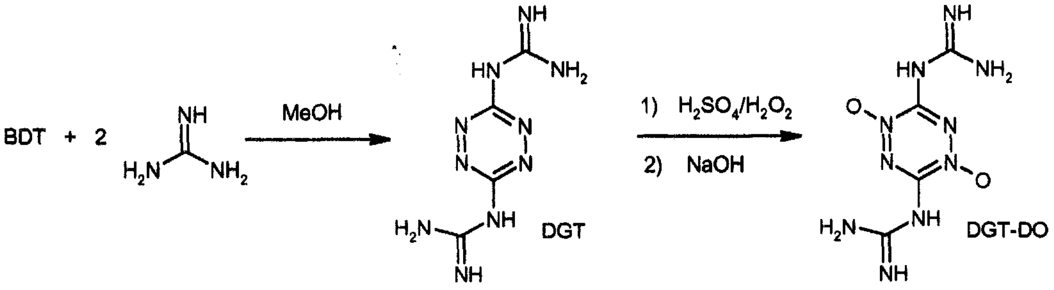

Figure 7. *Synthesis scheme of DGT and its oxidation to the di-N-oxide.*

	Diperchlorate Salt	Dinitrate Salt
Dv (km/s) [Density, g/cc]	8.07 [1.79]	7.31 [1.60]
H_{50} (cm), Type 12	24	116
P_{CJ} (kbar) [Density, g/cc]	312 [1.794]	284 [calc]
Onset (°C)†	265	226
Density (g/cm) †	1.90	1.72
Spark (0.36 J) †	> 0.36	> 0.36
Friction (BAM, kg) †	8.6	> 36

Table 2. *Explosive properties of the diperchlorate and dinitrate salts of DGT. †For pure explosive only.*

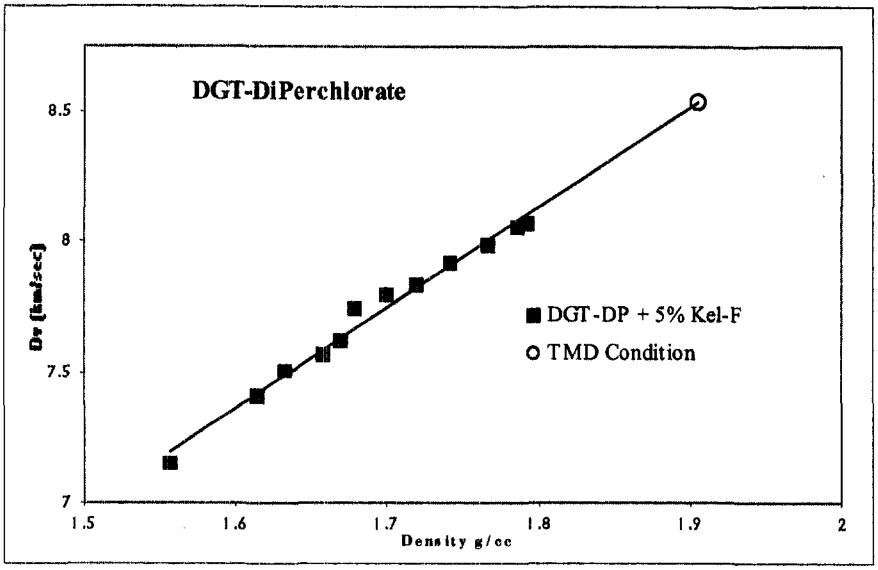

Figure 8. *Poly-rho data of the diperchlorate salt of DGT. Fitted line is extrapolated to the theoretical maximum density of this explosive.*

Furazan Explosives

The compound 3,4-diaminofurazan (DAF) is a useful precursor to two furazan explosives, namely 3,3'-diamino-4,4'-azoxyfurazan (DAAF), 3,3'-diamino-4,4'-azofurazan (DAAzF) along with a relatively unstable impurity, 3-amino-4-nitrofurazan (ANF, Figure 11) . DAF was first reported by our laboratory in 1968, but was later extensively examined by the Russians[4] who used a variety of peroxide reagents to form mixtures of DAAF, DAAzF and ANF. These mixtures were difficult to separate and purify, and the contaminant ANF depressed their stability. We found that DAAF could be synthesized fairly purely and in high yield by oxidizing DAF with sulfuric acid and hydrogen peroxide. This is followed by recrystallization from DMSO/water to remove trace ANF.

Pure orange-yellow DAAF has a DSC onset of 248°C and an X-ray crystal density of 1.747 g/cm^3. The heat of formation (ΔH_f) was measured to be +443 kJ/mol by combustion calorimetry. DAAF has a drop height (H_{50}) greater than 320 cm (2.5 kg, Type 12) and elicits no response to spark (>0.36 J) or friction (>36 kg, BAM). A Henkin critical temperature was determined to be 252°C for pure DAAF while DAAF formulated with 5 volume percent of Kel-F 800 binder has a critical temperature of 241°C.

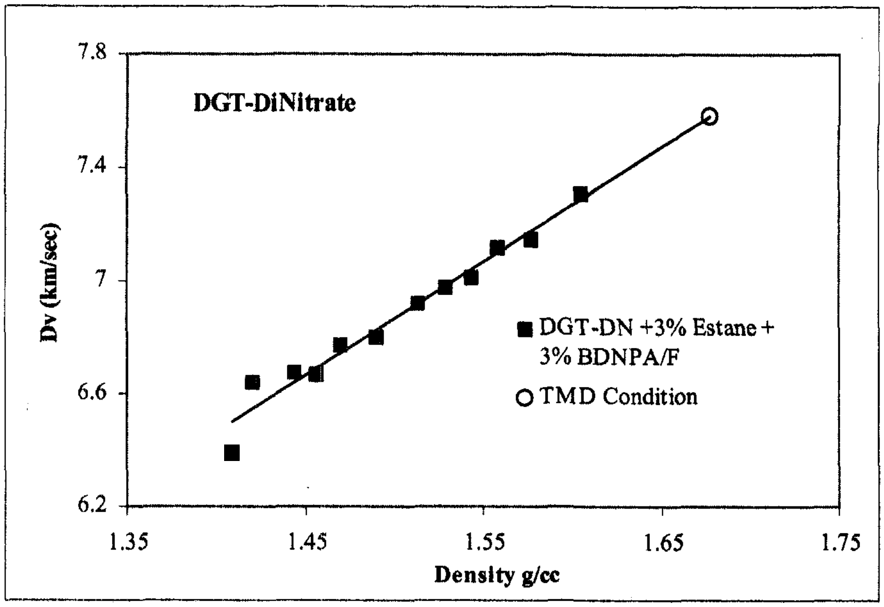

Figure 9. *Poly-rho data of the dinitrate salt of DGT. Fitted line is extrapolated to the theoretical maximum density of this explosive.*

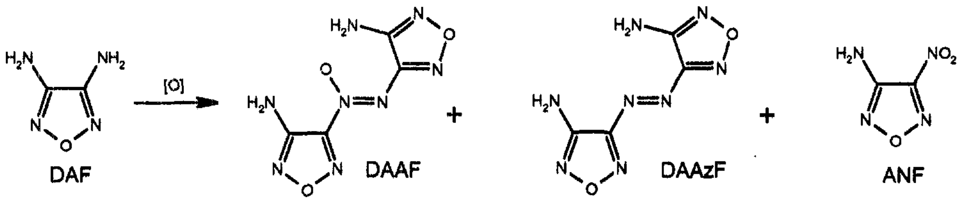

Figure 10. *The furazan precursor, 3,4-diaminofurazan (DAF), readily oxidizes to form mixtures of DAAF, DAAzF and ANF.*

A poly-rho test of DAAF performed at two diameters, 0.50 and 0.25 inches (0.50 inch poly-rho data are plotted in Figure 13) revealed that detonation velocity is relatively independent of diameter[5]. These data were further verified by detonating an unconfined rate stick of pellets at a density of 1.69 g/cm^3 and 3 mm in diameter atop a witness plate. A failure diameter of less than 3 mm is unprecedented in a material which is insensitive to impact. The detonation pressure (P_{CJ}) was estimated to be 299 kbar from a 0.50 inch diameter plate dent at a density of 1.69 g/cm^3.

In addition, the shock sensitivity of DAAF (with 5 wt. % Kel-F binder) was characterized by performing six wedge tests[5]. The resulting Pop plot demonstrated that DAAF is similar to HMX in terms of shock sensitivity. This is very unusual for an explosive that can not be initiated by impact and clearly bucks the sensitivity-performance relationship that is typical of traditional explosives.

The explosive DAAzF has excellent thermal properties having a DSC onset comparable to that of HNS (315°C) and a measured ΔH_f of +536 kJ/mol, which is greater than that of DAAF. DAAzF is synthesized by reducing DAAF with zinc and acetic acid to form the hydrazo intermediate, 3,3'-diamino-4,4'-hydrazofurazan (DAHF), followed by its oxidation to the azo-derivative (Figure 11). Despite its large internal energy, DAAzF is insensitive to impact (H_{50}>320 cm, Type 12), spark (>0.36 J) and friction (>36 kg, BAM). When compared to DAAF, DAAzF has lower detonation velocity and CJ pressure, presumably because the increase in the heat of formation is not sufficient to offset the loss of the one azoxy oxygen in the molecule (see Table 3). The poly-rho detonation velocities of DAAzF when shot as two different diameter rate sticks (0.50 and 0.25 inches, with 0.50 inch data plotted in Figure 12) were found to be dependent on diameter. But despite this dependence, a 3 mm diameter shot at a density of 1.65 g/cm^3 detonated cleanly with no confinement. A 0.50 inch diameter plate dent placed the detonation pressure at 262 kbar with a pellet density of 1.65 g/cm^3.

	PBX 9502	DAAF + 5% Kel-F	DAAzF + 5% Kel-F
Dv (km/s) [Density, g/cc]	7.71 [1.90]	7.98 [1.69]	7.56 [1.65]
H_{50} (cm), Type 12	> 320	>320	> 320
P_{CJ} (kbar) [Density, g/cc]	289 [1.895]	299 [1.69]	262 [165]
Onset (°C)†	~330	248	315
Failure Diameter (mm)	9	< 3	< 3
Density (g/cm) †	1.938	1.747	1.70
ΔHf (kJ/mol) †	-154	+443	+536

Table 3. *Explosive performance data of PBX 9502 (TATB with 5 wt. % Kel-F), DAAF and DAAzF with Kel-F binder. †For pure explosive only.*

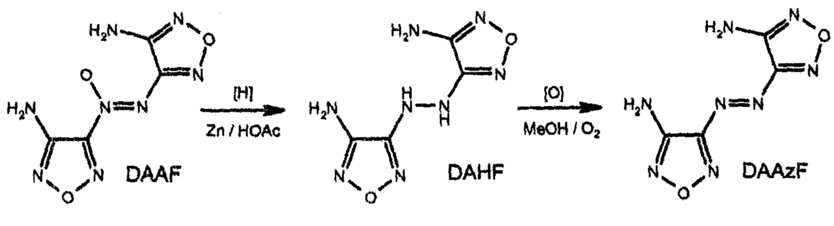

Figure 11. *Synthesis scheme of pure 3,3'-diamino-4,4'-azofurazan (DAAzF).*

While it is well known that TATB is greatly insensitive, its fairly large critical diameter of about 9 mm precludes its use in small explosive devices. Because DAAF and DAAzF have critical diameters of at least 3 mm and in some aspects have better explosive performances than TATB, we speculate that DAAF and DAAzF are more sensitive than TATB. Unfortunately it is difficult to accurately compare the sensitivities of these three explosives since all are quite insensitive. With the hopes of improving the explosive performance of TATB (e.g. critical diameter) without sacrificing its insensitivity, we investigated the explosive properties of DAAF and TATB mixtures as well as DAAzF and TATB mixtures. As one might expect, the addition of either DAAF or DAAzF to TATB might have a concomitant increase in sensitivity. However, the explosive formulator might appreciate the ability to tailor-make an insensitive explosive composition for a specific application while maintaining maximum insensitivity.

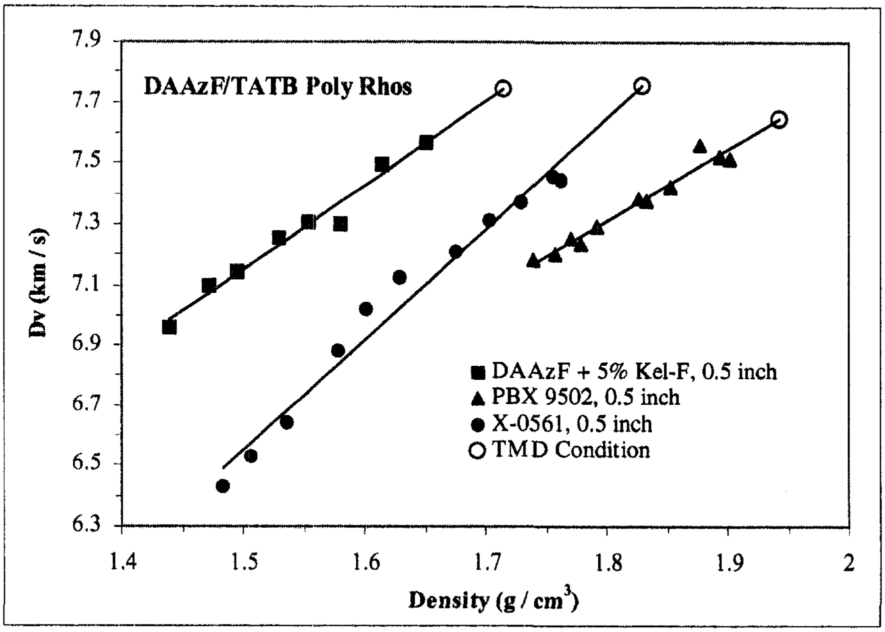

Figure 12. *Poly-rho data for X-0561, PBX-9502 and DAAzF with 5% Kel-F binder. All rate sticks are 0.5 inches in diameter and fitted lines terminate at theoretical maximum density condition (TMD).*

The first explosive mixture, X-0561, is composed by weight of 47.5% DAAzF, 47.5% TATB and 5% Kel-F 800 binder. The second mixture, X-0563, is composed of 47.5% DAAF, 47.5% TATB and 5% Kel-F 800 binder. Figures 12 and 13 have the poly-rho data for X-0561 and X-0563 respectively. For comparison, the poly-rho data for PBX 9502 (95% TATB + 5% Kel-F), DAAF and DAAzF (both with 5% Kel-F) are included in Figures 12 and 13. All poly-rhos were performed as 0.50 inch rate sticks, except for one additional X-0563 poly-rho performed as a 0.25 inch rate stick (Figure 13). With respect to detonation velocity, the X-0561 formulation appears to behave no differently than either DAAzF or TATB. However, a 0.25 inch (6.4 mm) poly-rho of X-0561 failed, thus suggesting that the critical diameter for that material is somewhere between 9 mm (for pure TATB) and 6.4 mm. For X-0563, the detonation velocity appears to be an average of the two pure materials, TATB and DAAF. The poly-rho experiment was repeated with success for a 0.25 inch rate stick; however, there is a slight reduction in detonation velocity between the 0.50 and 0.25 inch rate sticks, which is attributed to a diameter effect. Complete detonation of a 3 mm rate stick of X-0563 was found to be possible, thus demonstrating that the critical diameter of this explosive is at least 3 mm.

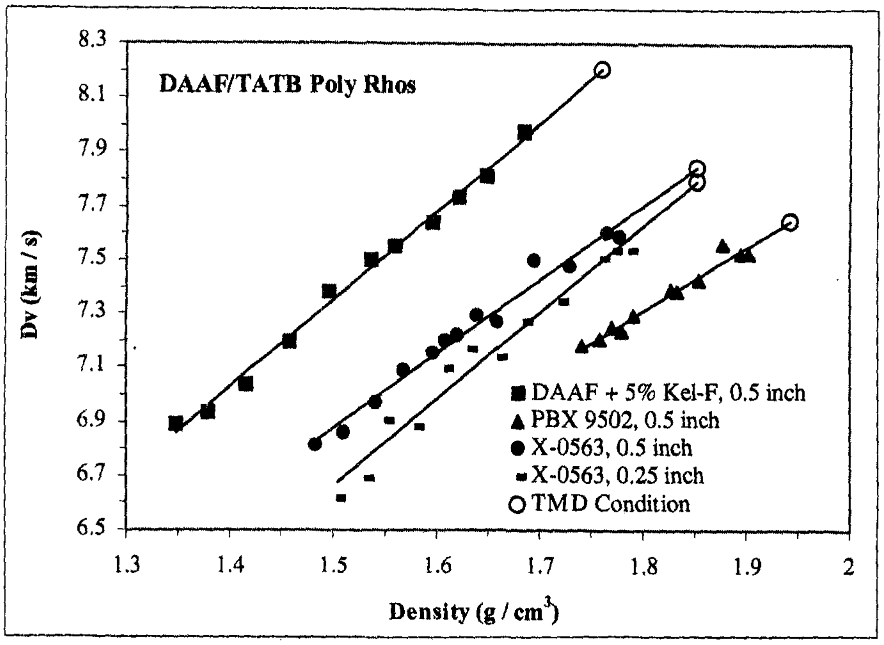

Figure 13. *Poly-rho data for X-0563, PBX-9502 and DAAF with 5% Kel-F binder. Both DAAF and PBX-9502 were performed as 0.50 inch rate sticks, while two poly-rhos were performed for X-0563 as 0.50 and 0.25 inch rate sticks. All fitted lines terminate at theoretical maximum density condition (TMD).*

Conclusion

Utilizing the useful precursor, 3,6-bis-(3,5-dimethylpyrazol-1-yl)-s-tetrazine (BDT), several useful energetic compounds based on the s-tetrazine system have been synthesized and studied. The compound, 3,3'-azobis(6-amino-s-tetrazine) (DAAT), was found to detonate as a half inch rate stick despite having no oxygen in the molecule. DAAT can be oxidized to give mixtures of N-oxide isomers (DAATO3.5) with an average oxygen content of about 3.5. DAATO3.5 burns at extremely high rates and with low dependency on pressure. The compound, 3,6-diguanidino-s-tetrazine (DGT), is synthesized by reacting BDT with guanidine in methanol. The dinitrate and diperchlorate salts of DGT have been characterized as explosives. The high-nitrogen explosives based on the furazan system, 4,4'-diamino-3,3'-azoxyfurazan (DAAF) and 4,4'-diamino-3,3'-azofurazan (DAAzF), were formulated with TATB in an effort to reduce its critical diameter without sacrificing its insensitivity.

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