Insensitive High-Nitrogen Compounds

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ABSRACT

The conventional approach to developing energetic molecules is to chemically place one or more nitro groups onto a carbon skeleton, which is why the term "nitration" is synonymous to explosives preparation. The nitro group carries the oxygen that reacts with the skeletal carbon and hydrogen fuels, which in turn produces the heat and gaseous reaction products necessary for driving an explosive shock. These nitro-containing energetic molecules typically have heats of formation near zero and therefore most of the released energy is derived from the combustion process. Our investigation of the tetrazine, furazan and tetrazole ring systems has offered a different approach to explosives development, where a significant amount of the chemical potential energy is derived from their large positive heats of formation. Because these compounds often contain a large percentage of nitrogen atoms, they are usually regarded as high-nitrogen fuels or explosives. A general artifact of these high-nitrogen compounds is that they are 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, several useful energetic compounds based on the s-tetrazine system have been synthesized and studied. Some of the first compounds are 3,6-diamino-s-tetrazine-1,4-dioxide (LAX-112) and 3,6-dihydrazino-s-tetrazine (DHT). LAX-112 was once extensively studied as an insensitive explosive by Los Alamos; DHT is an example of a high-nitrogen explosive that relies entirely on its heat of formation for sustaining a detonation. Recent synthesis efforts have yielded an azo-s-tetrazine, 3,3'-azobis(6-amino-s-tetrazine) or DAAT, which has a very high positive heat of formation.

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 too is a better explosive performer.

The recently discovered tetrazol derivative, 3,6-bis-(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz) was measured to have exceptional positive heats of formation and to be insensitive to explosive initiation. Because of its high burn rate with low sensitivity to pressure, this material is of great interest to the propellant community.

Introduction

The ideal explosive is one that is exceptionally brisant, has a very small failure or critical diameter, and possesses an enormously high detonation pressure, yet is entirely insensitive to impact, shock, friction or electric static discharge. Although no such explosive exists, the search for *insensitive* high-performance explosives continues. Unfortunately, an observed feature of traditional explosives is that performance runs parallel to sensitivity. The explosive CL-20, for example, is recognized as one of the best performing explosive with a reported detonation velocity (Dv) of 9.6 km/s. CL-20 is also well known for its sensitivity; the drop height for CL-20 ranges between 4 and 14 cm (2.5 kg, Type 12 impact machine). When CL-20 is compared with other explosives, namely HMX (9.1 km/s), tetryl (7.9 km/s), and TNT (6.9 km/s), which have impact heights that are approximately 24, 32 and 160 cm respectively, the performance-sensitivity correlation is readily observed.

For the past decade at the Los Alamos National Laboratory, we have focused on the synthesis of compounds high in nitrogen content and with large positive heats of formation. These compounds are noteworthy in that they represent a unique class of energetic materials that appear to contradict the performance-sensitivity correlation. Because these compounds often contain a large percentage of nitrogen atoms, they are usually referred to as high-nitrogen fuels or explosives. A significant amount of the chemical potential energy of these high-nitrogen compounds is derived from their high heats of formation (ΔH_f) and not from oxidation of carbon in the backbone. In addition, the increased nitrogen content in the molecular framework typically leads to high densities, and the reduced amounts of hydrogen and carbon allow the oxygen balance to be achieved more easily. Our investigation of the furazan, tetrazole and 1,2,4,5-tetrazine (also known as s-tetrazine) heterocycles has offered a different approach to energetic materials development and new energetic molecules with insensitive explosives characteristics.
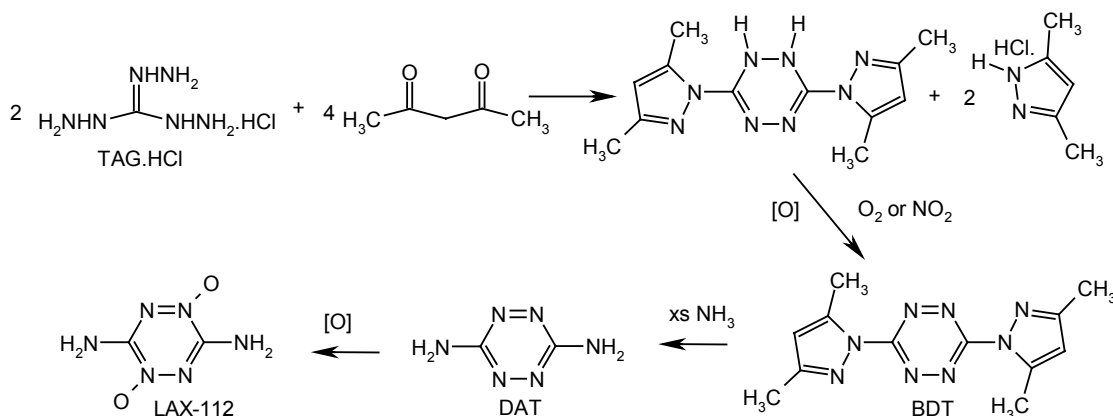
1,2,4,5-Tetrazines (Or s-Tetrazines)

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. One tetrazine compound that was extensively evaluated as an insensitive explosive (H_{50}=179, 2.5 kg, Type 12) in the early 1990's has been 3,6-diamino-s-tetrazine-1,4-dioxide or LAX-112 (Figure 1). Initial results for X-0535, a 95/5 formulation of LAX-112 with OXY 461 binder, were promising, but the explosive's metal-pushing performance as measured by a cylinder test was only marginally better than that of TATB (Table 1).
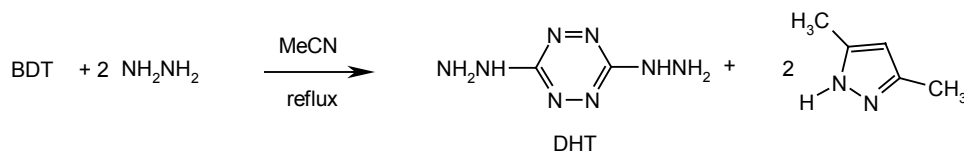
In the process of scaling up LAX-112 for evaluation, large quantities of intermediates were prepared. This allowed for a more thorough investigation by permitting access to materials containing the tetrazine ring. The precursor for LAX-112 and most tetrazines is the useful intermediate, 3,6-bis-(3,5-dimethyl-pyrazol-1-yl)-s-tetrazine (BDT). This compound is easily prepared from triaminoguanidine hydrochloride and 2,4-pentanedione followed by oxidation (Figure 1)[1]. LAX-112 is produced by the oxidation of 3,6-diamino-s-tetrazine, which is prepared by reacting ammonia with BDT.

A variety of other nucleophiles have been used to synthesize other energetic tetrazines including hydrazine to produce 3,6-dihydrazino-s-tetrazine (Figure 2, DHT)[2,3]. DHT 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); pressed pellets of DHT 0.50 inches in diameter detonate unconfined (Dv=7.54 km/s, ρ=1.56). Pellets 0.25 inches in diameter were not detonable (unconfined) when boosted with PBX 9501. DHT 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.

We had become interested in the synthesis of azo-s-tetrazines due 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 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). Reported works on the synthesis of tetrazine systems linked by an azo group are practically non-existent, with 3,3'-azobis(6-phenyl-s-tetrazine) and 3,3'-azobis[6-(4-chlorophenyl)-s-tetrazine] as the only reported compounds. However no physical properties or proof of structure were provided for these compounds.

Figure 1. *The important precursor of most tetrazine compounds, BDT, is synthesized from triaminoguanidine hydrochloride and 2,4-pentanedione followed by oxidation by atmospheric oxygen or nitrogen dioxide. LAX-112 is synthesized from BDT in two simple steps.*
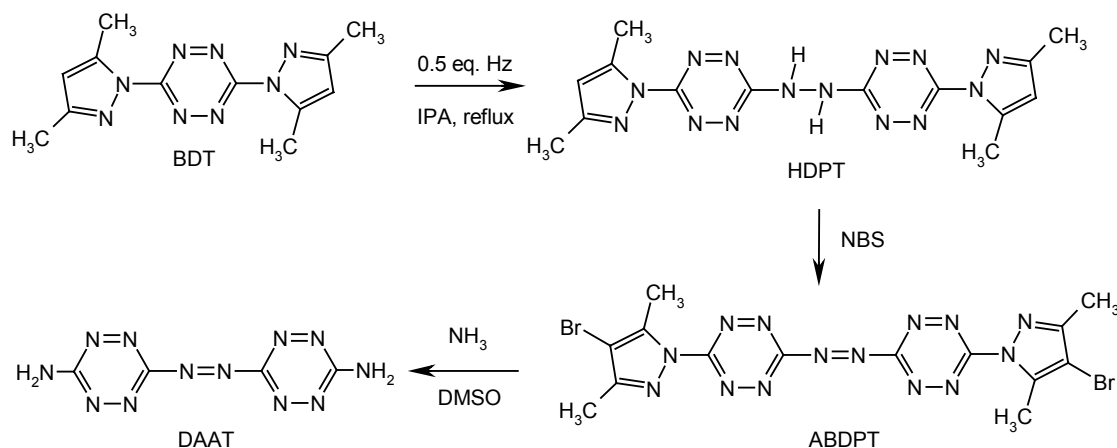

Figure 2. *Synthesis scheme of 3,6-dihydrazino-s-tetrazine (DHT).*

It was first believed that the synthesis of azo-s-tetrazines could be affected by the oxidative coupling of 3-amino-s-tetrazines. However, it has been previously shown that oxidation of 3-amino-s-tetrazines leads to the formation of *N*-oxides alpha to the amino group[4]. In the case of 3,6-diamino-s-tetrazine, *N*-oxides are formed at the 1 and 4 positions (LAX-112). The use of stronger oxidizers (hypofluorous acid, peroxytrifluoroacetic acid) can also oxidize an amino group to a nitro group when 3,6-diamino-s-tetrazine is the substrate. Under no circumstances have we observed the formation of an azo or azoxy linkage in our oxidation studies of amino-s-tetrazines. Thus the formation of the azo group in a tetrazine system was accomplished by a different synthetic approach[5].

The precursor, 3,3'-hydrazobis[6-(3,5-dimethylpyrazol-1-yl)-s-tetrazine] (HDPT) was synthesized by treatment of BDT with 0.5 equivalent of hydrazine (Figure 3). A variety of oxidizing reagents typically used to oxidize a hydrazo group to an azo moiety (Br_2, NO_2, MnO_2, HgO, HONO) did not lead to the formation of the azo group. Oxidation was only achieved with *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 acetonitrile yielded a precipitate which upon analysis showed that complete displacement of the 4-bromo-3,5-dimethylpyrazol-1-yl groups did not occur. However, when the reaction was conducted in dimethylsulfoxide (DMSO) followed by treatment of the reaction mixture with 2-propanol, a red-brown precipitate was isolated, which analyzed to be the bis-DMSO solvate of 3,3'-azobis(6-amino-s-tetrazine) (DAAT). 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 cyrstallography 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. We believed that this graphite-like structure would lead to a high density of the neat material. A preliminary density of 1.84 g/cm^3 was originally determined for pure DAAT, however recent gas pycnometry measurements have placed the density more accurately at 1.78 g/cm^3, which is likely to be the most dense C, H, N molecule known[6].

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 (the popular high-explosive HMX is 25 cm.), despite having no oxygen present in the molecule. The compound is insensitive to initiation by spark (>0.36 J) or friction (BAM, >36 kg). We are currently evaluating the oxidation of DAAT with oxygen transfer reagents to improve the density and explosives performance.
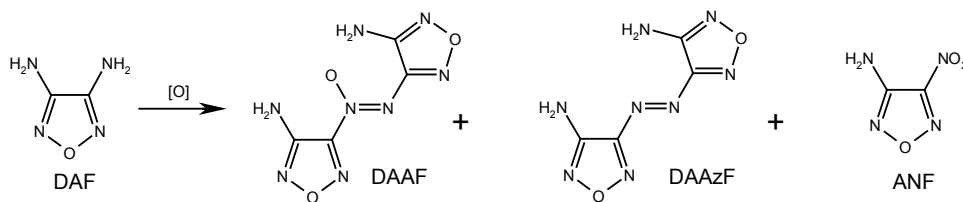
Furazans

The compound 3,4-diaminofurazan (DAF) is a useful precursor of most energetic furazan systems (Figure 4). DAF was first reported by our laboratory in 1968, but was later extensively examined by the Russians[7]. They oxidized DAF using a variety of peroxide reagents to form mixtures of 3,3'-diamino-4,4'-azoxyfurazan (DAAF), 3,3'-diamino-4,4'-azofurazan (DAAzF) and 3-amino-4-nitrofurazan (ANF). These mixtures were difficult to separate and purify, and the least stable contaminant, ANF, severely depresses the differential scanning calorimetry (DSC) onset of the more stable compounds, DAAF and DAAzF. We found that DAAF could be synthesized with only trace amount of ANF by oxidizing DAF with sulfuric acid and hydrogen peroxide. Fortunately the destabilizing ANF contaminant is easily

removed by recrystallization from DMSO/water. 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 at +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.

	PBX 9502	X-0535	DAAT	DAAF + 5% Kel-F
Dv (km/s) [Density, g/cc]	7.71 [1.90]	8.26 [1.81]	7.73 [1.78]*	7.98 [1.69]
H_{50} (cm), Type 12	> 320	179 †	70	>320
P_{CJ} (kbar) [Density, g/cc]	289 [1.895]	242 [1.63]	241 [1.78]*	299 [1.69]
Onset (°C)†	~330	245‡	252	248
Failure Diameter (mm)	9	< 6	--	< 3
Density (g/cm) †	1.938	1.834	1.78	1.747
ΔHf (kJ/mol) †	-154	+164	+862	+443
ΔHf (kJ/mol-atom) †	-6.42	+11.7	+43.1	+23.3
E_{19} (kJ/g)	1.04	1.16	--	1.22

*Table 1. Explosive performance data of PBX 9502 (TATB with 5 wt. % Kel-F), X-0535 (LAX-112 with 5 wt. % OXY 461 binder), DAAT and DAAF with Kel-F binder. †For pure explosive only *Calculated value. ‡ Critical temperature (Henkin Test)*
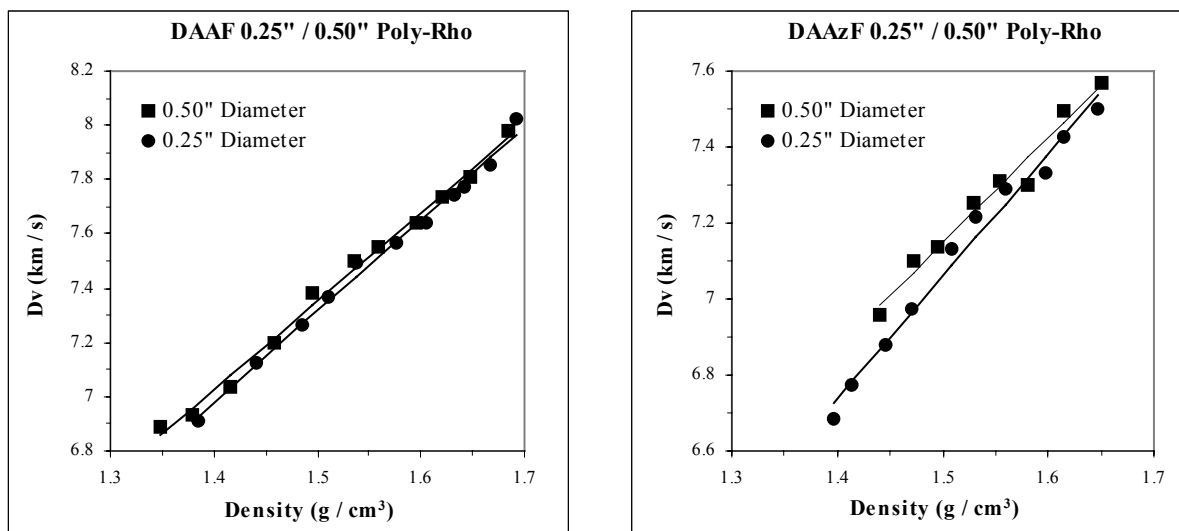

Figure 4. *The furazan precursor, 3,4-diaminofurazan (DAF), readily oxidizes to form mixtures of DAAF, DAAzF and ANF.*

The explosive performance properties of DAAF proved to be interesting[8]. A poly-rho test of DAAF—which measures detonation velocity for a series of pellets of varying densities—was performed at two diameters, 0.50 and 0.25 inches. As shown in Figure 5, these two diameters revealed that detonation velocity is relatively independent of diameter. 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. Complete detonation was achieved as evidenced by the witness plate. Unfortunately this test was too small to be instrumented accurately to determine detonation velocity. 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.

The shock sensitivity of DAAF (with 5 wt. % Kel-F binder) was characterized by performing six wedge tests[8]. Each test involves passing a carefully attenuated shock wave of known pressure through the wedge and following the progress of the shock wave by tracking its intersection with the wedge face[9]. This is experimentally performed by illuminating the wedge sample with an argon flash and photographing the wedge face with a streak camera. If the shock wave has sufficient strength to initiate an exothermic chemical reaction in the explosive, the chemical energy release feeds back into the shock

and causes it to accelerate. Eventually the accelerating shock front becomes a steady detonation wave. The shorter the run distance or run time from initial shock to detonation for a given explosive, the more sensitive the explosive is to shock. A plot of run distance to detonation versus input pressure (better known as a "Pop Plot") for DAAF is given in Figure 6. For comparison, the Pop plots of PBX 9502, PBX 9501 and PETN are also included in Figure 6. From the plots it is clearly seen 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 energy of DAAF with 5 volume percent Kel-F 800 binder at a density of 1.691 g/cm^3 was characterized by performing a standard 1-inch cylinder test[8]. This test consists of a 1.00-inch inside diameter, 0.10-inch wall copper tube filled with explosive and detonated at one end. The pressure of the explosive products expands the tube in a funnel shape, typically to about three times its initial diameter before it fragments. The metal-pushing ability of an explosive is the so-called "cylinder energy", which for DAAF was measured at 1.22 kJ/g, a value that lies between those of the TATB-based explosive, PBX 9502 (1.04 kJ/g) and the HMX-based explosive, PBX 9501 (1.58 kJ/g).
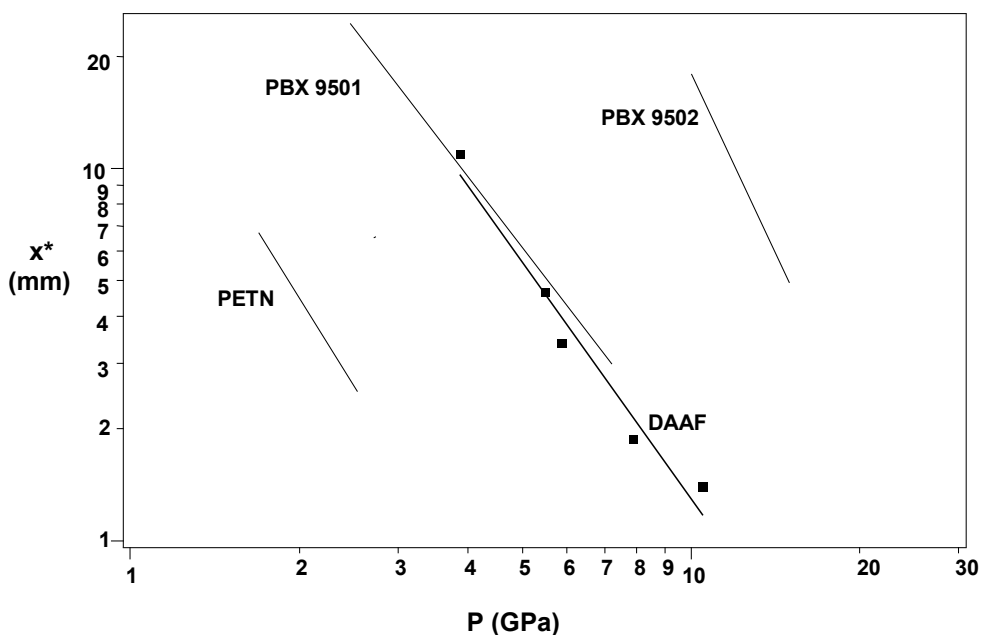

Figure 5. *Poly-rho results of DAAF and DAAzF pellets at 0.50 and 0.25 inches demonstrate that the detonation velocity is nearly independent of diameter down to 0.25 inches for DAAF, but it is more dependent for its analogue, DAAzF.*
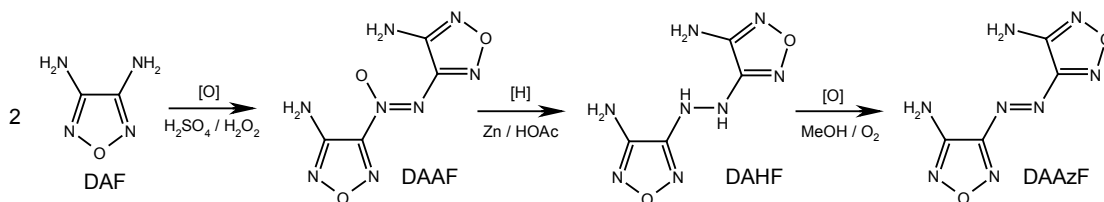
We were also interested in the related **azo**-compound, DAAzF, for its excellent thermal properties. DAAzF has a DSC onset comparable to that of HNS (315°C) and a higher calculated ΔH_f (+611 kJ/mol) than DAAF. The published procedure for preparing DAAzF yields inseparable mixtures of DAAF, DAAzF and ANF as did the reduction of DAAF with triphenylphosphine. Therefore a new method of synthesis was developed whereby DAAF is reduced 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 7).

This route also allowed us to examine the properties of the previously unknown hydrazine, DAHF. Solid DAHF undergoes slow air oxidation to DAAzF; however, oxidation proceeds more quickly when air is bubbled through a methanolic solution of DAHF. Interestingly, the ΔH_f of DAHF was found to be only +209 kJ/mol while the ΔH_f of DAAzF, measured at +536 kJ/mol. Likewise, the azoxy derivative, DAAF

has a heat of formation of +443 kJ/mol. This demonstrates that the internal energy of an energetic material can be greatly increased by incorporating the azo- or azoxy- linkage in the molecular framework.

Figure 6. *Run distance to detonation versus input pressure for DAAF. For comparison, similar experimental data for PETN, PBX 9501 and PBX 9502 have been included.*

Figure 7. *Synthesis scheme for pure 3,3'-diamino-4,4'-azofurazan (DAAzF).*

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 2). The poly-rho detonation velocities of DAAzF (mixed with 5 volume percent Kel-F 800 binder) determined at two different diameters (0.50 and 0.25 inches) were found to be more dependent on diameter than with DAAF (Figure 2). 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.

Here at Los Alamos National Laboratory, we are investigating mixtures of DAAF and TATB, and DAAzF and TATB with the hopes of improving the detonation characteristics of TATB without

sacrificing impact sensitivity or thermal stability. While it is well known that TATB is greatly insensitive, its fairly large critical diameter of about 9 mm limits the use of TATB in small, critical components. The addition of either DAAF or DAAzF to TATB formulations might decrease its critical diameter.

Tetrazoles

The molecule, 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz), which is likened as a hybrid of the tetrazole and s-tetrazine ring systems, is almost 80% nitrogen by weight (see Table 2). It is most conveniently prepared by treating BDT with commercially available anhydrous 5-aminotetrazole in hot sulfolane (Figure 8). BTATz is fairly stable, having a DSC onset of 264°C and is friction insensitive. Although pure BTATz is fairly sensitive to spark initiation at 0.36 J of capacitive energy, it is easily desensitized by addition of binder, such as Kel-F or polyethylacrylate (PEA). The impact sensitivity of BTATz was difficult to measure with accuracy and is perhaps suggestive of the odd characteristics of this high-nitrogen material. Positive impact results range from 32 cm of upwards to 200 cm on a 2.5 kg Type 12 machine, and yet most times the material was never entirely consumed or reacted by the impact. For this reason, a conservative H_{50} value of 32 cm was assigned to BTATz. Contrarily, pressed pellets of BTATz (0.50 inch) were found to be non-detonable when boosted by PBX 9501.

	TNT	HNS	DAAzF	BTATz
Dv (km/s) [Density, g/cc]	6.83 [1.64]	6.80 [1.60]	7.42 [1.60]	7.52 [1.76]*
H_{50} (cm), Type 12	154	54	> 320	32
P_{CJ} (kbar) [Density, g/cc]	189 [1.64]	200 [1.60]	262 [165]	223 [1.76]*
Onset (°C)†	240	315	315	264
Failure Diameter (mm)	3‡	~0.5	< 3	--
Density (g/cm) †	1.65	1.74	1.70	1.76
ΔHf (kJ/mol) †	-50.2	+78.2	+536	+883
ΔHf (kJ/mol-atom) †	-2.39	+2.06	+29.8	+40.1

*Table 2. Explosives data for BTATz and DAAzF. For comparison, additional data for TNT and HNS are included. †For pure explosive only. *Calculated value. ‡When TNT is pressed; critical diameter is approximately 14 mm when cast.*

BTATz burns at impressive rates and with lower than typical pressure effects (see Figure 9)[9]. At 1 atmosphere, BTATz has a burn rate of 0.56 cm/sec and increases to 7.5 cm/sec at 191 atmospheres. The pressure exponent over the same range of pressure calculates to 0.49, which has peaked interest in the propellant community. Like DHT, BTATz burns with little or no flame front, and in measurements performed at Sandia Laboratory, BTATz can sustain a burn front when packed in glass tubes as small as 250 microns in diameter[10].
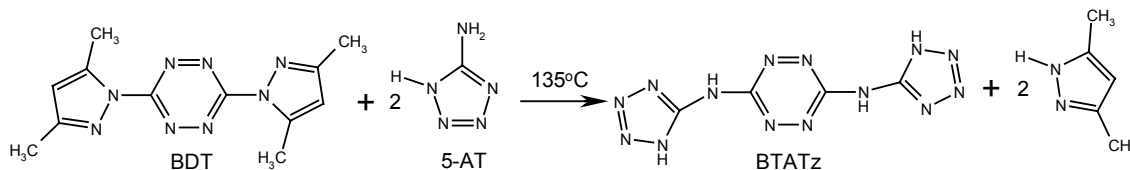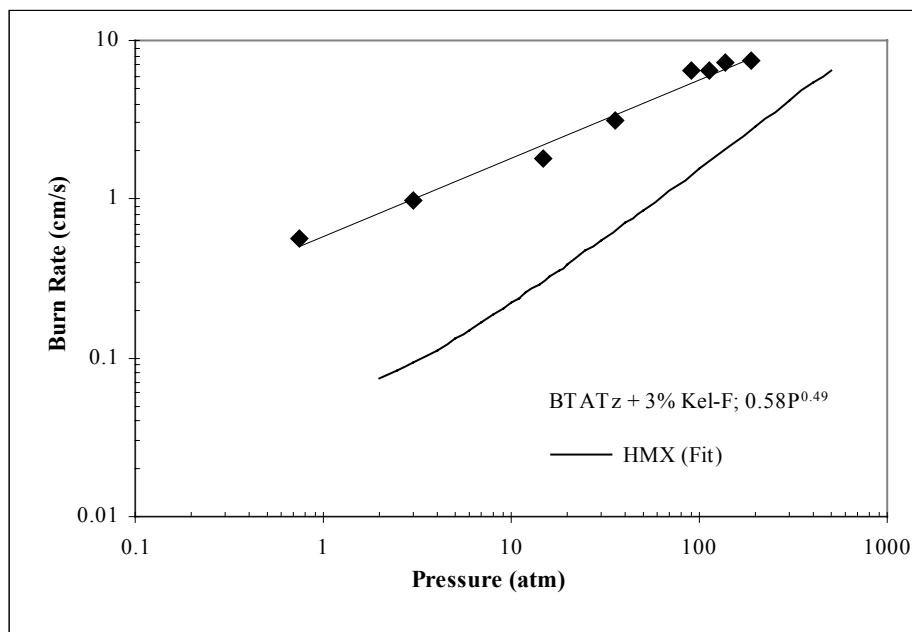

Figure 8. *Synthesis scheme of 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz).*

Conclusion

The utility of a variety of energetic high-nitrogen compounds as insensitive explosives has been described. High nitrogen explosives rely more on a large positive heat of formation rather than oxidation of the skeletal carbon for driving a detonation front. LAX-112, DHT and DAAT are examples of energetic high-nitrogen materials that belong to the s-tetrazines family. The furazans, DAAF and DAAzF, are insensitive to impact, yet both have critical diameters less than 3 mm. The compound, BTATz, is a highly energetic compound with exceptional burn rate properties, but appears to have a critical diameter greater than 0.5 inches.

Figure. 9 *Pressure-dependent burn rate data of BTATz with 3% Kel-F binder. For comparison the numerically fitted HMX burn rate profile is also provided.*

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