Methyl Sydnone Imine and Its Energetic Salts

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Methyl Sydnone Imine and Its Energetic Salts

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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.

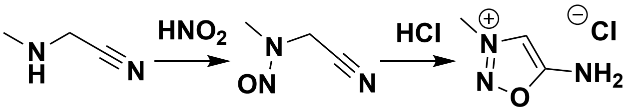
Introduction

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.[1–6] 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[7], ring or cage strain[8] or fuel and oxygen in the same molecule.[9]

The functional groups used in energetic materials are often very familiar to the chemist, such as nitro[10], azido[11], or nitrogen-rich heterocycles such as tetrazoles[12] and pentazoles.[13] 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.[14,15] 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,[16–20] while reports on new cations being paired with new energetic anions are comparatively more limited[21–24]. 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.[25] One such compound, methyl sydnone imine (MSI) chloride, was synthesized in 82% yield from 2-(methylamino)acetonitrile.[25] (Scheme 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.[25]



Scheme 1. Early synthesis of methyl sydnonimine chloride. Adapted from Daeniker and Druey.[25]

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.[26]

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.

Results and Discussion

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

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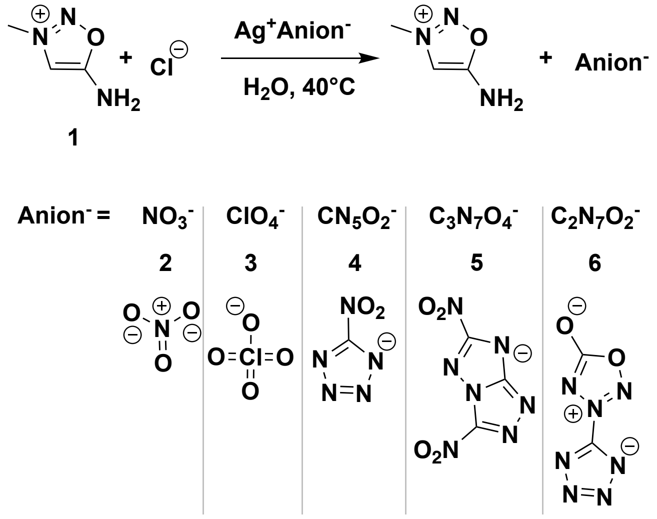
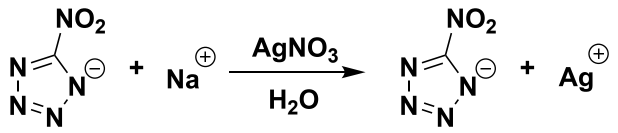
°C. After filtering off the white silver chloride precipitate, several energetic salts **2**-**6** were obtained after evaporation of the aqueous solution (Scheme 2). These salts of methyl sydnoneimine (MSI) include nitrate (**2**), perchlorate (**3**), nitrotetrazolate (**4**), 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazolate (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.



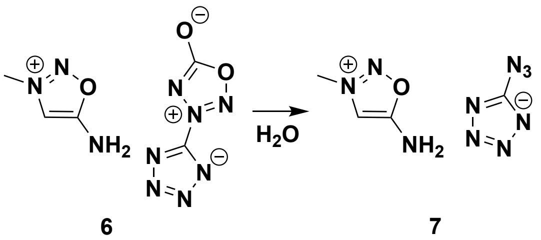
Scheme 2. Synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium salts **2**-**6** from **1**.

As a precursor to **4**, silver nitrotetrazole was synthesized from aqueous sodium nitrotetrazole prepared by a literature method,[27] treated with aqueous silver nitrate then filtered. (Scheme 3) The silver salts of DNTT and TAZ were prepared according to literature procedures.[16,28]



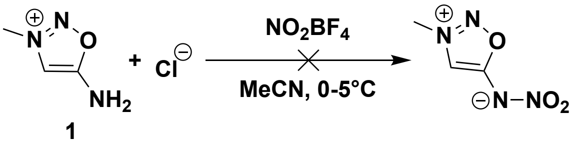
Scheme 3. Synthesis of silver nitrotetrazole from sodium nitrotetrazole.

During the synthesis of azasydnone salt **6**, partial decomposition of the azasydnone ring formed the azidotetrazole salt (**7**). (Scheme 4) Formation of azidotetrazole from tetrazole azasydnone was previously reported.[28] 5-Azidotetrazole is extremely explosive and this salt was only characterized by single-crystal X-Ray diffraction.[29,30]

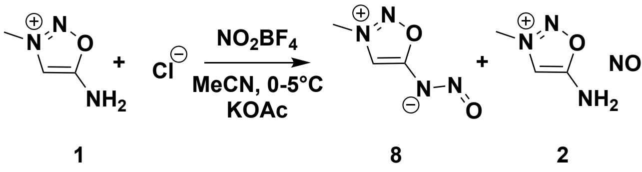


Scheme 4. Decomposition of **6** to 5-amino-3-methyl-1,2,3-oxadiazolium azidotetrazolate (**7**).

We attempted to form the zwitterionic nitroimide (Scheme 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. (Scheme 6)

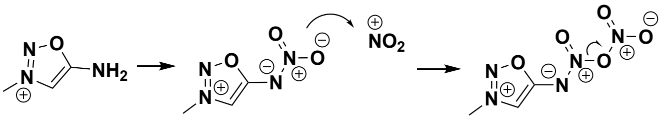


Scheme 5. Attempted synthesis of methyl sydnone nitroimide from **1**.



Scheme 6. Formation of 3-methyl-1,2,3-oxadiazolium nitrosoamide (**8**) and **2** from **1**.

A possible mechanism for the formation of the nitrosoimide (**8**) from 3-methyl-1,2,3-oxadiazolium chloride (**1**) is proposed in Scheme 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**).



Scheme 7. Possible reaction mechanism for the formation of the nitrosoamide **8** from **1**.

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_2O, which agree with the reported peaks in DMSO.[16] The ^{13}C peaks for tetrazole azasydnone salt (**6**) exist at 167.3 and 156.1 ppm as is common for tetrazoleazasydnone salts.[28] In the tetrazole azasydnone (**6**) sample, the carbon peak for the azidotetrazole formed by decomposition was observed at 159.5 ppm.[28] Attachment of the nitroso in **8** caused a slight downfield shift of the ^{13}C peak from 169.4 (in D_2O) to 173.8 (in CD_3CN) ppm. None of the anions carry any protons and all peaks in the ^1H 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.[25]

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}.[25,26,31,32] 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.[28,33,34] 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.[16]

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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-).

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-Kα 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-Kα 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.[35] The data were scaled and corrected for absorption using Sadabs.[36,37] The space groups were assigned using XPREP within the SHELXTL suite of programs[38], the structures were solved by direct methods and then refined by full-matrix least-squares against F^2 with all reflections using SHELXL2018.[39–41] 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. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C/N)$ with 1.5 for CH_3 and 1.2 for C-H and NH_2 units, respectively. For **4**, $U_{iso}(H)$ 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. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The structures for 5-amino-3-methyl-1,2,3-oxadiazolium salts **2-5** and **7** are shown in Fig. 1-Fig. 6 while 3-methyl-1,2,3-oxadiazolium nitrosoamide (**8**) is depicted in Fig. 7. Compounds **2-4** and **7** crystallized in the monoclinic system. (Table 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 colourless 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 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**.

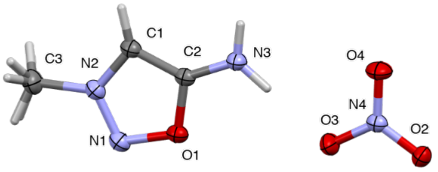

Fig. 1 Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium nitrate (**2**). Ellipsoids are drawn at the 50% probability level. Disorder of methyl H atoms is symmetry imposed by a mirror plane bisecting the cation.

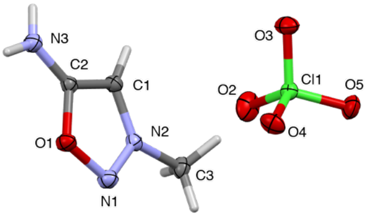

Fig. 2 Molecular unit 5-amino-3-methyl-1,2,3-oxadiazolium perchlorate (**3**). Ellipsoids are drawn at the 50% probability level.

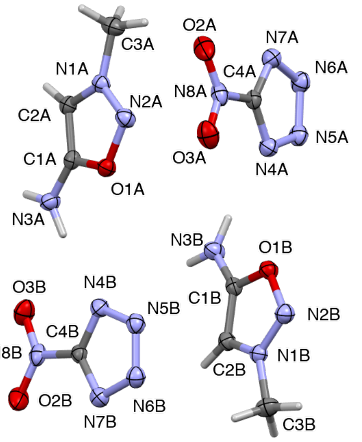

Fig. 3 Molecular units of 5-amino-3-methyl-1,2,3-oxadiazolium nitrotetrazolate (**4**). Ellipsoids are drawn at the 50% probability level.

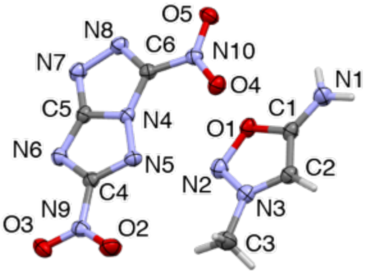

Fig. 4 Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium DNTT (**5**). Ellipsoids are drawn at the 50% probability level.

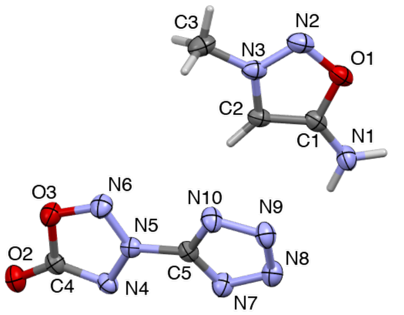

Fig. 5 Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium TAZ (**6**). Ellipsoids are drawn at the 50% probability level.

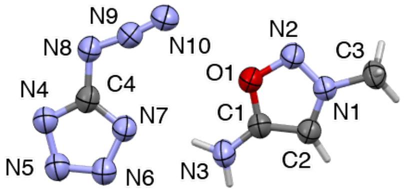

Fig. 6 Molecular unit of 5-amino-3-methyl-1,2,3-oxadiazolium azidotetrazolate (**7**). Ellipsoids are drawn at the 50% probability level.

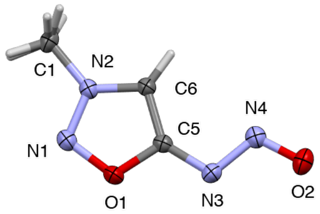

Fig. 7 Molecular unit of 3-methyl-1,2,3-oxadiazolium nitrosoamide (**8**). Ellipsoids are drawn at the 50% probability level. Disorder of methyl H atoms is symmetry imposed by a mirror plane bisecting the molecule.

Table 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
$\rho_{calc.}$ [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 x 0.13 x 0.09	0.55 x 0.17 x 0.13	0.14 x 0.11 x 0.07	0.24 x 0.20 x 0.13	0.21 x 0.11 x 0.05	0.15 x 0.02 x 0.01	0.31 x 0.22 x 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

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 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).[42]

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 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 temperature of 155 °C of the chloride salt **1** as reported by Daeniker.[25] The thermal stability of **3** exceeds PETN (165 °C), but falls short of RDX (205 °C) and TNT (295 °C).[42] 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.[29] Isolation of **7** was not attempted, which prevented further characterization.

Energetic Properties. The energetic properties of each of the compounds are recorded in Table 2. The method of Byrd and Rice (based on properties of individual energetic compounds derived from quantum mechanics), provided the heats of formation[43] and densities[44,45] of all compounds. These calculated densities agreed within 3% with those measured via X-ray crystallography at 150 K. The Gaussian09 program package[46] and the B3LYP spin-restricted Kohn-Sham density functional theory (KS-DFT)[47–50] with the 6-31G** Pople Gaussian basis set,[51–53] were used to determine gas phase geometries of each compound. Using these geometry data, the G3MP2(B3LYP)[54] electronic energy was determined which is required to compute the heat of formation. The Gutowski method[55] provided the heat of sublimation as determined from the molecular volume of each compound. The EXPLO5 V6.05.02 software package[56,57] 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).

Table 2. Energetic properties for all prepared 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}]^{calc}	1.639	1.789	1.642	1.749	1.677	1.565	1.618	1.654
$\Delta_f H^o$ [kJ mol^{-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 (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.

Experimental

General Methods. All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics, Fisher Scientific Co LLC) if not stated otherwise. Melting and decomposition points were measured with a TA Instruments SDT Q600 TGA/DSC using heating rates of 5 °C•min^{-1}. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AV-III-400-HD (5mm BBFO SmartProbe) and Bruker AV-III-500-HD (5mm BBFO Cryoprobe Prodigy) Avance DRX NMR spectrometers. All chemical shifts are quoted in ppm relative to TMS (^{1}H, ^{13}C). Infrared spectra were measured with a PerkinElmer Spectrum Two FT-IR spectrometer. Transmittance values are described as "strong" (s), "medium" (m) and "weak" (w). Mass spectra were measured using an Agilent 1260 Infinity II Quaternary LC instrument. Sensitivity data were determined using a BAM (Bundesanstalt für Materialforschung) friction tester (Reichel & Partner Gmbh) and OZM BAM Fall Hammer BFH-10 instrument.

Caution: The described compounds **2-8** are energetic materials with sensitivity to various stimuli. While we encountered no issues in the handling of these materials, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthened equipment) should be used at all times.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2024994 (**2**), CCDC-2024995 (**4**), CCDC-2024996 (**3**), CCDC-2024997 (**5**), CCDC-2025852 (**8**), CCDC-2025853 (**7**), and CCDC-2035560 (**6**). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

General procedures for the preparation of 2-8. Silver 3,6-dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazolate (DNTT), silver tetrazole azasydnone, and sodium nitrotetrazole were prepared according to the literature.[16,28,60]

Synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium nitrate (2). 5-Amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) (150 mg, 1.1066 mmol) was dissolved in water (20 ml) and silver nitrate (1 equiv, 188 mg) in an aqueous solution was added. The mixture was shielded from light and stirred overnight at 40 °C. Silver chloride formed as a white precipitate and was removed from the aqueous solution using a syringe filter (1 µm). The aqueous solution was evaporated, yielding (**2**) (158 mg, 0.9747 mmol, 88% yield). **DSC:** 135 °C (dec.). **IR:** $\tilde{\nu}$ = 3187 (m), 3007 (m), 2283 (w), 1747 (w), 1683 (m), 1606 (m), 1488 (w), 1459 (m), 1332 (s), 1280 (s), 1170 (m), 1078 (m), 1040 (m), 994 (m), 923 (m), 828 (m), 761 (w), 720 (m), 658 (s), 612 (s) cm^{-1}. ^{1}H NMR (500 MHz, D_2O): δ (ppm) 8.6 (s, 2H, $-NH_2$), 7.6 (s, 1H, -CH), and 4.4 (s, 3H, $-CH_3$) ppm. ^{13}C NMR (500 MHz, D_2O): δ (ppm) 169.6 (1C, -*C*-NH_2), 103.7 (1C, -N-*C*H), and 39.9 (1C, -N-*C*H_3) ppm. C, H, N analysis (%): $C_3H_6N_4O_4$ (162.11), calculated: C 22.23, H 3.73, N 34.56; found: C 21.4, H 3.6, N 33.3. MS (ESI^+) *m/z*: 100.1 $[M + H]^+$; (ESI^-) *m/z*: 62.1 $[M - H]^-$.

Synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium perchlorate (3). 5-Amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) (100 mg, 0.7377 mmol) was dissolved in water (20 ml) and silver perchlorate (1 equiv, 153 mg) in an aqueous solution was added. The mixture was shielded from light and stirred overnight at 40 °C. Silver chloride formed as a white precipitate and was removed from the aqueous solution using a syringe filter (1 µm). The aqueous solution was evaporated, yielding (**3**) (145 mg, 0.7266 mmol, 98 % yield). **DSC:** 187 °C (dec.). **IR:** $\tilde{\nu}$ = 3388 (m), 3338 (m), 3291 (m), 3228 (w), 3161 (m), 3066 (w), 2558 (w), 2463 (w), 2391 (w), 1650 (s), 1584 (w), 1483 (m), 1456 (w), 1415 (m), 1386 (w), 1325 (w), 1295 (w), 1182 (w), 1135 (m), 1049 (s), 933 (s), 769 (w), 738 (s), 697 (w), 620 (s), 610 (m) cm^{-1}. ^{1}H NMR (500 MHz, D_2O): δ (ppm) 8.5 (s, 2H, $-NH_2$), 7.6 (s, 1H, -CH), and 4.4 (s, 3H, $-CH_3$) ppm. ^{13}C NMR (500 MHz, D_2O): δ (ppm) 169.6 (1C, -*C*-NH_2), 103.9 (1C, -N-*C*H), and 40.0 (1C, -N-*C*H_3) ppm. C, H, N analysis (%): $C_3H_6N_3O_5Cl$ (199.55), calculated: C 18.06, H 3.03, N 21.06; found: C 17.63, H 3.03, N 20.71. MS (ESI^+) *m/z*: 100.1 $[M + H]^+$; (ESI^-) *m/z*: 99.1 $[M - H]^-$.

Synthesis of Silver Nitrotetrazolate. Special warning: Silver nitrotetrazolate is EXTREMELY SENSITIVE. Sodium nitrotetrazolate dihydrate ($NaNO_2CN_4{\cdot}2H_2O$, 300 mg, 1.7335 mmol) was dissolved in water (20 ml) and treated with an aqueous solution of silver nitrate (1 equiv, 295 mg). The mixture was shielded from light and stirred overnight. Silver nitrotetrazolate (350 mg, 1.5772 mmol, 91% yield) formed as a white precipitate, was filtered and dried overnight on a static discharge mat behind a protective blast shield.

Synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium nitrotetrazolate (4). 5-Amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) (214 mg, 1.5772 mmol) was dissolved in water (20 ml) and silver nitrotetrazolate (1 equiv, 350 mg) in an aqueous solution was added. The mixture was shielded from light and stirred overnight at 40 °C. Silver chloride formed as a white precipitate and was removed from the aqueous solution using a syringe filter (1 µm). The aqueous solution was evaporated, yielding (**4**) (191 mg, 0.8919 mmol, 56.6 % yield). **DSC:** 135 °C (dec.). **IR:** $\tilde{\nu}$ = 3261 (m), 3143 (m), 3056 (m), 2849 (w), 2460 (w), 2291 (w), 1679 (s), 1661 (s), 1584 (w), 1540 (s), 1504 (m), 1459 (m), 1436 (s), 1415 (s), 1315 (s), 1295 (m), 1185 (s), 1157 (m), 1092 (m), 1077 (w), 1051 (w), 1043 (w), 941 (m), 835 (s), 768 (w), 745 (s), 698 (w), 668 (m), 608 (m) cm^{-1}. ^{1}H NMR (500 MHz, D_2O): δ (ppm) 8.6 (s, 2H, $-NH_2$), 7.5 (s, 1H, -CH), and 4.7 (s, 3H, $-CH_3$) ppm. ^{13}C NMR (500 MHz, D_2O): δ (ppm) 169.4 (1C, -*C*-NH_2), 167.4 (1C, -*C*-NO_2) 103.6 (1C, -N-*C*H), and 39.9 (1C, -N-*C*H_3) ppm. C, H, N analysis (%): $C_4H_6N_8O_3$ (214.15), calculated: C 22.44, H 2.82, N 52.33; found: C 22.0, H 2.8, N 51.6. MS (ESI^-) *m/z*: 100.1 $[M + H]^+$; *m/z*: 114.1 $[M - H]^-$.

Synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium 3,6-Dinitro-[1,2,4]triazolo[4,3-b][1,2,4]triazolate (DNTT) (5). 5-Amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) (100 mg, 0.7377 mmol) was dissolved in water (20 ml) and silver dinitrotriazolo triazole (DNTT) (1 equiv, 225.7 mg) in an aqueous solution was added. The mixture was shielded from light and stirred overnight at 40 °C. Silver chloride formed as a white precipitate and was removed from the aqueous solution using a syringe filter (1 µm). The aqueous solution was evaporated, yielding (**5**) (200 mg, 0.6707 mmol, 91.0 % yield). **DSC:** 135 °C (dec.). **IR:** $\tilde{\nu}$ = 3331 (m), 3205 (w), 3110 (m), 2980 (m), 2886 (m), 2630 (w), 2232 (w), 2171 (w), 1964 (w), 1673 (m), 1596 (w), 1542 (m), 1508 (m), 1482 (s), 1456 (s), 1392 (s), 1344 (s), 1321 (s), 1282 (s), 1202 (m), 1186 (m), 1172 (m), 1119 (m), 1076 (s), 1000 (m), 988 (m), 920 (m), 858 (s), 797 (m), 754 (s), 734 (m), 627 (m), 606 (m), 567 (m) cm^{-1}. ^{1}H NMR (500 MHz, D_2O): δ (ppm) 8.7 (s, 2H, -NH_2), 7.5 (s, 1H, -CH), and 4.3 (s, 3H, $-CH_3$) ppm. ^{13}C NMR (500 MHz, D_2O): δ (ppm) 169.4 (1C, -*C*-NH_2), 164.3 (1C, -*C*-NO_2), 161.8 (1C, -*C*-NO_2), 142.8 (1C, -N-*C*=N-), 103.5 (1C, -N-*C*H), and 39.7 (1C, -N-*C*H_3) ppm. C, H, N analysis (%): $C_6H_6N_{10}O_5$ (298.18), calculated result: C 24.17, H 2.03, N 46.97; found: C 24.0, H 2.1, N 45.3. MS (ESI^+) *m/z*: 100.1 $[M + H]^+$; (ESI^-) *m/z*: 198.1 $[M - H]^-$.

Synthesis of 5-amino-3-methyl-1,2,3-oxadiazolium tetrazole azasydnone (6). 5-Amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) (100 mg, 0.7377 mmol) was dissolved in water (20 ml) and silver tetrazoleazasydnone (0.957 equiv, 185 mg, 0.7063 mmol) in an aqueous solution was added. The mixture was shielded from light and stirred overnight at 40 °C. Silver chloride formed as a white precipitate and was removed from the aqueous solution using a syringe filter (1 µm). The aqueous solution was evaporated, yielding (**6**) (123 mg, 0.4839 mmol, 68.5 % yield). **DSC:** 112 °C (dec.). **IR:** $\tilde{\nu}$ = 3154 (m), 3126 (m), 2948 (m), 2243 (w), 2135 (m), 1926 (w), 1786 (s), 1666 (s), 1614 (m), 1586 (m), 1455 (s), 1428 (m), 1399 (s), 1316 (s), 1261 (s), 1227 (m), 1191 (m), 1176 (m), 1122 (m), 1085 (w), 1077 (m), 1022 (w) cm^{-1}. ^{1}H NMR (500 MHz, D_2O): δ (ppm) 8.6 (s, 2H, -NH_2), 7.5 (s, 1H, -CH), and 4.7 (s, 3H, $-CH_3$) ppm. ^{13}C NMR (500 MHz, D_2O): δ (ppm) 169.4 (1C, -*C*-NH_2), 167.0 (1C, -*C*-O^-), 156.0 (1C, -*C*-N_4), 103.6 (1C, -N-*C*H), and 39.9 (1C, -N-*C*H_3) ppm. C, H, N, O analysis (%): $C_5H_6N_{10}O_3$ (254.17), calculated result: C 23.63, H 2.38, N 55.11; found: C 24.0, H 3.3, N 50.1. MS (ESI^-) *m/z*: 100.1 $[M + H]^+$; *m/z*: $C_2N_7O_2$ $[M - H]^-$.

Nitration of 3-methyl-1,2,3-oxadiazolium with nitrosonium tetrafluoroborate. 5-Amino-3-methyl-1,2,3-oxadiazolium chloride (**1**) (100 mg, 0.7377 mmol) was slurried in acetonitrile (25 ml) cooled to 0-5 °C. Potassium acetate (5 equiv, 362 mg) was added to the mixture as a buffer. Nitronium tetrafluoroborate (2 equiv, 196 mg) was added to the mixture and stirred overnight. The mixture was filtered and evaporated, giving a mixture of 3-methyl-1,2,3-oxadiazolium nitrate (**2**) and 3-methyl-1,2,3-oxadiazolium nitrosoamide (**8**).

3-methyl-1,2,3-oxadiazolium nitrosoamide (**8**): ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 8.1 (s, 1H, -CH) and 4.3 (s, 3H, $-CH_3$) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ (ppm) 173.8 (1C, -*C*-N-NO), 105.6 (1C, -*C*H), and 39.9 (1C, -N-*C*H_3) ppm. $C_3H_5N_4O_2$ (129.10). MS (ESI^-) *m/z*: 129.0 $[M - H]^-$.

Conclusions

In summary, seven energetic compounds were derived from the methyl sydnone imine cation. Despite its mechanical sensitivity,

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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.

Conflicts of interest

There are no conflicts to declare.

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