REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
15-06-2022	Final Report	1-Oct-2018 - 31-Jan-2022

4. TITLE AND SUBTITLE
Final Report: Molecular Structure and Dynamics: Disruptive Energetic Materials: The Synthesis and Stabilization of High-Nitrogen compounds and Next-Generation Energetic Materials

5a. CONTRACT NUMBER
W911NF-18-1-0463

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Purdue University
Sponsored Program Services
155 S Grant Street
West Lafayette, IN 47907 -2114

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
73236-CH.8

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Davin Piercey
UU	UU	UU	UU		19b. TELEPHONE NUMBER 765-494-1504

RPPR Final Report
as of 28-Jun-2022

Agency Code: 21XD

Proposal Number: 73236CH **Agreement Number: W911NF-18-1-0463**
INVESTIGATOR(S):

Name: Davin Piercey
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Organization: **Purdue University**
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Country: USA

DUNS Number: 072051394 EIN: 356002041
Report Date: 30-Apr-2022 Date Received: 15-Jun-2022
Final Report for Period Beginning 01-Oct-2018 and Ending 31-Jan-2022
Title: Molecular Structure and Dynamics: Disruptive Energetic Materials: The Synthesis and Stabilization of High-Nitrogen compounds and Next-Generation Energetic Materials
Begin Performance Period: 01-Oct-2018 **End Performance Period:** 31-Jan-2022
Report Term: 0-Other

Submitted By: Davin Piercey Email: dpiercey@purdue.edu
Phone: (765) 494-1504

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 2 **STEM Participants:** 8

Major Goals: In this work various thrusts for disruptive energetic materials are covered. These thrusts include such work as the preparation of all-nitrogen heterocycles, methodology for the stabilization of high-N and all-N systems, and synthetic routes to functional groups that have the potential to be used in the creation of energetic materials of very high performance. This work will cover all steps from the development of new synthetic methods for high-N and all-N chemistry, work on model systems to demonstrate methods of stabilizing molecules with unprecedented nitrogen and energy content, the synthesis of functional energetics and the calculation and measurement of energetic properties of the prepared molecules.
Under this work we are working towards:
a) New insights on the stabilization of energetic materials towards mechanical and thermal stimuli.
b) New synthesis strategies to energetic functional groups and backbones that push the limits of performance.
c) New functional energetic materials that meet performance requirements of the Army and contributing to the Army's mission.
d) New energetic materials based on all-nitrogen backbones such as pentazoles furthering the understanding of these materials and pushing the limits of energetic performance.

Accomplishments: Please see uploaded pdf

Training Opportunities: Participation in numerous conferences since the start of this grant including:
NTREM
IPS
FEM
GRC

Results Dissemination: Please see attached pdf for publication listing during this grant

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Two provisional patents obtained from this effort and one new energetic material transitioned to Picatinny Arsenal for further testing.

For more details see the pdf.

PARTICIPANTS:

Participant Type: Faculty
Participant: Davin Piercey
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Participant: Matthew Gettings
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
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Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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Participant: Ashank Sethia
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Matthew Giroux
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Michael Thoenen
Person Months Worked: 8.00 **Funding Support:**

RPPR Final Report
as of 28-Jun-2022

Project Contribution:
National Academy Member: N

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemistry; A European Journal
Publication Identifier Type: DOI Publication Identifier: 10.1002/chem.202002664
Volume: Issue: First Page #:
Date Submitted: 8/31/21 12:00AM Date Published: 6/1/20 12:00PM
Publication Location:
Article Title: Tetrazole Azasydnone (C2N7O2H) And Its Salts: High?Performing Zwitterionic Energetic Materials Containing A Unique Explosophore
Authors: Matthew Lee Gettings, Michael T Thoenen, Edward F. C. Byrd, Jesse J. Sabatini, Matthias Zeller, Davin
Keywords: Azasydnone 5-(5-oxido-1,2,3,4-oxatriazol-3-ium-3-yl)tetrazol-1-ide Energetic materials Explosive heterocycles
Abstract: We show the ability of a nitrilimine prepared from 3-amino-5-nitro-1,2,4-triazole to undergo various cyclization 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. New materials prepared were characterized both chemically (multinuclear NMR, IR, mass spectrometry, and elemental analysis) and energetically, with sensitivities and performances reported.
Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ChemistryOpen
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1002/open.202000053
Volume: 9 Issue: 8 First Page #: 806
Date Submitted: 6/15/22 12:00AM Date Published: 5/1/20 4:00PM
Publication Location: Chemistry Europe
Article Title: Sensitive Energetics from the N -Amination of 4-Nitro-1,2,3-Triazole
Authors: Dominique R. Wozniak, Benjamin Salfer, Matthias Zeller, Edward F. C. Byrd, Davin G. Piercey
Keywords: amination reactions energetic materials heterocycles N-amines primary explosives
Abstract: Recent publications demonstrate exciting new uses of azasydnones in the development of energetic materials. Facile synthesis routes support a remarkabe 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.
Distribution Statement: 4-Distribution authorized to the Department of Defense and U.S. DoD contractors only
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 28-Jun-2022

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: RSC Advances
Publication Identifier Type: DOI Publication Identifier: 10.1039/D1RA00953B
Volume: 11 Issue: 29 First Page #: 17710
Date Submitted: 6/15/22 12:00AM Date Published:
Publication Location: OK, United Kingdom
Article Title: 3-Methyl-1,2,3-triazolium-1N-dinitromethylylide and the strategy of zwitterionic dinitromethyl groups in energetic materials design
Authors: Dominique R. Wozniak, Matthias Zeller, Edward F. C. Byrd, Davin G. Piercey
Keywords: energetic materials, triazoles,
Abstract: 3-Methyl-1,2,3-triazolium-1N-dinitromethylylide, an exemplary zwitterionic energetic molecule, is the first fully-studied energetic material making use of the zwitterionic dinitromethyl functional group. This compound has impact and friction sensitivities of 8 J and 144–160 N respectively with a detonation velocity of 8162 m s?1.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Inorganic Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.inorgchem.1c00469
Volume: 60 Issue: 11 First Page #: 7607
Date Submitted: 6/15/22 12:00AM Date Published: 5/2/21 4:00AM
Publication Location: Online
Article Title: 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, Davin G
Keywords: energetic materials
Abstract: The latest member of the azole family, the pentazolate or cyclo-N5?, has received increased attention since its first mass-spectral detection by Christe et al. in 2002. As it is carbon- and hydrogen-free, the pentazolate anion can release large amounts of energy while simultaneously decomposing to environmentally friendly nitrogen gas. Due to these attractive qualities, cyclo-N5? and related compounds are essential in the advancement of high-energy-density materials (HEDMs) research. This review aims to provide a consolidated report on all research done on cyclo-N5?, with a focus on pentazoles as energetic materials and on their experimental synthesis. Included in this review are the following: ? the historical significance of cyclo-N5?; ? precursors of cyclo-N5?; ? synthesis routes of cyclo-N5? with a focus on arylpentazole precursors; ? factors affecting the stability of cyclo-N5?; ? energetic performances of current energetic cyclo-N5?-containing compounds; and ? future possible exp
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: New Journal of Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1039/D0NJ05354F
Volume: 45 Issue: NA First Page #: 2228
Date Submitted: 6/15/22 12:00AM Date Published: 1/11/21 10:00AM
Publication Location: London, United Kingdom
Article Title: Methyl sydnone imine and its energetic salts
Authors: Matthew L. Gettings, Edward F. C. Byrd,Matthias Zeller, Davin Piercey
Keywords: energetic materials, sydnones
Abstract: Several energetic salts of the 5-amino-3-methyl-1,2,3-oxadiazolium cation were synthesized and characterized. Structures are confirmed by IR, 1H and 13C 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 that of 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 facile syntheses. This is the first exploration of sydnone imines as components of energetic materials.
Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 28-Jun-2022

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Energetic Materials Frontiers
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1016/j.enmf.2020.11.002
Volume: 1 Issue: 3 First Page #: 136
Date Submitted: 6/15/22 12:00AM Date Published: 3/11/21 5:00AM
Publication Location: China
Article Title: Azasydnones and their use in Energetic Materials
Authors: MatthewGettings, DavinPiercey
Keywords: Azasydnone 5-(5-Oxido-1,2,3,4-oxatriazol-3-ium-3-yl)tetrazol-1-ide Energetic materials Heterocycles High nitrogen compounds
Abstract: Recent publications demonstrate exciting new uses of azasydnones in the development of energetic materials. Facile synthesis routes support a remarkabe 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.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Engineering
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1016/j.eng.2020.05.019
Volume: 6 Issue: 9 First Page #: 981
Date Submitted: 6/15/22 12:00AM Date Published: 10/26/20 8:00AM
Publication Location: china
Article Title: Review of the Current Synthesis and Properties of Energetic Pentazolate and Derivatives Thereof
Authors: Dominique R.Wozniak, Davin G.Piercey
Keywords: pentazoles, energeic materials
Abstract: The latest member of the azole family, the pentazolate or cyclo-N5?, has received increased attention since its first mass-spectral detection by Christe et al. in 2002. As it is carbon- and hydrogen-free, the pentazolate anion can release large amounts of energy while simultaneously decomposing to environmentally friendly nitrogen gas. Due to these attractive qualities, cyclo-N5? and related compounds are essential in the advancement of high-energy-density materials (HEDMs) research. This review aims to provide a consolidated report on all research done on cyclo-N5?, with a focus on pentazoles as energetic materials and on their experimental synthesis. Included in this review are the following: ? the historical significance of cyclo-N5?; ? precursors of cyclo-N5?; ? synthesis routes of cyclo-N5? with a focus on arylpentazole precursors; ? factors affecting the stability of cyclo-N5?; ? energetic performances of current energetic cyclo-N5?-containing compounds; and ? future possible exp
Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

Partners

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RPPR Final Report
as of 28-Jun-2022

I certify that the information in the report is complete and accurate:
Signature: Davin Piercey
Signature Date: 6/15/22 4:20PM

Grant or Contract Number: W911NF-18-1-0463
Date Prepared: April 15, 2022.
Project Title: **Disruptive Energetic Materials: The Synthesis and Stabilization of High-Nitrogen compounds and Next-Generation Energetic Materials.**
Final Summary Report
Period of Performance: October 1 2018-July 31, 2021 (money ran out Jan 2021)
Principle Investigator:
Prof. Davin Piercey
765-494-1504
dpiercey@purdue.edu
Purdue University

Section I: Project Summary

1. Overview of Project

In this work various thrusts for disruptive energetic materials are covered. These thrusts include such work as the preparation of all-nitrogen heterocycles, methodology for the stabilization of high-N and all-N systems, and synthetic routes to functional groups that have the potential to be used in the creation of energetic materials of very high performance. This work will cover all steps from the development of new synthetic methods for high-N and all-N chemistry, work on model systems to demonstrate methods of stabilizing molecules with unprecedented nitrogen and energy content, the synthesis of functional energetics and the calculation and measurement of energetic properties of the prepared molecules.

Under this work we are working towards:

a) New insights on the stabilization of energetic materials towards mechanical and thermal stimuli.
b) New synthesis strategies to energetic functional groups and backbones that push the limits of performance.
c) New functional energetic materials that meet performance requirements of the Army and contributing to the Army's mission.
d) New energetic materials based on all-nitrogen backbones such as pentazoles furthering the understanding of these materials and pushing the limits of energetic performance.

2. Activities and Accomplishments

During the time period since the grant has been awarded, all thrusts have all had investigation and will be covered in turn. Unfortunately this grant was terminated after 2 years of performance so not all the work proposed was able to be completed as the work was proposed for 3 years.

Thrust 1: Energetic materials containing zwitterionic and highly-charged functionalities.

Initially under this thrust, a new energetic anion consisting of both thermally and mechanically stabilizing structural motifs was targeted. The 1,3-bis(nitroimido)-1,2,3-triazolate anion is known to be thermally stable however is quite mechanically sensitive with impact and friction sensitivities comparable to primary explosives. We are currently seeking to produce this material, however containing a *C*-amine and *C*-nitro group on the parent heterocyclic ring.

Figure 1 details the prospective synthesis route for the synthesis of this material

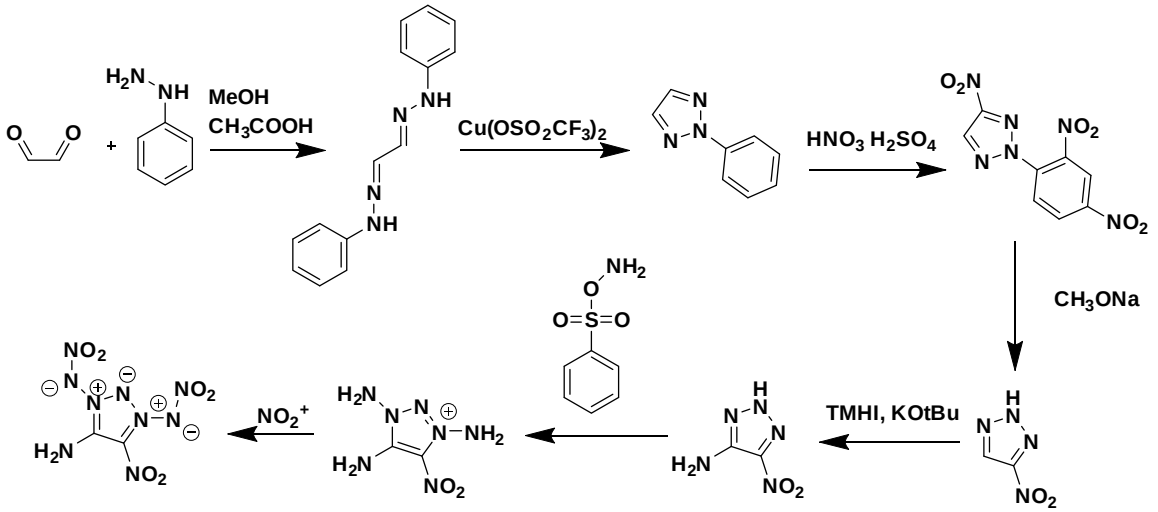


Figure 1: Synthesis of 4-amino-5-nitro-1,3-bis(nitroimido)-1,2,3-triazolate anion

We successfully reached the immediate precursor for this material, the 1,3,4-triamino-5-nitro-1,2,3-triazolium cation upon the amination of 4-amino-5-nitro-1,2,4-triazole with *O*-tosylhydroxylamine. Figure 2 shows the mass spec of this material (m/z: 160, M+) as well as the only diaminated product (m/z: 145, M+H)

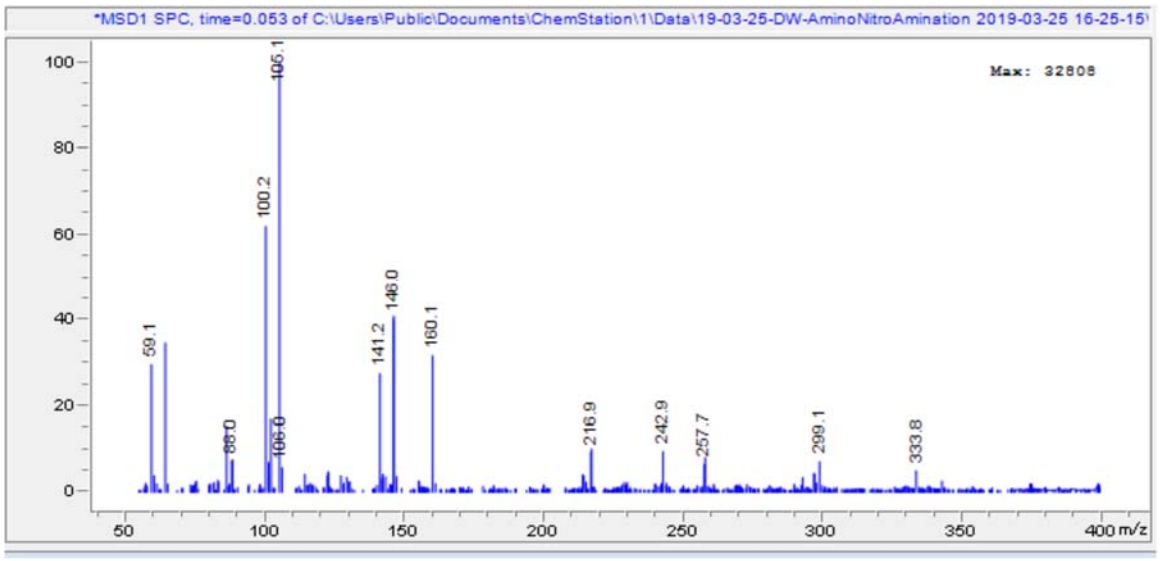
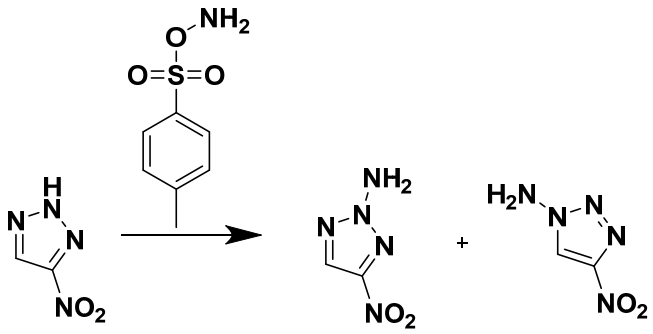


Figure 2: Mass spec of the 4-amino-5-nitro1,3-bis(nitroimido)-1,2,3-triazolate anion

Unfortunately this material appeared to be unstable and formed in only small amounts; all attempts at isolation have led to loss of the material.

With 4-nitro-1,2,3-triazole in hand from this synthetic route, we also sought to attempt first *N*-amination using *O*-tosylhydroxylamine before using TMHI (trimethylhydrazinium iodide) for *C*-amination, giving an alternate route to the 1,3,4-triamino-5-nitro-1,2,3-triazolium cation. We were unable to achieve di-*N*-amination regardless of reaction conditions, however we did isolate the neutral energetic molecules 1-amino-4-nitro-1,2,3-triazole and 2-amino-4-nitro-1,2,3-triazole. (Scheme 2)



Scheme 2: The O-tosylhydroxylamine amination of 4-nitro-1,2,3-triazole.

These materials have been fully characterized as energetic materials in addition to traditional chemical characterization and a manuscript on them has been published in *Chemistry Open*.[2] Both aminated compounds are quite sensitive towards impact and friction, with sensitivities comparable to primary explosives. Detonation performances are comparable to PETN and lower than RDX. Full publication will be emailed to program manager Jim Parker by email.

Table 1: Energetic performances of 2-amino-4-nitro-1,2,3-triaole and 1-amino-4-nitro-1,2,3-triazole

	2-amino-4-nitro-1,2,3-triazole	1-amino-4-nitro-1,2,3-triazole	RDX	PETN	$Pb(N_3)_2$
Formula	$C_2H_3N_5O_2$	$C_2H_3N_5O_2$	$C_3H_6N_6O_6$	$C_5H_8N_4O_{12}$	N_6Pb
FW / [g mol^{-1}]	129.08	129.08	222.12	316.13	291.3
IS / [J][a]	<1	<1	7.5	3	2.5-4
FS / [N][b]	16-18	14-16	120	60	0.1-1
N / [%][c]	24.99	24.99	37.84	17.7	28.9
Ω / [%][d]	-43.38	-43.38	-21.61	-10.12	-11.0
T_{dec} / [°C][e]	100	175	205	165	ca. 315
ρ / [g·cm^{-3}][f]	1.766	1.721	1.858	1.8	-
ρ / [g·cm^{-3}]^{calc}	1.677	1.694	-	-	4.8
$\Delta_f H_m^o$ / [kJ mol^{-1}] [g]	276.4	282.7	86.3	-561	450.1
EXPLO6					
$-\Delta_{Ex}U^o$ / [kJ kg^{-1}][h]	-5226	-5255	-5740	-6012	1569
T_{det} / [K][i]	3576	3630	3745	3958	3401
P_{CJ} / [kbar][j]	296	282	336	308	338
V_{det} / [m s^{-1}][k]	8602	8425	8801	8429	5920
V_o / [L kg^{-1}][l]	797	802	783	743	252

[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] energy of explosion; [i] explosion temperature; [j] detonation pressure; [k] detonation velocity; [l] volume of detonation gases (assuming only gaseous products).

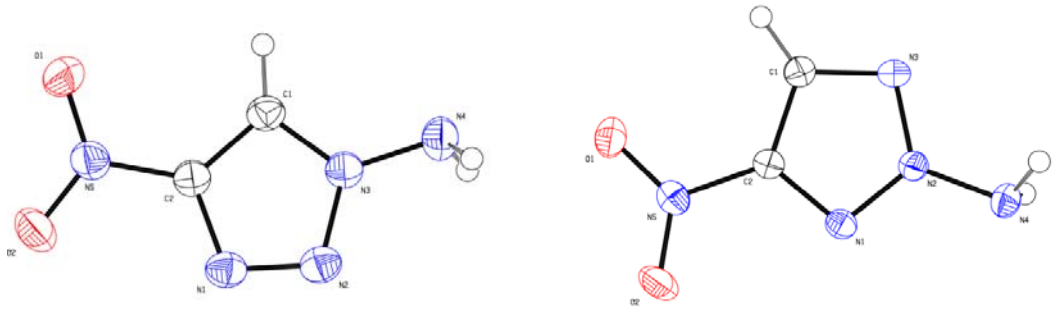
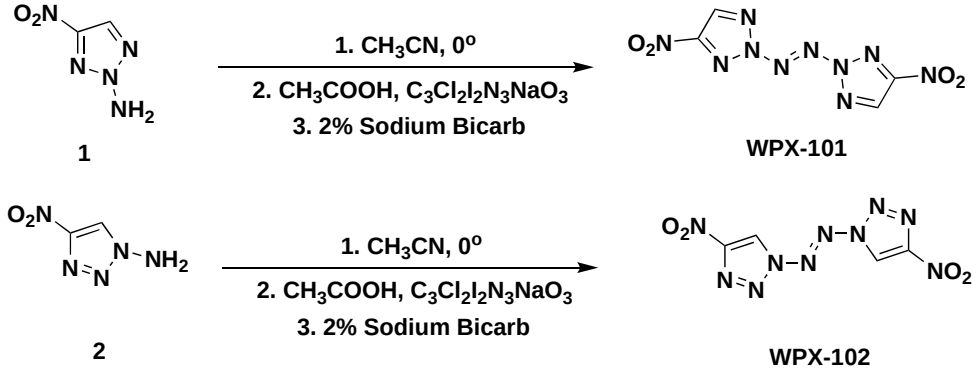


Figure 3: Molecular units of 2-amino-4-nitro-1,2,3-triaole and 1-amino-4-nitro-1,2,3-triazole

With these energetic amino compounds in hand, we chose to azo couple them to get the corresponding azo compounds possessing extended chains of catenated nitrogen atoms. (Scheme 3)



Scheme 3: The azo coupling of 2-amino-4-nitro-1,2,3-triazole and 1-amino-4-nitro-1,2,3-triazole

Both of these materials have been fully characterized including single-crystal X-Ray (Figure 3) and a manuscript on them has been published in *Organic Letters.* Their performance data can be found in table 2.

Table 2: Energetic performances of WPX-101 and WPX-102.

	WPX-101	**WPX-102**	**HMX**	**RDX**
Formula	$C_4H_2N_{10}O_4$	$C_4H_2N_{10}O_4$	$(CH_2NNO_2)_4$	$C_3H_6N_6O_6$
FW / [g mol^{-1}]	254.13	254.13	296.16	222.12
IS / [J][a]	4.0-4.5	<1	7	7.5
FS / [N][b]	36-40	<5	112	120
N / [%][c]	55.12	55.12	37.84	37.84
Ω / [%][d]	-31.48	-31.48	-21.61	-21.61
T_{dec} / [°C][e]	227	160	275	205
ρ / [g·cm^{-3}][f]	1.840	1.818	1.905	1.858
ρ / [g·cm^{-3}]^{calc}	1.766	1.780	-	-
$\Delta_f H_m^o$ / [kJ mol^{-1}] [g]	841.4	866.4	74.8	86.3
EXPLO6				
$-\Delta_{Ex}U°$ / [kJ kg^{-1}][h]	-6036	-6112	-5700	-5740
T_{det} / [K][i]	4405	4481	4117	3745
P_{CJ} / [kbar][j]	354	349	378	336
V_{det} / [m s^{-1}][k]	9068	9014	9193	8801
V_o / [L kg^{-1}][l]	743	747	763	783

[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] energy of explosion; [i] explosion temperature; [j] detonation pressure; [k] detonation velocity; [l] volume of detonation gases (assuming only gaseous products).

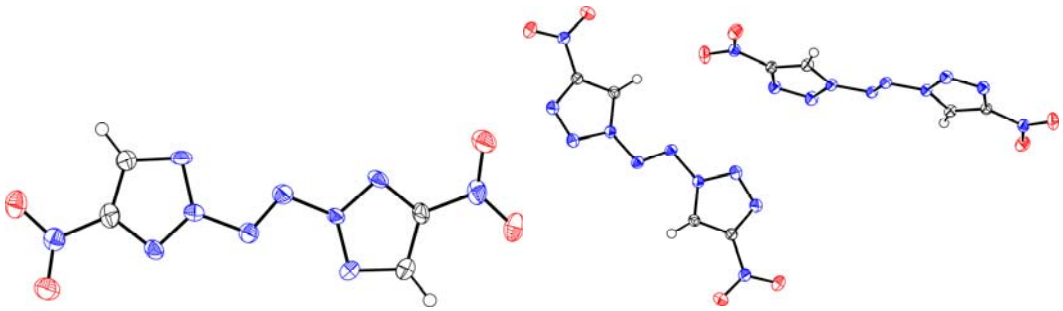


Figure 3: Molecular units of WPX-101 and WPX-102.

2,2'-azobis(4-nitro-1,2,3-triazole) or WPX-101, is very thermally stable decomposing at 227 ºC and performances between RDX and HMX while having and impact sensitivity of 4-4.5J making it more sensitive than RDX. This is an interesting high-performing secondary explosive. 1,1'-azobis(4-nitro-1,2,3-triazole) or

WPX-102 possess higher sensitivities (< 1 J, <5 N) being comparable to primary explosives. Interestingly, this material easily undergoes a deflagration to detonation transition, it snaps loudly when ignited and half a milligram of this material detonated violently when determining its thermal stability of 160 °C. It may be an interesting metal free primary explosive as evidenced by its ability to initiate RDX.

Tetrazole azasydnone

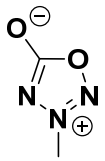
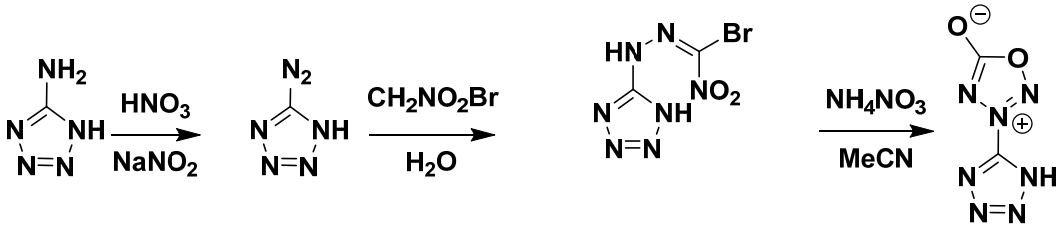


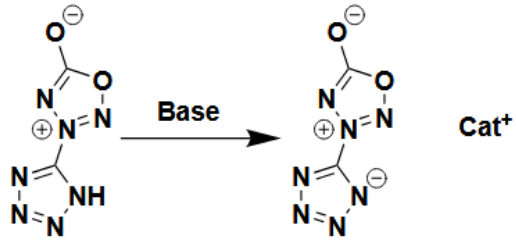
Figure 4: The zwitterionic azasydnone ring.

The azasydnone ring (Figure 4) 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 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. We sought to explore a nitrogen-rich azasydnone by building up an azasydnone on a tetrazole ring. This target was chosen in discussion with Jesse Sabatini at ARL.



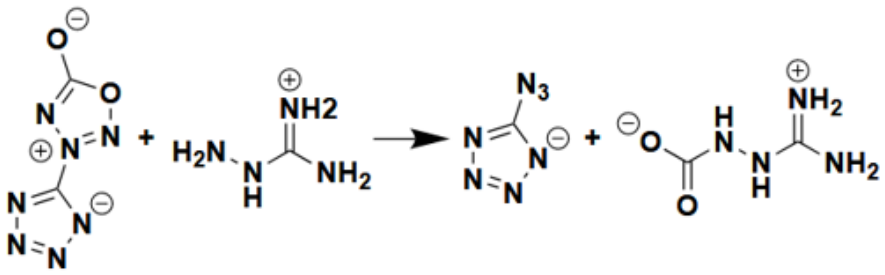
Scheme 4: The synthesis of tetrazole azasydnone

The synthesis of tetrazoleazasydnone was effectively accomplished by the synthesis route shown in scheme 4. 5-aminotetrazole was dissolved in dilute nitric acid and sodium nitrite added to form the diazotetrazole. To this was added bromonitromethane resulting in coupling via the activate methylene group giving the bromonitrohydrazone. After extraction of this hydrazone followed by cyclization with ammonium nitrate in acetonitrile, tetrazoleazasydnone was obtained. It was purified by a series of extractions and several energetic salts were prepared from this material either by acid base or metathesis methods from already prepared salts. (Scheme 5)



Scheme 5: The synthesis of tetrazole azasydnone salts by acid base chemistry.

The ammonium, hydroxylammonium, hydrazinium, guanidinium, silver, sodium, aminoguanidinium and triaminoguanidinium salts were all attempted to be prepared. Interestingly, the tetrazoleazasydnone material proved to be extremely sensitive towards sodium cations. The addition of sodium hydroxide to the free acid led to immediate decomposition and even using a sodium-loaded ion exchange resin to exchange the tri-*n*-butylammonium salt led to complete decomposition. The azasydnone ring also is destroyed by nucleophiles, and many of the salts partially decomposed during synthesis, especially aminoguanidinium, triaminoguanidinium and hydrazinium. In the case of the aminoguanidinium and triaminoguanidinium, azidotetrazole was identified in the decomposition products. (Scheme 6)



Scheme 6: The decomposition products of aminoguanidinium tetrazoleazasydnone. 2-guanidinium-1-aminocarboxylate monohydrate was determined by X-Ray crystallography.

The energetic properties of the various energetic derivatives are shown in Table 3. The tetrazoleazasydnone anion has been abbreviated as TAZ, and the counterion for each salt is listed as the table header. Single-crystal X-Ray structures were obtained for most compounds, and a representative structure is shown in Figure 3

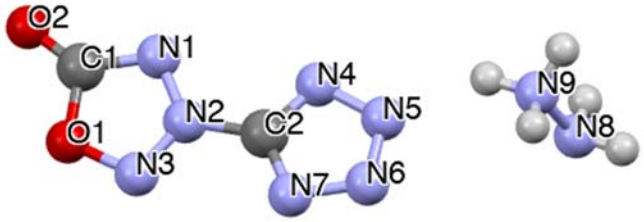


Figure 3: molecular unit of hydrazinium tetrazoleazasydnone.

Table 3: Energetic performances of energetic tetrazole azasydnones

	HTAZ	**NH_4^+**	**$N_2H_5^+$**	**Ag^+**	**NH_4O^+**	**$CH_6N_3^+$**	**$CH_7N_4^+$**	**$CH_9N_6^+$**	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	-12.22	-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}]^{calc}	1.842	1.744	1.694	-	1.796	1.655	1.654	1.642	-
$\Delta_f H^o$ [kJ kg^{-1}] [g]	2698.1	1372.9	2044.3	-	1467.2	-129.41	1366.4	2051.6	316.55
EXPLO5 V6 $-\Delta_{Ex}U^\circ$ [kJ kg^{-1}] [h]	-4999.4	-3873.8	-4458.7	-	-4767.1	-2859.9	-3410.0	-4003.4	-5740
T_{det} [K] [i]	3841.3	2907.7	3112.2	-	3383.4	2238.1	2540.5	2762.7	3745
P_{CJ} [kbar] [j]	326.911	249.018	292.232	-	312.423	206.739	224.274	254.654	336
$V_{Det.}$ [m s^{-1}] [k]	8906.2	8222.4	8803.9	-	8822.7	7736.2	8009.0	8473.7	8801
V_o [L kg^{-1}] [l]	763.7	845.9	870.6	-	829.9	880.8	863.8	894.8	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 (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 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.[62] and the EXPLO5 V6 database. † **$CH_7N_4^+$** and **$CH_9N_6^+$** salts showed evidence of decomposition forming azidotetrazole.

The salts of tetrazoleazasydnone may also be compared with their nitrotetrazole and azidotetrazole analogs for a general comparison of the azasydnone explosophore with the traditional nitro and azido explosophores. All TAZ

salts had greater densities than analogous azidotetrazoles. Densities of many but not all exceeded their nitrotetrazole analogs 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. In general, energetic nitrogen-rich salts of tetrazoleazasydnone tend to decompose around 150-160 ^{o}C and performances are generally lower than that of RDX, with the highest performer being the free acid, HTAZ. However due to other azasydnones being reported in the literature to have higher thermal stabilities than what we have seen, we suspect the lower thermal stabilities here are not general to the azasydnone ring, and other energetic azasydnones should be explored We have done so and will discuss them later in this report.

Of all TAZ compounds prepared, the metal-free primary explosive **HTAZ** and silver salt **AgTAZ** 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 4 compares these primary explosives to sensitivities and performances of triazine triazide (TTA), DBX-1, lead styphnate, and lead azide. HTAZ is a metal-free primary explosive which can be safely handled unlike TTA, which suffers from sublimation issues and hyper primary sensitivity.[4] 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 HTAZ and AgTAZ, 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 ^{o}C. Thus, decomposition temperatures of 150-160 ^{o}C are tolerable.

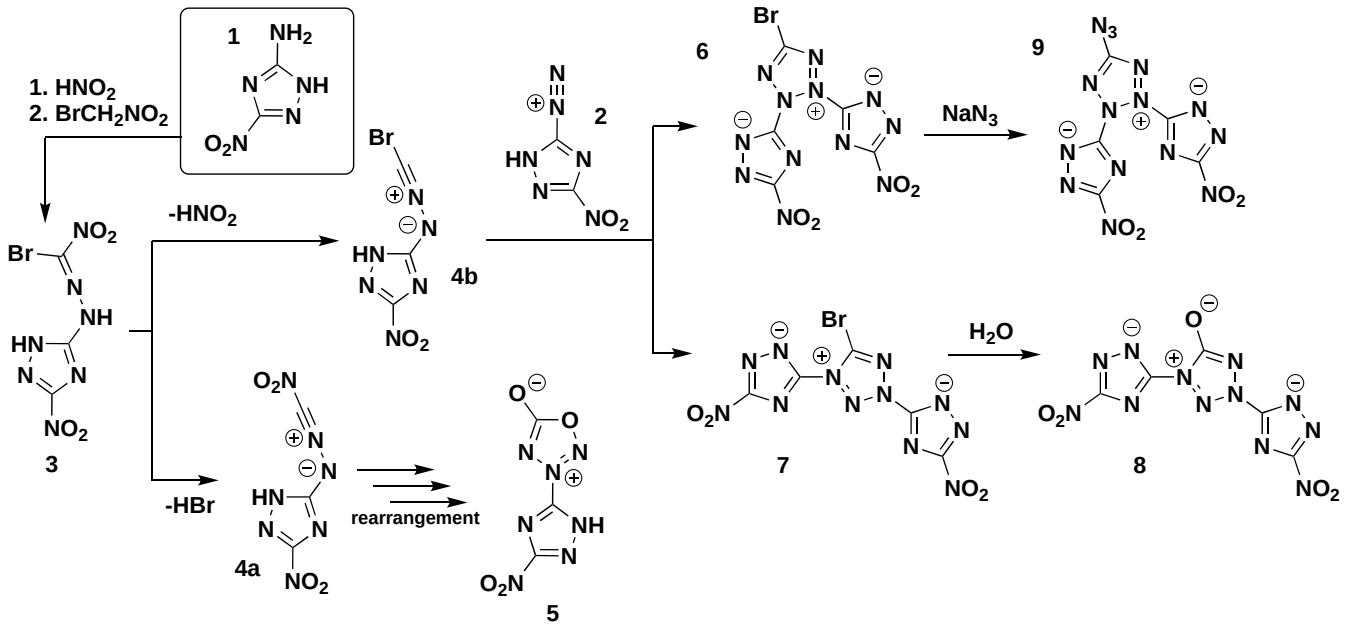
Table 4: Energetic performances of primary explosive energetic tetrazole azasydnones compared to well-known primary explosives.

Compound	**HTAZ**	**TTA**	**AgTAZ**	**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	-	-	-	8330	-
V_{det} [m s^{-1}]	8906	6900	-	~7000	5300	4900

The silver-containing AgTAZ primary detonates when ignited in only the smallest amounts and is reminiscent of silver azide. Jesse Sabatini has organized a transition of this material to Picatinny arsenal and we prepared and shipped them 3g of this material. This work has been published in *Chemistry, A European Journal* and the lead-free primaries are the subject of a provisional patent application.

Nitrotriazole azasydnone

Following the success of the tetrazoleazasydnone above, we sought to bring the same chemistry to an energetic triazole instead of tetrazole. An ice-cold aqueous solution of ANTA (**1**) was treated with a solution of sodium nitrite acidified with nitric acid, forming the diazonium . Bromonitromethane was added, forming bromonitrohydrazone (**3**) after stirring for 18 hours. From this product, all compounds in this work were prepared. Scheme 7 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 products identified. Salts of 3-azasydnone-5-nitro-1,2,4-triazole (**5**) were prepared analogously to tetrazole azasydnone by stirring an acetonitrile solution of hydrazone **3** over ammonium nitrate in a similar procedure to our previous work. This product results from elimination of hydrobromic acid from bromonitrohydrazone (**3**) forming nitro nitrilimine (**4a**). Nitronitrilimine then rearranges to azasydnone **5**. This material crystalized by slow evaporation from an aqueous solution. **5** crystallized as colorless blades in monoclinic space group *C2* (Z=6) (**Error! Reference source not found.**4) with crystal density of 1.748 g·cm^{-3}.



Scheme 7. Synthesis of compounds (**3**-**9**), from ANTA (**1**).

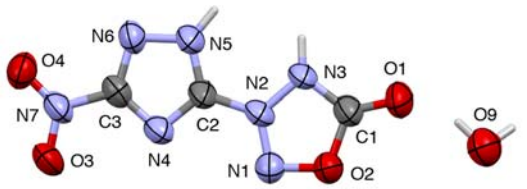
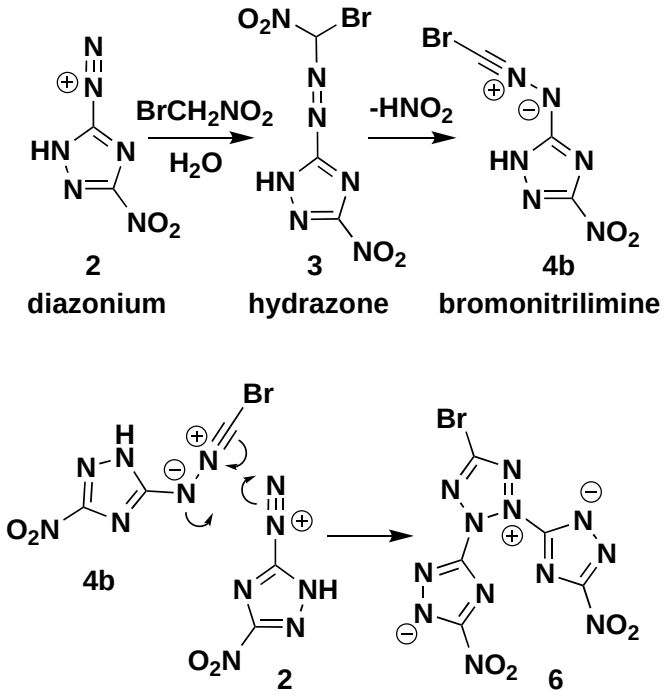


Figure 4. Crystal structure of HNTAZ monohydrate (**5**). Ellipsoids are drawn at the 50% probability level.

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**).

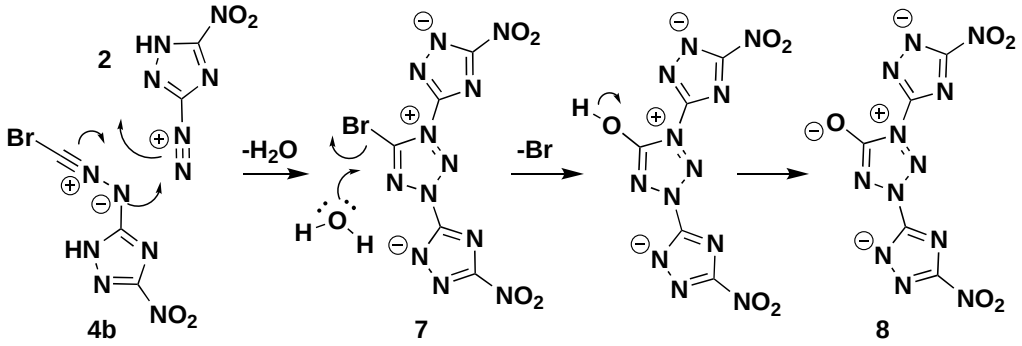
We suspect that {2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazolium}ate anion (**6**) formed as a result of bromonitrilimine **4b** undergoing a 2+3 cycloaddition reaction with 5-diazo-3-nitro-1,2,4-triazole (**2**). (Scheme 8). This result is unique in that to the best of our knowledge, and extensive literature searching, it marks the first report of tetrazole being generated by cycloaddition of nitrilimine with diazonium compound. Furthermore, it's a rare example of suspected bromonitrilimine intermediate and search of literature revealed only a few examples of this class of intermediates.



Scheme *8*. Possible reaction mechanism for formation of compound **6**

Based on regiochemistry of bromonitrilimine **4b** undergoing cyclization with diazonium **2**, two products are capable of being formed; {2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-

bromotetrazolium}ate anion (**6**) as well as {1,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazolium}ate anion (**7**). Based on ^{13}C-NMR spectroscopy experiments and comparison with pure crystalized **6a**, we were unable to detect significant amounts of 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-oxotetrazolium}ate anion **8** were obtained while attempting to purify crude sodium salt of **5**. This anion results from hydrolysis of sought-after {1,3-di(5-nitro-1,2,4-triazole-3-ide)-5-bromotetrazolium}ate anion (**7**) in water. (Scheme 9).



Scheme 9. Possible reaction mechanism for hydrolysis of **7**, forming **8**

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. Crystal structure of **8** (Figure 5) crystallizes in space group $P\bar{1}$ with 2 units in cell and density of 1.735 g·cm^{-3}.

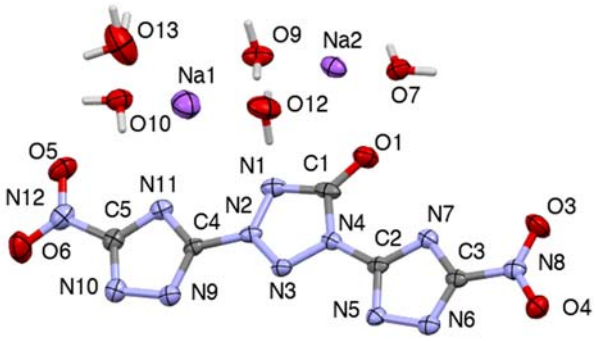


Figure 5. Crystal structure of compound (**8**). Ellipsoids are drawn at 50% probability level. Water and triazole N coordinating bonds to sodium atoms are hidden to make structure more clear.

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**) followed 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 solution of tri-n-butylammonium nitrate and extraction with ethyl acetate semi-selectively extracted residual **6** as its butylammonium salt, leaving solution of pure **5**

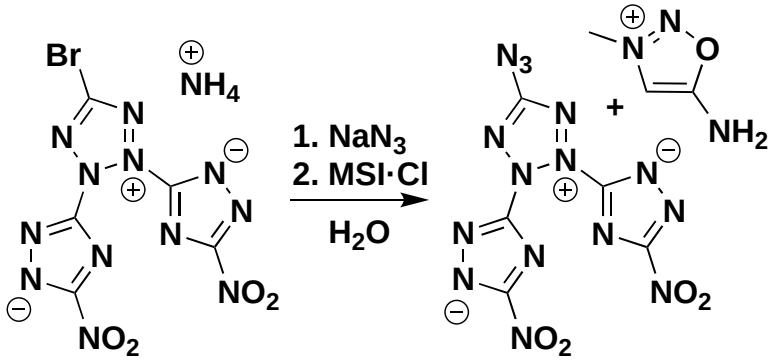
(as mixture of its ammonium salt with ammonium nitrate). Further addition of butylammonium nitrate allowed extraction into ethyl acetate of pure butylammonium salt (**5b**) of **5**. Use of ion exchange resin allowed preparation of salts **5**(**c-i**) sodium (**5c**), ammonium (**5d**), hydroxylammonium (**5e**), hydrazinium (**5f**), guanidinium (**5g**), aminoguanidinium (**5h**), and diaminoguanidinium (**5i**). Nitrate impurities found in **5c** were removed by redissolving material in acetone then filtered through syringe. Structure for NTAZ sodium salt (**5c**) had density of 1.836 $g \cdot cm^{-3}$. 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 crystalized after repeated attempts.

During 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 work. 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 Table 5. Thermogravimetric analysis (TGA) captured thermal behavior of compounds. Unfortunately, TGA traces of most salts of **5** did not reveal 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 $kJ \cdot mol^{-1}$), resulting in lower values for detonation pressure (239 kbar) and velocity (7840 $m \cdot s^{-1}$) as compared with the other compounds. 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 crystallographic analysis. Calculated densities for the remaining NTAZ salts ranged 1.711 $g \cdot cm^{-3}$ (diaminoguanidinium) (**5i**) to 1.840 $g \cdot cm^{-3}$ (hydroxylammonium) (**5e**).

Based on calculated densities (or crystallographic densities when available) and heats of formation, detonation performances were obtained using EXPLO5 software. All compounds exceeded TNT performance (P_{CJ} = 194 kbar, $V_{Det.}$ = 6824 $m \cdot s^{-1}$). Among NTAZ compounds, hydroxylammonium salt (**5e**) had highest detonation pressure (325 kbar) and detonation velocity (8749 $m \cdot s^{-1}$). Compounds **5**, ammonium (**5d**), and hydrazinium (**5f**) salts had comparable detonation pressures (286-289 kbar) and velocities (8360-8503 $m \cdot s^{-1}$). However, their lack of chemical stability as shown by partial decomposition to azidotriazole, and hygroscopicity 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, no 2,3-disubstituted tetrazole has ever been studied as energetic material. We found it to react with sodium azide in aqueous solution to generate {2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-azidotetrazolium}ate anion (**9**). Addition of 5-amino-3-methyl-1,2,3-oxadiazolium chloride to the reaction mixture led to crystallization of 5-amino-3-methyl-1,2,3-oxadiazolium salt (**9b**). (Scheme 10). **9b** crystalizes in $P2_1/n$ space group with 4 units in unit cell and density of 1.707 $g \cdot cm^{-3}$. (Figure 6)



6a **9b**

Scheme 10. Formation of azido complex MSI salt (**9b**) from **6a**

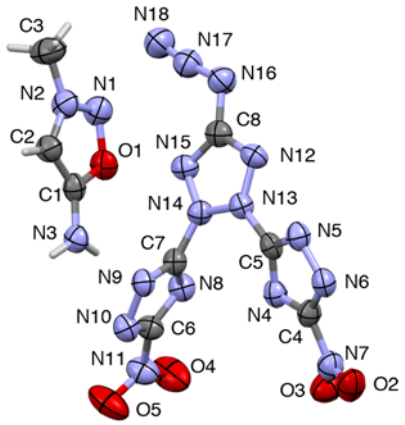


Figure 6. Crystal structure of azido compound MSI salt (**9b**). Ellipsoids are shown at 50% probability level.

9b exhibits ^{13}C signals at 163.9, 163.3 and 148.9 ppm for the anion. ^{13}C signals for the cation matched those previously reported.

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

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 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 very hygroscopic, which prevented further analysis. Methyl sydnone imine salt (**9b**) of {2,3-di(5-nitro-1,2,4-triazole-3-ide)-5-azidotetrazolium}ate anion (**9)** showed good thermal stability (170 °C) and is a representative member of a new class of energetic tetrazoles which also demonstrated novel nitrilimine chemistry during its synthesis.

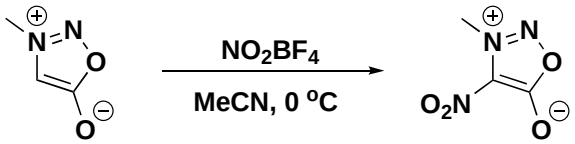
Table 5. Energetic properties for prepared energetic compounds, **5** and **5c-5i**.

	5	**5c**	**5d**	**5e**	**5f**	**5g**	**5h**	**5i**	**TNT**
Formula	$C_3HN_7O_4$	$C_3N_7O_4Na$	$C_3H_4N_8O_4$	$C_3H_4N_8O_5$	$C_3H_5N_9O_4$	$C_4H_6N_{10}O_4$	$C_4H_7N_{11}O_4$	$C_4H_8N_{12}O_4$	$C_7H_5N_3O_6$
FW[g mol^{-1}]	199.09	221.07	216.12	232.11	231.13	258.16	273.17	288.18	227.13
IS [J] [a]	ND	20	15	ND	ND	>40	ND	ND	15
FS [N] [b]	ND	>360	>360	ND	>324	>360	ND	ND	>353
N [%][c]	49.25	44.35	51.85	48.28	54.54	54.26	56.40	58.32	18.50
Ω [%][d]	-20.09	-18.09	-29.61	-20.68	-31.15	-43.38	-43.92	-44.41	-73.96
T_{dec} [°C] [e]	ND	145	105	ND	170	200	175	175	295
ρ [g·cm^{-3}] [f]	1.748	1.836	-	-	-	-	-	-	-
ρ [g·cm^{-3}][calc]	1.886	2.232	1.828	1.840	1.774	1.733	1.722	1.711	1.654
$\Delta_f H^o$ [kJ mol^{-1}] [g]	266.82	41.87	108.27	154.75	252.45	73.15	179.35	287.47	-59.4
EXPLO5 $-\Delta_{Ex}U°$ [kJ kg^{-1}] [h]	-4898	-4609	-4176	-4902	-4593	-3445	-3719	-3974	-4427
T_{det} [K] [i]	3946	3607	3099	3514	3294	2667	2783	2882	3222
P_{CJ} [kbar] [j]	286	239	289	325	288	224	236	246	194
$V_{Det.}$ [m s^{-1}] [k]	8360	7840	8451	8749	8503	7788	7977	8150	6824
V_o [L kg^{-1}] [l]	752	570	773	768	806	796	820	840	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 (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 energy of explosion; i explosion temperature; j detonation pressure; k detonation velocity; l volume of detonation gases (assuming only gaseous products)

Methylnitrosydnone

In these experiments we attempted to prepare nitromethylsydnone from 3-methylsydnone. (Scheme 11). This would be another zwitterionic energetic material.



Scheme 11: Proposed synthesis route to 4-nitro-3-methylsydnone

Reactions were monitored by mass spec however no product was identified. This nitration was also attempted using mixed acid which led to a bright yellow nitration mixture (precursor is colorless). While this was taken to be a good sign of nitration, upon the quenching of the reaction mixture with water, all yellow color was lost. This does not bode well for the aqueous stability of this nitrosydnone. No product was detected by mass spec in these or any other nitration conditions of 4-nitro-3-methylsydnone.

Methylsydnoneimine salts

As an energetic cation, the sydnone imines have never been investigated for their utility in energetic materials. With the methylsydnoneimine hydrochloride in hand for the nitration effort reported in our last annual report, we prepared several energetic salts of this novel cation via metathesis reactions with silver salts. After filtration of the precipitated silver chloride the

aqueous solution was evaporated down yielding the pure energetic methylsydnoneimine salt. Figure 8 shows the crystal structure of a variety of energetic salts that have been prepared.(nitrate, perchlorate, nitrotetrazolate, dinitrotriazolotriazolate, 5-azasydnonetetrazolate) In general these salts were of low thermal stability and performances as a result of their low density.(Table 6) This work was published in *New Journal of Chemistry.*

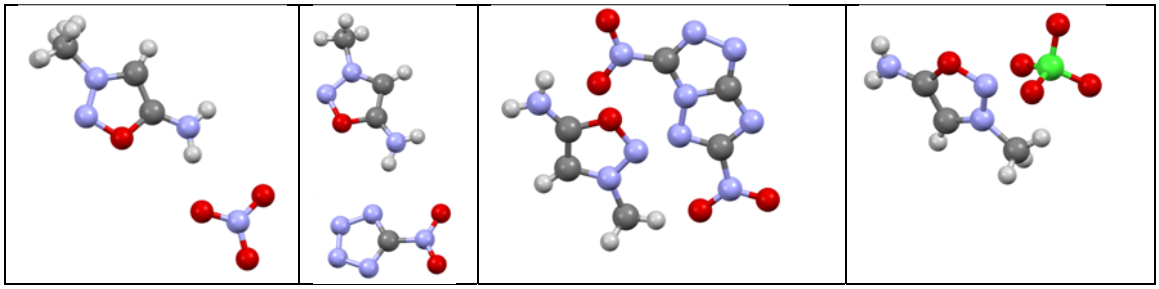


Figure 8: Molecular units of energetic azasydnone imines that have been crystalized.

Table 6. Energetic properties for all prepared compounds. Calculated densities shown when X-ray diffraction densities were unavailable.

	nitrate	**perchlorate**	**NT**	**DNTT**	**TAZ**	**TNT***
Formula	$C_3H_6N_4O_4$	$C_3H_6N_3O_5Cl$	$C_4H_6N_8O_3$	$C_6H_6N_{10}O_5$	$C_5H_6N_{10}O_3$	$C_7H_5N_3O_6$
FW[g mol^{-1}]	162.11	199.55	214.15	298.18	254.18	227.13
IS [J] [a]	> 40	1-2	> 40	> 40	> 35**	15
FS [N] [b]	> 360	36	> 360	> 360	> 160**	> 353
N [%][c]	33.29	21.06	51.63	45.32	50.1	18.5
Ω [%][d]	-49.35	-28.06	-59.77	-53.66	-62.95	-73.96
T_{dec} [°C] [e]	135	187	135	135	112**	295
ρ [g·cm^{-3}] [f]	1.612	1.826	1.607	1.725	1.633	ND
ρ [g·cm^{-3}]^{calc}	1.639	1.789	1.642	1.749	1.677	1.654
$\Delta_f H^o$ [kJ kg^{-1}] [g]	-780.0	-209.1	1562.3	1492.2	1709.2	-261.3
EXPLO5						
$-\Delta_{Ex}U°$ [kJ kg^{-1}] [h]	-4328	-5180	-4370	-4610	-3980	-4427
T_{det} [K] [i]	2973	3682	3113	3337	2964	3222
P_{CJ} [kbar] [j]	215	290	211	243	201	194
$V_{Det.}$ [m s^{-1}] [k]	7537	8074	7572	7865	7418	6824
V_o [L kg^{-1}] [l]	821	750	802	740	773	633

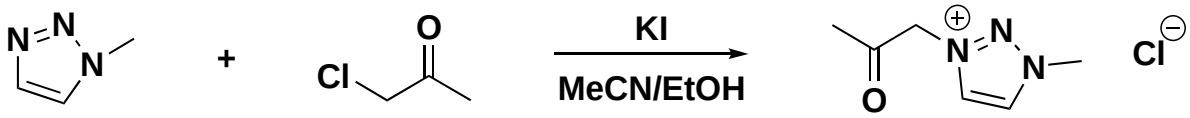
ND: not determined; a) impact sensitivity (BAM drophammer (1 of 6)); b) friction sensitivity (BAM friction tester (1 of 6)); c) nitrogen content; d) oxygen balance (Ω = (xO–2yC–1/2zH)M/1600); e) decomposition temperature from DSC (β = 5 °C); f) from X-ray diffraction; g) calculated heat of formation; h) energy of explosion; i) explosion temperature; j) detonation pressure; k) detonation velocity; l) volume of detonation gases (assuming only gaseous products). *Values based on Refs [58,59] and the EXPLO5 V6.05.02 database. ****6** showed evidence of decomposition forming azidotetrazole.

Zwitterionic dinitromethyl containing energetic materials: On triazole

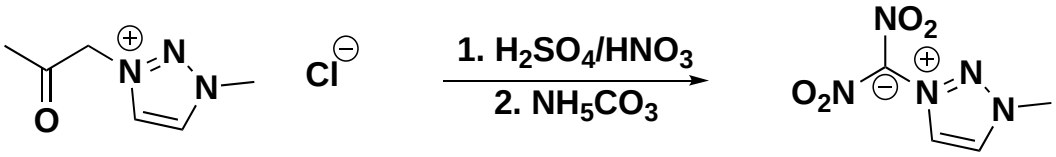
Dinitromethyl groups are often used in energetic materials to increase the performance as a result of their high oxygen content and generally high densities. Energetic materials that include a dinitromethyl functional group are often high performing and are also an efficient

method of creating energetic salts once the acidic proton is removed. Due to these properties, dinitromethyl groups were seen as potential new building blocks for zwitterionic molecules, which could potentially both impart energy while helping increase stability through electrostatic interactions.

For this work, we hypothesized that addition of a dinitromethyl group onto a positively charged heterocycle would produce a zwitterionic energetic material, with a possible energetic utility comparable to *N*-oxides or *N*-nitroimides. Outside of this work, very few zwitterionic dinitromethyl containing compounds have been synthesized and fully characterized and to the best of our knowledge there is no full energetic characterization of a material containing this unique functional group. In this work we sought to report the first full energetic characterization of an azolium dinitromethylylide for preliminary investigation of the utility of this functional group in energetic materials design. This molecule was fully characterized and found to be a sensitive energetic material.



Scheme 12. Synthesis of 1-acetonyl-3-methyl-1,2,3-triazolium chloride



Scheme 13. Synthesis of 3-methyl-1,2,3-triazolium-1N-dinitromethylylide.

1-methyl-1,2,3-triazole was alkylated using excess chloroacetone in acetonitrile with potassium iodide catalyst (Scheme 12). Nitration of 1-acetonyl-3-methyl-1,2,3-triazolium chloride using 98% H_2SO_4 and 100% HNO_3 led to the obtaining of 3-methyl-1,2,3-triazolium-1N-dinitromethylylide as a solid after purification by extraction with ethyl acetate. (scheme 13)

^{1}H and ^{13}C NMR spectra were collected for the product. The proton spectra of the precursor 1-methyl-1,2,3-triazole showed the *N*-CH_3 peak at 4.06 ppm and the two heterocyclic hydrogens at 8.03 and 7.71 ppm. These peaks shifted downfield in the product to 4.47, 9.27 and 9.00 ppm respectively. The carbon spectra shows a similar shift, with the I *N*-CH_3 peak moving from 36.10 ppm in the precursor to 41.20 ppm in the product. The heterocyclic carbon peaks shift from 133.42 and 125.60 ppm to 135.88 and 132.77 ppm respectively. The C-$(NO_2)_2$ peak appears at 130.20 ppm.

Colorless crystals of 3-methyl-1,2,3-triazolium-1N-dinitromethylylide were obtained through slow evaporation from ethyl acetate over several days at room temperature (Figure 9). 3-methyl-1,2,3-triazolium-1N-dinitromethylylide crystallizes in the orthorhombic space group C*mca* with a density of 1.757 g cm^{-3}.

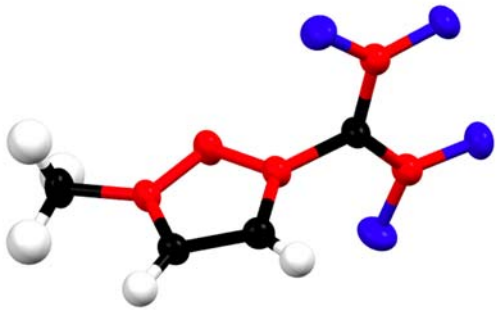


Figure 9. ORTEP plot of compound3-methyl-1,2,3-triazolium-1*N*-dinitromethylylide**.** Ellipsoids are drawn at the 50% probability level.

3-methyl-1,2,3-triazolium-1N-dinitromethylylide has a calculated heat of formation of 224.1 kJ mol^{-1}, detonation pressure of 272 kbar, and detonation velocity of 8162 ms^{-1}. Heat of formation was calculated using the Byrd and Rice method and energetic performances calculated using EXPLO5. 3-methyl-1,2,3-triazolium-1N-dinitromethylylide has impact and friction sensitivities of 8 J and 144-160 N respectively. These classify 3-methyl-1,2,3-triazolium-1N-dinitromethylylide as sensitive energetic materials with a sensitivity comparable to RDX (IS: 7J; FS 120N) and a performance higher than TNT. 3-methyl-1,2,3-triazolium-1N-dinitromethylylide decomposes at 150 ^{o}C. As a demonstrative molecule for zwitterionic molecules based on azolium dinitromethylylides, 3-methyl-1,2,3-triazolium-1N-dinitromethylylide is not thermally stable enough for practical use as it falls short of the 180 ^{o}C threshold desired for thermal stability but does show promising stability toward mechanical stimuli. In conclusion, a new zwitterionic energetic material was produced containing a unique azolium dinitromethylylide functional group and it was characterized for the first time as an energetic material. This type of compound has previously been synthesized but none were characterized for their energetic performances and stabilities. 3-methyl-1,2,3-triazolium-1N-dinitromethylylide possesses mechanical stabilities comparable to that of RDX and HMX and energetic performances higher than TNT. These properties bode well for the consideration of the zwitterionic azolium dinitromethylylide functional group in the toolkit of functional groups for energetic materials design**.**

<u>Thrust 2: 1,2,3,4-tetrazine-1,3-dioxides as stable high-performing energetic materials.</u>

I have previously used the reaction of nitroacetonitrile with a diazonium to generate an annulated 1,2,4-triazine. (*tert*-Butyl-*NNO*-azoxy)acetonitrile is isoelectronic (Figure 10) to nitroacetonitrile and if precedent holds, should generate 1,2,4-triazines in an analogous manner as shown in Scheme 14. The presence of a t-butylazoxy group next to an amine would ideally allow the closure of a 1,2,3,4-tetrazine-1,3-dioxide upon nitration.

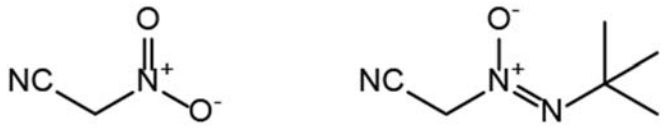
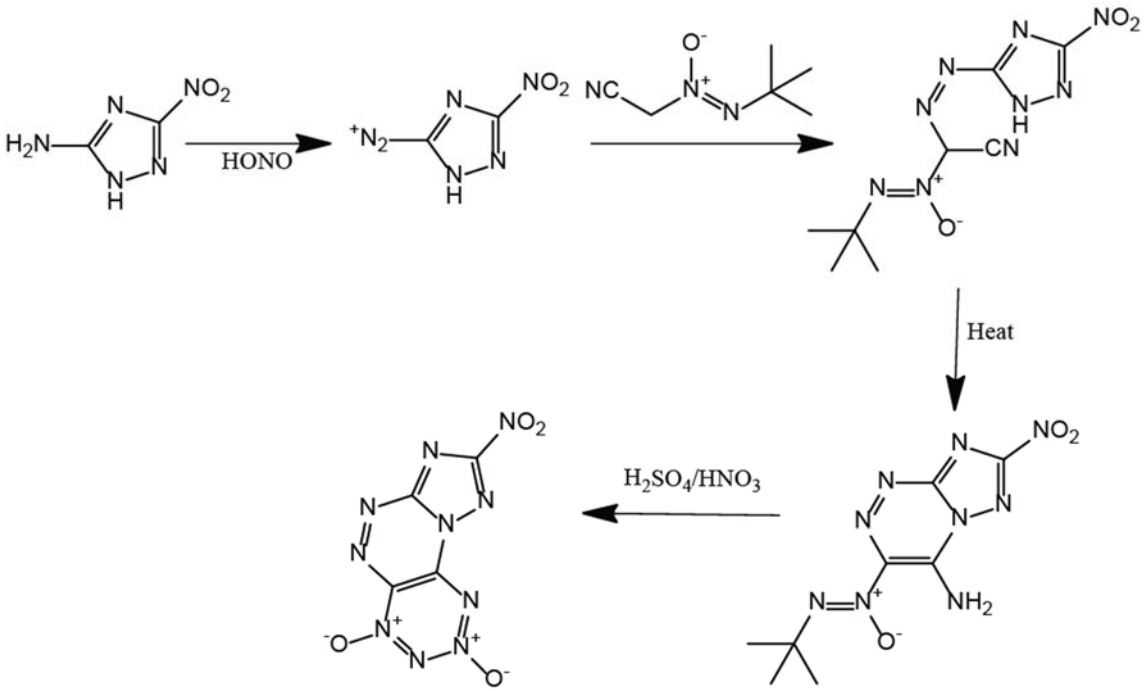
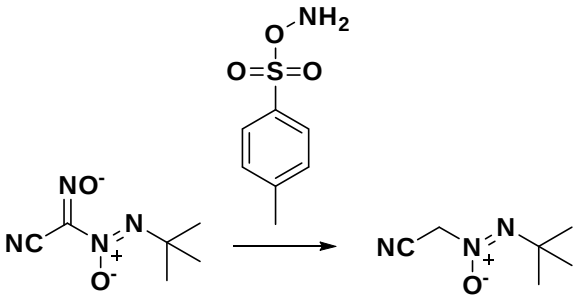


Figure 10. Nitroacetonitrile and isoelectronic (*tert*-Butyl-*NNO*-azoxy)acetonitrile



Scheme 14. Route to a new TDO-based energetic via (*tert*-Butyl-*NNO*-azoxy)acetonitrile.

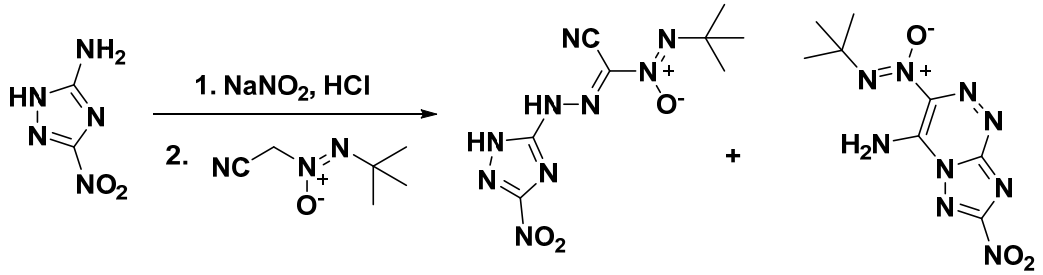
Unfortunately, the synthesis of (*tert*-Butyl-*NNO*-azoxy)acetonitrile based on the Russian literature has proven to be more difficult than the literature communicates. The troublesome step is shown in Scheme 15 below.



Scheme 15. The preparation of (*tert*-Butyl-*NNO*-azoxy)acetonitrile

While yields of over 70% are claimed in the paper, in our hands we got only a small fraction of this and often recovered large amounts of starting material. The distillation described for its purification also led to suspected decomposition as a result of the large amount of impurities present and a pure product was not isolated by distillation. For this reason, this precursor has not been as available as expected for a literature-published material.

Our best results with this material have been by taking the crude solution of it in dichloromethane and quantifying the (*tert*-Butyl-*NNO*-azoxy)acetonitrile content by quantitative NMR and using the impure solution direct in reaction with a diazonium of an energetic heterocycle (in this case, 3-amino-5-nitro1,2,4-triazole). For this, depending on conditions, we identified either the open or closed form structures (Scheme 16) based on mass spec and NMR analysis. Unfortunately due to the issues preparing the (*tert*-Butyl-*NNO*-azoxy)acetonitrile only a limited number of experiments were performed to date, and neither compound was isolated pure, only as very crude mixtures.

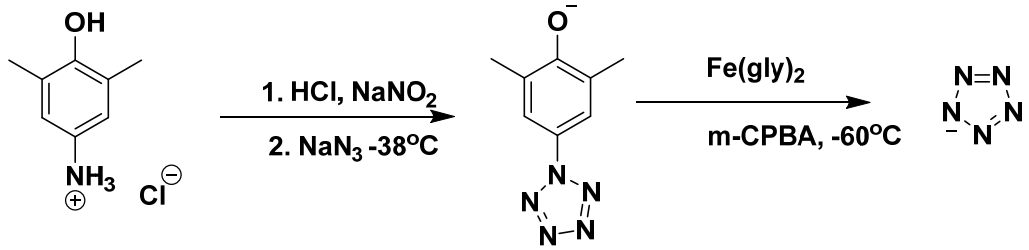


Scheme 16. Reaction of ANTA's diazonium with (*tert*-Butyl-*NNO*-azoxy)acetonitrile

Unfortunately during this work, a paper was published by Tartakovsky at the Zelinsky institute in Russia doing exactly what we were working on.

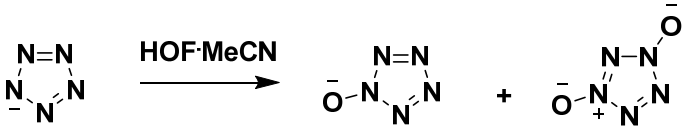
The work detailed in this paper indicates the final material will not undergo a cyclization upon nitration to form a 1,2,3,4-tetrazine-1,3-dioxide and due to issues duplicating the literature preparation of the precursor material we were unable to verify this for ourselves.

Thrust 3: Pentazole oxides and stabilized nitrogen ring systems.



Scheme 17. The preparation of the pentazolate anion

Under this thrust we attempted to duplicate the literate preparation of pentazolate salts (Scheme 17) where we would then subject them to oxidation with hypofluorous acid, HOF to form their oxides (Scheme 18).

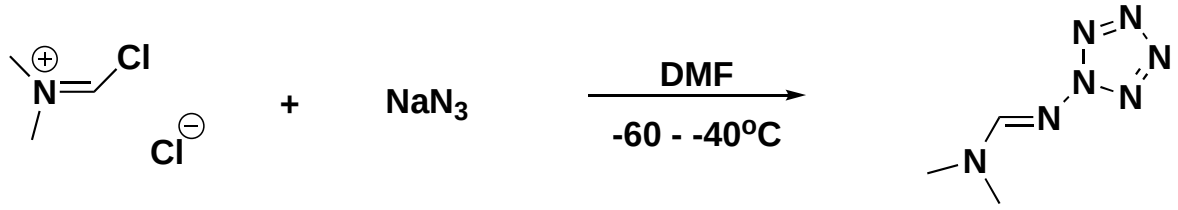


Scheme 18. The oxidation of the pentazolate anion to its oxides using hypofluorous acid.

While the authors state that the pentazolate ion in the sodium pentazolate prepared is easily detected by mass spec, we have had extensive difficulty in duplicating their work and detecting any formed pentazolates.

The preparation of the phenylpentazole does not proceed as they state, and what we observe in the mass spec after the addition of the azide to the diazonium of 2,6-dimethyl-4-aminophenol is the corresponding nitro, azido and coupled products. No phenyl pentazole has been detected by their method. In the event that we were just having issues determining the presence of the pentazole by mass spec, we have subjected this crude product to cleavage by their literature procedure, yet still no pentazole has been detected. We have had multiple people attempt this procedure by literature means, including myself, and have been unable to duplicate it.

The failure of the literature procedure to prepare the pentazolate anion has been a major hamper to this thrust however we also explored a new alternative preparation based on a recent paper in *Angewandte Chemie* (Scheme 19)



Scheme 19. Alternative preparation of a pentazole.

We duplicated the literature preparation of this pentazole-containing material and conducted numerous experiments by treating it with hypoflourous acid to generate oxides. Despite extensive effort we were unable to detect any formation of pentazole oxides.

3. Findings and Conclusions

The work has been completed under this grant due to the 3rd year of funding being cancelled. Thrust 1 contained the majority of the positive results from this final period. We obtained multiple new zwitterionic energetic materials including nitrotriazole azasydnone and its salts. While this

material is likely of little Army interest they are of chemical interest due to the unique azasydnone structural motif. Furthermore the discovery of the unique 2,3-disubstituted bromotetrazole prepared in this work will offer new routes to this unique class of unexplored heterocyclic systems offering unique new energetic materials. 3-methyl-1,2,3-triazolium-1N-dinitromethylylide was also prepared as an exemplary member of a new class of energetic compounds the azolium dinitromethylides.

Thrust 2 was not extensively pursued during this effort due to the Zelinsky Institute researchers beating us to the target intermediate and showing that the final step does not work as documented in the last annual report. We have verified this for ourselves and are unlikely to continue down this new path of preparing 1,2,3,4-tetrazine,1,3-dioxides.

Thrust 3 was built around the literature preparation of pentazolate salts being reproducible, allowing further chemistry based on this. Unfortunately that does not seem to be the case and as a result we have pivoted to the oxidation of other substituted pentazoles that are available. All attempted routes so far have failed to give pentazole oxides.

4. Plans and Upcoming Events

This project was cancelled after 2 of 3 proposed years in the proposal and the 2nd year of funding has been spent. As such there is no more plans for this effort.

5. Transitions and Impacts

3g of silver tetrazoleazasydnone was delivered to Picatinny Arsenal in Fall 2020.
The PhD student whose stipend was funded by this work has received a job offer at ONR and will be transitioning there once her PhD is complete.

6. Collaborations

Jesse Sabatini at ARL has been collaborated with on the azasydnone and sydnone target selections.
Ed Byrd at ARL has been collaborated with for computational densities and heats of formation of prepared materials.

7. Personnel

Principal investigator:

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Sponsored Program Services
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spsofg@purdue.edu
Phone: (765) 494-6204

Team Members: N/A
Subs: N/A

8. Students

1 graduate student has been supported for stipend and chemicals by this project during the entire project (Dominique Wozniak) as well as numerous undergraduate students. Another PhD student (Matthew Gettings) has had his chemicals covered for work covered under this grant. His stipend came from elsewhere. One staff scientist has his chemicals covered for work under this grant.

9. Technology Transfer

None during this effort

10. Products, Publications, Patents, License Agreements, etc.

All archival publications during this effort

1. Wozniak, D. R.; Salfer, B.; Zeller, M.; Byrd, E. F. C.; Piercey, D. G."Sensitive Energetics from the *N*-Amination of 4-Nitro-1,2,3-Triazole" *Chem. Open.* **2020**, *9,* 806-811. Peer reviewed. Federal support acknowledged
2. Gettings, M. L.; Thoenen, M. T.; Byrd, E. F. C.; Sabatini, J. J.; Zeller, M; Piercey, D. G. *Chem. Eur. J.* **2020** "Tetrazole Azasydnone (C2N7O2H) And Its Salts: High-Performing Zwitterionic Energetic Materials Containing A Unique Explosophore" *Chemistry- A European Journal.* **2020,** *26*[64], 14530-14535. Peer reviewed. Federal support acknowledged
3. Wozniak, D. R.; Salfer, B.; Zeller, M.; Byrd, E. F. C.; Piercey, D. G." Tailoring Energetic Sensitivity and Classification Through Regioisomerism" *Org. lett. 2020. Organic Letters*, **2020,** *22*[22]**,** 9114-9117. Peer reviewed journal. Federal support acknowledged
4. Dominique Wozniak, Davin G. Piercey. "Review of the Current Synthesis and Properties of Energetic Pentazolate and Derivatives Thereof" *Engineering.* **2020**, *6*[9], 981-991. Peer reviewed. Federal support acknowledged
5. Dominique Wozniak, Matthias Zeller, Edward F. C. Byrd, Davin G. Piercey. "3-methyl-1,2,3-triazolium-1N-dinitromethylylide and the strategy of zwitterionic dinitromethyl groups in energetic materials design " *RSC Advances* **2021**, 11, 17710-17714. Peer reviewed. Federal support acknowledged
6. Matthew L. Gettings, Sarah Davis, Ashank Sethia, Matthias Zeller, Edward Byrd, Davin G. Piercey. "Heterocyclic Nitrilimines and Their Use in the Synthesis of Complex High-Nitrogen Materials" *Inorg. Chem*. **2021,** *60*, 7607-7611. Peer reviewed. Federal support acknowledged
7. Matthew L. Gettings, Matthias Zeller, Edward Byrd, Davin G. Piercey. "Methylsydnone Imine and its Energetic Salts" New J. Chem. **2021**, *45*, 2228-2236. Peer reviewed. Federal support acknowledged Peer reviewed. Federal support acknowledged

11. Point of Contact in Army

Jesse Sabatini (jesse.j.sabatini.civ@army.mil)

12. Acknowledgement/Disclaimer

This work was sponsored by the Army Research Office (ARO), under grant number W911NF-18-1-0463 The views and conclusions contained herein are those of the authors only and should not be interpreted as representing those of ARO, the U.S. Navy or the U.S. Government.

Section II: Project Metrics

Grant or Contract Number: W911NF-18-1-0463
Date Prepared: April 15, 2022.
Project Title: **Disruptive Energetic Materials: The Synthesis and Stabilization of High-Nitrogen compounds and Next-Generation Energetic Materials.**
Final Summary Report
Period of Performance: October 1 2018-July 31, 2021 (money ran out Jan 2021)
Principle Investigator:
Prof. Davin Piercey
765-494-1504
dpiercey@purdue.edu
Purdue University

Metrics

Number of faculty supported under this project during this reporting period: 1

Number of post-doctoral researchers supported under this project during this period: 0

Number of graduate students supported under this project during this reporting period: 1 fully (stipend +chemicals+analytics) 1 partially (chemicals+analytics)

Number of undergraduate students supported under this project during this period: 5

Number of scientists / engineers / technicians supported under this project during this reporting period: 1 partially (this grant covered his chemicals and analytics for work covered under this grant, but his salary comes from elsewhere)

Number of refereed publications during this reporting period for which at least 1/3 of the work was done under this effort: 7 published

Number of publications (all) during this reporting period: 7

Number of patents during this reporting period: 2 (provisional)

Number of M.S. students graduated during this reporting period: 0

Number of Ph.D. students graduated during this reporting period: 0 (none graduated during this effort, but 2 graduated soon after the ending of this)

Awards received during this reporting period: 0

Invited talks given: 1 (general, not specific to this funded project)

Conferences at which presentations were given (not including invited talks above): 2

1. Financial information

Part of Thrust 2, the use of (*tert*-Butyl-*NNO*-azoxy)acetonitrile in the preparation of 1,2,3,4-tetrazine-1,3-dioxides was also covered under a Navy grant and this was communicated to the ARO program manager Jim Parker on Feb 13, 2019 by email and the Navy program manager Chad Stolz on Feb 6, 2019. This part of work was deemphasized in both grants due to reasons described above and in previous reports (it does not work).

	Total Budget	**Obligated This Period**	**Obligated Cumulative**	**Expended This Period**	**Expended Cumulative**	**Grant/ Contract Period of Performance**
6.1 (Basic Research Funding)	**$ 412,653**		**$ 412,653**		$ 412,652.99	**10/1/2018-1/31/2022**
6.2 (Applied Research Funding)						
Total (if both 6.1 and 6.2 funding was used)						

2. Administrative notes and other items of interest

Nothing to report