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LDRD – Final Report
Borazine Precursors for Boron Nitride anti Friction Coatings for MEMS

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Borazine Precursors for Boron Nitride anti Friction Coatings for MEMS

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Abstract

2,4,6-Triazidoborazine is an explosive material that contains no carbon or oxygen. There is very little discussion of this material in the open literature, and due to the nature of this class of compounds, it is possible that a sophisticated adversary could produce and deploy this material. This work was undertaken to understand this material's chemical and explosive properties. This paper documents the experimental procedure and results of this LDRD.

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Acronyms

DIMEADAB	Dimethylaminodiazidoborazine, $H_3N_3B_3(N_3)_2(N(CH_3)_2)$
IMS	Ion Mobility Spectroscopy
LANL	Los Alamos National Laboratories
NMR	Nuclear Magnetic Resonance
PETN	Pentaethryritol tetranitrate
SNL	Sandia National Laboratories
TAB	2,4,6-Triazidoborazine, $H_3N_3B_3(N_3)_3$
TMS	Trimethylsilyl, $(H_3C)_3Si$-
TRIMTAB	1,3,5-Trimethyl-2,4,6-triazidoborazine

Borazine Precursors for Boron Nitride anti Friction Coatings for MEMS

1.0 Introduction

Borazine molecules consist of a core 6-membered ring of alternating boron and nitrogen atoms with exocyclic substituents. The parent borazine ($B_3N_3H_6$), shown in Figure 1, is known as 'inorganic benzene' due to chemical properties similar to benzene.[1]

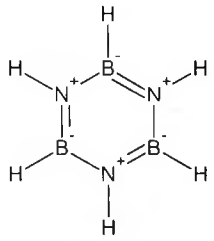


Figure 1. Borazine, $B_3N_3H_6$

Borazine may be used to produce boron nitride, a non-oxide ceramic material that in its hexagonal form has properties similar to graphite and may be used as a solid state lubricant.

One route to the synthesis of borazine is by the addition hydrogen to 2,4,6-trichloroborazine using a hydriding reagent such as sodium borohydride,[2] as shown in Figure 2.

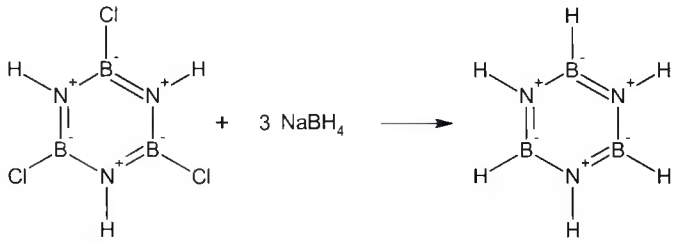


Figure 2. Reaction to synthesize Borazine

2,4,6-Trichloroborazine is readily produced by the reaction of boron trichloride with ammonium chloride in refluxing chlorobenzene,[3] as shown in Figure 3.

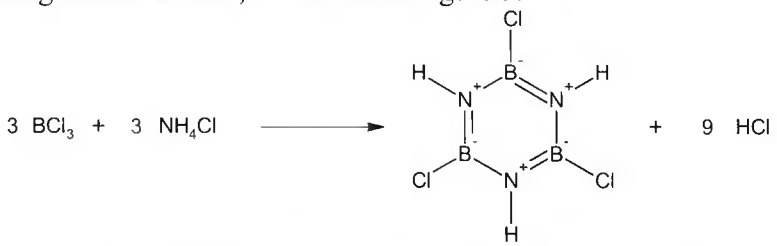


Figure 3. Reaction to synthesize 2,4,6-Trichloroborazine

The boron-chlorine bond in 2,4,6-trichloroborazine is highly labile and may be used to introduce different substituents to the borazine ring by metathesis reactions, aminations, or transaminations.[1]

Metathesis reactions using trimethylsilyl reagents can be used to replace the chlorine on the borazine ring with amine or pseudohalogen groups. Trimethylsilyl chloride is a volatile by-product that can be removed from the resulting product using vacuum techniques. This can minimize the amount of contamination found in molecular precursors used to produce boron nitride articles. The reaction of 2,4,6-trichloroborazine with hexamethyldisilazane shown in Figure 4 demonstrates this condensation.[4]

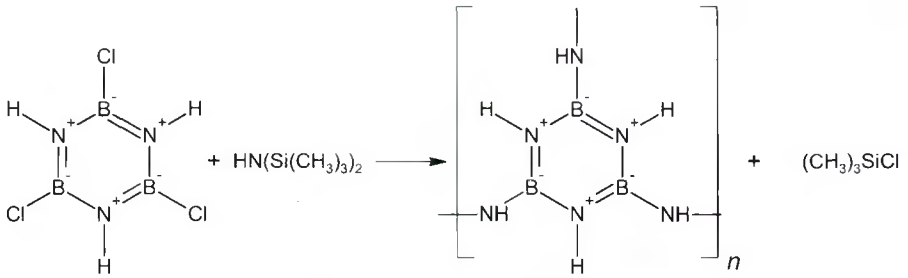


Figure 4. Poly(aminoborazine) Synthesis

The search for a borazine-based molecular precursor that would readily decompose and would not contain carbon or oxygen lead to the investigation of 2,4,6-triazidoborazine, Figure 5. This molecule could be readily synthesized from 2,4,6-trichloroborazine and trimethylsilyl azide. This molecule might be used to form boron nitride films and powders.

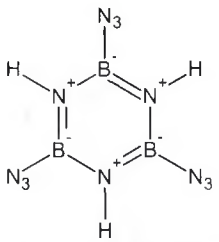


Figure 5. 2,4,6-Triazidoborazine

It was also discovered that when more than 200 milligrams of this material was heated above its melting point, it detonated. This molecule is a novel energetic material with no prior discussion in the open literature until 1999, and no further discussion in the open literature as of this writing in 2008.

2.0 Background

2.1 Early Synthetic Attempts

The first reported attempt at the synthesis of 2,4,6-triazidoborazine (TAB) was by Muszkat, et.al., in 1963.[5] These workers used 2,4,6-trichloroborazine and excess sodium azide in acetonitrile. An impure white solid that did not melt up to 300°C was isolated from the reaction, and detonation usually occurred during attempts at purification.

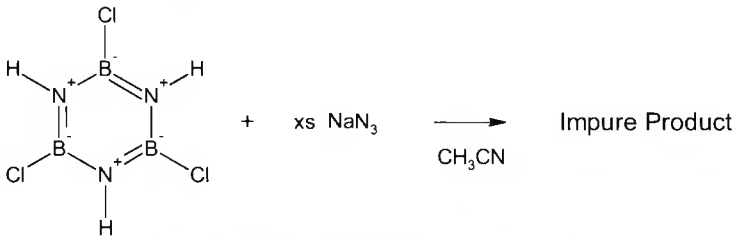


Figure 6. Sodium azide/acetonitrile reaction scheme

The second mention of TAB was in a patent by Keith, et.al.,[6] describing a synthetic pathway using 2,4,6-trichloroborazine and excess sodium azide in refluxing chlorobenzene for 2 days. No characterization data was provided. The product detonated when exposed to flame.

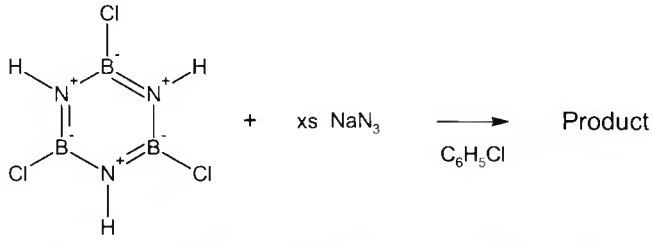


Figure 7. Sodium azide/chlorobenzene reaction scheme

These reactions are probably limited by the low solubility of sodium azide in the solvents selected for this reaction.

2.2 Current Synthetic Approach

The reaction of trimethylsilyl azide $(H_3C)_3SiN_3$ with 2,4,6-trichloroborazine in diethyl ether was described by Paine, et.al., in 1999.[7] This reaction produces TAB in almost quantitative yield.

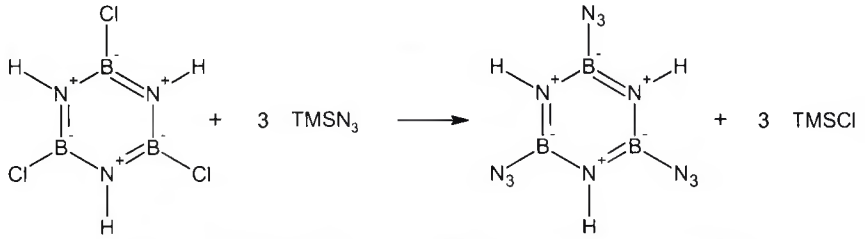


Figure 8. Trimethylsilyl azide/diethyl ether reaction scheme

TAB was fully characterized by single crystal x-ray diffraction, ^{11}B and ^{1}H nuclear magnetic resonance spectroscopy, infrared and mass spectroscopy, and elemental analysis. TAB melts at 152°C.

During the course of forming boron nitride powders from TAB, it was observed that whenever more than 200 milligrams was heated under a static atmosphere, detonation occurred above the melting point of TAB.

Preliminary explosive safety testing was performed by Los Alamos National Laboratories for the 1999 paper; drop-height and friction testing placed this material as more sensitive than PETN. The electrostatic discharge testing produced a value of 0.36J, which is a value considered to be nonsensitive to human electrostatic discharge.

3.0 Current Interest and Goals

3.1 Novel Energetics

There may be some interest in energetic materials that are not typical and are not widely known. These atypical explosives could become replacements for current explosives, may have niche applications, could confound current detection schemes, and may have less of a long-term environmental impact. TAB may fill some or all of these rolls.

In 2006, discussions between SNL and LANL about the TAB tested for the 1999 Inorganic Chemistry paper revealed that those tests might not have been conducted in an environment completely free of oxygen and water. LANL commented that TAB might be 'a borderline primary-secondary' explosive. It was clear that known pure material should be tested to confirm the previous results and provide further explosive characteristic information.

3.2 Goals of this LDRD

The goals of this LDRD were two-fold; the primary goal was to investigate the energetic characteristics of TAB, and the secondary goal was to investigate the use of these materials for molecular precursors for solid state lubricants for MEMS devices.

To accomplish the primary goal, the following objectives were developed:

1. Establish the infrastructure to synthesize boron-based energetic materials
2. Perform explosive safety testing on TAB
3. Expand, if possible, the suite of borazine explosives
4. Determine the decomposition profile
5. Determine the response to TAB of common, field-deployed explosive detection equipment

To accomplish the secondary goal, the following objectives were developed:

a. Attempt to coat common substrates to form boron nitride films
b. Develop tribological reference materials to test boron nitride films
c. Investigate any unexpected developments for possible exploitation in other arenas

As the secondary goals for the LDRD were tangential to the primary goals, the secondary goals were not pursued with vigor.

4.0 Experimental Results

4.1 Infrastructure, Synthesis, and Safety Testing

Borazine molecules are air and moisture sensitive. The synthesis of these molecules requires specialized apparatus and techniques common to air-sensitive chemical synthesis. To permit this synthesis, specialized glassware, Schlenk lines, and gloveboxes were purchased and installed. Examples of the hardware acquired are shown in Figure 9 and Figure 10;

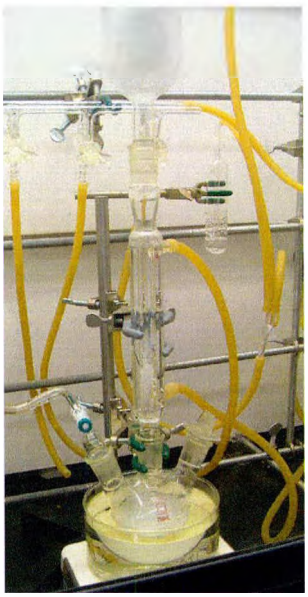


Figure 9. Apparatus for the synthesis of 2,4,6-Trichloroborazine

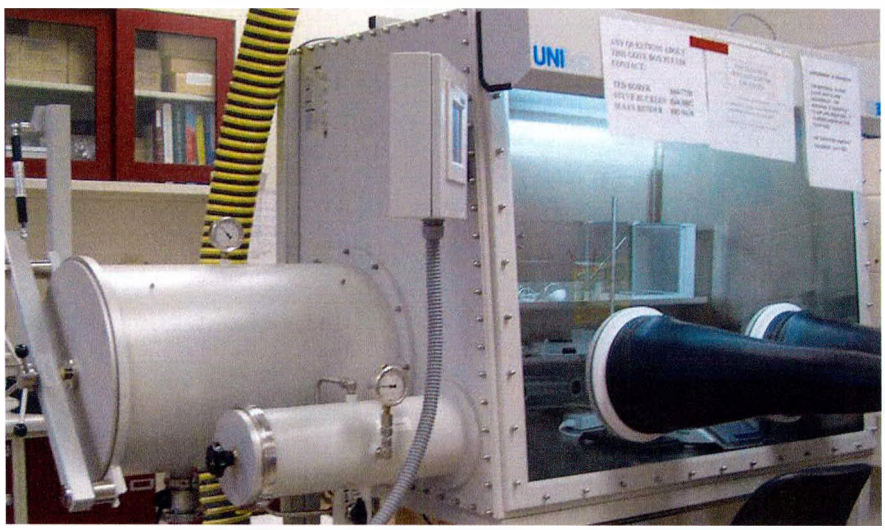


Figure 10. Glovebox for gross manipulations of solid reactants

Once this apparatus was installed, the synthesis of precursor materials commenced. With the approval of the Sandia Explosives Safety and Explosives Development Committees, the synthesis of TAB was performed according to the literature.

A sample of freshly prepared TAB was submitted to LANL for safety testing; the tests requested were differential scanning calorimetry (DSC), drop height, friction sensitivity, electrostatic discharge, and vacuum stability. It was emphasized to LANL that the handling of this material in air should be minimized during the testing process.

The results of the impact testing are shown below. TAB has 50% drop height value at 12.1 cm. This result is much lower than the result reported in the 1999 Inorganic Chemistry paper, which was 16.5 cm.

IMPACT SENSITIVITY TESTING Type 12

The 50% drop height is determined using a 2.5 kg weight and the "Bruceton up/down method."

SAMPLE	Lab # / LIMs #	50% Height (cm)	σ Log Units	% RH	Temp. (°C)
Triazidoborazine	50545/ 070205005	12.1	0.081	18.6	23.9
PETN 94-01B	Na	15.8	0.150	28	16.7
TNT 22391 Lot 2	Na	242.4	0.04	15.0	20.0
HMX Standard (HOL 83L 030 050)	Na	23.1	0.030	38.0	18.0

The results of the friction testing are shown below. TAB has a <0.5 response at 50% Load in kg. This result is much lower than the result reported in the 1999 Inorganic Chemistry paper, which was 10.6 kg.

FRICTION SENSITIVITY TESTING

The 50% load in kg is determined using the "Bruceton up/down method."

SAMPLE	Lab # / LIMs #	50% Load in kg	σ Log Units	% RH	Temp. (°C)
Triazidoborazine	50545/ 070205005	< 0.5	Na	20.1	22.0
PETN Standard (94-01B)	Na	7.0	1.704	16.5	21.8

The results of the electrostatic discharge testing are shown below. TAB has a <0.00125 J response. This result is also much lower than the result reported in the 1999 Inorganic Chemistry paper, which was 0.36 J.

ABL SPARK SENSITIVITY TESTING

SAMPLE	Lab # / LIMs #	TIL (Threshold of Initiation Limit)*	% RH	Temp. (°C)
Triazidoborazine	50545/ 070205005	0.00125*	20.5	21.3
PETN Standard (94-01B)	Na	0.0625 Joules	9.0	61.0

LANL then requested that the vacuum stability and DSC tests be cancelled due to the extreme sensitivity of TAB to these safety tests.

From this set of testing, it was concluded that the initial set of tests performed by LANL on TAB for the 1999 paper was done using impure and/or partially oxidized material.

TAB was declared to be a primary explosive by LANL as a result of this testing.

DSC measurements were performed at SNL. A result is shown in Figure 11. The melting point of this material is shown at 153°C; there is a secondary endotherm at 235°C, and an exotherm at 390°C.

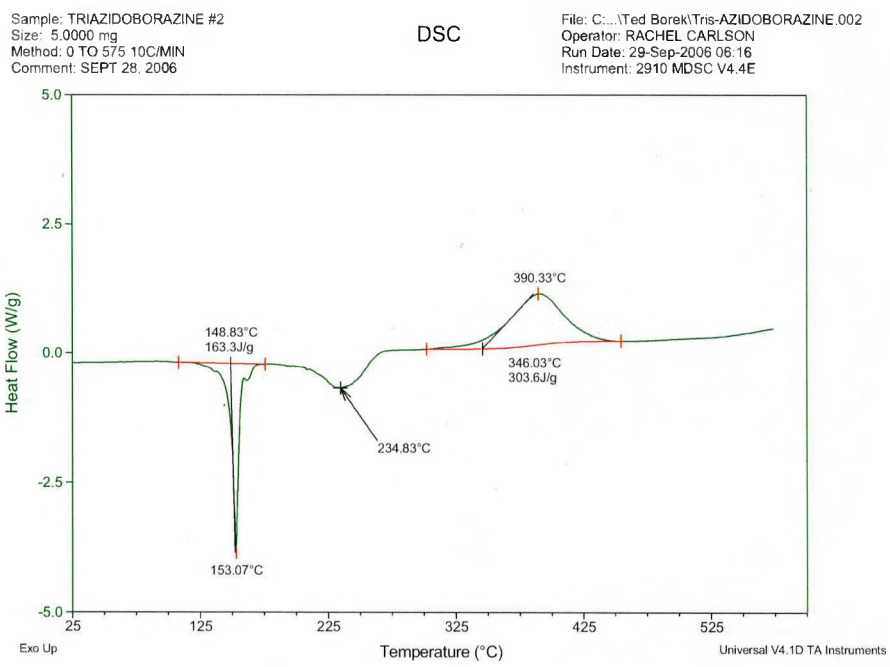


Figure 11. DSC measurement of TAB

4.2 Expanding the Suite

Since TAB exhibited energetic properties, it was of interest to expand the suite of borazine azides to determine if any other boron-based explosives may be found. The first attempt at expanding this suite of molecules was to produce 1,3,5-trimethyl-2,4,6-triazidoborazine (TRIMTAB). 1,3,5-Trimethyl-2,4,6-trichloroborazine is readily synthesized from methylammonium hydrochloride and boron trichloride in refluxing chlorobenzene.

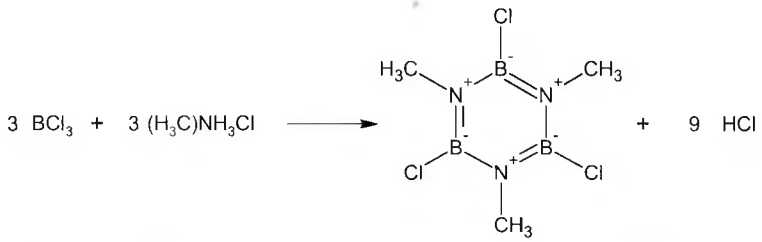


Figure 12. Synthesis scheme for 1,3,5-Trimethyl-2,4,6-trichloroborazine

The synthesis of TRIMTAB was reported by Muszkat;[5] their product was described as a waxy solid that liquefied at ~100°C. However, when TRIMTAB was synthesized using $TMSN_3$; the resulting product was found to be a liquid which was distilled at 133°C @ 1-3 mTorr.

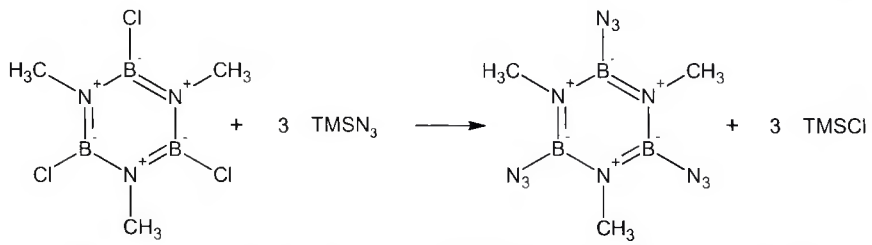


Figure 13. Synthesis scheme for 1,3,5-Trimethyl-2,4,6-triazidoborazine

This synthesis of TRIMTAB produced a previously unknown borazine azide.

Characterization data was then collected. NMR data on TRIMTAB are shown in Table 1.

Table 1. NMR Results, TRIMTAB

Nucleus	Shift
^{1}H	2.93, singlet
^{11}B	25.75, singlet
^{13}C	30.77, singlet
solvent, $CDCl_3$	

This molecule was dissolved in chloroform, and analyzed by gas chromatograph/mass spectrometry. One non-solvent peak was observed, and the mass spectrum for this peak is shown in Figure 14. The parent ion at m/z of 246 is observed, as well as the expected isotopic distribution for a molecule containing boron (10B:11B, 18.2:81.8).

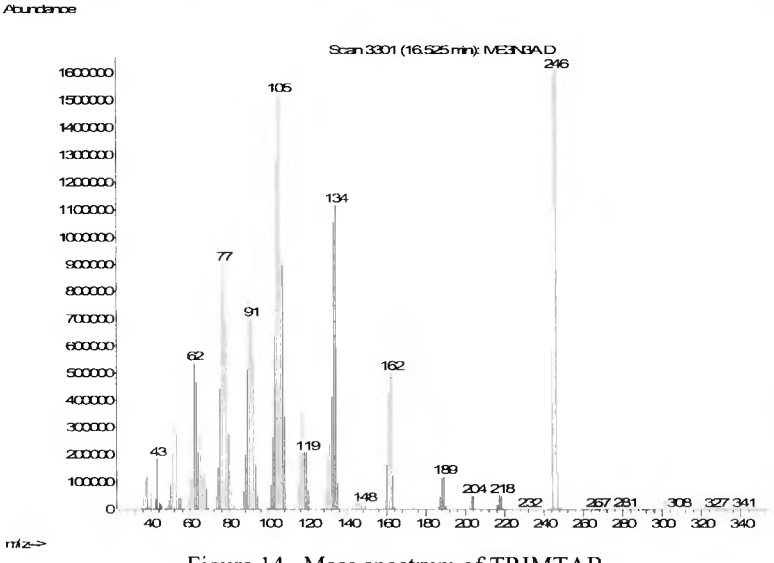


Figure 14. Mass spectrum of TRIMTAB

The infrared spectrum of this material is shown in Figure 15; the azide stretch at 2150 cm^{-1} is evident.

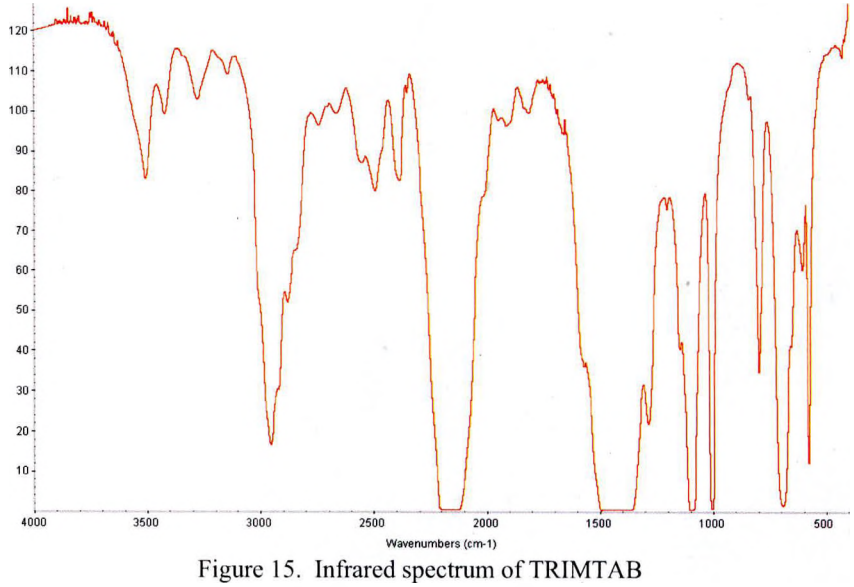


Figure 15. Infrared spectrum of TRIMTAB

This material was destroyed when it was learned that TAB was a primary explosive. No further testing was performed.

It is possible to substitute one of the chlorine atoms on the borazine ring with a dimethylamino group. This would provide a route to a diazido borazine. 2-Dimethylamino-4,6-dichloro-borazine was made according to the literature procedure[8]. This material is a crystalline solid, and as there was no previously reported crystal structure, a structure was determined and reported to the literature.[9]

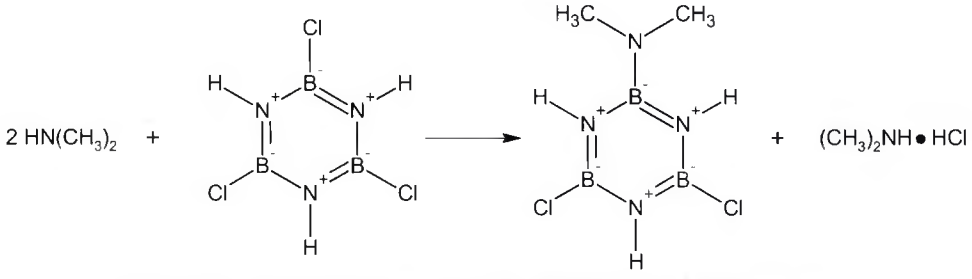


Figure 16. Synthesis scheme for 2-Dimethylamino-4,6-dichloroborazine

The synthesis of 2-dimethylamino-4,6-diazidoborazine (DIMEADAB) was attempted as in the two previous examples with the parent chloro compound and $TMSN_3$; the resulting product was found to be a white solid with a melting point of 62-64°C.

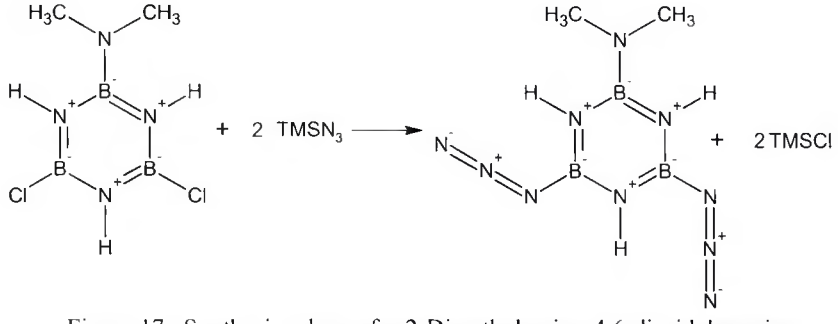


Figure 17. Synthesis scheme for 2-Dimethylamino-4,6-diazidoborazine

This synthesis of DIMEADAB produced a previously unknown borazine azide.

Characterization data was then collected. NMR data on DIMEADAB are shown in Table 2. This material was impure per the ^{11}B NMR results, and was destroyed without further examination when TAB was determined to be a primary explosive.

Table 2. NMR Results, DIMEADAB

Nucleus	Shift
^{1}H	Multiple
^{11}B	29.83, 26.64, and 24.47, singlets
^{13}C	36.78, singlet
solvent, $CDCl_3$	

One other material that was synthesized is worth noting. 1,3,5-Trimethyl-2,4,6-(tris-(dimethylamino)borazine may be used a reagent for subsequent transamination reactions. This molecule was made according to the literature procedure.[10] This material is a crystalline solid, and as there was no previously reported crystal structure, a structure was determined and reported to the literature.[11]

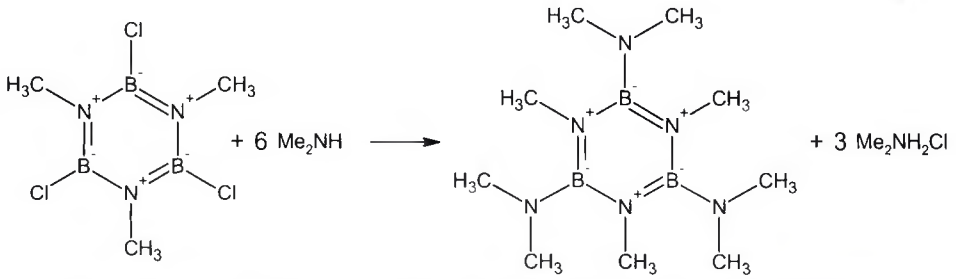
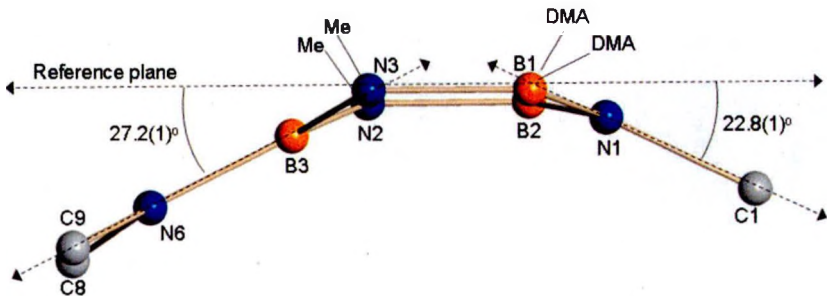


Figure 18. Synthesis scheme for 1,3,5-Trimethyl-2,4,6-tris(dimethylamino)borazine

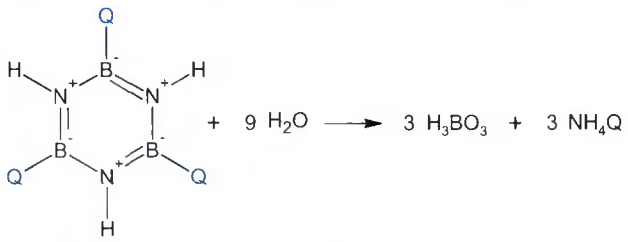


The unusual feature of this molecule is the deviation from planarity that crystalline borazine species typically exhibit.

4.3 Decomposition Profile

Borazine molecules in general are air and moisture sensitive; it is of interest to determine the decomposition profile of TAB in order to assess its performance for field applications.

The reaction of borazines with water could proceed in this manner:



This reaction may also proceed in moist air. The decomposition products do not resemble the starting materials, and are not indicative of the structure of the parent material.

An examination of the oxidation of 1,3,5-trimethyl-2,4,6-tris(dimethylamino)borazine in air as interrogated by infrared analysis was conducted at SNL. In this experiment, the borazine was exposed to laboratory air for 2 minutes and for longer than 10 minutes. The spectra obtained after these air exposures, along with the spectrum of unexposed borazine, are shown in below. Changes are seen in the IR spectra even with the two-minute exposure, and the original borazine bands have nearly disappeared after the 10-minute-plus air exposure. The material remaining after the 10-minute-plus air exposure consists of borate and, possibly, nitrate species and absorbed water.

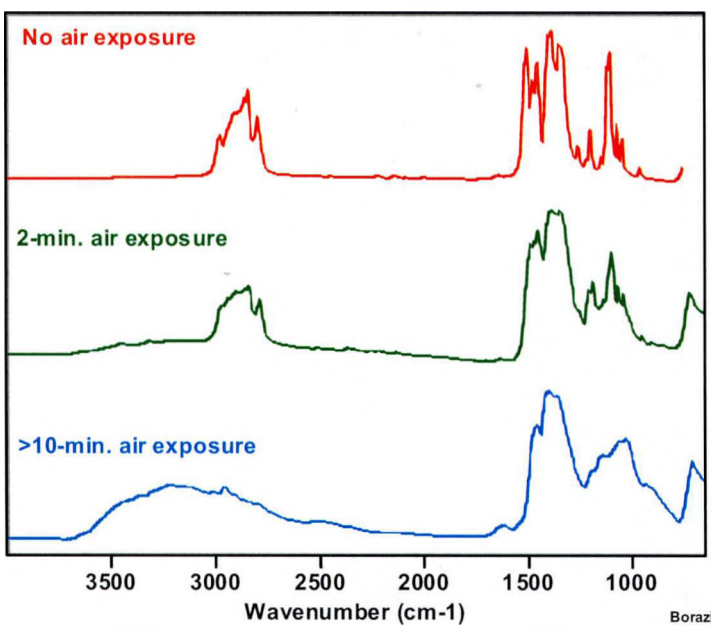


Figure 19. Infrared analysis of the oxidation of 1,3,5-trimethyl-2,4,6-tris(dimethylamino)borazine

4.4 Detection

A sample of TAB was used to challenge an ion mobility spectrometer, a device that is commonly used to in deployed explosive detection devices. Evaluation was done using an Ionscan 400B ion mobility spectrometry S#861650 in negative mode. The unit was autocalibrated in 2 passes following a reset of the absolute pressure transducer. A verification run was performed using a negative mode verification stick and was normal. The operating parameters for the IMS unit are listed below.

Table 3. Ionscan 400B operating parameters

IMS tube temperature	110°C
Inlet temperature	240°C
Desorber temperature	233°C
Calibrant temperature	65°C
DPT signal	0.07 kPa
Flow	351 cc/min
High voltage	-2046 V

Sample introduction was from the cloth swipes. All swipes were checked before sample runs to verify initial cleanliness and lack of any nonstandard peaks. Both a solution of the TAB sample in acetonitrile and a solid sample of the material were analyzed. The TAB material was dissolved in acetonitrile immediately before evaluation. Not all of the TAB material dissolved in the acetonitrile and the solution was not quantified. The solid material was transferred by swab from the container to the swipe immediately before evaluation on the IMS. The containers were kept closed at all times samples were not being actively transferred to reduce atmospheric decomposition.

The acetonitrile solution of TAB sample showed a large peak at a time of 7.40 ms that was not present with a blank swipe. This peak was earlier than the Ionscan 400B location for the explosive nitrate peaks at 7.90 to 8.00 msec. The first graph below plots the first solution sample versus a blank swipe with the nitrate location indicated. The peak at 10.38 msec on the blank wipe is the system internal calibrant. Most of the other peaks are present in both the blank swipe run and the TAB solution and are probably not significant.

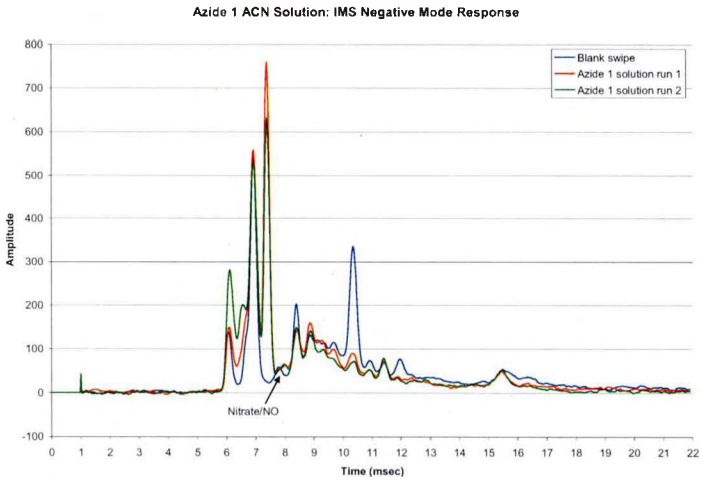


Figure 20. IMS scan of TAB/acetonitrile

The second graph plots the blank swipe (in black) and the difference between the blank swipe and the average response of the 2 solution runs (in red). The peak at 7.40 msec is clearly significantly different from the blank swipe. Less clear, but perhaps also significant is a peak in this graph at 6.55 msec which appears in the plot above as a leading broadening of the swipe peak at 6.98 msec in the first solution run and a duplex to this peak in the second solution run. This may be a decomposition product forming since it appears to be increasing with time of the TAB material in acetonitrile solution.

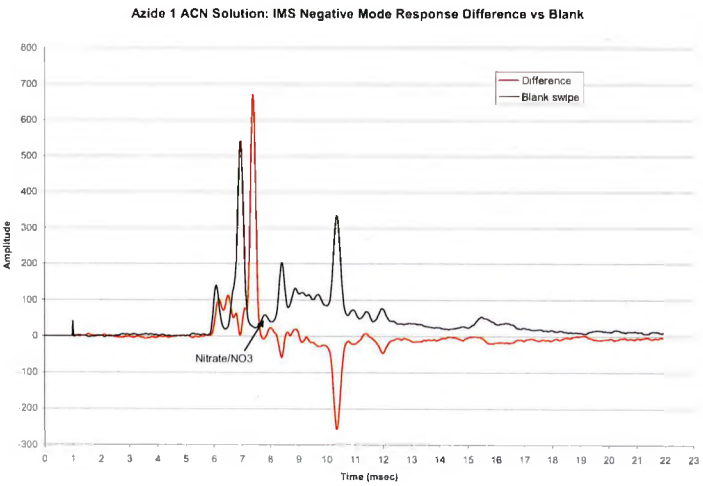


Figure 21. IMS scans of TAB/acetonitrile, difference plots

The solid sample of TAB showed a much different response from the acetonitrile solution. The peak at 7.40 msec present in the solution sample is not present but a strong peak at 11.50 msec appears which did not occur in the solution sample. There is a smaller but still significant peak at 6.60 msec that does not occur with the blank swipe. The differences between the blank swipe and the solid TAB sample may be more clearly shown in the second graph which plots the blank swipe (in black) and the difference between the blank swipe and the average response of the 2 solid runs (in red). The two significant peaks appear above the zero baseline. The solid sample appears to give a cleaner peak at 6.55-6.60 msec than was obtained from the solution sample.

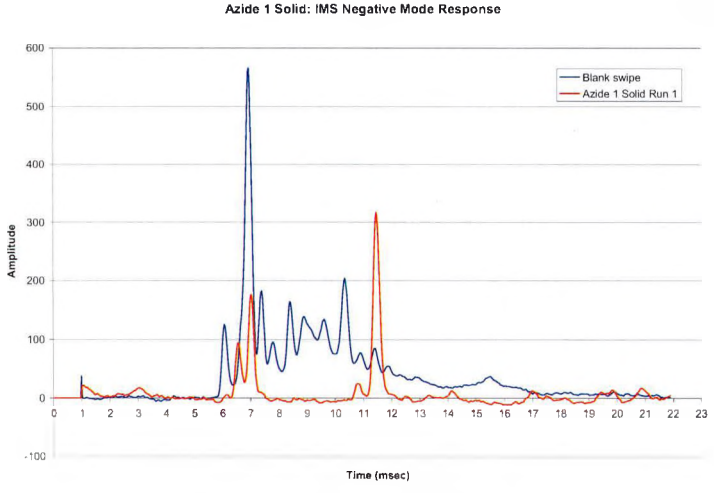


Figure 22. IMS of solid TAB

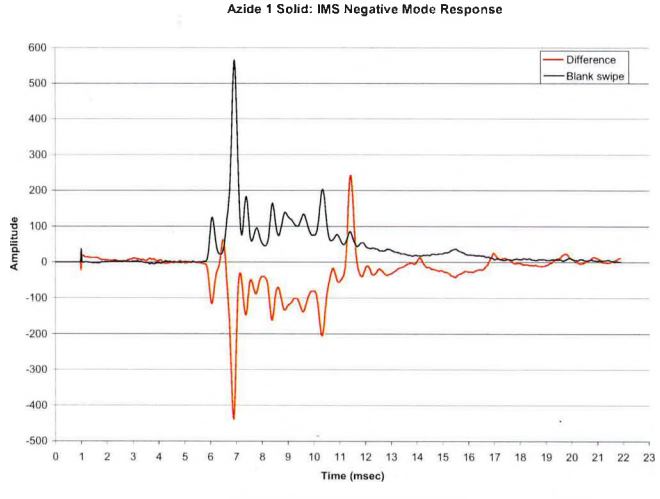


Figure 23. IMS of solid TAB, difference plots

In both the solution and solid samples, no channels or substances defined as explosive were obtained. Data for the graphs was obtained by taking one of the series of IMS spectra obtained for each run. These are averaged for the results displayed by the Ionscan but differences are often clearer with a single scan. The same blank swipe and sample scan were used to minimize time differences.

5.0 Discussion

The tests performed on TAB revealed that this molecule is a primary explosive. It is unusual among primaries as it has a readily accessible melting point (152-154°C) that is lower than the onset of the decomposition exotherm (346°C). This may permit this material to be cast in place.

Other explosive properties, such as detonation velocity and pressure, need to be experimentally determined. One can estimate these properties, as was done by Cooper,[12] using the elemental formula and density of the material, or solely on the density.

(1) Based on elemental formula ($H_3B_3N_{12}$) and density (1.58-g/cm^3), the detonation properties are:

Detonation Pressure, P_{CJ}, 21.3-GPa
Detonation Velocity, D, 7.15-km/s

(2) Based only on density (1.58-g/cm^3), the detonation properties are:

Detonation Pressure, P_{CJ}, 24.9-GPa
Detonation Velocity, D, 7.71-km/s

These compare to values of several other common explosives.

Table 4. Density, Detonation Velocity and Pressures

Explosive	Density (g/cm_3)	Detonation Velocity (km/s)	Detonation Pressure (GPa)
Borazine		Estimated values	
TAB, $H_3N_3B_3(N_3)_3$	1.58	7.15 to 7.71	21.3 to 24.9
Secondary Explosives		Actual values	
ANFO	0.84	4.65	5.8
Comp-B	1.7	7.8	28
HMX	1.89	9.11	39
PETN	1.7	8.08	30.7
RDX	1.76	8.62	32.5
TNT	1.63	6.95	19.5
Nitromethane (liquid)	1.13	6.3	13
Primary Explosives			
Lead Azide	3.66	4.42	15.5
Lead Styphnate	2.9	5.2	19.5

The decomposition of TAB, TRIMTAB, or DIMEADAB were not examined. It was observed that TAB could be destroyed with water with some evolution of heat. No attempt was made to characterize the resulting solutions. This remains to be completed.

In an effort to reduce the friction and electrostatic discharge sensitivity, an effort to formulate TAB with a common polymer is being investigated. Once an acceptable formulation is produced, testing to determine detonation velocity and pressure will be performed.

6.0 Conclusion

Sandia is in possession of a unique explosive that has had limited discussion in the open literature. The tests performed on TAB revealed that this molecule is a primary explosive. It is possible to expand on the set of azidoborazines using the modern synthetic scheme. Previously described azidoborazines and their properties enumerated in the older literature may not be correct. This suggests that an entire class of explosive and/or energetic materials may be available to exploit if the proper resources are applied.

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