CHEMISTRY OF COMPLEX HIGH-NITROGEN MATERIALS

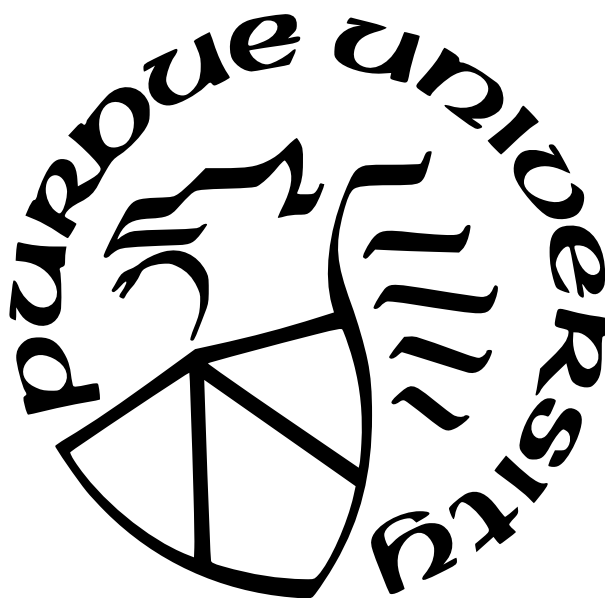by

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To my wife and children

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ABSTRACT

This dissertation is a compilation of five manuscripts which were peer-reviewed and accepted for publication in several international scientific journals, including *Zeitschrift für Anorganische und Allgemeine Chemie ZAAC* (Germany), *Chemistry-A European Journal* (several European nations), *Energetic Materials Frontiers* (China), *New Journal of Chemistry* (U.K.), and *Inorganic Chemistry* (U.S.). The extensive research was achieved during the three year graduate research program as part of the Purdue Energetics Research Center (PERC).

Chemistry of Complex High-Nitrogen Materials begins with a brief background on a few high explosive materials and their applications, followed by synthesis routes and characterization methods of energetic materials. Several new complex high-nitrogen materials where synthesized and presented in the following chapters. These novel energetics include several nitrilimines, triazoles, tetrazoles, methyl sydnone imines, azasydnones, and an annulated heterocycle. Their energetic properties are discussed and compared with other well-known explosive materials.

1. INTRODUCTION

1.1 Background

Although the physics payload of a nuclear weapon attracts much attention, a vital component of the weapon design remains the insensitive high explosive (IHE). This energetic material must be thermally stable, mechanically insensitive, endure decades of radiation without decomposing, and provide sufficient energy upon detonation. These weapons could be exposed to fire or accidental drop from an aircraft. For example, in both aircraft accidents in Palomares, Spain (1966) and Thule Air Base, Greenland (1968) the high-explosives within the nuclear weapons detonated, causing wide-spread dispersal of plutonium.[1]–[3] In the event of such accidents, an insensitive high explosive remains a critical feature in order to mitigate the risk of releasing plutonium into the environment.[4]

1,3,5-triamino-2,4,6-trinitrobenzene (TATB) serves as an insensitive high-explosive in nuclear weapons.[5] (Figure 1.1) First reported in 1888, this unique energetic material is well known for its thermal stability (360 °C decomposition temperature) and insensitivity.[4], [6], [7] The vicinal amino and nitro groups lead to strong intermolecular and intramolecular hydrogen bonding network. Furthermore, its molecules stack as a planar system within the crystal. The very strong hydrogen bonding network coupled with a planar crystal system greatly reduces mechanical sensitivity.[8] Consequently, following the nuclear accidents at Palomares and Thule, TATB was selected as an insensitive high-explosive replacement in nuclear weapons. Moreover, in the last 50 years, TATB has been incorporated into many formulations of plastic-bonded explosives (PBX).[4]
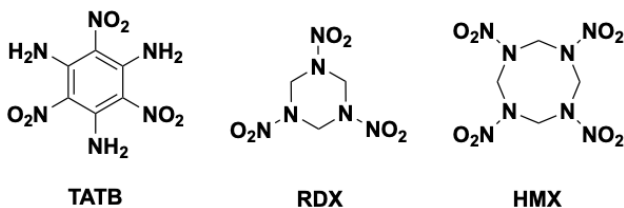
Figure 1.1. Structure of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), hexogen (RDX), and octogen (HMX).

Other extensively known insensitive high explosives include hexogen (RDX) and octogen (HMX). Both of these N-nitro (nitramines) explosives were widely used throughout WWII and today, like TATB, are found in variations of PBX.[9], [10] The popular plastic explosive, C4, contains 90% RDX.[9] Although RDX currently remains a significant HE for military use, HMX exceeds its detonation performance.[10] HMX is a high melting explosive, but the expensive production costs inhibit widespread utilization beyond any military applications.[10]

While the history of such materials is quite interesting, the scope of this manuscript is constrained to the simple chemistry of certain novel complex high-nitrogen materials. Hence, the title and straightforward transition to synthesis routes.

1.2 Synthesis Routes
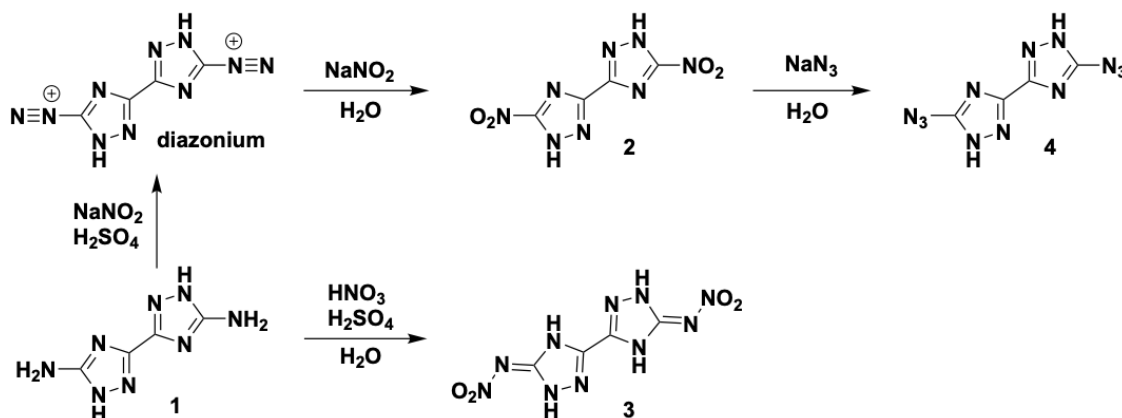
Scheme 1.1. Amines of 3,3′-diamino-5,5′-bis(1H-1,2,4-triazole) (DABT) (**1**) forming derivatives with nitro (**2**), azido (**4**), and nitroimide (**3**) substituents.[11]

Compounds supporting amine substituents are useful precursors in the synthesis of a wide variety of energetic products. Common substituents which can contribute towards energetic performance includes the nitro (-NO$_2$), azido (-N$_3$), and nitroimide (-N-NO$_2$) groups. For example, several energetic molecules are easily obtained from 3,3′-diamino-5,5′-bis(1H -1,2,4-triazole) (DABT) (**1**).[11] (Scheme 1.1) Treating an aqueous solution of **1** with sodium nitrite and sulfuric acid causes both amines to be replaced by nitro groups, via Sandmeyer-

type reaction, producing 3,3 -dinitro-5,5 -bis(1H-1,2,4-triazole) (**2**). Shown in the transformation to **2** is the highly unstable diazonium (–N≡N+) intermediate. Furthermore, both nitro groups of compound **2** may be substituted with azides upon addition of sodium azide, forming 3,3 -diazido-5,5 -bis(1H-1,2,4-triazole) (**4**). Alternatively, treatment of **1** with a mixture of nitric and sulfuric acids leads to nitration of the amines forming nitroimides (**3**). Similar strategies to those shown in Figure 1.1 may be applied to many other nitrogen-rich moieties. Elements of this strategy are employed throughout the remaining chapters.

1.3 Characterization of New Energetic Molecules

The molecular structure of energetic materials determines its chemical characteristics as well as its energetic performances. It's often useful to explore the molecular structure to gain insight into how a molecule will behave, and various functionalities and moieties have known effects on performance and stability of the energetic material. The structure of each compound is elucidated by analytical techniques including electrospray ionization mass spectrometry, spectroscopy (infrared, ^{1}H and ^{13}C nuclear magnetic resonance), and elemental analysis. Successful single-crystal x-ray diffraction analysis confirms the structure of each compound as well as their experimental densities. Crystallographic data is published in the Cambridge Crystallographic Data Centre (CCDC). A hybrid computational and experimental approach was followed to obtain these explosive parameters. Using the experimental crystal density and the computed heat of formation gives a hybrid experimental-computational detonation velocity and detonation pressure. Measured densities from crystallographic analysis are used to calculate the heats of formation and lattice enthalpies. The method of Byrd and Rice (based on properties of individual energetic compounds derived from quantum mechanics), obtained the heats of formation[12] and densities[13], [14] of all compounds. Optimized molecular geometries were computed from the Gaussian09 program package[15] using the B3LYP spin-restricted Kohn-Sham density functional theory (KS-DFT)[16]–[19] with the 6-31G** Pople Gaussian basis set.[20]–[22] Using the optimized geometry, the G3MP2(B3LYP)[23] energy is determined for electronic energy required to compute the heat of formation. The Gutowski method[24] provided the heat of sublimation

as determined from molecular volume. The heats of formation as well as density are input parameters for the EXPLO5 software. All detonation performance data (explosive energy and temperature, detonation pressure, detonation velocity, and volume of detonation gases) are calculated using EXPLO5 software.[25], [26] This methodology represents a hybrid strategy of blending computational heat of formation and experimental density data. Computational tools play an important role in the development of new energetic materials.

1.4   Computation of Energetic Performances

Computation of energetic performance data is achieved via EXPLO5 software.[27]–[29] This benchmark computer program is used globally, which is beneficial when comparing explosives characterized by various researchers worldwide. EXPLO5 calculates the detonation properties using "Becker-Kistaikowsky-Wilson (BKW) equation of state for gaseous detonation products and Cowan-Fickett equation of state for solid carbon".[27]–[29] Among the many output performance data for C-H-N-O type explosives, this software provides the calculated detonation pressure at the Chapman-Jouget point (P_{CJ}) and detonation velocity. Whenever a detonation performance comparison is made with benchmark explosives (eg. RDX, HMX, PETN, TNT, etc.) these two parameters (P_{CJ} and V_{Det}) are nearly exclusively used.

Crystal packing densities affect the calculated detonation performance of energetic materials. Wang et al. provide the following equations for detonation velocity (D) and detonation pressure (P) which show both detonation parameters are proportional to density (ρ) [30] such that,

$$D[\text{km·s}^{-1}] = \Phi^{0.5}(1.011 + 1.312 \cdot \rho \ [\text{g·cm}^{-3}])$$
$$\Phi = N \cdot \overline{M}^{0.5} Q^{0.5}$$
$$P[\text{GPa}] = 1.558 \cdot \Phi \cdot \rho^2 \ [\text{g·cm}^{-3}]$$

where "Φ is the characteristic value of explosives, N are the moles of gas produced per gram of explosives, $\overline{M}$ is an average molar weight of detonation products, and Q is the estimated heat of detonation".[30] Detonation velocity is proportional to density, while detonation pressure is proportional to density squared.[30] Therefore, single-crystal x-ray analysis serves not only

to unambiguously prove the molecular structure, but provides further insight into how these compounds are likely to perform upon detonation due to their experimental determination of density. However, beyond energetic performance, the suitability of explosophores may be constrained based upon their mechanical sensitivities and thermal stabilities.

1.5   Sensitivity and Thermal Stability

Further characterization of new energetic materials requires testing sensitivities toward impact and friction as well as thermal stabilities. Regarding impact, an insensitive secondary material will require >40 J of energy while a primary explosive may only require <4 J. A calibrated mass is dropped from a measured height, which is converted/calibrated to equivalent Joules impact. This is determined by releasing a drop-hammer (or *fallhammer*) of mass (m) from various heights (h) onto a sample of energetic material. The impact energy (in Joules) is calculated using $E = mgh$, where g is the gravitational constant. This is an experimental technique which doesn't correlate perfectly with any computational methods. There are several techniques for testing impact sensitivity. Dried material placed between two steel cylinders are held in place by a steel ring. Positive indications of decomposition include: audible bang or snap, escaping smoke when pulling cylinders apart, or dark trace residue after impact. A single positive result out of six repetitions validates the sensitivity. Tests are repeated by gradually lowering the energy (either by reducing the drop-hammer mass and/or drop height) until six negative results (using same energy) are achieved.

Sensitivity to friction is determined via a friction test apparatus. In this configuration the apparatus drags a porcelain peg over a small sample of dried material, which is placed on a porcelain plate of standard friction coefficient. Standard masses are placed at calibrated positions on the apparatus arm and a chart provided by the manufacturer lists the equivalent Newtons of force. Visual indications of decomposition include dark decomposition lines, a bright spark or flash, in addition to an audible snap or crackling. While an insensitive material requires >360 N of friction force, primary explosives typically have friction sensitivities <10 N. Similar to impact testing, a single positive result out of six repetitions determines the sensitivity. Friction is reduced by selecting lighter masses and/or placement of the mass

closer toward the machine. These tests follows the NATO standard for both impact[31] and friction[32] sensitivity tests. Relative sensitivities should only be compared with results derived from the same testing standard.

Energetic materials may need to be stored in arid environments at elevated temperatures for protracted periods of time, and any inherent thermal instability could have catastrophic consequences. Thermal stability is recorded via thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC). Samples should first be thoroughly dried then stored in a vacuum sealed desiccator (over a drying agent such as drierite or P_2O_5) for several days. Only a few milligrams of prepared dry material is necessary for collecting sufficient data for determining the decomposition temperature. The weight percent (relative to starting mass) is recorded as the temperature continues to increase at a rate typically of 5 °C/min. The weight percent plot trace should indicate a sharp mass loss near the onset of decomposition. Multiple samples are run as needed in order to improve the confidence in the data.

Sensitivity tests are useful for determining the safety of an energetic material and potential uses. Highly sensitive materials may be useful primaries capable of initiating and forming a sufficient shockwave necessary to cause insensitive secondary explosive material to detonate. Through the study of various energetic molecules, some important sensitivity trends emerge. For example, energetic azides are often quite sensitive, which precludes their use as insensitive high explosives.[33] Unfortunately, azides tend to inhibit molecular packing in the crystal lattice structure, which lowers the density and reduces the energetic performance.

Nitrotetrazole (as well as protonated DNTT and NTAZ) is acidic. The nitro group is electron withdrawing, which lowers the pKa, thereby making it acidic. For comparison, nitrotetrazole has a pKa of -0.8 and therefore is more acidic than either the protonated 5-H tetrazole (pKa = 4.9) or acetic acid (pKa = 4.75). Nitrotetrazole is more acidic than either of these compounds due to the electron withdrawing nature of the nitro group.

An energetic molecule containing an acidic proton usually has higher detonation performance, but relatively low mechanical or thermal stability as compared to its salts. For this reason, a series of energetic salts are often explored which may improve mechanical and

thermal stabilities.[34], [35] Acidic explosophores may be deprotonated by treatment with a base such as ammonia or hydroxylamine. Upon deprotonation, energetic salts may improve their stabilities when combined with nitrogen rich cations.

1.6 Heterocycles Investigated

1.6.1 Triazole and Tetrazole

In addition to the 1,2,4-triazole[11] another common energetic moiety is the tetrazole.[36] Both five-membered heterocycles form the backbone of a wide variety of catenated nitrogen systems. By replacing a carbon on the triazole, the tetrazole enjoys a higher heat of formation due to increased nitrogen content, which contributes to overall energetic performance. However, this added benefit of a driving force toward the formation of N_2 nitrogen gas comes at the cost of reduced stability. Instability of high-nitrogen systems is a result of the lone pair of electrons on each nitrogen atom.[37] The lone pair may donate to neighboring antibonding sigma orbitals.[37] This explains why it's easier for tetrazoles to achieve the lower activation energy (as manifested by lower stability and higher sensitivity), which triggers the explosives to form the detonation products. In aromatic nitrogen-rich heterocycles, stability is improved by inclusion of substituents, which help separate the pi and sigma bonds of the heterocycle ring.[37] Furthermore, the 1,2,4-triazole remains a useful framework since it has the advantage of enabling substituents attached on either or both of the ring carbons. Several novel energetic tetrazoles and 1,2,4-triazoles are found in each of the following chapters.

1.6.2 Azasydnone Formation

In addition to tetrazole and 1,2,4-triazole, three of the subsequent chapters explore the cyclization and unique attributes of the azasydnone heterocycle. As an energetic functional group, azasydnones have the possibility to incorporate notable benefits such as high densities and good thermal stability due to zwitterionic motif leading to enhanced packing in the crystal lattice due to strong intermolecular hydrogen bonding in the network.[39] Additionally, the inclusion of two oxygen atoms improves the formation of detonation products.[39] An
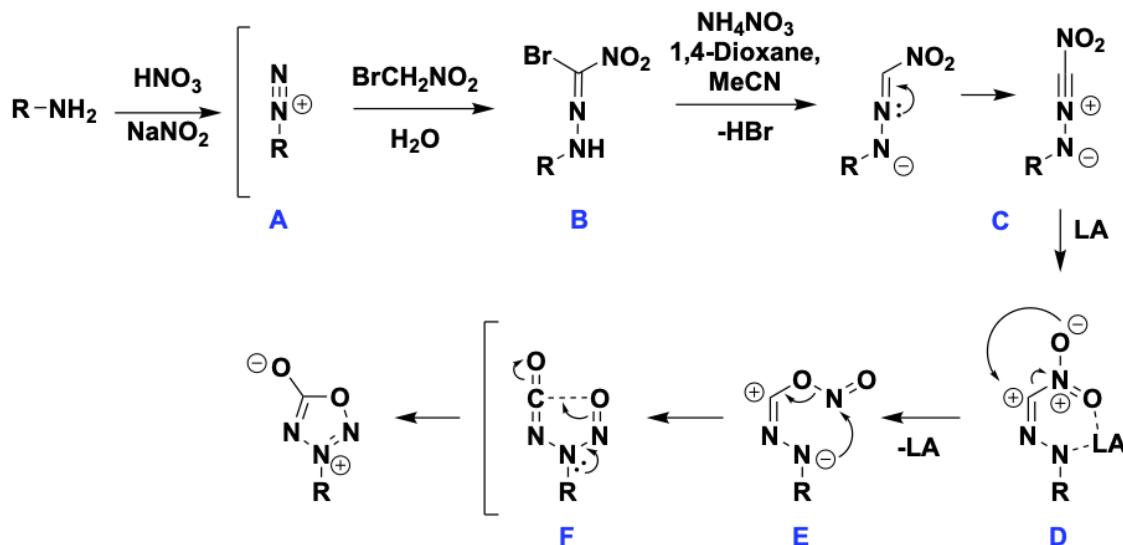
Figure 1.2. Plausible reaction mechanism for azasydnone ring. Adapted from Zhilin et al.[38]

explanation of the reaction mechanism leading to the formation of the azasydnone moiety was proposed by Zhilin et al and is shown in Figure 1.2.[38] Zhilin's reaction mechanism was based on nitrosonium tetrafluoroborate in trifluoro acetic acid with potassium nitroform as the nitro source. An adaptation of the reaction mechanism is presented in Figure 1.2. The main transformations occurring are diazotization, azo coupling, elimination, and double rearrangement.[38] Initially, the amine reacts with nitrous acid (formed by reacting nitric acid with sodium nitrite) to form the diazonium compound (**A**). Bromonitromethane then reacts with the diazonium giving the bromonitrohydrazone compound (**B**). After isolating **B** as dried material and redissolving in either acetonitrile or 1,4-dioxane, the mixture was stirred with excess ammonium nitrate, causing hydrobromic acid to be released from (**B**). The electron withdrawing nature of the remaining nitro group, leads to a lone pair of electrons from the azo group to form the C≡N triple bond of nitronitrilimine intermediate (**C**). Finally, in the presence of a lewis acid (**C**) gives the intermediate cyclic structure (**D**).[38] In the presence of the lewis acid (HBr), the -N=C-NO$_2$ moiety (**D**) rearranges from a nitro compound to an organic nitrite carbocation (**E**). This species then forms cyclic intermediate (**F**), while a lone pair of electrons from the R-N nitrogen forms a sigma bond with the freed nitro group. The second rearrangement occurs when the pi bond electrons from the N=O

double bond shift away from the nitrogen toward the more electronegative oxygen, forming a sigma O-C bond, closing the oxatriazole ring with the exocyclic oxygen. The formation of the azasydnone is complete. The resulting negative charge on the exocyclic oxygen and positive charge on the central nitrogen are unique features of the zwitterionic compound.

1.6.3   Azasydnone Decomposition

Unfortunately, decomposition of the azasydnone has been reported in the literature as well as several of the following chapters. In such instances, azido compounds often result from the decomposition of the azasydnone, leading to more sensitive products. An insightful decomposition mechanism of the azasydnone ring to azide has been proposed by Dalinger.[40] Figure 1.3 is an adaptation of this decomposition mechanism and applied to 3-azasydnone-5-nitro-1,2,4-triazole (NTAZ) found in Chapter 6. This scheme could also be representative of a similar phenomena occurring during the tetrazole azasydnone (TAZ) synthesis (Chapter 3) since azidotetrazole was also observed in some energetic salts of TAZ upon standing. Specifically, azidotetrazole appeared in the ^{13}C NMR spectra of aminoguanidinium and triaminoguanidinium salts of TAZ. (Chapter 3) Similarly, 3-azido-5-nitro-1,2,4-triazole appeared in the ^{13}C NMR spectra of NTAZ. (Chapter 6) Even during the synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium (MSI) TAZ, crystal structures of MSI azidotetrazolate were obtained. (Chapter 5) Therefore, since similar findings are discovered in several chapters of this manuscript, it is appropriate to present such a reaction mechanism in order to aid in understanding of the recurring appearance of azides. It is rather tragic that the amine is both a necessary precursor to the formation (Figure 1.2) of the azasydnone as well as its possible assassin. (Figure 1.3).

In this mechanism[40], an amine attacks the azasydnone carbon. Electrons move within the ring, resulting in cleavage of the C-O sigma bond, which opens the ring. Ring opening leads to formation of more stable C=N and N=O pi bonds. (pathway A) The exocyclic oxygen loses its negative charge to form the C=O pi bond. Subsequent hydrolysis leads to the formation of an oxotetrazole ring. Elimination of isocyanic acid (HNCO) leaves the azide substituent. Alternatively, following addition of an amine to the azasydnone carbon,
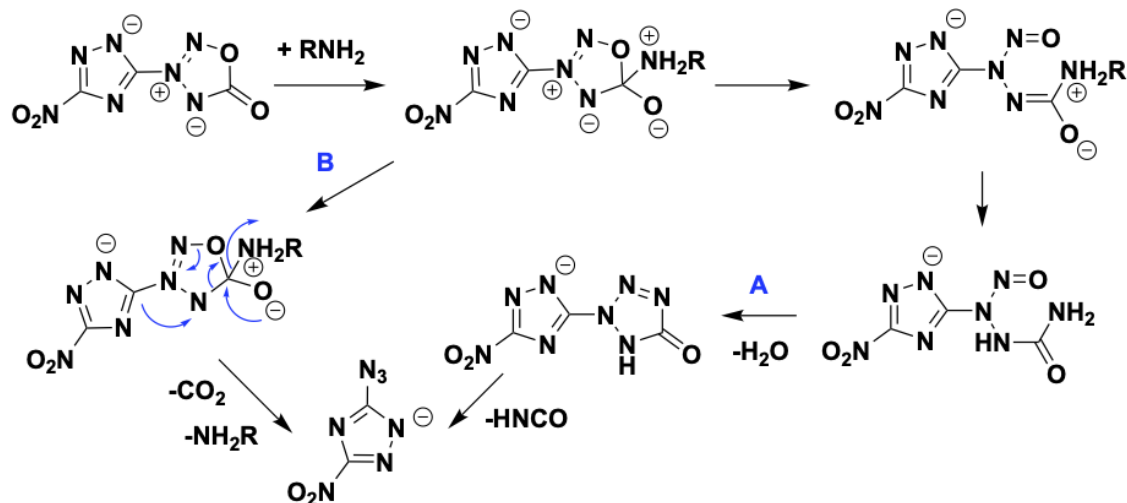
Figure 1.3. Possible decomposition mechanism of azasydnone to azide substituent. Adapted from Dalinger et al.[40]

formation of an oxotetrazole intermediate is bypassed, resulting in the simple elimination of carbon dioxide and amine. (pathway B) This mechanism may be the root cause of the instability observed in azasydnone compounds with counterions containing nucleophiles (eg. diaminoguanidinium).

1.7 Bridged and Annulated Structures

Many nitrogen-rich energetic compounds contain several nitrogen atoms catenated to form a series of N-N bonds.[34] Familiar five-membered heterocyles are formed as pyrazoles (1,2-diazole), imidazoles (1,3-diazole), triazoles, and tetrazoles. Such heterocycles may be combined as bicyclic or tricyclic systems in order to achieve even higher nitrogen content. These catenated structures are commonly formed either by bridging multiple heterocycles via C-N or C-C bonds or as a structure of fused rings (annulated). As compared to bridged heterocycles, the annulated systems often have increased heats of formation, higher densities (and hence greater detonation performance), and improved thermal stabilities.[34], [35] Consequently, annulated heterocycles are a promising high-density structures within the field of new energetic material design. For example, 3,6,7-Triamino-[1,2,4]triazolo[4,3-b][1,2,4]triazole (TATOT) remains a very promising non-toxic energetic cation.[35], [41],

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[42] (Figure 1.4) Two annulated 1,2,4-triazoles form the base structure. This compound is easily prepared from inexpensive commercially-available precursors.[35] Furthermore, many TATOT salts have high performance as a result of high densities, as well as good thermal and mechanical stabilities.
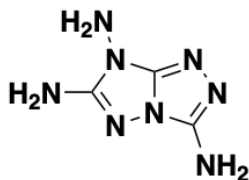
Figure 1.4. 3,6,7-Triamino-[1,2,4]triazolo[4,3-b][1,2,4]triazole (TATOT).

1.8 Energetic Salts

Cations used in energetic salts discussed herein include ammonium, hydroxylammonium, and hydrazinium as well as nitrogen-rich species (e.g., guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium). Ammonium, hydroxylammonium, and hydrazinium are sometimes effective in improving the sensitivity of highly sensitive compounds including azides.[33] Relative to other nitrogen-rich salts, hydroxylammonium usually has higher density and therefore, greater detonation performance, but lower thermal stability because it's a relatively reducing cation Ammonium is less nucleophilic and less reducing than hydroxylammonium and hydrazinium. Hydrazinium is reducing but provides higher heats of formation due to increased nitrogen content and is more thermally stable.

Forming energetic salts of a nitrogen-rich energetic acidic compound have been shown to improve thermal stability, while maintaining detonation performance.[43] These cations are capable of increasing detonation performance due to increased nitrogen content. However, some cations may inhibit packing in the crystal structure, thereby reducing densities. Unfortunately, the aminated nitrogen-rich salts cause decomposition of tetrazole azasydnones.[44] (see Chapter 3) The relatively high densities observed in metallic salts (eg. copper, silver, and sodium) is somewhat misleading since their heavy mass is effectively dead weight, energetically speaking. Incorporating copper or silver often causes the resultant heavy metal

salts to be extremely sensitive and must be handled with care. Several sensitive primary explosives incorporate metals (eg. Lead azide[45], Lead styphnate[45], copper-based DBX-1[46], silver azide[47], silver nitrotetrazole[48], and silver fulminate[49]). Further examples of these salts are presented in Chapters 2, 3, and 6.

Although less common, energetic salts (such as nitrate or perchlorate) of a nitrogen rich cation can enhance the energetic properties. Oxygen in both of these anions serve as oxidizers, which react with carbon and hydrogen to form detonation products upon detonation and improves the energy release during detonation. Aside from the enriched oxygen content, both anions can improve thermal stability. Beyond nitrate and perchlorate, incorporating deprotonated nitrotetrazole anion with its high-nitrogen content can drive the heat of formation higher. Chapter 5 discusses several energetic salts of a nitrogen rich cation in greater detail.

1.9   Chapter Previews

Chapter 2 covers the synthesis of the 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazolate anion from TATOT. As shown in Figure 1.4, TATOT incorporates one amine bonded to nitrogen and two amines bonded to carbon atoms on the annulated heterocycle. The addition of two C-NO$_2$ substituents and elimination of the N-amine from TATOT was achieved via Sandmeyer reaction. From this new annulated heterocyclic compound, a series of energetic salts was prepared which were fully characterized by mass spectrometry, multinuclear NMR spectroscopy, single-crystal X-Ray diffraction, and differential scanning calorimetry. Impact and friction tests proved each of these energetic materials exhibit low-sensitivities. The high-performance of all compounds was confirmed by calculated detonation performance, as determined from the calculated heats of formation. This research was the basis of my first paper, which was published in *ZAAC* (*Journal of Inorganic and General Chemistry*).[50] I was invited by researchers from the University of Pardubice to present this paper at the *New Trends in Energetic Materials* (NTREM) Conference in Czech Republic.[51] I was also invited to present the manuscript at the *International Pyrotechnics Society* (IPS) Seminar in Colorado. Unfortunately, both conferences were cancelled due to the COVID-19 pandemic.

Chapter 3 details the synthesis of tetrazole azasydnone (TAZ), which is the first compound comprising both an azasydnone and a tetrazole ring. Advertised as an environmentally friendly zwitterionic primary explosive, tetrazole azasydnone and its silver salt are lead-free potential replacements for primary explosives. Eleven other energetic salts of TAZ were synthesized and characterized. This work was published and featured on the cover of *Chemistry-A European Journal.*[44] Furthermore, the significance of this work has captured the attention of SynFacts.[52] More than three grams of the silver tetrazole azasydnone has been prepared for shipment to Picatinny Arsenal for their further analysis and characterization because of promising primary explosive properties. Both Purdue and the Army Research Lab (ARL) published press releases announcing the impact of this exciting new energetic compound and has been widely circulated on social media platforms such as Twitter. The detonation of silver tetrazole azasydnone may be viewed on the Piercey Research Group website: https://www.davinpiercey.com/agtazdet/. I presented this work as part of the virtual *Soft Materials Symposium* during Summer 2020 at Purdue University.

Chapter 4 reviews the little-known heterocycle (azasydnone) and its use in energetic materials. The azasydnone ring has more traditionally found use in pharmaceuticals, however a recent flurry of papers has shown there is now broad interest in this heterocycle within the energetics and broader chemical community. For this reason a brief review on this unique nitrogen-rich heterocycle is necessary as its use in tailored materials is growing rapidly. In this chapter, we reviewed the state of the art of azasydnone use in energetic materials prior to our novel work in this area. Additionally, their detonation performances are compared with tetrazole and azide analogs. This chapter ties in appropriately with Chapters 3 and 6 since several zwitterionic compounds were synthesized based on the azasydnone motif. This work was published in *Energetic Materials Frontiers.*[53]

Chapter 5 discusses the synthesis and characterization of several energetic salts of the methyl sydnone imine cation. New energetic cations remain less common than new energetic anions when salt-based energetic materials are considered, so any new energetic cation greatly expands the range of possible energetic salts available. This is of particular interest because the sydnone imine based cationic heterocycle may potentially improve oxygen balance of energetic materials based on this unique cation and this also marks the first use of this

heterocyclic system in energetic materials. Consequently, this study is unique in that it is the first to investigate the use of sydnone imines in energetic salts. This chapter also explores the behavior upon nitration of this unique heterocyclic system. This work was published in *New Journal of Chemistry.*[54]

Chapter 6 showcases the first synthesis of nitrotriazoleazasydnone (NTAZ) via the rearrangement of a *C*-nitronitrilimine, including seven new azasydnone salts and records their energetic performances. As a fascinating byproduct, the chapter reports the first known example of a nitrilimine to cyclize with a diazonium to form a 2,3-disubstituted tetrazole. Although nitrilimines are known widely for their use in traditional organic compound synthesis, they are rather unexplored for N-N bond forming reactions. Multiple new high-nitrogen heterocyclic energetic species were synthesized via nitrilimine chemistry, resulting in the formation of several novel high-nitrogen energetic compounds including a fifteen-nitrogen tri-heterocyclic system based around an azidotetrazole core. These complex heterocyclic products were obtained in a minimal number of steps from an easily-generated bromonitrohydrazone and offers an exemplary route to new high-nitrogen compounds and N-N bond forming reactions. This work has been peer-reviewed, submitted with revisions, and awaiting final acceptance for publication in *Inorganic Chemistry.*

Chapter 7 provides a brief summary of the previous chapters. The principle findings from each of the publications are captured. Where possible, common themes from the research are highlighted among the work achieved from annulated heterocyles, tetrazoles, azasydnones, methyl sydnone imines, 1,2,4-triazoles, and nitrilimines. This final chapter in *Chemistry of Complex High-Nitrogen Materials* is arranged as an abbreviated compilation of syntheses, characterization, and performance.

The following chapters of this dissertation record my unique contribution to the energetic materials community and the broader scientific body of knowledge.

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2. SYNTHESIS AND CHARACTERIZATION OF SALTS OF THE 3,6-DINITRO-[1,2,4] TRIAZOLO [4,3-b] [1,2,4] TRIAZOLATE ANION: INSENSITIVE ENERGETIC MATERIALS AVAILABLE FROM ECONOMICAL PRECURSORS

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2.1 Abstract

In this work, the treatment of 3,6,7-triamino-[1,2,4]- triazolo[4,3-b][1,2,4]triazole (TATOT) [2] with sulfuric acid and sodium nitrite results in elimination of the *N*-amine and the formation of the new energetic anion 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazolate (DNTT) via nitro-Sandmeyer chemistry. This new energetic anion is available in a convenient and inexpensive three-step process from inexpensive commercial starting materials. Several nitrogen rich salts of this material have been prepared and their chemical (infrared, Raman, NMR, single-crystal X-ray) and energetic (impact, friction, thermal) properties determined. As a rule, this class of energetic salts are insensitive energetic materials.

2.2 Introduction

Within the field of new energetic materials design, various performance and safety requirements drive energetic materials development including high mechanical or thermal stability, high performances, or a high degree of environmental safety. As these goals are pursued, the syntheses of these new 'designer' energetic materials often become an extensive number of steps long which translates to an energetic material that is far too expensive to be used in practice. This issue is best exemplified by the explosive octanitrocubane, [3] which despite possessing excellent detonation performance has a complex synthesis so complex as

to render the final material entirely useless in practice. Within preparatory energetic materials chemistry there is a strong need for synthetic transformations on readily-available precursors to create the next generation of energetic materials.

Unfortunately, the synthesis of new energetic materials to meet ever-increasing performance requirements requires often rather complex heterocyclic backbones. These complex structures often have correspondingly long/expensive syntheses. One of the promising structural motifs for high density (and as such, high performance) of an energetic material is annulated heterocycles, but these often have even more complex syntheses.

3,6,7-Triamino-[1,2,4]triazolo[4,3-b][1,2,4]triazole (TATOT) has been shown to be a very promising energetic cation in the design of new energetic materials. [2], [4], [5] This moiety has the advantage that it is prepared in an easily-scaled two-step two pot procedure; first inexpensive guanidinium chloride is reacted with hydrazine hydrate giving triaminoguanidinium chloride. [2] This is then reacted with economical cyanogen bromide giving the 3,6,7-triamino-[1,2,4]triazolo[4,3-b][1,2,4]triazole system. Salts of this annulated heterocycle are generally high-density with high thermal and mechanical stabilities, and often have high performance. Additionally, this energetic cation has been shown to be entirely non-toxic. [2]

The ease of preparation of the TATOT heterocycle, consisting of two annulated 1,2,4-triazole rings, led us to use it as the basis of this effort toward new annulated-heterocycle based energetic materials.

The TATOT system possesses three amine moieties, two bound to carbon and one bound to nitrogen. In this work we subjected this material to Sandmeyer reaction reactions which resulted in the loss of the N-amine, and formation of two C-NO$_2$ groups forming the 3,6-dinitro-[1,2,4]triazolo[4,3-b]- [1,2,4]triazolate anion. With this new material in hand we prepared a series of energetic salts which were chemically characterized by single-crystal X-ray diffraction, multinuclear NMR spectroscopy, differential scanning calorimetry, and mass spectrometry. These all proved to be low-sensitivity energetic materials as determined by their experimental impact and friction sensitivities. Heats of formation for all compounds were calculated and used to determine theoretical detonation performances, confirming that all prepared materials are high-performing energetic materials.

2.3 Results and Discussion

2.3.1 Syntheses

The precursor 3,6,7-triamino-[1,2,4]triazolo[4,3-b][1,2,4]triazole (TATOT) was prepared according to literature procedures. [2] Triaminoguanidinium hydrochloride was reacted with cyanogen bromide in a hydrochloric acid solution at elevated temperature. After cooling, the precipitate of TATOT hydrochloride that formed is neutralized with a solution of sodium carbonate, yielding neutral TATOT. [2] A dilute sulfuric acid solution of TATOT when added to a concentrated solution of sodium nitrite at elevated temperature was found to result in the loss of the *N*-amine and the *C*-amines underwent Sandmeyer chemistry yielding the dinitro annulated triazole, 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazole (HDNTT) (Scheme 2.1).
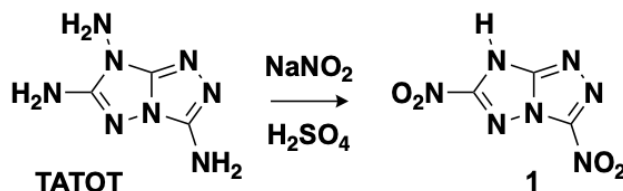
Scheme 2.1. Synthesis of HDNTT (**1**).

When increasing concentrations of TATOT in sulfuric acid were used in this reaction, the reaction produced a large amount of uncharacterized entirely insoluble material, likely coupling products of extended structure due to the reactivity of diazonium intermediates toward precursor amines. In order to obtain **1** in good yields and without byproduct formation the TATOT solution must be kept dilute. After diazotization, the reaction was acidified and the acidic HDNTT (**1**) was extracted using ethyl acetate. The evaporation of this solution yielded extremely-deliquescent HDNTT as an oil. Attempting to dry this oil over Drierite or P_2O_5 in a desiccator or on a high-vacuum line failed to remove water from the material. The HDNTT oil was dissolved in water and treated with sodium hydrogen carbonate, and after purification from residual hydrogen carbonate yielded the sodium salt of 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazolate (**2**) as a hygroscopic solid (Figure 2.1).

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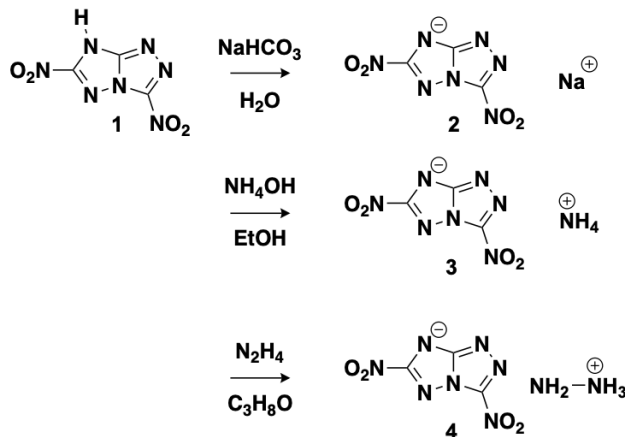
Figure 2.1. Synthesis of DNTT salts of **2**-**4** from **1**.

When the HDNTT oil was treated with ammonium hydroxide and evaporated, the ammonium salt (**3**) was obtained as similar extremely deliquescent oil and was unable to be isolated in a form sufficient for energetic characterization. The hydrazinium salt (**4**) was attempted to be prepared by adding hydrazine hydrate to a solution of HDNTT in 2-propanol, however the initially-flocculent precipitate of the hydrazinium salt absorbed atmospheric moisture within minutes and became a sticky oil. By NMR this compound also exhibited significant decomposition and was not characterized further.

The sodium salt (**2**) was used to prepare the silver salt (**5**) via a metathesis reaction with aqueous silver nitrate (Figure 2.2).
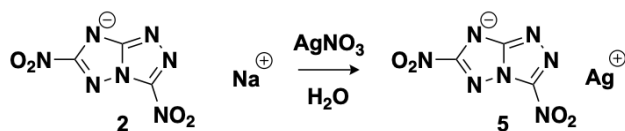
Figure 2.2. Synthesis of DNTT (**5**) from **2**.

By thermogravimetric analysis (TGA), the silver salt (**5**) was found to exist as a hemi-hydrate and this material was used for the further preparation of all energetic salts. Energetic salts were prepared by reaction with the corresponding chloride salt of the energetic cation (Figure 2.3 and Figure 2.4) in aqueous solution, followed by filtration of the precipitated

silver chloride, evaporation of the solvent and drying of the residual solid in a desiccator over Drierite.
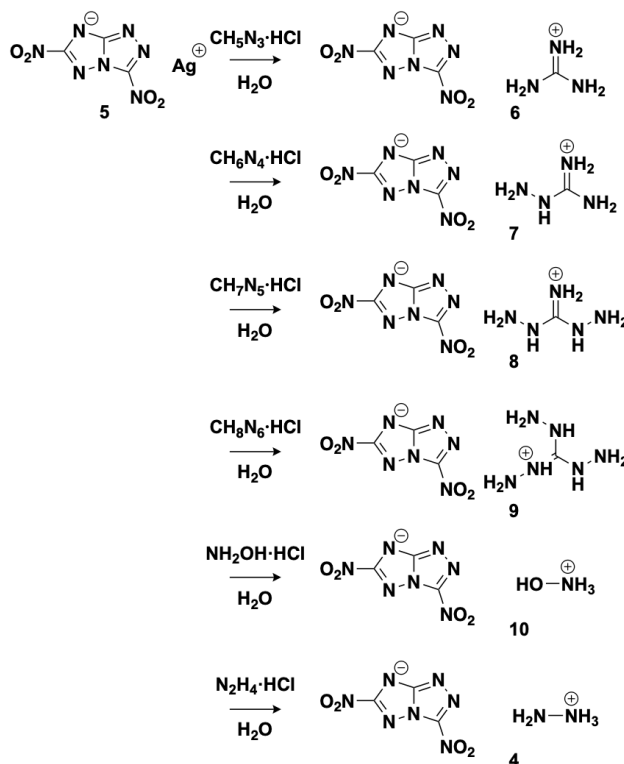
Figure 2.3. Synthesis of DNTT salts **4**, **6-10** from **5**.
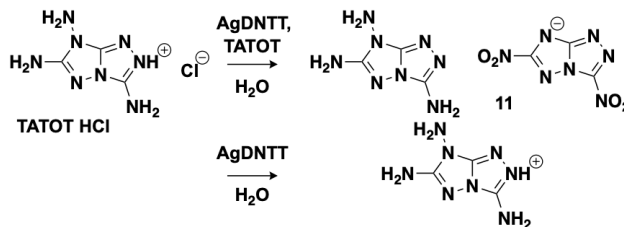
Figure 2.4. Synthesis of TATOT · DNTT · TATOT (**11**).

The hydroxylammonium (**10**) and hydrazinium (**4**) salts were unable to be isolated in a pure form. In both cases, on evaporation of the aqueous solution after filtration of the silver chloride, the residual gummy solid darkened and gas bubbles were observed. NMR indicated the presence of new impurities and we suspect there is nitro group reduction or displacement occurring. The diaminoguanidinium (**8**) and triaminoguanidinium (**9**) salts also darkened

slightly but only trace impurities were detected by NMR spectroscopy. The guanidinium (**6**), aminoguanidinium (**7**), and TATOT (**11**) salts of the DNTT anion were isolated as bright yellow solids. In the case of **11**, when one equivalent of TATOT hydrochloride was reacted with one equivalent of silver DNTT, after the silver chloride was filtered off and the solution evaporated to dryness, the crystals obtained consisted of TATOT DNTT co-crystallized with a second molecule of neutral TATOT. After this initial synthesis, all further preparations of **11** had an equivalent of neutral TATOT included to always form this product.

2.3.2   Spectroscopy

The signals of the $C_3N_7O_4^-$ anion appears in the ^{13}C spectra at 165.1, 163.1, and 143.1 ppm. The 165.1 and 163.1 ppm peaks correspond to the carbons with nitro groups while the 143.1 peak is attributed to the central carbon. The chemical shifts of the terminal carbons are shifted downfield relative to the peaks at $\delta =$ 158.5 and 149.1 ppm reported for TATOT.[2] There remains only a slight upfield shift of the central carbon peak from 143.5 ppm of TATOT. [2] The proton spectra of all compounds compare well with literature data on other materials containing the corresponding cations.

2.3.3   Mass Spectrometry

The $C_3N_7O_4^-$ anion was observed at 198 m/z in negative mode ESI for all prepared compounds **1**–**11**.

2.3.4   Single Crystal X-ray Analysis

Data for guanidinium DNTT (**6**) and TATOT · DNTT · TATOT (**11**) were collected using a Bruker Quest diffractometer with kappa geometry, a copper target I-μ-S microsource X-ray tube (Cu-K_α radiation, $\lambda = 1.54178$ Å), a laterally graded multilayer (Goebel) mirror single crystal for monochromatization, and a Photon2 CMOS area detector. Data for diaminoguanidinium DNTT (**8**) and triaminoguanidinium DNTT (**9**) were collected with a Bruker Quest diffractometer with a fixed chi angle, a molybdenum wavelength fine focus sealed X-ray tube (Mo-K_α radiation, $\lambda = 0.71073$ Å), a single crystal curved graphite inci-

Table 2.1.
Crystallographic data and structure refinement details for **6**, **8**, **9**, and **11**.

	6	8	9	11
Formula	$C_3N_7O_4 \cdot CH_6N_3$	$C_3N_7O_4 \cdot CH_8N_5$	$C_3N_7O_4 \cdot CH_9N_6$	$C_3H_6N_8 \cdot C_3N_7O_4 \cdot C_3H_6N_8$
FW [g·mol^{-1}]	258.19	288.22	303.24	506.38
Crystal System	orthorhombic	monoclinic	monoclinic	monoclinic
Space Group	$Pbca$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	8.2089 (2)	8.5604 (6)	12.076 (1)	22.7370 (6)
b [Å]	12.8092 (4)	14.7253 (11)	6.8987 (6)	5.3574 (2)
c [Å]	18.3773 (5)	9.8929 (7)	13.7956 (11)	16.3703 (3)
α [°]	90	90	90	90
β [°]	90	114.740 (3)	99.157 (4)	106.5675 (12)
γ [°]	90	90	90	90
V [Å^3]	1932.36 (9)	1132.59 (14)	1134.65 (16)	1911.30 (9)
Z	8	4	4	4
ρ calcd.[g·cm^{-3}]	1.775	1.690	1.775	1.763
T [K]	150	150	150	150
Crystal shape	Plate	Block	Plate	Plate
Color	Orange	Brown	Colorless	Yellow
Crystal size [mm]	0.24×0.21×0.07	0.47×0.39×0.25	0.38×0.25×0.05	0.20×0.17×0.01
R_1/wR_2 (all data)	0.0478 /0.1208	0.0491 /0.1114	0.0723 /0.1129	0.0672 /0.1469
R_1/wR_2 (I>2σ)	0.0449 /0.1177	0.0379 /0.1034	0.0483 /0.1037	0.0565 /0.1406
S^c	1.055	1.034	1.105	1.050
No. of reflec.	2067	4342	3601	4006
Parameters	183	332	345	364
Restraints	6	567	565	66

dent beam monochromator, and a Photon100 CMOS area detector. Both instruments are equipped with Oxford Cryosystems low temperature devices. Examination as well as data collection were performed at 150 K. Data were collected, reflections were indexed and processed using APEX3. [6] The data were scaled then corrected for absorption using Sadabs. [7], [8] The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs [9] then refined by full-matrix least-squares against F^2 with all reflections using SHELXL2018. [10]–[12] The structure for guanidinium DNTT (**6**) is shown in Figure 2.5.

For guanidinium DNTT (**6**) hydrogen atom positions were refined and all N–H bond lengths were restrained to a target value of 0.88(2) Å. For diaminoguanidinium DNTT (**8**), triaminoguanidinium (**9**) and TATOT · DNTT · TATOT (**11**) the bond lengths of all sp^2 hybridized primary amino N–H groups were restrained to be similar to each other, as were the bond lengths of all sp^3 hybridized primary amino N–H groups and of all secondary
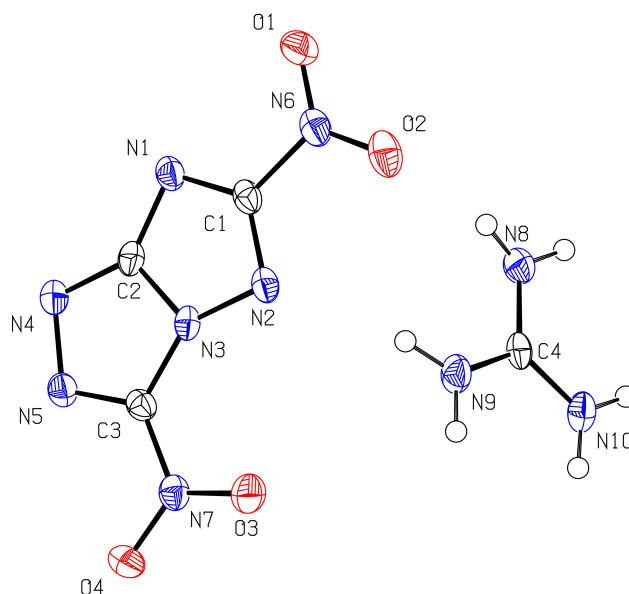
Figure 2.5. Molecular unit of guanidinium DNTT (**6**). Ellipsoids are drawn at the 50% probability level.

amino N–H groups. $U_{iso}(H)$ values were set to 1.2 or 1.5 times $U_{eq}(N)$ in all structures. The structures for **8** and **9** are shown in Figure 2.6 and Figure 2.7, respectively.

In both the structures of diaminoguanidinium DNTT (**8**) and triaminoguanidinium DNTT (**9**) the DNTT moieties are disordered by a pseudo-mirror operation. In both structures the two disordered moieties were restrained to have each a similar arrangement. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratios refined to 0.9598(11) to 0.0402(11) for diaminoguanidinium DNTT (**8**) and to 0.8944(18) to 0.1056(18) for triaminoguanidinium DNTT (**9**). The structure for **11** is shown in Figure 2.8.

The crystallographic data and structure refinement details for **6**, **8**, **9**, and **11** are summarized in Table 2.1. Complete crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre. [13]

2.3.5 Thermal Behavior

The thermal behaviors of all salts prepared were investigated by combination differential scanning calorimetry – thermogravimetric analysis (DSC/TGA). All measurements were
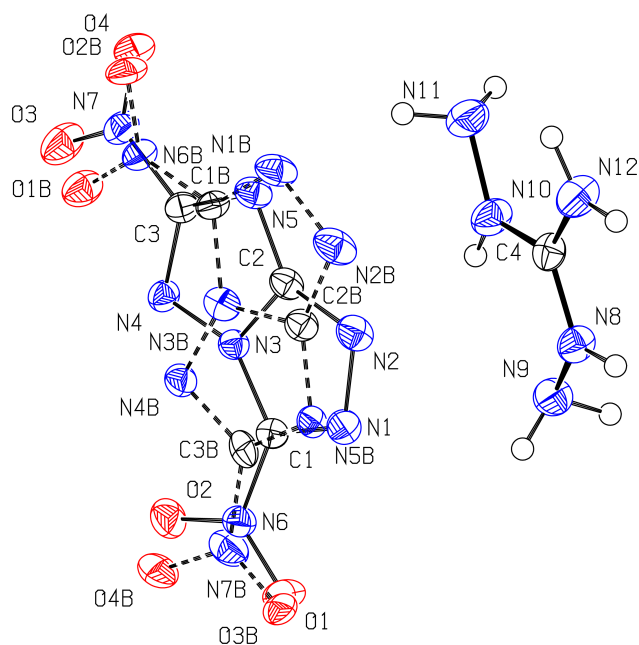
Figure 2.6. Molecular unit of diaminoguanidinium DNTT (**8**). Ellipsoids are drawn at the 50% probability level.
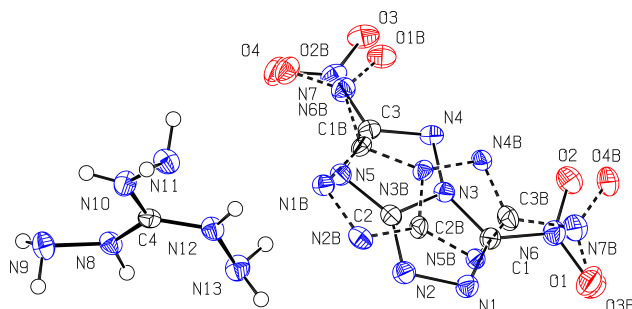
Figure 2.7. Molecular unit of triaminoguanidinium DNTT (**9**). Ellipsoids are drawn at the 50% probability level.

conducted with a heating rate of 5 $K \cdot min^{-1}$. Decomposition temperatures for **5**, **6**, and **11** were observed near 210°C, while the remaining salts decomposed below 180°C, demonstrating insufficient thermal stability for practical use. As mentioned previously, salts **4** and **10** appeared to decompose near room temperature during evaporation and darkened. Not surprisingly, the DSC profile of **10** records the lowest decomposition temperature at 90°C without a sharp onset. The differential scanning calorimeter indicated a well-defined onset of decomposition at 209°C for **6**, which also revealed a sudden drop in heat flow at constant
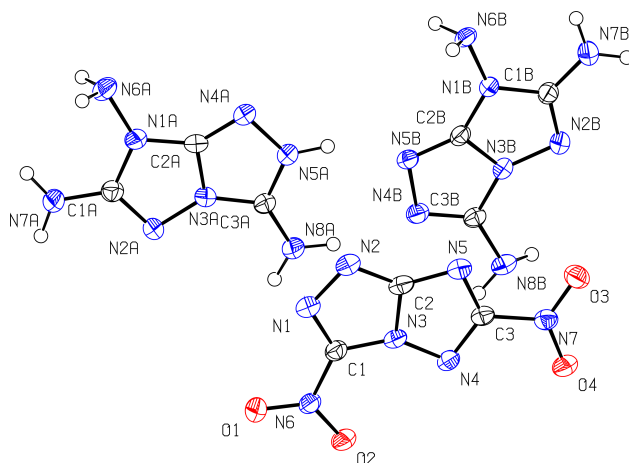
Figure 2.8. Molecular unit of TATOT · DNTT · TATOT (**11**). Ellipsoids are drawn at the 50% probability level.

weight, indicating a melting temperature at 135°C. Decomposition temperature appears to trend with increasing nucleophilicity of the counterion; while the guanidinium salt is one of the most stable, the triaminoguanidinium salt with its hydrazine moieties is one of the least stable.

2.3.6 Energetic Properties

The energetic properties of the DNTT compounds are summarized in Table 2.2. The density [14], [15] and heats of formation [16] of all materials were calculated using the method of Byrd and Rice, based on correlations of quantum mechanically derived properties of isolated energetic molecules with experimental heats of formation and crystalline densities. The calculated densities were within 3.5% of the densities determined crystallographically. The molecular geometries were optimized using the B3LYP spin-restricted Kohn–Sham density functional theory (KS-DFT) [17]–[20] with the 6-31G** Pople Gaussian basis set, [21]–[23] using the Gaussian09 program package. [24] For the computation of the electronic energy required to compute the heat of formation, the G3MP2(B3LYP) [25] energy is obtained on the optimized geometry. Finally the heat of sublimation, using the Gutowski method, [26] was calculated from the molecular volume (determined from the volume contained within the .001 electron per bohr^3 isosurface of the electron density of each of the isolated molecular

Table 2.2.
Energetic properties for all prepared compounds.

	1	2	4	5	6	7	8	9	10	11
Formula	$C_3HN_7O_4$	$NaC_3N_7O_4$	$C_3H_5N_9O_4$	$AgC_3N_7O_4$	$C_4H_6N_{10}O_4$	$C_4H_7N_{11}O_4$	$C_4H_8N_{12}O_4$	$C_4H_9N_{13}O_4$	$C_3H_4N_8O_5$	$C_9H_{13}N_{23}O_4$
FW [g·mol^{-1}]	199.08	221.07	231.13	305.95	258.16	273.17	288.19	303.2	232.12	507.36
IS [J]$^{a)}$	ND	>40	>40	>40	>40	>40	>40	>40	>40	>40
FS [N]$^{b)}$	ND	180	192	120	>240	192	>288	216	>288	>360
N [%]$^{c)}$	49.26	44.36	54.55	32.05	54.27	56.42	58.34	60.07	48.29	63.39
Ω [%]$^{d)}$	-20.1	-14.5	-31.15	-10.5	-43.38	-43.92	-44.41	-44.85	-20.68	-64.6
T_{dec}[°C]$^{e)}$	ND	150	160	210	209	178	150	135	90	215
ρ [g·cm^{-3}]$^{f)}$	ND	ND	1.775	ND	1.775	ND	1.690	1.775	1.845	1.763
ρ [g·cm^{-3}]$^{(calcd.)}$	1.901	2.254	1.790	–	1.747	1.735	1.724	1.714	1.857	1.737
$\Delta_f H°$ [kJ·kg^{-1}]$^{g)}$	2215.5	–	1371.9	–	498.7	840.4	1152.9	1437.5	942.5	2376.8
ΔH_L [kJ·mol^{-1}]$^{h)}$	–	–	-140.51	–	-137.59	-136.26	-135.03	-133.89	-141.23	-124.63
EXPLO5										
$-\Delta_{Ex}U°$ [kJ·kg^{-1}]$^{i)}$	-5836	–	-4864	–	-3658	-3899	-4119	-4346	-5166	-4008
T_{det} [K]$^{j)}$	4339	–	3422	–	2760	2868	2969	2989	3632	2844
P_{CJ} [kbar]$^{k)}$	377	–	303	–	246	246	244	288	339	257
V_{Det} [m·s^{-1}]$^{l)}$	9250	–	8667	–	8064	8107	8110	8722	8908	8366
V_o [L·kg^{-1}]$^{m)}$	734	–	805	–	793	819	841	855	767	794

a) Impact sensitivity (BAM drophammer (1 of 6)); b) Friction sensitivity (BAM friction tester (1 of 6)); c) Nitrogen content;
d) Oxygen balance (Ω = (xO–2yC–1/2zH)M/1600); e) Decomposition temperature from DSC (β = 5 °C);
f) From X-ray diffraction; g) Calculated heat of formation; h) Lattice enthalpy; i) Energy of explosion;
j) Explosion temperature; k) Detonation pressure; l) Detonation velocity; m) Volume of detonation gases
(assuming only gaseous products). n) ND = not determined.

units and subsequently added together).

When crystal densities were available they were used in place of the calculated densities with the calculated heats of formation to determine detonation performance using the EXPLO5 software package. [27], [28]

All of the calculated detonation pressures and velocities were greater than those of TNT (P_{CJ} = 194 kbar, V_{Det} = 6824 m·s^{-1}). The highest calculated detonation parameters are observed in **1** (P_{CJ} = 377 kbar, V_{Det} = 9250 m·s^{-1}) and **10** (P_{CJ} = 339 kbar, V_{Det} = 8908 m·s^{-1}). Both of these energetic materials exceed RDX performance (P_{CJ} = 336 kbar, V_{Det} = 8801 m·s^{-1}) and compare well to HMX performance (P_{CJ} = 378 kbar, V_{Det} = 9193 m·s^{-1}).

2.3.7 Mechanical Sensitivities

For initial safety testing, the impact and friction sensitivity tests of the prepared nitrogen-rich salts were carried out. [29], [30] The impact sensitivity tests were carried out according to STANAG 4489 [31] and were modified according to instruction[32] using a self-constructed BAM (Bundesanstalt für Materialforschung[30]) drophammer setup. The friction sensitivity tests were carried out according to STANAG 4487[33] and were modified according to instruction[34] using a BAM friction tester. Regrettably, the extreme deliquescence of **1** prevented characterization of its energetic properties. Impact sensitivities for all other recorded compounds were >40 J, which are considered "insensitive".[35] During friction testing **5** was the most sensitive (>120 N) while **11** was the least sensitive to friction (>360 N). Overall, compounds **2**, **4**–**10** may be classified "sensitive" to friction.[35]

2.4 Conclusions

This paper demonstrates the simple synthesis of the annulated heterocyclic system 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazole and the availability of a series of energetic salts from it. The prepared salts were characterized as energetic materials where they were found to be generally of low mechanical sensitivity, however thermally they were only highly-stable when paired with a non-nucleophilic cation. When paired with a cation containing nucleophilic groups, the stability of the produced energetic salt declined dramatically. These materials were fully characterized by infrared, Raman, and multinuclear NMR spectroscopy. The molecular structure of the DNTT anion has been confirmed by several X-ray crystal structures obtained. The calculated energetic performances for these materials are greater than those of TNT, while they fall slightly short of RDX performance.

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3. TETRAZOLE AZASYDNONE ($C_2N_7O_2H$) AND ITS SALTS: HIGH-PERFORMING ZWITTERIONIC ENERGETIC MATERIALS CONTAINING A UNIQUE EXPLOSOPHORE

Authors: Matthew L. Gettings, Michael T. Thoenen, Edward F. C. Byrd, Jesse J. Sabatini, Matthias Zeller, and Davin G. Piercey

3.1 Abstract

We report the first compound containing both a tetrazole and an azasydnone ring, a unique energetic material. Several energetic salts of the tetrazole azasydnone were synthesized and characterized, leading to the creation of new secondary and primary explosives. Molecular structures are confirmed by ^{1}H and ^{13}C NMR, IR spectroscopy, and X-ray crystallographic analysis. The high heats of formation, fast detonation velocities, and straightforward synthesis of energetic azasydnones should capture the attention of future energetics research.

3.2 Introduction

The synthesis of high-energy density materials is important in the design of explosive materials.[2] While much attention has been placed on the synthesis of secondary explosives, the synthesis of materials that fit into the primary explosive category receives significantly less attention. Primary explosives, however, are ubiquitous, as they are present in detonators and percussion primers. These systems are important ignition train energy systems that convert mechanical stimuli into rapid chemical energy to ignite many small-, medium- and large caliber explosive and propellant munitions found in both military and commercial sectors. Although mercury, lead and silver fulminate were early primary explosives employed in detonators and primers, these materials are no longer used due to their inherent instability and hypersensitivity. Today, in-service detonator and primer mixtures contain significant

amount of lead azide and/or lead styphnate.[3] While the compounds function reliably, lead is a well-documented toxin to both the environment and human health.[4] Lead has been found to be present in significant numbers on many military and civilian firearm training facilities, and the US Environmental Protection Agency has called for strict limits on these ranges in an effort to protect the groundwater supply, environmental and human health.[5],[6]

Driven by the EPA regulations and the need to protect and improve human and environmental health, recent efforts have been devoted toward developing lead-free primary explosive alternatives. Two such compounds that have been subject to intense investigation is the copper-based material DBX-1[3] and the metal-free triazine triazide (TTA).[3] (Figure 3.1) While copper has been shown to be a significant improvement over lead, it is still plagued by toxicity issues, and the current synthesis of DBX-1 is problematic. Due to its metal-free nature, TTA would be an ideal primary explosive candidate due to its low toxicological profile. Unfortunately, TTA is classified as a hyperprimary, is very dangerous to isolate and handle, and has been shown to sublime at temperatures commonly encountered during processing of primary explosive mixtures. Thus, there remains a continued interest in developing high-energy primary explosive materials that are capable of being handled safely, while still possessing low toxicity and possessing enough sensitivity to undergo reliable detonation when desired.

Figure 3.1. Structures of copper(I) 5-nitrotetrazole (DBX-1) and 2,4,6-azido-1,3,5-triazine (TTA).

High-nitrogen heterocycles make up the backbone of many energetic materials.[7],[8],[9] Heterocycles such as tetrazoles[10], [11], tetrazines[12]–[15], triazoles[16]–[18] and triazines[19], [20] have all found extensive use in the design of new energetic materials. Their nitrogen content contributes to the energetic properties of these materials due to high heats of formation as a result of the thermodynamic driving force of nitrogenous compounds towards

the formation of nitrogen gas. Having an appropriate oxygen balance (enough oxygen in the molecule to oxidize C and H to CO_2, CO and H_2O) also contributes to energetic output, and for compounds possessing ring or cage strain, this can further contribute energy to the final energetic material. Unfortunately, high-nitrogen heterocycles have some disadvantages in energetic materials; in some cases as nitrogen content increases, sensitivities increase,[21] and increasing nitrogen content can also decrease the opportunity to functionalize the molecule. For example, in tetrazole-based energetic materials, oxygen balances are often low[11], [22] as a result of the tetrazole ring only having (usually) two accessible sites for functionalization and incorporation of oxidizing moieties. The density of an energetic material is an important factor affecting final performance of the energetic material, and as the number of N-N bonds increase, the number of polarized bonds can decrease, reducing molecular motivation for crystal packing in high-density arrangements.[23]

Energetic materials containing zwitterionic and charged structures are an important method of increasing density[24], and in some cases stability[25], [26] of energetic materials. Incorporating these charged structures allows high-density materials to form based on high-nitrogen backbones through the introduction of charged structures. For example, when diaminodinitropyrazine is oxidized to its oxide, LLM-105, the introduction of zwitterionic N-oxide results in improved density and energetic performances.[27]–[30] N-oxides[25] are not the only method of introducing a zwitterionic system to energetic material, and N-nitroimides[26], and nitrodiazine oxides[31] have all been used to prepare high-performing, dense, energetic materials.

In order to improve simultaneously the oxygen balance, and density of high-nitrogen energetic materials, one can also introduce an oxygen atom within the ring. This has the advantage of increasing oxygen balance and setting up polarized bonds allowing high densities. While this strategy has been very well explored in the 2-carbon 5-membered heterocycles with oxadiazole-based energetic materials,[32]–[35] introducing an oxygen to a 5-membered 1-carbon heterocycle is less explored as an energetic backbone.(Figure 3.2)

The azasydnone can be considered as a tetrazole in which a ring nitrogen has been replaced by an oxygen, with an additional exocyclic oxygen on the carbon atom. This means they are an oxygen-balanced hybrid of azide and CO_2, and when functionalized on the
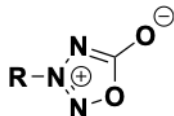
Figure 3.2. Azasydnone structure.

ring nitrogen also adopt a zwitterionic structure. Despite having these molecular features conducive to high performance, they have been much less studied as energetic materials. Recently, some beautiful work by Sheremetev et al.[36] has pioneered the use of this unique heterocyclic system in energetic materials. While published studies on the energetic properties of azasydnones are relatively limited compared to other heterocyclic energetic backbones[36]–[46] they have been explored as nitric oxide donors in pharmaceuticals.[47]–[49] its detonation products by pushing electrons, without needing to move atoms, an important criteria in the development of primary explosives.[50]

In this work we synthesized an azasydnone ring on the 5-position of the tetrazole ring giving tetrazoleazasydnone. Several energetic salts of this structure were also prepared. These energetic materials were characterized by X-ray diffraction, infrared spectroscopy, NMR spectroscopy, and DSC. Computational calculations predicting energetic performance confirm exceedingly high energetic properties of this class of materials. We demonstrated the ability of this unique class of compounds to be used as a backbone of high-performing energetic materials and novel primary explosives.

To an acidic solution of 5-aminotetrazole in water was added sodium nitrite forming a solution of the EXTREMELY SENSITIVE diazotetrazole. Large dilutions of water (200 ml) : 5-aminotetrazole (800 mg) were used for this step of the synthesis given that crystals of diazotetrazole are known to detonate upon crystallization.[51] To this solution was added bromonitromethane and the solution stirred overnight forming hydrazone **2**. (Figure 3.3) Hydrazone **2** was extracted into ethyl acetate and evaporated. Ring closure of **2** to tetrazole azasydnone was performed in dioxane by stirring over solid ammonium nitrate until full conversion of **2** to azasydnone **3**. (Figure 3.3)

After cyclization, the reaction was evaporated and the resultant oil redissolved in water leaving an oily residue and solution of tetrazole azasydnone (**3**) in water. Strong acidification
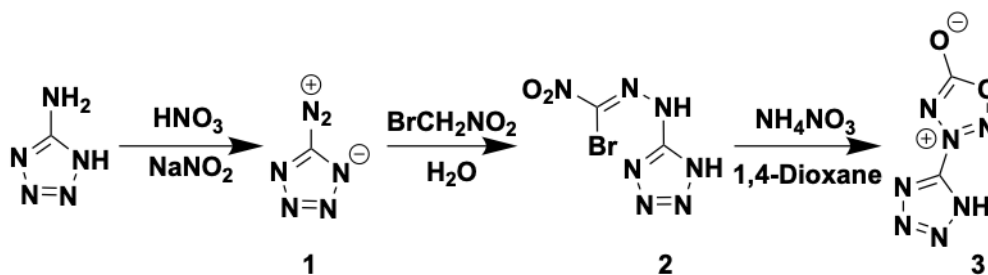
Figure 3.3. Synthesis of TAZ (**3**).
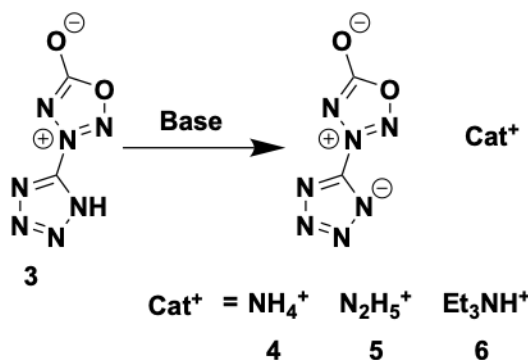
Figure 3.4. Synthesis of TAZ salts **4**-**6** from **3**.
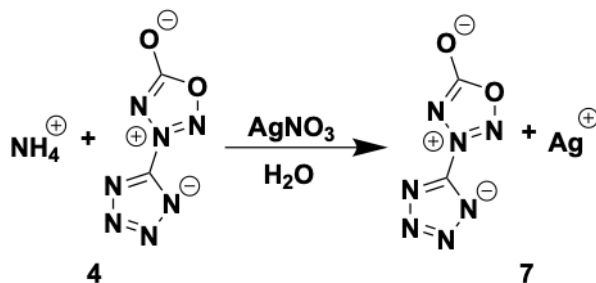
Figure 3.5. Synthesis of TAZ salt **7** from **4**.

of the solution with nitric acid after filtration and discarding of the oily solids allowed extraction of pure **3** into ethyl acetate.

From either pure solutions of tetrazole azasydnone or the aqueous filtrate we produced the ammonium (**4**), hydrazinium (**5**) and triethylammonium (**6**) salts of **3** by simply adding the aqueous base until the solution was slightly basic. Evaporation of the solution and recrystallization gave pure salts. (Figure 3.4) Reaction of **4** with aqueous silver nitrate pre-

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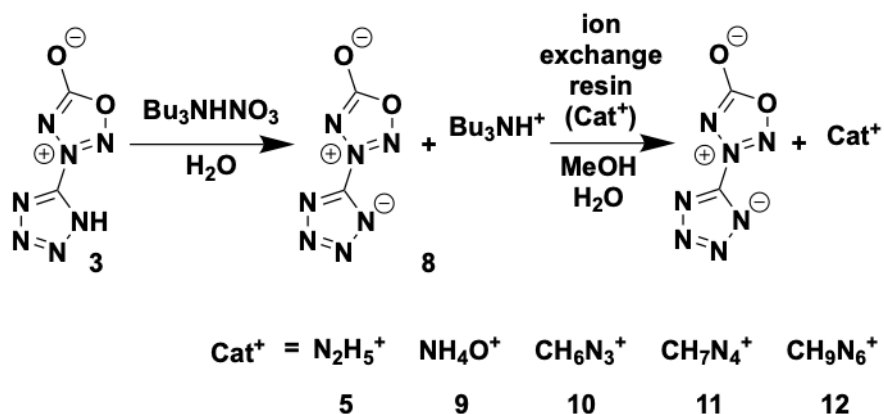
Figure 3.6. Synthesis of TAZ salts **5**, **9**-**12** from **8**.
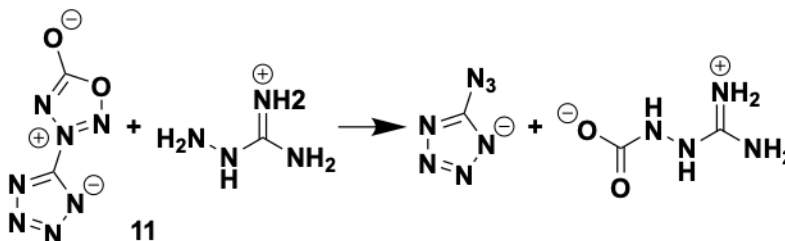
Figure 3.7. Decomposition of **11**, forming azidotetrazole and zwitterionic 2-guanidinium-1-aminocarboxylate monohydrate.

cipitated the silver salt **7** which detonates with violence upon flame-test (Figure 3.5). Video of detonation of **7** against a copper plate available at www.davinpiercey.com/AgTAZdet

To prepare additional energetic compounds, butylammonium salt (**8**) was prepared from **3** in aqueous solution, extracted into ethyl acetate and evaporated giving oily **8**. Butylammonium salt **8** was run through Amberlyst 15$^{\text{TM}}$ ion exchange resin loaded with the appropriate cation to obtain hydroxylammonium (**9**), guanidinium (**10**), aminoguanidinium (**11**) and triaminoguanidinium (**12**) tetrazoleazasydnones. (Figure 3.6)

After evaporation of water, while hydroxylammonium (**9**) and guandinium salts (**10**) were isolated pure, triaminoguanidinium and aminoguanidinium salts showed extensive decomposition. As all crystal structures were obtained by ether diffusion into a methanolic solution of the salt, we hoped to obtain the non-decomposed azasydnone salt crystal in this manner, but actually obtained a crystal of zwitterionic 2-guanidinium-1-aminocarboxylate monohydrate.[55], [56] This supports the hypothesis that the more nucleophilic triamino and

Figure 3.8. Synthesis of TAZ salts **9**, **11**, and **12** from **7**. Salts **11** and **12** underwent partial decomposition.

Figure 3.9. Molecular unit of ammonium TAZ (**4**). Ellipsoids are drawn at the 50% probability level.
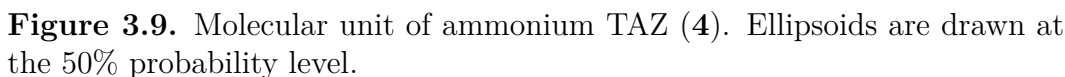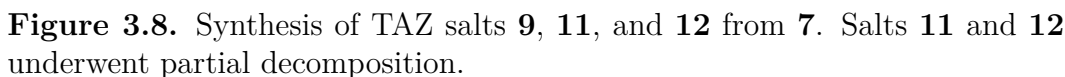
aminoguanidinium cations are attacking the C on the azasydnone, eliminating azidotetrazole. To confirm this, the addition of ammonium azidotetrazolate[57] to a NMR tube containing partially-decomposed aminoguanidinium tetrazoleazasydnone showed the suspected azidotetrazolate peak increase (Figure 3.7). As this manuscript was in preparation, other researchers[37] reported the destruction of azasydnones forming azido compounds as well.

Compounds **9**, **11**, and **12** were also attempted to be prepared by reaction of silver salt **7** with the corresponding chloride salt in water, followed by filtration of silver chloride and evaporation to obtain products. In the case of **9** this improved yield, and in the case of **11** and **12**, the same decomposition forming azidotetrazole was seen. (Figure 3.8) The crystal structures for **4**, **5**, and **10** are shown in Figures 3.9-3.11.
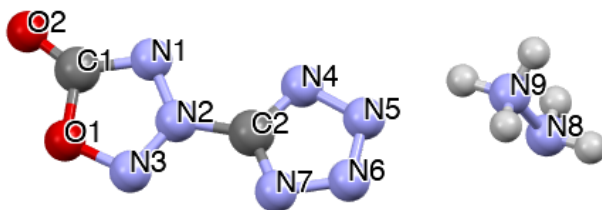
Figure 3.10. Molecular unit of hydrazinium TAZ (**5**). Ellipsoids are drawn at the 50% probability level.
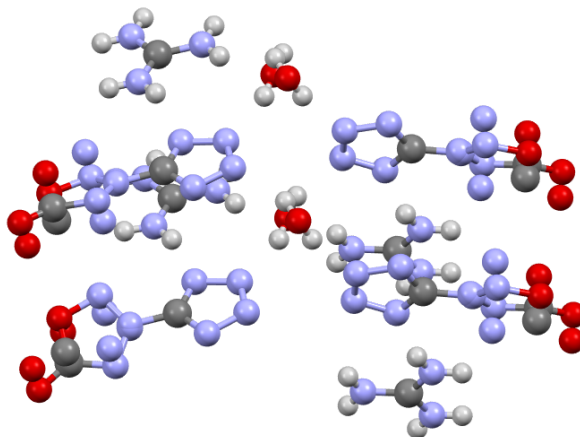
Figure 3.11. Molecular unit of guanidinium TAZ monohydrate (**10**). Ellipsoids are drawn at the 50% probability level.

The salts of tetrazoleazasydnone may also be compared with their nitrotetrazole and azidotetrazole analogs. All TAZ salts had greater densities than analogous azidotetrazoles.[57]–[62] Densities of **4**, **5**, and **10**-**12** exceeded their nitrotetrazole analogs and **3** exceeded the density of RDX (1.820 g $\cdot$ cm^{-3}).[57]–[62] This indicates, that overall as an explosophore in energetic materials, that the azasydnones should be considered as important as the ubiquitous nitro group given the high probability of being higher density, which is one of the most crucial determinants of explosive performance.

The free acid (**3**) and silver (**7**) salts were more sensitive than RDX (7 J, 120 N). (Table 3.2) Among TAZ compounds, **3** had best detonation performance (327 kbar, 8906 m/s), comparable to RDX (336 kbar, 8801 m/s). The free acid **3** had the highest heat of formation, which despite its lower nitrogen content, had the greatest calculated density.

Table 3.1.

Sensitivities and performance of HTAZ and Silver TAZ compared to TTA, DBX-1, lead azide (LA), and lead styphnate (LS).[3], [52], [53]

Com- pound	3	TTA	7	DBX-1	LA	LS
IS [J]	2	<2.5	3	0.036	2.5−4	<2.5
FS [N]	10	0.1	14	0.1	0.1−1	0.1
T_{dec}[°C]	160	187	150	337	315	282
ρ [g·cm^{-3}]	1.84	1.54	–	2.58	4.80	3.00
P_{CJ} [kbar]	327	–	–	–	–	–
V_{Det} [m·s^{-1}]	8906	6900	–	∼7000	5300	4900

Of all TAZ compounds prepared, the metal-free primary explosive **3** and silver salt **7** are the best candidates to serve as a primary explosive replacement. The toxicity of lead underscores the importance of removing lead from primary explosive mixtures. Table 3.1 compares these primary explosives to sensitivities and performances of triazine triazide (TTA), DBX-1, lead styphnate, and lead azide.

Compound **3** is a metal-free primary explosive which can be safely handled unlike TTA, which suffers from sublimation issues and hyper primary sensitivity.[3], [52] Although **3** and **7** have lower densities than the in-service lead salts (lead azide, lead styphnate), less of the metal-free compound (**3**) is required to attain the gas generation necessary for a primer composition in the formulation mixture. Removal of the metal entirely remains a critical goal due to the inherent toxicity of lead. While it is true that the decomposition temperatures of lead azide and lead styphnate are higher than **3**, lower decomposition temperatures are tolerated in primer compositions. Tetrazene, a known and ubiquitous sensitizer in primary explosive mixtures, has a decomposition temperature of 118.6 °C.[63] Thus, decomposition temperatures of 150-160 °C are tolerable.

The silver salt (**7**) also has a reasonable sensitivity with respect to primary explosive power. The impact sensitivity of **7** is similar to PETN (3 J), while remaining sensitive to friction. Silver salts enjoy very high densities, which allows sufficient amount of material to fit into a primer cup (i.e. usually only accommodates 30-40 mg of mixture). Silver salts, like

Table 3.2.

Energetic properties for all prepared energetic compounds. Calculated densities shown when X-ray diffraction densities were unavailable.

	3	4	5	7	9	10	11	12	RDX*
Formula	$C_2HN_7O_2$	$C_2H_4N_8O_2$	$C_2H_5N_9O_2$	$Ag\cdot C_2N_7O_2$	$C_2H_4N_8O_3$	$C_3H_6N_{10}O_2$ $\cdot H_2O$	$C_3H_7N_{11}O_2$	$C_3H_9N_{13}O_2$	$C_3H_6N_6O_7$
FW [g·mol^{-1}]	155.08	172.11	187.12	261.94	188.11	214.15	229.16	259.19	222.12
IS [J]$^{a)}$	2	>40	>40	3	>40	>40	>40 †	1 †	7.5
FS [N]$^{b)}$	10	>360	>180	14	>360	>360	>360†	>64†	120
N [%]$^{c)}$	63.23	65.11	67.37	37.43	59.57	60.33	67.23	70.25	37.84
Ω [%]$^{d)}$	-25.79	-37.18	-38.47	-15.27	-25.52	-48.24	-52.36	-52.47	-21.6
T_{dec} [°C]$^{e)}$	160	155	155	150	130	151	150†	160†	205
ρ [g·cm^{-3}]$^{f)}$	ND	1.716	1.750	ND	ND	1.598	ND	ND	1.858
ρ [g·cm^{-3}]$^{(calcd.)}$	1.842	1.744	1.694	–	1.796	1.655	1.654	1.642	–
$\Delta_{\text{f}}H°$ [kJ·kg^{-1}]$^{g)}$	2698.1	1372.9	2044.3	–	1467.2	-129.41	1366.4	2051.6	316.55
EXPLO5									
$-\Delta_{\text{Ex}}U°$ [kJ·kg^{-1}]$^{h)}$	4999	3874	4459	–	4767	2860	3410	4003	5740
T_{det} [K]$^{i)}$	3841	2908	3112	–	3383	2238	2541	2763	3745
P_{CJ} [kbar]$^{j)}$	327	249	292	–	312	207	224	255	336
V_{Det} [m·s^{-1}]$^{k)}$	8906	8222	8804	–	8823	7736	8009	8474	8801
V_o [L·kg^{-1}]$^{l)}$	764	846	871	–	830	881	864	895	783

ND not determined; a) Impact sensitivity (BAM drophammer (1 of 6)); b) Friction sensitivity (BAM friction tester (1 of 6));
c) Nitrogen content; d) Oxygen balance ($\Omega = (\text{xO–2yC–1/2zH})\text{M}/1600$); e) Decomposition temperature from DSC ($\beta = 5$ °C);
f) From X-ray diffraction; g) Calculated heat of formation; h) Energy of explosion; i) Explosion temperature;
j) Detonation pressure; k) Detonation velocity; l) Volume of detonation gases (assuming only gaseous products).
*Values based on Ref.[54] and the EXPLO5 V6 database. †**11** and **12** showed evidence of decomposition forming azidotetrazole.

copper-based primaries (e.g. DBX-1) are significantly less toxic than lead[3], [52] and will likely have lower toxicity than lead-based energetic compounds.[64]

In summary, several energetic salts of the novel tetrazole azasydnone (TAZ) were synthesized and characterized for their energetic properties. The metal-free compound **3** and silver salt **7** are potential replacements for primary explosives. Their energetic performances are comparable to in-service primary explosives (e.g. lead azide and lead styphnate) with the benefit of reduced toxicity. Specifically, the silver salt prepared during this study may be an interesting primary explosive due to its high sensitivity and demonstrated ability to undergo a deflagration to detonation transition.

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4. AZASYDNONES AND THEIR USE IN ENERGETIC MATERIALS

Authors: Matthew L. Gettings and Davin G. Piercey

4.1 Abstract

Recent publications demonstrate exciting new uses of azasydnones in the development of energetic materials. Facile synthesis routes support a remarkable variety of substituents for various uses. This heterocycle enjoys several inherent benefits as an explosophore: high nitrogen content, balanced oxygen content, high thermal stability, and high densities and detonation performance. The thermal behavior and combustion analysis of azasydnones reveals two azasydnone compounds as possible fillers in propellants.

4.2 Introduction

Among energetic materials, azasydnones are less well known although their usefulness as nitric oxide donors in pharmaceuticals is more fully established.[2] However, recent interest in azasydnones as energetic materials underscores the utility of this unique class of compounds to be used in various fields. Since 2018, several papers on the energetic properties of azasydnones have been published.[2]–[7] Clearly, azasydnones are of interest in the energetic materials community and it's important to understand this emerging trend of a unique heterocycle in new energetic materials design. The base heterocyclic backbone of azasydnones (more formally known as 3-R-1,2,3,4-oxatriazol-5-ones) is the oxatriazole ring.[4] (Figure 4.1) The exocyclic oxygen on azasydnone is similar to the sydnone structure. However, the azasydnone structure has an additional nitrogen on the heterocyclic structure, which replaces a carbon on the sydnone.[3] [4] Exchanging a carbon for nitrogen improves the oxygen balance on the molecule as well as the heat of formation, benefiting detonation

performance. High-nitrogen content also increases the positive enthalpy of formation and detonation performance.[8]

Figure 4.1. Zwitterionic azasydnone resonance structures.

Oxygen balance remains an important feature for energetic materials. Materials having a negative oxygen balance (fuel rich) require an oxidizing agent (or air) for complete formation of detonation products such as CO_2, N_2, H_2O, and CO.[8] Azasydnones have the advantage of being oxygen balanced, which makes them very useful as an explosophoric material because they are able to burn in oxygen-deficient environments, making them also of high interest as propellants.[5]
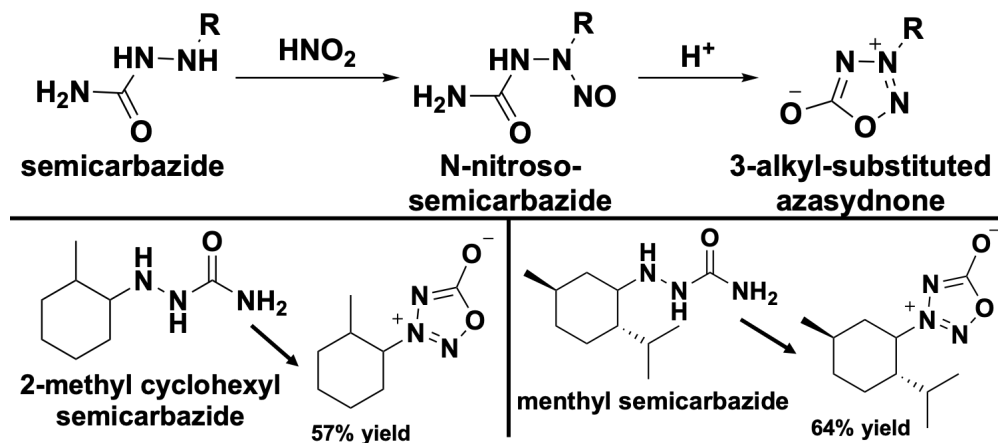
4.3 Syntheses

Figure 4.2. Early synthesis of two azasydnones by Boyer.[9], [10]

Azasydnones may be synthesized via multiple routes and are capable of supporting a remarkable variety of substituents.[9], [11]–[17] An early synthesis (Figure 4.2) obtained two azasydnone compounds by treating semicarbazides in ice-cold aqueous solution with nitrous

acid, forming an *N*-nitroso-semicarbazide intermediate and upon heating (>60 °C), cyclized the azasydnone with release of ammonia gas.[9]
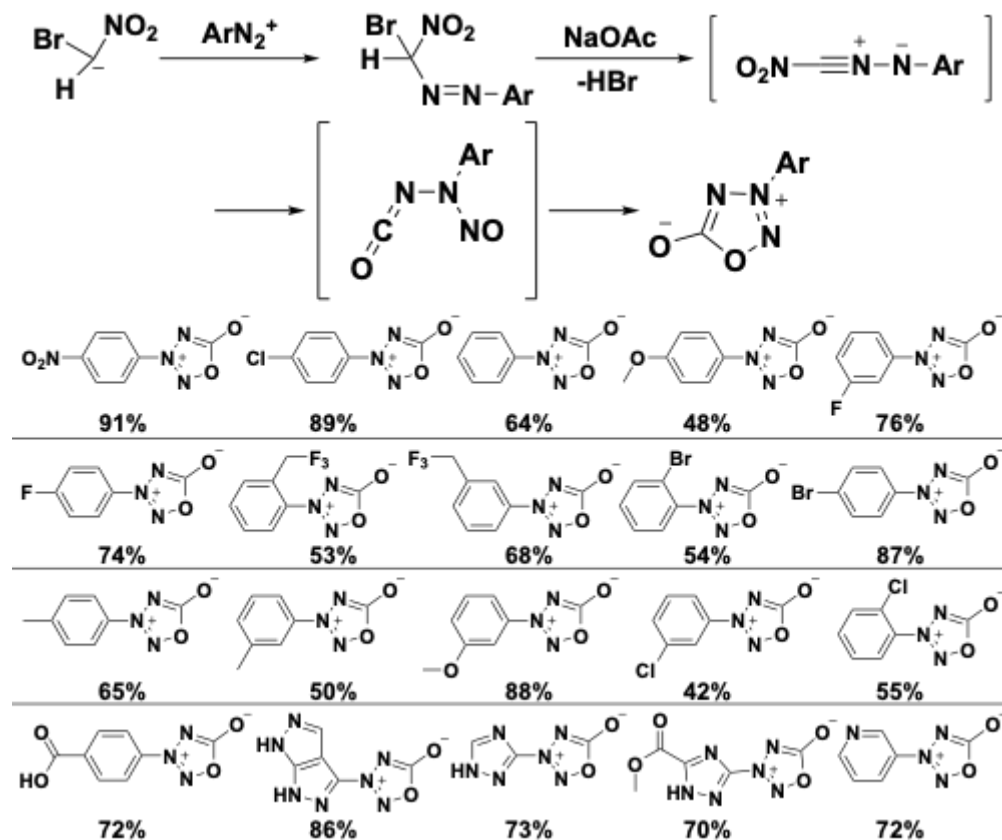

Figure 4.3. Shevelev synthesized 20 azasydnones with aryl substituents (42–91% yields).[10], [11]

In 1999, Shevelev et al. synthesized 20 arylazasydnones (Figure 4.3) by first azo coupling arenediazonium salts with bromonitromethane, forming hydrazone intermediates.[11] (Figure 4.3) Following extraction from the reaction mixture, the hydrazones were dissolved in acetonitrile, dimethylformamide or 1,4-dioxane and cyclized into the azasydnone ring in the presence of solid ammonium nitrate.[11]

Other previous methods used potassium diazomethanedisulphonate, $N_2C(SO_3K)_2$, (Figure 4.4) or nitroform, $C(NO_2)_3$, (Figure 4.5) to achieve coupling and hydrazone formation with arenediazonium salts.[10], [13], [14]
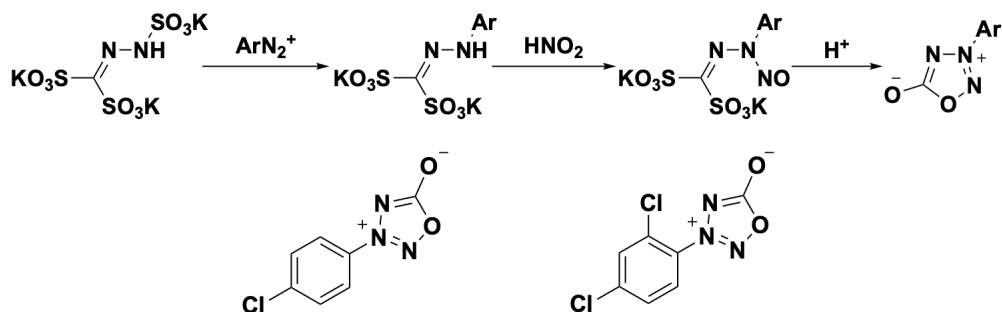
Figure 4.4. Synthesis of azasydnones by Farrar (yields not reported).[10], [14]
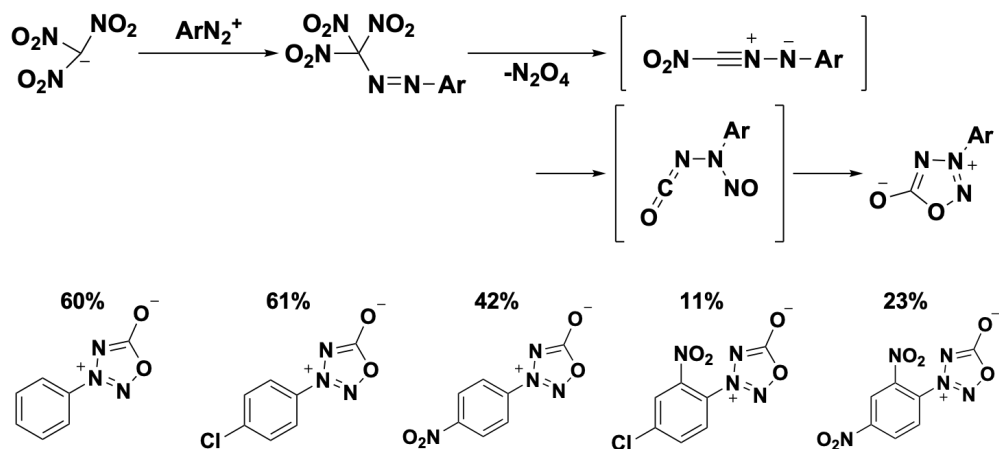

Figure 4.5. Synthesis of azasydnones by Martynova.[10], [13]

However, the recent paper by Zhilin et al. provides a more convenient one-pot synthesis of azasydnones starting with amines, used for synthesizing over 20 furoxanylazasydnones and furazanlyazasydnones.[2] (Figure 4.6) This method avoids isolation of hazardous intermediates, inefficient multi-step syntheses, and leverages unstable diazonium salts for ring closure.[2] Azasydnones may be produced easily on a gram-scale,[2] however as of yet there has been no literature-documented large scale preparation of such materials.
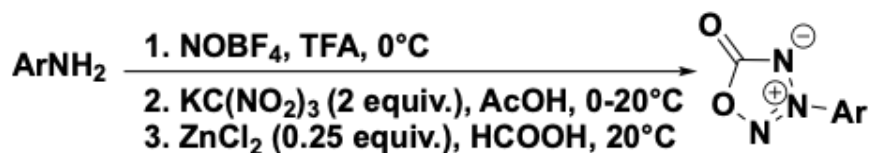

Figure 4.6. Synthesis of azasydnones from arylamines.[2]
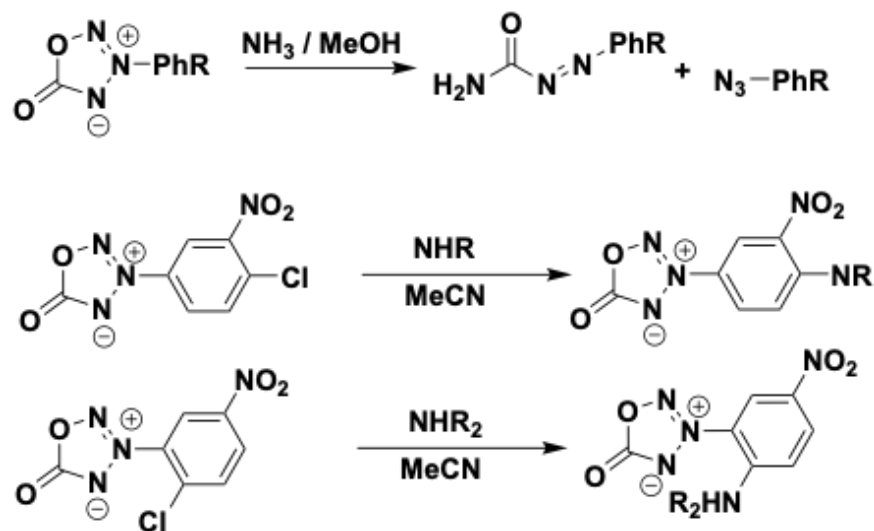
Figure 4.7. Reaction of chloronitrophenyl azasydnones with ammonia (top), amines (middle), and cycloaliphatic amines (bottom).[6]
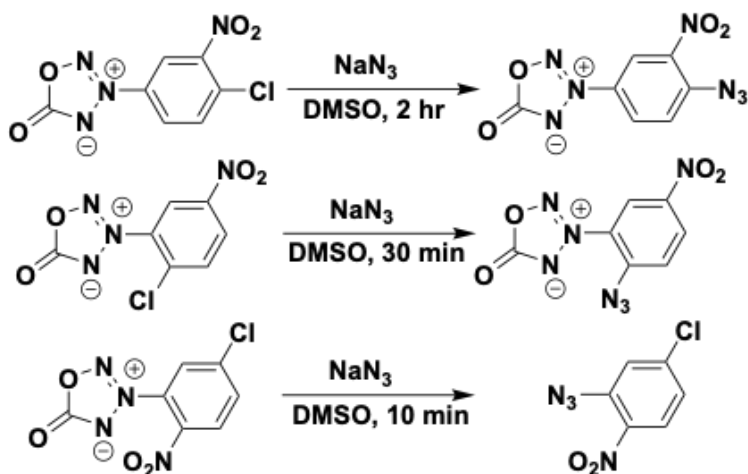
Figure 4.8. Regioselectivity of azide placement on chloronitrophenyl azasydnone.[6]

The recent work of Dalinger et al. explored nucleophilic aromatic substitution (S_NAr) reactions of several azasydnone derivatives.[6] Azasydnones with chloro/nitrophenyl substituents treated with high excess (70 equiv.) amines in methanol or acetonitrile led to the destruction of the azasydnone ring, forming arylazides and azocarboxamides.[6] (Figure 4.7) In fact, excess ammonia favored formation of azides over azocarboxamides by 3:1.[6] However, the azasydnone was not destroyed at lower molarities (1.5 equiv.).[6] Regioselectivity of the phenyl azasydnone was also observed.[6] Azasydnones attached either para or

ortho to the chloro substituent and treated with cycloaliphatic amines, resulted in chloride replacement with the amine while the azasydnone remained intact.[6] Similarly, the azide replaced the choloride in the para and ortho positions.[6] (Figure 4.8) However, when chloride was positioned meta to the azasydnone, the azasydnone ring opened or was replaced by the azide.[6] Furthermore, the position of the chloro and nitro substituents on the phenyl ring (relative to azasydnone) had a significant effect on the reaction rates, spanning 10 minutes to 2 hours.[6]

4.4 Performance

Improved thermal stability is a notable advantage for azasydnones. The azasydnone structure increases the melting and decomposition temperature significantly as compared to azido and tetrazole groups (Figure 4.9) when functionalizing the same backbone (Table 4.1).[3] 4-nitrophenyl azasydnone melted at 167 °C then decomposed near 236 °C, while the azide decomposed near 164 °C (after melting at 70 °C), and the tetrazole did not melt before decomposing near 193 °C.[3] Several other azasydnone compounds were more thermally stable than similar tetrazoles and azide structures.[3] Furthermore, a study conducted by Serushkin et al. also reported a significant rise in melting temperatures of (di)nitropyrazole moeties when nitro groups were swapped with the azasydnone.[5]
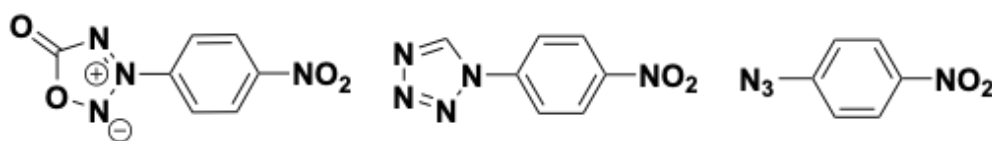
Figure 4.9. Structures of analogous azasydnone, tetrazole, and azide nitrophenyl compounds.[3]

The zwitterionic heterocycle exhibits notable advantages over tetrazoles and azides with respect to density and detonation performance.[3] First, the azasydnone compounds have greater crystal packing densities than the corresponding tetrazoles or azides with the same nitrophenyl substituents.[3] Azasydnones achieve higher density due to enhanced capacity for molecular packing in the crystal structure as a result of the zwitterionic struc-

Table 4.1.

Energetic performance of azasydnones compared to tetrazole and azide analogs with nitrophenyl substituents.

Substituent		Tetrazole	Azide	Azasydnone
4-Nitrophenyl	$T_{dec}[°C]^a$	193	164	236
	ρ [g·cm^{-3}]^b	1.606	1.571	1.714
	V_{Det} [km·s^{-1}]^c	6.49	6.56	6.76
	P_{CJ} [GPa]^d	14.0	14.2	17.4
	IS [J]^e	24	34	64
	FS [N]^f	>360	>360	>360
3-Nitrophenyl	$T_{dec}[°C]^a$	151	164	237
	ρ [g·cm^{-3}]^b	1.586	1.587	1.710
	V_{Det} [km·s^{-1}]^c	6.47	6.61	6.77
	P_{CJ} [GPa]^d	13.9	14.5	17.5
	IS [J]^e	>50	22	13
	FS [N]^f	>360	>360	>360

[a] Decomposition temperature. [b] Density. [c] Calculated detonation velocity. [d] Calculated detonation pressure. [e] Impact Sensitivity. [f] Friction Sensitivity.

ture allowing for strong intramolecular interactions to form and heavier molecular mass.[3] Second, crystal packing densities affect the calculated detonation performance of energetic materials. This is because, generally, greater crystalline density of the energetic material results in faster detonation velocity and higher detonation pressure.[18] Specifically, detonation velocity is proportional to density, while detonation pressure is proportional to density squared.[19] Consequently, azasydnones have faster calculated detonation velocities and higher detonation pressures compared to the corresponding nitro, azide, and tetrazole analog compounds.[3] (Table 4.1) Replacing the tetrazole moiety with azasydnone on 4-nitrophenyl improved the detonation velocity by 270 m·s^{-1}.[3] In fact, all of the azasydnones in that paper show faster detonation velocities than their analogs, including dinitrobenzenes (1,3-DNB and 1,4-DNB).[3] The greater density, improved oxygen balance, and positive enthalpy of formation for azasydnones explains the faster calculated detonation velocities.[3]

A recent synthesis proved effective in forming the azasydnone on tetrazole.[7] (Figure 4.10) Densities for several energetic salts of tetrazole azasydnone (TAZ) surpassed the analogous nitrotetrazole salts.[7] The calculated detonation velocity of the metal-free (and non-toxic) HTAZ surpassed triazine triazide (TTA), DBX-1, lead azide, and lead styph-
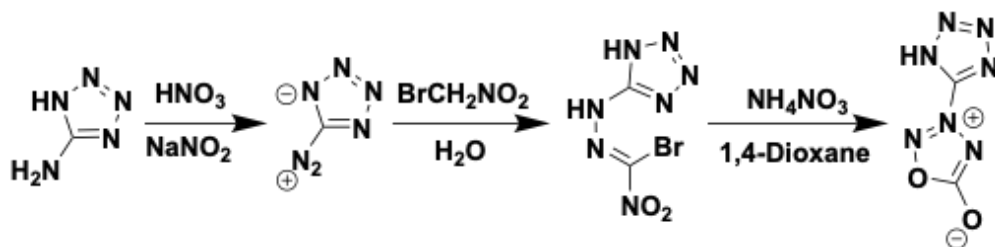
Figure 4.10. Synthesis of tetrazole azasydnone (HTAZ).[7]

nate.[7] Silver TAZ performed well as a primary explosive in multiple detonation tests.[7] Both the metal-free HTAZ and silver salt may be suitable primary explosive replacements.[7]
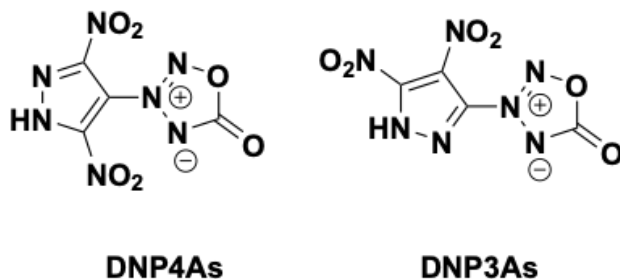
DNP4As   **DNP3As**

Figure 4.11. Structures of DNP4As and DNP3As.[5]

Serushkin et al, reported thermal behavior of five azasydnone compounds with (di)nitropyrazole or nitrophenyl substituents.[5] Altering the substituents on an energetic heterocycle will impact the thermal stability and combustion behavior.[5] The combustion study also revealed low pressure-dependence on burn rates for 3-(3,5-dinitropyrazol-4yl) azasydnone (DNP4As) and 3-(4,5-dinitropyrazol-3-yl) azasydnone (DNP3As).[5] (Figure 4.11) Burn rate of the energetic material and how the burn rate changes with pressure are critical for developing effective propellants.[5] The burning rate, r_b, is dependent on pressure, p, according to

$$r_b \; [\mathrm{mm \cdot s^{-1}}] = b \cdot p^n$$

where, b is a coefficient and n is the index of the burn rate.[8] Propellants typically have n values ranging 0.2-0.6.[8] The indices of burn rate for both azasydnone DNP4As ($n = 0.59$) and DNP3As ($n = 0.52$), are possible good candidates for next generation of propellants.[5]

4.5 Conclusion

In summary, this unique zwitterionic heterocycle may be synthesized via several methods and enjoys several distinct advantages over tetrazoles and azides: greater densities, greater thermal stability, and improved oxygen-balance. Consequently, the azasydnones which were mentioned have higher calculated detonation velocities and detonation pressures than their tetrazole or azide analogs. Finally, two dinitropyrazol azasydnones have burn rates which are characterized by low pressure-dependence. The low values of both indices of burn rates for these azasydnones may indicate suitable applications as a new series of propellants. However, azasydnones have not been as widely studied as many other energetic materials. Therefore, azasyndones remain excellent candidates for further research into their synthesis, characterization, and performance.

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5. METHYL SYDNONE IMINE AND ITS ENERGETIC SALTS

Authors: Matthew L. Gettings, Edward F. C. Byrd, Matthias Zeller, and Davin G. Piercey

5.1 Abstract

Several energetic salts of the 5-amino-3-methyl-1,2,3-oxadiazolium cation were synthesized and characterized. Structures are confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy, and X-ray crystallography. The perchlorate salt was thermally stable, with a crystal density of 1.826 g·cm^{-3} and its calculated energetic performance exceeded TNT. Except for the perchlorate, these salts are mechanically insensitive. This work explored the methyl sydnone imine cation as a suitable energetic compound, which was quickly obtained through fascile syntheses. This is the first exploration of sydnone imines as components of energetic materials.

5.2 Introduction

The replacement of currently-used energetic materials with materials that are either higher performing, more stable, or less toxic is an intense area of current research.[2]–[7] When one considers types of energetic materials, in general 3 major strategies are used to impart energy content to a molecule: high heats of formation[8], ring or cage strain[9] or fuel and oxygen in the same molecule.[10] The functional groups used in energetic materials are often very familiar to the chemist, such as nitro[11], azido[12], or nitrogen-rich heterocycles such as tetrazoles[13] and pentazoles.[14] However, as the quest for energetic materials of tailored sensitivity and performance continues, many functional groups and systems not traditionally considered explosophores have been investigated, including materials entirely lacking such traditional energetic functional groups.[15], [16] While the contributions towards energy content of a nitro group or azide are straight forward (improving oxygen balance or heat of formation) the reality is that any functional group consisting of nitrogen and oxygen has the potential to contribute positively towards energetic properties of the final material.

Salt based energetic materials often show homogeneity of design when their cations are considered, especially as energetic anions are more common than energetic cations; this has resulted in a multitude of new energetic anions being reported over the years,[17]–[21] while reports on new cations being paired with new energetic anions are comparatively more limited[22]–[25]. As a result, new energetic cations open up a wide range of energetic materials when paired with the wide variety of energetic anions already in use. In 1962, Daeniker and Druey synthesized and characterized 35 5-amino-1,2,3-oxadiazlium (sydnone imine) salts.[26] One such compound, methyl sydnone imine (MSI) chloride, was synthesized in 82% yield from 2-(methylamino)acetonitrile.[26] (Figure 5.1) 2-(Methylamino)acetonitrile was treated with nitrous acid forming the *N*-nitroso intermediate. Acidification in various solvents (e.g. acetone, tetrahydrofuran, ether, etc.) results in closure to the sydnone ring.[26]
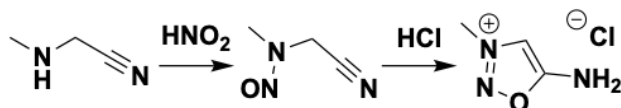

Figure 5.1. Early synthesis of methyl sydnone imine chloride.[26]

Later, in 1977 Vohra et al. improved this synthesis. A methanolic solution of *N*-nitroso(2-methylamino)acetonitrile was treated with HCl gas and the solvent evaporated. Following an acetone rinse, 5-amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) is obtained via recrystallization from ethanol in 90-92% yield.[27] This cation has the advantage of containing an oxygen atom which many energetic cations do not. This has the potential to result in improved oxygen balance of the prepared energetic materials. Additionally, we hypothesized that the dipolar C-O and N-O bonds would allow the formation of dense energetic structures. This sydnone imine based cationic heterocycle has never been used in an energetic material and would serve to exemplarily indicate the promise (or lack thereof) of sydnone imines in energetic materials. In this work we explored energetic materials based on the MSI cation for the first time, as well as investigating its behaviour during nitration.

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5.3 Results and Discussion

5.3.1 Synthesis

In a first step, an aqueous solution of 5-amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) was treated with an equivalent amount of several silver salts of energetic anions and warmed to 40 °C. After filtering off the white silver chloride precipitate, several energetic salts **2-6** were obtained after evaporation of the aqueous solution (figure 5.2). These salts of methyl sydnoneimine (MSI) include nitrate (**2**), perchlorate (**3**), nitrotetrazolate (**4**), 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazolate (DNTT) (**5**), and tetrazole azasydnone (TAZ) (**6**). Yields for **2**, **3** and **5** were greater than 87%, while **4** and **6** were obtained in 57% and 68% yield, respectively.
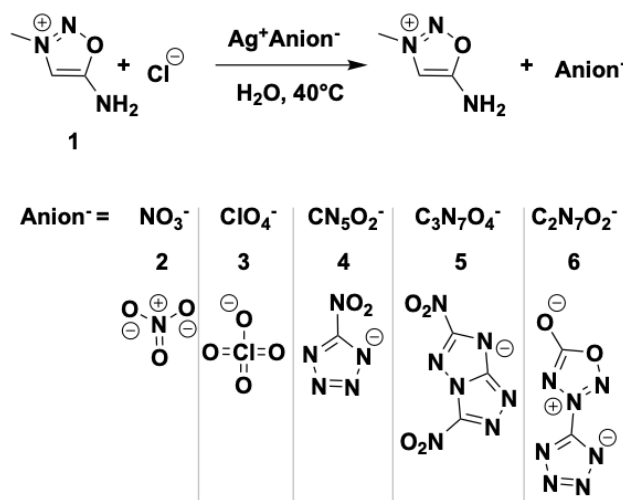

Figure 5.2. Synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium salts **2**–**6** from **1**.

As a precursor to **4**, silver nitrotetrazole was synthesized from aqueous sodium nitrotetrazole prepared by a literature method,[28] treated with aqueous silver nitrate then filtered. (Figure 5.3) The silver salts of DNTT and TAZ were prepared according to literature procedures.[17], [29]

During the synthesis of azasydnone salt **6**, partial decomposition of the azasydnone ring formed the azidotetrazole salt (**7**). (Figure 5.4) Formation of azidotetrazole from tetrazole azasydnone was previously reported.[29] 5-Azidotetrazole is extremely explosive and this salt was only characterized by single-crystal X-Ray diffraction.[30], [31]
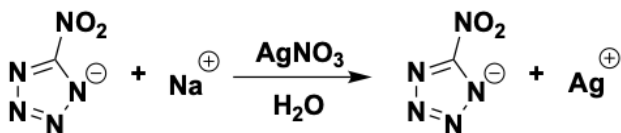
81

Figure 5.3. Synthesis of silver nitrotetrazole from sodium nitrotetrazole.
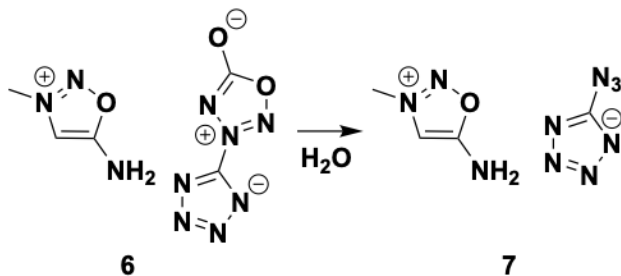

Figure 5.4. Decomposition of 6 to 5-amino-3-methyl-1,2,3-oxadiazolium azidotetrazolate (**7**).

We attempted to form the zwitterionic nitroimide (Figure 5.5) by the treatment of **1** with nitronium tetrafluoroborate in acetonitrile at 0-5 °C. Without addition of a potassium acetate buffer, only unidentified decomposition products were formed. With the addition of potassium acetate, we saw instead the formation of both the nitrosoimide (**8**) and the nitrate salt (**2**) as identified by single-crystal X-ray analysis. (Figure 5.6)
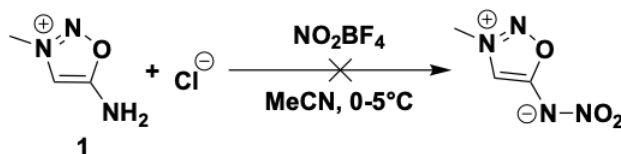
Figure 5.5. Attempted synthesis of methyl sydnone nitroimide from **1**.

A possible mechanism for the formation of the nitrosoimide (**8**) from 3-methyl-1,2,3-oxadiazolium chloride (**1**) is proposed in Figure 5.7. We propose that after transient formation of the nitroimide (detected by MS) a second nitronium cation reacts with the nitro group of the nitroimide. After elimination of nitrate, the zwitterionic nitrosoimide (**8**) is formed. Nitrate and excess starting material pair to form 3-methyl-1,2,3-oxadiazolium nitrate (**2**).

Figure 5.6. Formation of 3-methyl-1,2,3-oxadiazolium nitrosoimide (**8**) and **2** from **1**.

Figure 5.7. Possible reaction mechanism for the formation of the nitrosoimide **8** from **1**.

5.3.2 Spectroscopy

In the ^{13}C NMR the three carbon signals of the 5-amino-3-methyl-1,2,3-oxadiazolium cation occur at 169.6, 103.9, and 40.0 ppm. The ^{13}C peaks for the DNTT salt (**5**), appeared at 164.3, 161.8, and 142.8 ppm in D$_2$O, which agree with the reported peaks in D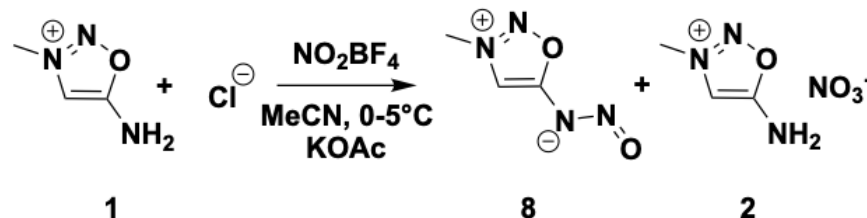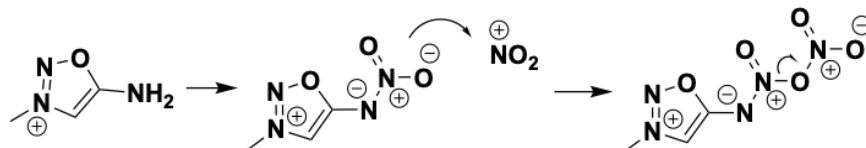MSO.[17] The ^{13}C peaks for tetrazole azasydnone salt (**6**) exist at 167.3 and 156.1 ppm as is common for tetrazoleazasydnone salts.[29] In the tetrazole azasydnone (**6**) sample, the carbon peak for the azidotetrazole formed by decomposition was observed at 159.5 ppm.[29] Attachment of the nitroso in **8** caused a slight downfield shift of the ^{13}C peak from 169.4 (in D$_2$O) to 173.8 (in CD$_3$CN) ppm. None of the anions carry any protons and all peaks in the ^{1}H NMR spectra of this series match those of the MSI cation (8.6, 7.6, and 4.4 ppm), matching the signals reported in Daeniker's 1962 manuscript.[26]

Broad band of N-H stretches appear in the IR spectra at 3400-3100 cm^{-1} for compounds **2-7**. The stretches for the oxadiazole ring include 1683-1650 (C-O), 1483-1450 (C-N), 1325-1182 (N-O), 1295-1256 (N=N), and 1078-1049 (N-N) cm^{-1}.[26], [27], [32], [33] For compounds **6** and **7**, the tetrazole ring has IR stretches at 1455 (C=N), 1428-1399 (C-N), 1261 (N=N), and 1022 (N-N) cm^{-1}, which agree with the literature.[29], [34], [35] The azide stretch is found at 2135 cm^{-1} for compound **7**. The other stretches for the azasydnone on **6** include 1786 (C-O), 1585 (C=N), 1316 (C-N), 1227 (N=N), 1085-1077 (N-N), and 1191-1175 (N-O)

cm^{-1}. The stretches for the DNTT annulated heterocycle of **5** include 1542-1482 (C=N), 1392-1321 (C-N), 1077-988 (N-N), and 1202-1186 (N-O) cm^{-1}, matching the literature.[17]

5.3.3 Mass Spectrometry

The 5-amino-3-methyl-1,2,3-oxadiazolium ($C_3H_6N_3O$) cation was observed at 100.1 m/z in (ESI$^+$) for compounds **2**-**7**. The nitrosoamide compound **8** was detected at 129.0 m/z in (ESI$^-$). As a result of decomposition of the tetrazole azasydnone zwitterion of **6**, the presence of azidotetrazole (CN_7^-) was detected at 110 m/z in (ESI$^-$).

Table 5.1.
Crystallographic data and structure refinement details for **2**-**8**.

	2	3	4	5	6	7	8
Formula	$C_3H_6N_3O\cdot$ NO_3	$C_3H_6N_3O\cdot$ ClO_4	$C_3H_6N_3O\cdot$ CN_5O_2	$C_3H_6N_3O\cdot$ $C_3N_7O_4$	$C_3H_6N_3O\cdot$ $C_2N_7O_2$	$C_3H_6N_3O\cdot$ CN_7	$C_3H_4N_4O_2$
FW [g·mol^{-1}]	162.12	199.56	214.17	298.21	254.20	210.19	128.10
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space Group	$P2_1/m$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$Cmc2_1$
a [Å]	5.7481 (6)	19.5213 (6)	24.1038 (10)	7.2060 (4)	5.2488 (8)	8.4296 (13)	6.1158 (7)
b [Å]	5.8420 (7)	5.1844 (1)	5.0060 (2)	9.3911 (5)	13.9673 (14)	5.5977 (9)	9.1928 (9)
c [Å]	9.9504 (11)	14.8287 (5)	15.4562 (7)	9.4448 (5)	14.1051 (18)	19.058 (3)	9.3984 (10)
α [°]	90	90	90	71.6516 (19)	90	90	90
β [°]	91.390 (5)	104.6857 (11)	108.365 (3)	85.772 (2)	90	96.392 (10)	90
γ [°]	90	90	90	71.196 (2)	90	90	90
V [Å^3]	334.04 (6)	1451.73 (7)	1770.01 (13)	574.01 (5)	1034.1 (2)	893.7 (2)	528.39 (10)
Z	2	8	8	2	4	4	4
$\rho_{\text{calcd.}}$ [g·cm^{-3}]	1.612	1.826	1.607	1.725	1.633	1.562	1.610
T [K]	150	150	150	150	150	150	150
Crystal shape	Block	Needle	Block	Block	Fragment	Needle	Block
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Yellow
Crystal size [mm]	0.15×0.13 ×0.09	0.55×0.17 ×0.13	0.14×0.11 ×0.07	0.24×0.20 ×0.13	0.21×0.11 ×0.05	0.15×0.02 ×0.01	0.31×0.22 ×0.20
R_1 (obs.)	0.036	0.025	0.029	0.043	0.040	0.092	0.034
wR_2 (all data)	0.105	0.071	0.077	0.107	0.097	0.301	0.091
S	1.15	1.05	1.03	1.02	1.01	0.97	1.07
No. of reflec.	764	2673	3112	4208	3434	1744	1077
Parameters	72	117	290	243	164	137	56
Restraints	0	0	6	37	0	0	1
CCDC	2024994	2024996	2024995	2024997	2035560	2025853	2025852

5.3.4 Single-crystal X-ray Analysis

Data for **2**, **4** and **7** were collected using a Bruker Quest diffractometer with kappa geometry, a copper target I-μ-S microsource X-ray tube (Cu-K$_\alpha$ radiation, $\lambda = 1.54178$ Å), a laterally graded multilayer (Goebel) mirror single crystal for monochromatization, and a Photon3 CMOS area detector. Data for **3**, **5**, **6** and **8** were collected with a Bruker Quest diffractometer with a fixed chi angle, a molybdenum wavelength fine focus sealed X-ray tube (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å), a single crystal curved graphite incident beam monochromator, and a Photon2 CMOS area detector. Both instruments are equipped with Oxford Cryosystems low temperature devices. Examination as well as data collection were performed at 150 K. Data were collected, reflections were indexed and processed using APEX3.[36] The data were scaled and corrected for absorption using Sadabs.[37], [38] The space groups were assigned using XPREP within the SHELXTL suite of programs[39], the structures were solved by direct methods and then refined by full-matrix least-squares against F^2 with all reflections using SHELXL2018.[40]–[42] C-bound H atoms were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for alkene C-H and moieties, and 0.98 Å for CH$_3$ moieties, respectively. N-H bond distances were either constrained to 0.88 Å (**7**, **8**) or freely refined (**2**, **3**, **4**, **5**). For **4**, N-H distances were restrained to be similar to each other. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C/N})$ with 1.5 for CH$_3$ and 1.2 for C-H and NH$_2$ units, respectively. For **4**, $U_{\text{iso}}(\text{H})$ values were refined for the amine H atoms. In **5**, the anion exhibits minor disorder with two alternative orientations. The two disordered moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Equivalent atoms in the major and minor moiety were constrained to have identical ADPs. Subject to these conditions the occupancy ratio refined to 0.9467(10) to 0.0533(10). Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2025852, 2025853, 2024994 to 2024997, and 2035560 contain the supplementary crystallographic data for this paper.
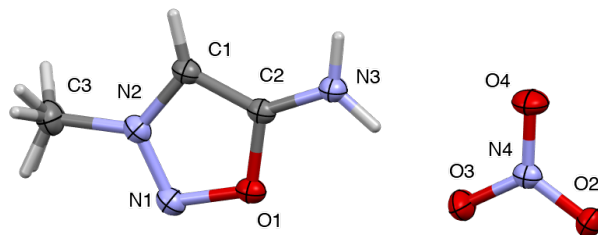
Figure 5.8. Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium nitrate (**2**). Ellipsoids are drawn at the 50% probability level. Disorder of methyl H atoms is symmetry imposed by a mirror plane bisecting the cation.
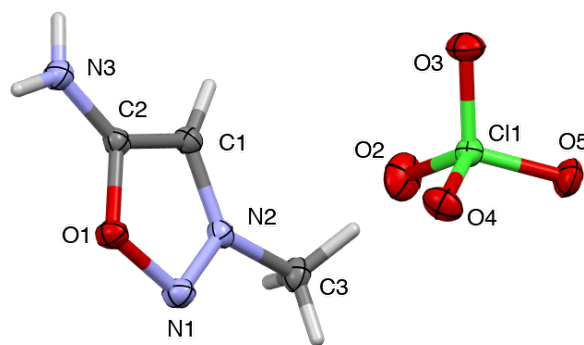

Figure 5.9. Molecular unit 5-amino-3-methyl-1,2,3-oxadiazolium perchlorate (**3**). Ellipsoids are drawn at the 50% probability level.

The structures for 5-amino-3-methyl-1,2,3-oxadiazolium salts **2**-**7** are shown in Fig. 5.8-Fig. 5.13 while 3-methyl-1,2,3-oxadiazolium nitrosoamide (**8**) is depicted in Fig. 5.14. Compounds **2**-**4** and **7** crystallized in the monoclinic system. (Table 5.1) Orthorhombic crystal structures were observed in crystals of **6** and **8**, whereas **5** aligned in a triclinic arrangement. Compound **2** crystalized in space group $P2_1/m$ with 2 formula units in the unit cell and a density of 1.612 g·cm^{-3} at 150 K. At ambient temperature the density was remeasured and found to be 1.562 g·cm^{-3}. Among the seven crystals obtained, **3** had the greatest densities of 1.826 g·cm^{-3} at 150 K and 1.763 g·cm^{-3} at ambient temperature. **4** crystallized in colorless blocks in the monoclinic space group $P2_1/c$ (Z=8) and densities of 1.607 g·cm^{-3} (150K) and 1.567 g·cm^{-3} (ambient). The sole triclinic system in the series was found in crystals of **5** (space group $P\bar{1}$ and Z=2), which achieved the second greatest densities: 1.725 g·cm^{-3} (150K) and 1.677 g·cm^{-3} (ambient). Colorless fragments of **6** (space
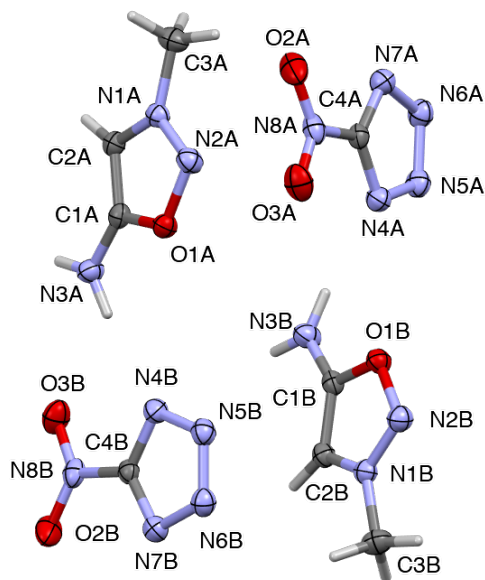
Figure 5.10. Molecular units of 5-amino-3-methyl-1,2,3-oxadiazolium nitrotetrazolate (**4**). Ellipsoids are drawn at the 50% probability level.

group $P2_12_12_1$ with 4 formula units) provided densities of 1.633 g·cm⁻³ (150K) and 1.591 g·cm⁻³ (RT). The monoclinic space group $P2_1/n$ of **7** formed as tiny needles having the least density of 1.562 g·cm⁻³. Yellow block-shaped crystals of **8** (space group $Cmc2_1$ and Z=4) had densities of 1.610 g·cm⁻³ (150K), comparable to similar densities of **2** and **4**.

5.3.5 Mechanical Sensitivities

Overall the salts of methyl sydnone imine were insensitive to impact and friction stimuli. The azidotetrazolate salt (**7**) was not isolated as a pure compound, and only as an impurity in the tetrazoleazasydnone salt, which prevented characterization of its mechanical sensitivity. The perchlorate (**3**) had the greatest sensitivity to impact (1-2 J) and friction (36 N). (Table 5.2) The sensitivity of (**6**) may be due to the presence of impurities of azidotetrazole (**7**). **3** was more sensitive than PETN (3 J, 60 N) and RDX (7.5 J, 120 N).[43]
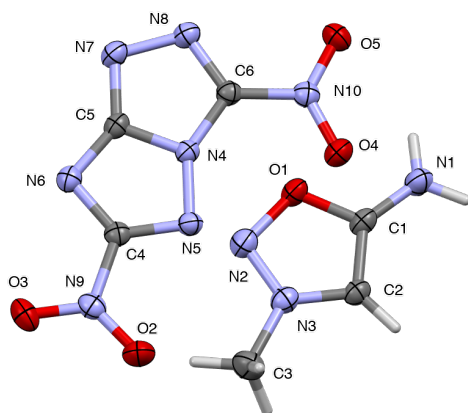
Figure 5.11. Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium DNTT (**5**). Ellipsoids are drawn at the 50% probability level.
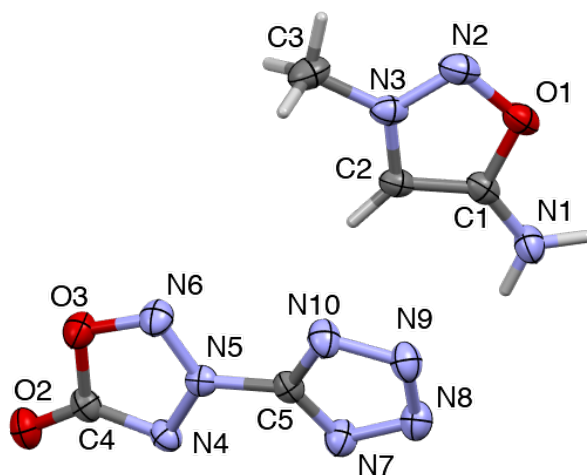
Figure 5.12. Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium TAZ (**6**). Ellipsoids are drawn at the 50% probability level.

5.3.6 Thermal Behavior

Combination differential scanning calorimetry – thermogravimetric analysis (DSC/TGA) with heating rates of 5 °K·min^{-1} were used to record the thermal behavior of all prepared compounds. Decomposition temperatures for each of the MSI compounds are shown in Table 5.2. Three salts of MSI decomposed near 135 °C. The most thermally stable compound was **3**, which decomposed near 187 °C. This is an improvement from the reported decomposition
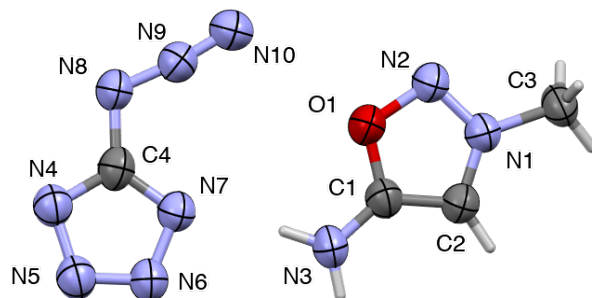
Figure 5.13. Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium azidote-trazolate (**7**). Ellipsoids are drawn at the 50% probability level.
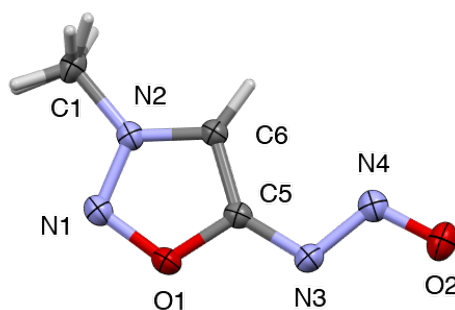
Figure 5.14. Molecular unit of 3-methyl-1,2,3-oxadiazolium nitrosoimide (**8**). Ellipsoids are drawn at the 50% probability level. Disorder of methyl H atoms is symmetry imposed by a mirror plane bisecting the molecule.

temperature of 155 °C of the chloride salt **1** as reported by Daeniker.[26] The thermal stability of **3** exceeds PETN (165 °C), but falls short of RDX (205 °C) and TNT (295 °C).[43] Unfortunately, **6** was the least thermally stable, decomposing at 112 °C. The lower thermally stability of **6** is likely due to the decomposition of the azasydnone ring, forming the azidotetrazole salt (**7**). Azidotetrazolate salts are known to be thermally very sensitive.[30] Isolation of **7** was not attempted, which prevented further characterization.

5.3.7 Energetic Properties

The energetic properties of each of the compounds are recorded in Table 5.2. The method of Byrd and Rice (based on properties of individual energetic compounds derived from quantum mechanics), provided the heats of formation[46] and densities[47], [48] of all

Table 5.2.

Energetic properties for all prepared energetic compounds. Calculated densities shown when X-ray diffraction densities were unavailable.

	2	3	4	5	6	7	8	TNT*
Formula	$C_3H_6N_4O_4$	$C_3H_6N_3O_5Cl$	$C_4H_6N_8O_3$	$C_6H_6N_{10}O_5$	$C_5H_6N_{10}O_3$	$C_4H_6N_{10}O$	$C_3H_4N_4O_2$	$C_7H_5N_3O_6$
FW [g·mol^{-1}]	162.11	199.55	214.15	298.18	254.18	210.17	128.10	227.13
IS [J]$^{a)}$	>40	1-2	>40	>40	>35**	ND	ND	15
FS [N]$^{b)}$	>360	36	>360	>360	>160**	ND	ND	>353
N [%]$^{c)}$	33.29	21.06	51.63	45.32	50.1	66.65	43.74	18.5
Ω [%]$^{d)}$	-49.35	-28.06	-59.77	-53.66	-62.95	-76.13	-74.94	-73.96
T_{dec}[°C]$^{e)}$	135	187	135	135	112**	ND	ND	295
ρ [g·cm^{-3}]$^{f)}$	1.612	1.826	1.607	1.725	1.633	1.562	1.610	ND
ρ [g·cm^{-3}]$^{(calcd.)}$	1.639	1.789	1.642	1.749	1.677	1.565	1.618	1.654
$\Delta_f H°$ [kJ·kg^{-1}]$^{g)}$	-126.4	-41.7	334.6	444.9	434.4	698.4	286.8	-59.4
EXPLO5								
$-\Delta_{Ex}U°$ [kJ·kg^{-1}]$^{h)}$	-4328	-5180	-4370	-4610	-3980	-4321	-5241	-4427
T_{det} [K]$^{i)}$	2973	3682	3113	3337	2964	3006	3455	3222
P_{CJ} [kbar]$^{j)}$	215	290	211	243	201	205	222	194
V_{Det} [m·s^{-1}]$^{k)}$	7537	8074	7572	7865	7418	7683	7645	6824
V_o [L·kg^{-1}]$^{l)}$	821	750	802	740	773	802	771	633

ND not determined; a) Impact sensitivity (BAM drophammer (1 of 6)); b) Friction sensitivity (BAM friction tester (1 of 6));
c) Nitrogen content; d) Oxygen balance ($\Omega = $ (xO–2yC–1/2zH)M/1600); e) Decomposition temperature from DSC ($\beta = 5$ °C);
f) From X-ray diffraction; g) Calculated heat of formation; h) Energy of explosion; i) Explosion temperature;
j) Detonation pressure; k) Detonation velocity; l) Volume of detonation gases (assuming only gaseous products).
*Values based on ref.[44], [45] and the EXPLO5 V6 database. **6 showed evidence of decomposition forming azidotetrazole.

compounds. These calculated densities agreed within 3% with those measured via X-ray crystallography at 150 K. The Gaussian09 program package[49] and the B3LYP spin-restricted Kohn-Sham density functional theory (KS-DFT)[50]–[53] with the 6-31G** Pople Gaussian basis set,[54]–[56] were used to determine gas phase geometries of each compound. Using these geometry data, the G3MP2(B3LYP)[57] electronic energy was determined which is required to compute the heat of formation. The Gutowski method[58] provided the heat of sublimation as determined from the molecular volume of each compound. The EXPLO5 V6.05.02 software package[59], [60] provided the detonation performance data from the calculated heats of formation based on crystal densities (when available) or calculated densities otherwise.

In addition to high mechanical sensitivity and good thermal stability, **3** exhibits the strongest calculated detonation performance ($P_{CJ} = 290$ kbar, $V_{Det} = 8074$ m/s) of the

energetic salts. The high-density perchlorate anion of **3** leads to higher density (1.826 g·cm^{-3}) and improved oxygen balance relative to the other compounds in this series. MSI DNTT (**5**) with its density of 1.725 g·cm^{-3} and strong detonation performance (P_{CJ} = 243 kbar, V_{Det} = 7865 m/s), serves as an insensitive alternative to **3**. Both **3** and **5** benefit from the most (five) oxygen atoms in their structures. All of the MSI salts have greater detonation performance than TNT (P_{CJ} = 194 kbar, V_{Det} = 6824 m/s), but fall short of PETN (P_{CJ} = 308 kbar, V_{Det} = 8429 m/s).

5.4 Conclusions

In summary, seven energetic compounds were derived from the methyl sydnone imine cation. Despite its mechanical sensitivity, the perchlorate salt possessed the greatest thermal stability and strongest calculated energetic performance of the series. Although the DNTT salt was less thermally stable (135 °C), its detonation velocity and pressure were the highest among the insensitive compounds. This study was the first on the use of sydnone imines in energetic salts. Due to their low densities and sensitivity towards thermal stimuli this class of compounds does not present itself as useful in energetic materials.

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6. HETEROCYCLIC NITRILIMINES AND THEIR USE IN THE SYNTHESIS OF COMPLEX HIGH-NITROGEN MATERIALS

Authors: Matthew L. Gettings, Sarah E Davis Finch, Ashank Sethia, Edward F. C. Byrd, Matthias Zeller, and Davin G. Piercey

6.1 Abstract

In this work we show the ability of a nitrilimine prepared from 3-amino-5-nitro-1,2,4-triazole to undergo various cycloaddition and rearrangement reactions giving a beautiful diversity of nitrogen-rich heterocyclic products. This chemistry includes the first cyclization of a nitrilimine with a diazonium species giving a tetrazole; a previously unknown transformation as well as leading to the creation of several new energetic materials with backbones not available by traditional techniques in the energetics field. The new materials prepared were characterized both chemically (multinuclear NMR, IR, MS, EA) as well as energetically with sensitivities and performances reported.

6.2 Introduction

Energetic materials (all of propellants, explosives and pyrotechnics) fundamentally straddles both the academic and practical realms. On one hand, we have materials that are on the borderline of existence where the unique structures of these materials can contribute to fundamental understanding of molecular stability[1]–[3], and on the other ever higher performing and higher stability propellants and explosives are sought for real-world applications.[4]–[7]

The increasing complexity of high-performance energetic materials must be balanced against the feasibility of production. For example, although octanitrocubane[8] is high-performing, its long synthesis has a yield over ten steps of less than one percent, which is impractical for large-scale production. Shorter synthesis translates to reduced costs and

increased chances of adoption. Chemical transformations allowing the synthesis of complex products in a minimal number of steps therefore allow 'innately scalable' energetic synthesis.

Despite the ability of nitrilimines to be generated simply and ability to undergo a wide variety of reactions, they are rather unexplored in new energetic materials discovery work. The dipolarity of nitrilimines, and their potential to undergo a diverse array of reactions,[9], [10] can allow formation of novel high-nitrogen compounds. Both hydrazonyl halides and 2,5-disubstituted tetrazoles are known precursors to nitrilimines.[9] The inherent utility of these dipolar nitrilimine compounds is their capacity to perform 1,3-dipolar cycloaddition type reactions.[9] In fact, nitrilimines undergo cycloaddition reactions to form 1,2,4-triazoles,[9], [11]–[13] 1,2,3-triazoles,[14], [15] pyrazoles,[9], [10], [16], [17] and tetrazines[18], [19] which are useful backbones for the synthesis of energetic materials.[9] Beyond energetics, nitrilimines play important roles in polymer synthesis and biochemistry including protein ligation, peptide stapling, and as chemosensors in fluorescent imaging.[9] Despite vast literature reporting various nitrilimines, C-bromonitrilimines are exceedingly rare.[20]–[22] Furthermore, there has been no known example of a nitrilimine to cyclize with a diazonium to form a tetrazole.

Brilliant work of other researchers showcase facile synthesis of exciting new energetics based on nitrilimine chemistry, including formation of azasydnones.[23]–[28] Energetic materials based on tetrazole azasysdnone have been previously reported by our group.[29] Continuing with our work on azasydnones[29], [30] we now report three new energetic species which were easily synthesized from 3-amino-5-nitro-1,2,4-triazole (ANTA) via nitrilimine chemistry.
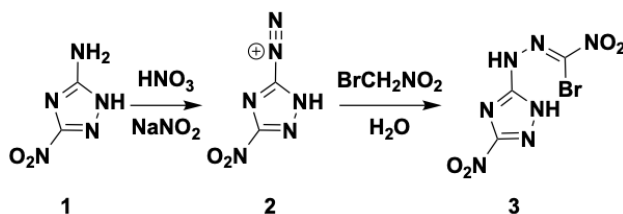

Figure 6.1. Synthesis of hydrazone (**3**) from ANTA (**1**).

An ice-cold aqueous solution of ANTA[31] was treated with a solution of sodium nitrite acidified with nitric acid, forming the diazonium (**2**). (Figure 6.1) Bromonitromethane was

added, forming bromonitrohydrazone (**3**) after stirring for 18 hours. From this product, all compounds in this work were prepared.
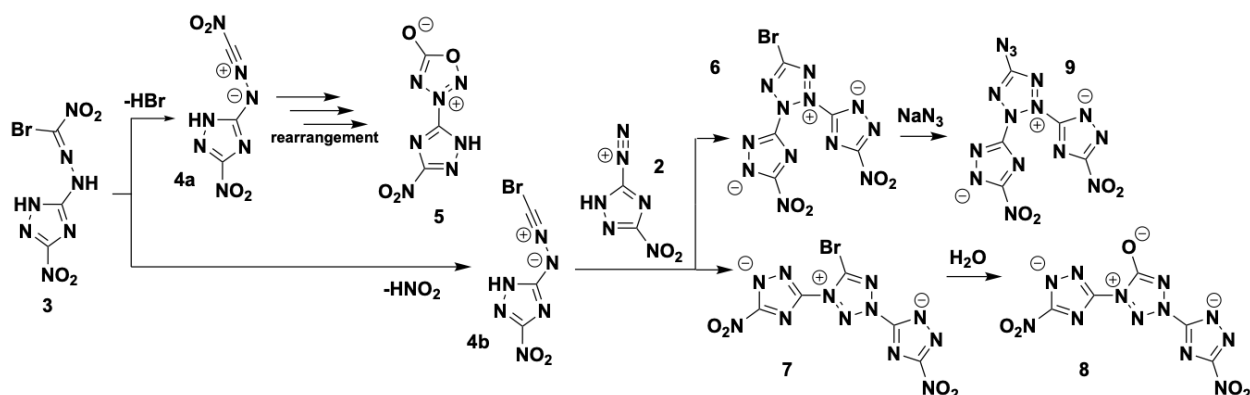

Figure 6.2. Synthesis of compounds (**4-9**), from hydrazone (**3**).

Figure 6.2 illustrates the diversity of products prepared in this work. From hydrazone **3**, elimination of either hydrobromic acid or nitrous acid was found to be possible as a result of the products identified. Salts of the 3-azasydnone-5-nitro-1,2,4-triazole (**5**) were prepared analogously to tetrazole azasydnone[29] by stirring an acetonitrile solution of hydrazone **3** over ammonium nitrate in a similar procedure to our previous work.[29] This product results from elimination of hydrobromic acid from the bromonitrohydrazone (**3**) forming the nitro nitrilimine (**4a**). The nitronitrilimine then rearranges[23] to the azasydnone **5**. This material was able to be crystalized by slow evaporation from an aqueous solution. **5** crystallized as colorless blades in the monoclinic space group *C2* (Z=6) (Figure 6.3) with a crystal density of 1.748 g·cm^{-3}.
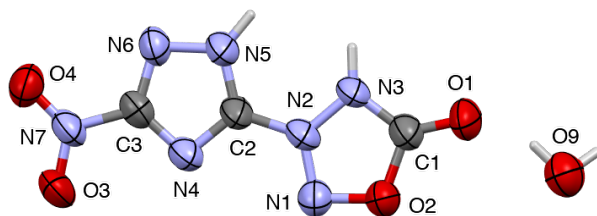

Figure 6.3. Crystal structure of HNTAZ monohydrate (**5**). Ellipsoids are drawn at the 50% probability level.

In the ^{13}C NMR, the three peaks of **5** and its salts occur at 167.1, 162.7, and 151.1 ppm. The 162.7 ppm peak of the C-NO$_2$ shifted downfield from the ANTA precursor (159.8 ppm). The azasydnone carbon peak of **5** closely matches ^{13}C peaks for other azasydnones.[24], [27], [28] The ^{1}H NMR spectra of **5b**-**5i** match those of the cations found in literature.[32]

However unlike in our related work with tetrazoleazasydnone, two additional unique products were identified which we suspect result from elimination of nitrous acid from bromonitrohydrazone **3**, forming bromonitrilimine (**4b**).
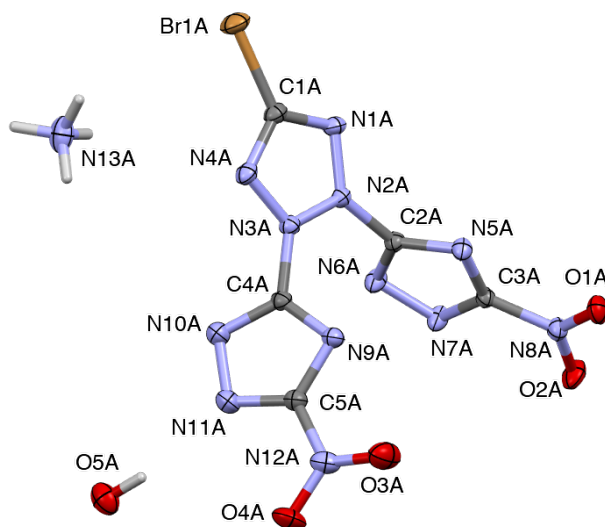

Figure 6.4. Crystal structure of the ammonium salt (**6a**). Ellipsoids are shown at the 50% probability level.

The ammonium salt (**6a**) of the 2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazoliumate anion (**6**) was first detected in crude solutions of (**5**) by mass spectrometry. Crystals of ammonium salt **6a** (Figure 6.4) were readily obtained via slow evaporation of crude aqueous solution of **5** during workup. Based on single-crystal X-ray diffraction, the crystal density of **6a** was 1.933 g·cm^{-3}.

^{13}C NMR experiments of **6a** consistently report three peaks at 163.3, 148.6, and 146.2 ppm. For **6a**, the *C*-NO$_2$ carbon of each triazole (163.3 ppm) shifted downfield from **5** (161.4 ppm). However, the peak of the second triazole carbon (148.6 ppm) bonded to the tetrazole shifted upfield from **5** (151.1 ppm), where it's bonded to the azasydnone ring. The carbon peak of chlorotetrazole[33] is reported at 150.8 ppm.
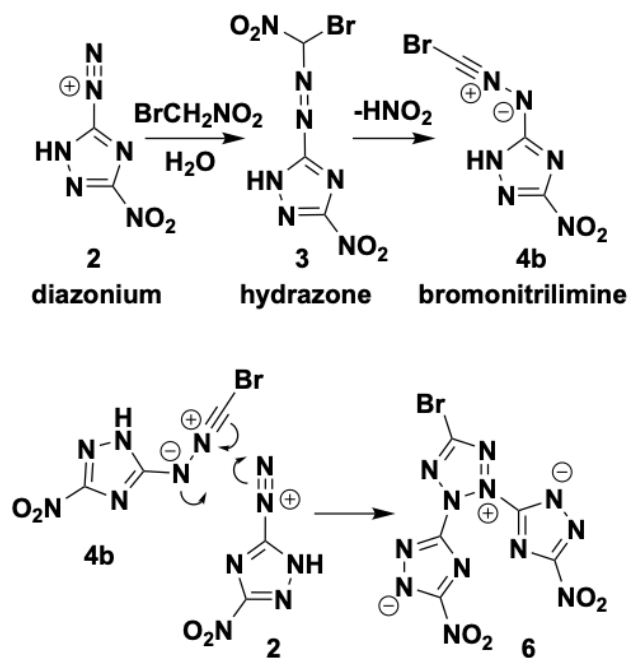
Figure 6.5. Possible reaction mechanism for the formation of compound **6**.

The ammonium salt **6a** decomposed near 185°C and was "sensitive"[34] to impact (>5 J), yet insensitive (>360 N) to friction.
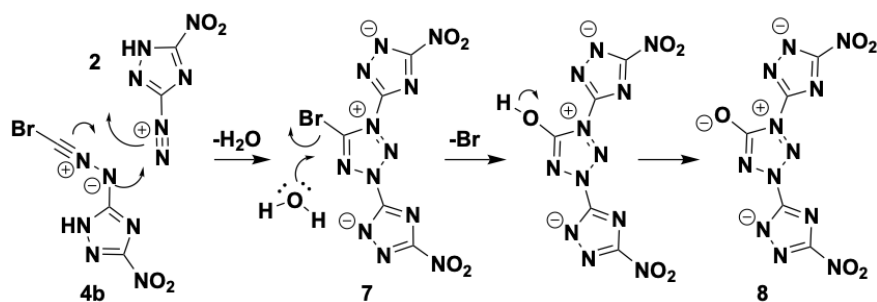
Figure 6.6. Possible reaction mechanism for the hydrolysis of **7**, forming **8**.

We suspect that the 2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazoliumate anion (**6**) formed as a result of bromonitrilimine **4b** undergoing a 2+3 cycloaddition reaction with 5-diazo-3-nitro-1,2,4-triazole (**2**). (Figure 6.5). This result is unique in that to the best of our knowledge, and extensive literature searching, it marks the first report of a tetrazole being generated by cycloaddition of a nitrilimine with a diazonium compound.[9] Furthermore, it

is a rare example of a suspected bromonitrilimine intermediate and a search of the literature revealed only a few examples of this class of intermediates.[20]–[22]
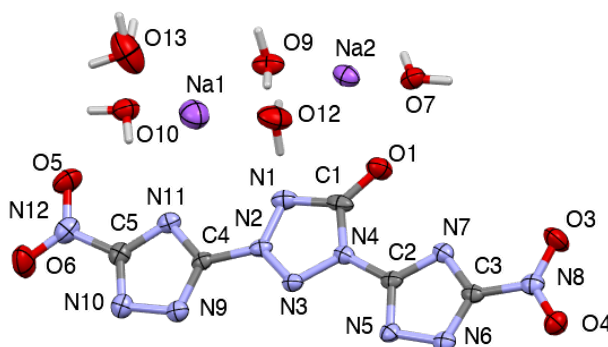

Figure 6.7. Crystal structure of compound (**8**). Ellipsoids are drawn at the 50% probability level. Water and triazole N coordinating bonds to sodium atoms are hidden to make structure more clear.

Based on regiochemistry of bromonitrilimine **4b** undergoing cyclization with diazonium **2**, two products are capable of being formed; the 2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazoliumate anion (**6**) as well as 1,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazoliumate anion (**7**). Based on ^{13}C-NMR spectroscopy experiments and comparison with pure crystalized **6a**, we were unable to detect significant amounts of the latter anion (**7**) in any experiments during separation of pure salts of **5** and **6**. Serendipitously, crystals of disodium (**8a**) 1,3-di(5-nitro-1,2,4-triazole-3-ide)-5-oxotetrazoliumate anion **8** were obtained while attempting to purify crude sodium salt of **5**. This anion results from hydrolysis of the sought-after 1,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazoliumate anion (**7**) in water. (Figure 6.6). Despite reviewing mass spectrometry data from roughly 50 experiments that were performed in which salts of **5** and **6** were prepared for characterization, anion **8** was only detected in traces in a handful of experiments, and the few crystals of this material (**8a**) obtained were insufficient for any analytics other than single-crystal X-ray. The crystal structure of **8** (Figure 6.7) crystallizes in space group $P\overline{1}$ with 2 units in the cell and a density of 1.735 g·cm^{-3}.

In general, despite occasional appearance of **8**, treatment of aqueous 3-diazo-5-nitro-1,2,4-triazole (**2**) with bromonitromethane, extracting crude bromonitrohydrazone (**3**) fol-
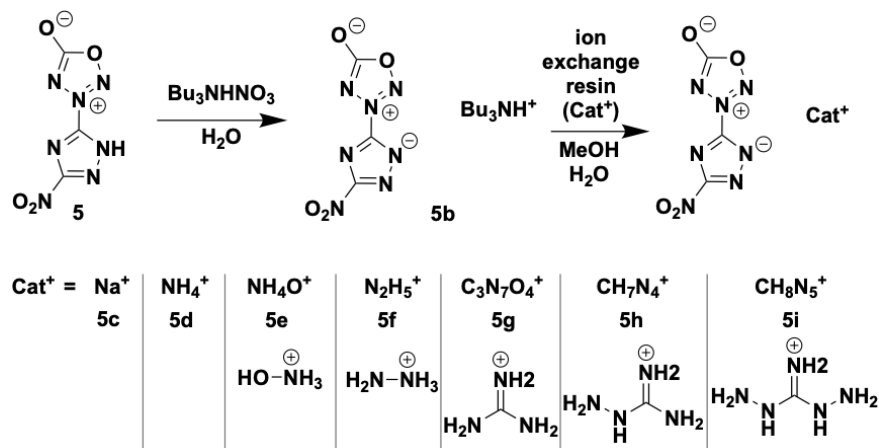
Figure 6.8. Synthesis of NTAZ salts (**5b**-**5i**) from HNTAZ (**5**).

lowed by its rearrangement over ammonium nitrate in acetonitrile gives **5** and **6** as their ammonium salts (**5a** and **6a**). When a solution of the two is allowed to slowly evaporate, ammonium salt **6a** is isolated pure. Careful addition of a solution of tri-n-butylammonium nitrate and extraction with ethyl acetate semi-selectively extracted residual **6** as its butylammonium salt, leaving a solution of pure **5** (as a mixture of its ammonium salt with ammonium nitrate). Further addition of butylammonium nitrate allowed extraction into ethyl acetate of pure butylammonium salt (**5b**) of **5**. Use of an ion exchange resin allowed preparation of salts **5**(**c-i**) (Figure 6.8) sodium (**5c**), ammonium (**5d**), hydroxylammonium (**5e**), hydrazinium (**5f**), guanidinium (**5g**), aminoguanidinium (**5h**), and diaminoguanidinium (**5i**). Nitrate impurities found in **5c** were removed by redissolving the material in acetone then filtered through a syringe. The structure for NTAZ sodium salt (**5c**) (Figure 6.9) had density of 1.836 g·cm^{-3}. Crystals of **5c** formed as colorless flakes in monoclinic space group P_c with 4 units. However, due to their extreme deliquescency several salts (**5e**, **5f**, and **5i**) were unable to be fully characterized and only sodium salt was able to be crystallized after repeated attempts.

During the synthesis of salts of **5** we observed evidence of decomposition to 3-azido-5-nitro-1,2,4-triazole by mass spectrometry (M-H, ESI$^-$, 154 m/z), which matches decomposition of azasydnone to azide as seen in our previous paper[29] as well as the work of
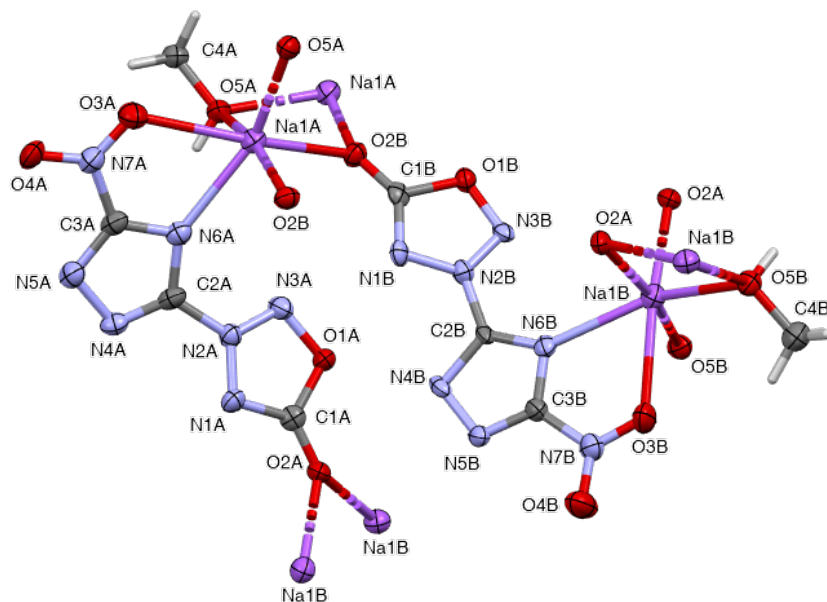
Figure 6.9. Crystal structure of the NTAZ sodium salt (**5c**). Ellipsoids are shown at the 50% probability level.

Dalinger.[27] This effect was particularly pronounced when attempting salts of nucleophilic cations such as hydrazinium and hydroxylammonium.

Full chemical characterization and energetic properties for all prepared compounds may be found in Supporting Information. Thermogravimetric analysis (TGA) captured thermal behavior of these compounds. Unfortunately, TGA traces of most of the salts of **5** did not reveal a sharp mass loss, as a result of partial decomposition to their azides and hygroscopicity. Some dehydration was observed in TGA traces as well. All prepared compounds had negative oxygen balances (fuel rich). The most oxygen balanced salt was sodium (**5c**) (-18 %), but its heat of formation was rather low (41.9 kJ·mol^{-1}), resulting in lower values for detonation pressure (239 kbar) and velocity (7840 m·s^{-1}) as compared with the other compounds. The remaining salts were "insensitive" to friction, although hydrazinium salt (**5f**) showed some sensitivity (>324 N). Hygroscopicity of the hydroxylammonium (**5e**), aminoguanidinium (**5h**), and diaminoguanidinium (**5i**) salts prevented accurate sensitivity characterization. As mentioned earlier, densities for **5** and **5c** were obtained from crystal-

lographic analysis. Calculated densities for the remaining NTAZ salts ranged 1.711 g·cm^{-3} (diaminoguanidinium) (**5i**) to 1.840 g·cm^{-3} (hydroxylammonium) (**5e**).
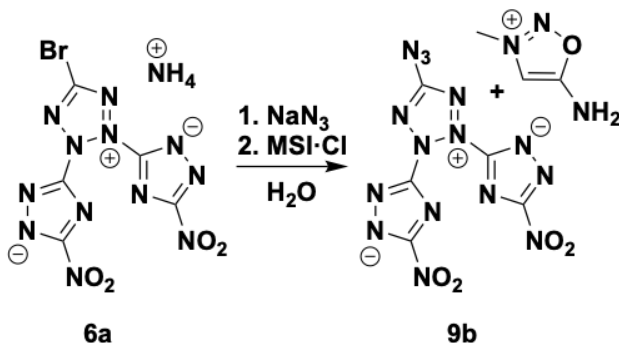

Figure 6.10. Formation of the azido complex MSI salt (**9b**) from **6a**.

Based on calculated densities (or crystallographic densities when available) and heats of formation, detonation performances were obtained using EXPLO5 software.[35], [36] All compounds exceeded TNT performance (P_{CJ} = 194 kbar, V_{Det}= 6824 m·s^{-1}). Among the NTAZ compounds the hydroxylammonium salt (**5e**) had the highest detonation pressure (325 kbar) and detonation velocity (8749 m·s^{-1}). Compounds **5**, ammonium (**5d**), and hydrazinium (**5f**) salts had comparable detonation pressures (286-289 kbar) and velocities (8360-8503 m·s^{-1}). However, their lack of chemical stability as shown by partial decomposition to the corresponding azidotriazole, and hygroscopicity will preclude their use as practical energetic material despite their nice performances.

Compound **6** is unique in that its high nitrogen system is unprecedented in energetic materials. While 2,3-disubstituted tetrazoles are well known in the literature,[37]–[39] no 2,3-disubstituted tetrazole has ever been studied as an energetic material. We found it to react with sodium azide in aqueous solution to generate the 2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-azidotetrazoliumate anion (**9**). The addition of 5-amino-3-methyl-1,2,3-oxadiazolium chloride[40] to the reaction mixture led to crystallization of the 5-amino-3-methyl-1,2,3-oxadiazolium salt (**9b**). (Figure 6.10). **9b** crystalizes in the $P2_1/n$ space group with 4 units in the unit cell and a density of 1.707 g·cm^{-3}. (Figure 6.11)

9b exhibits ^{13}C signals at 163.9, 163.3 and 148.9 ppm for the anion. The ^{13}C signals for the cation matched those previously reported.[40]
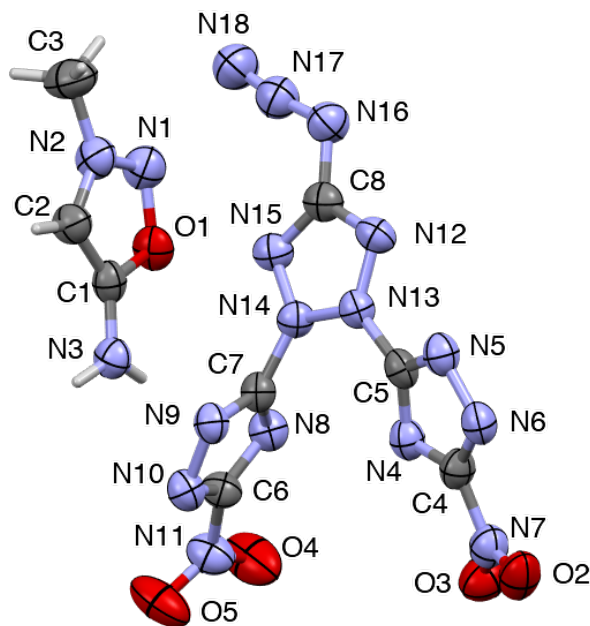
Figure 6.11. Crystal structure of the azido compound MSI salt (**9b**). Ellipsoids are shown at the 50% probability level.

Thermal decomposition of the MSI salt (**9b**) was observed as an abrupt mass loss near 170 °C in our TGA instrument. As expected, MSI salt of the azido compound (**9b**) exceeded detonation performance (255 kbar, 8063 m·s^{-1}) of ammonium salt **6a** (254 kbar, 7481 m·s^{-1}).

6.3 Conclusions

In conclusion, nitrilimines derived from 3-amino-5-nitro-1,2,4-triazole (ANTA) were used to synthesize a series of high-nitrogen energetic compounds. This work demonstrates a novel synthesis of 2,3-disubstituted bromotetrazoles with applicability to new energetic materials synthesis. We report the first synthesis of nitro triazoleazasydnone and several energetic salts. Several compounds were characterized and their energetic properties were reported. Unfortunately, several NTAZ salts proved to be very hygroscopic, which prevented further analysis. The methyl sydnone imine salt (**9b**) of the 2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-azidotetrazoliumate anion (**9**) showed good thermal stability (170 °C) and is a rep-

resentative member of a new class of energetic tetrazoles which also demonstrated novel nitrilimine chemistry during its synthesis.

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7. SUMMARY

7.1 Chapter Reviews

In Chapter 2, nine energetic salts of DNTT anion were synthesized and characterized. These include sodium, ammonium, hydrazinium, silver, guanidinium, aminoguanidinium, diaminoguanidinium, triaminoguanidinium, hydroxylammonium, and TATOT DNTT cocrystal. Each of the synthesis routes required only affordable precursors following straightforward processes. Three compounds demonstrated good thermal stability (>180 ºC). All of the compounds were insensitive to impact (>40 J). Several salts were considered "sensitive" to friction. Both HDNTT and the hydroxylammonium salts surpassed RDX and are close to HMX performance. All of the DNTT salts exceeded calculated detonation pressure and velocity for TNT. However, HDNTT was deliquescent, which prevent analysis of thermal stability as well as friction and impact sensitivities. Hydroxylammonium salt began to decompose at room temperature.

In Chapter 3, tetrazole azasydnone (TAZ) as well as its energetic salts were obtained and analyzed. Particular attention focused on the metal-free (HTAZ) and the silver salt (silver TAZ) as primary explosives. The Army Research Lab has expressed such interest that further research and characterization of silver tetrazole azasydnone (TAZ) has been transitioned to Picatinny Arsenal. Formation of azasydnones remains a unique strategy in energetics design which, unfortunately, appear limited by their reactivity with nucleophiles. When compared with their azidotetrazole analogs, all of the TAZ salts had greater densities. Moreover, five TAZ salts had higher densities than the same salts of nitrotetrazole.

Chapter 4 explored the use of azasydnones in energetic materials. Azasydnones may be synthesized through several methods, yet only recent papers examined their energetic properties. A recent (2018) thermal stability and combustion study proposed two isomeric dinitropyrazole azasydnones as potential candidates in propellants due to the thermal stabilities and low pressure-dependence of their burn rates.

Chapter 5 reported the synthesis and characterization of seven new energetic salts of methyl sydnone imine (MSI). This research remains quite notable as the first investigation of this new energetic cation, which may greatly expand the range of possible energetic salts

available. Linking back to Chapter 2, the DNTT salt stood out with the highest detonation performance. The greatest thermal stability (187 °C) was recorded for the perchlorate salt. Unfortunately, the MSI salts were plagued by low densities and poor thermal stabilities.

Chapter 6 revealed the generation of heterocyclic nitrilimines and their utilization in the synthesis of several new high-nitrogen energetic materials. A series of energetic nitrogen-rich salts of nitro triazoleazasydnone was prepared. Moreover, an unexpected formation of rather exotic zwitterionic tetrazoles was observed. This publication showcased the fifteen-nitrogen 2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-azidotetrazoliumate anion.