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TECHNICAL REPORT

Novel Energetic Materials for Counter WMD Applications

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HDTRA1-07-1-0024

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14. ABSTRACT The goal of this work was to advance the fundamental understanding of exciting and newly discovered novel energetic materials via syntheses and theoretical/empirical calculations. These energetic molecular compounds and salts derived primarily from, but not limited to, azoles including pyrazoles, 1,2,3- and 1,2,4-triazoles, tetrazoles, nitroiminotetrazolates, 5,5'-azobis(tetrazolates), 5-nitroaminotetrazoles, and nitroamino triazoles were thoroughly characterized by determining melting point, viscosity (if appropriate), thermal (DSC and TGA) and hydrolytic stability, density, thermodynamic properties, and impact sensitivity concomitantly with spectroscopic and elemental analysis. Additionally, energetic monomer and polymer salts from 1-vinyl-1,2,4-triazole derivatives and azoles with pentafluorosulfanyl substituents were treated similarly. By taking advantage of criteria that have impact on such characteristics as density, enthalpy of formation, oxygen balance and melting point/thermal stability, new energetic compounds were designed. Calculations were used to predict density and heat of formation (allowing prediction of detonation energies, specific impulse, etc.) prior to developing synthetic routes and carrying out the laboratory work.					
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Executive Summary - HDTRA1-07-1-0024

I. Research Objectives

- Discover/develop new types of high-energy materials
 - Pentafluorosulfanyl-containing (SF_5) salts
 - Energetic polymer salts
 - Dense high nitrogen molecular and ionic materials
- Utilize theoretical or empirical calculations to predict thermochemical properties and density
 - Gaussian 03 (Revision D.01); Cheetah 5.0
 - Ye, C.; Shreeve, J. M. "Rapid and Accurate Estimation of Densities of Room Temperature Ionic Liquids and Salts," *J. Phys. Chem. A*, 2007, 111, 1456-1461. *Ibid.*, "A New Atom/Group Volume Additivity Method to Compensate for the Impact of Strong Hydrogen Bonding on Densities of Energetic Materials," *Journal of Chemical and Engineering Data*, 2008, 53(2), 520-524.
- Desirable properties
 - Density $\geq 2 \text{ g cm}^{-3}$; MP $> 200^\circ\text{C}$; positive heat of formation; high hydrolytic and thermal stabilities; oxygen balance ≥ 0 ; decomposition velocity and pressure $\geq \text{RDX}$

II. Summary of topics addressed

Pentafluorosulfanyl-containing (SF_5) salts

- A. Pentafluorosulfanyl (SF_5)-containing energetic salts
- B. Synthesis of pentafluorosulfanyl (SF_5)-pyrazole and 1,2,3-triazole and their derivatives as energetic materials by click chemistry
- C. 5-(1,2,3-Triazol-1-yl)-tetrazoles derivatives of an azido-tetrazole *via* click chemistry

Energetic polymer salts

- A. Energetic monomer and polymer salts from 1-vinyl-1, 2, 4-triazole derivatives

Dense high nitrogen molecular and ionic materials

- A. Structure and synthesis of energetic salts of N, N'-dinitrourea (DNU)
- B. Impact insensitive dianionic dinitrourea salts: The $\text{CN}_4\text{O}_5^{2-}$ anion paired with nitrogen-rich cations
- C. Energetic ionic liquids based on anionic rare earth nitrate complexes

- D. Energetic nitrogen-rich Cu(II) and Cd(II) 5,5'-azobis(tetrazolate) complexes
- E. Nitroamino triazoles: nitrogen-rich precursors of stable energetic salts
- F. Energetic ethylene and propylene-bridged bis(nitroiminotetrazolate) salts
- G. Energetic salts of 3-nitro-1,2,4-triazole-5-one (NTO), 5-nitroaminotetrazole and other nitro-substituted azoles
- H. The synthesis of di(aminoguanidine) 5-nitroimino-tetrazolate; some diprotic or monoprotic acids as precursors of energetic salts
- I. 1,3-Diazido-2-(azidomethyl)-2-propylammonium salts

III. Work Accomplished

The goal of this work was to advance the fundamental understanding of exciting and newly discovered novel energetic materials via syntheses and theoretical/empirical calculations. These energetic molecular compounds and salts derived primarily from, but not limited to, azoles including pyrazoles, 1,2,3- and 1,2,4-triazoles, tetrazoles, nitroiminotetrazolates, 5,5'-azobis(tetrazolates), 5-nitroaminotetrazoles, and nitroamino triazoles were thoroughly characterized by determining melting point, viscosity (if appropriate), thermal (DSC and TGA) and hydrolytic stability, density, thermodynamic properties, and impact sensitivity concomitantly with spectroscopic and elemental analysis. Additionally, energetic monomer and polymer salts from 1-vinyl-1,2,4-triazole derivatives and azoles with pentafluorosulfanyl substituents were treated similarly. By taking advantage of criteria that have impact on such characteristics as density, enthalpy of formation, oxygen balance and melting point/thermal stability, new energetic compounds were designed. Calculations were used to predict density and heat of formation (allowing prediction of detonation energies, specific impulse, etc.) prior to developing synthetic routes and carrying out the laboratory work. A very large number of stable, energetic materials were synthesized. Two of the new compounds, ethylamine bis(nitroiminotetrazole) and dihyrazinium ethylaminebis(nitroiminotetrazolate), that have detonation properties, thermal stabilities, densities, enthalpies of formation and impact sensitivities that are very competitive with both RDX and HMX, were selected for further testing.

Generalizations that arise from this lengthy study include the following points:

Introduction of the SF₅ group increased density remarkably and thus enhanced the detonation performance of energetic materials relative to the CF₃ group. SF₅-containing materials exhibited detonation properties similar to TNT. Thermal and hydrolytic stabilities are acceptable. Polymer salts of N-vinyl triazolium monomeric salts were prepared by polymerization of the N-vinyl-1,2,4-triazolium monomer or by protonation of poly(1-vinyl-1,2,4-triazole with inorganic or organic acids. Polymer salts exhibit higher thermal stabilities and higher densities than their monomer precursors.

DNU dianion salts are impact insensitive (>40 J). They exhibited reasonable physical properties, such as relatively high densities (1.51 to 1.67 g/cm³). Their calculated detonation velocities (7521 to 8909 m/s) and detonation pressures (19.6 to 29.1 kJ/mol) were comparable to those of TNT, TATB, and ADN. Given the ready preparation of DNU and lower impact sensitivity of the salts, they could be potential alternatives to costly dinitramide salts (M⁺N(NO₂)₂)⁻. Monodinitrourea salts also have

low decomposition temperatures, but display higher densities, heats of formation, and detonation pressures and velocities.

All of the dicationic nitroimino salts exhibited higher thermochemical values than their monocationic analogues - heats of formation, detonation pressures and velocities, and specific impulse. Nitroimino tetrazoles were considerably more energetic than their nitroimino triazole counterparts; however, the triazoles are more stable thermally. In general, thermal stability of a salt is enhanced over the parent compound. Comparison of 1-nitroamino-1,2,3-triazolates and 4-nitroamino-1,2,4-triazolates with common cations shows that the 1,2,4-triazolates in general are more stable thermally, and the 1,2,3-analogues invariably have higher heats of formation

IV. Compounds worthy of further work

Two compounds were found to have properties competitive with RDX and/or HMX and have been relegated to further study (vide infra).

V. Personnel Supported

Dr. Hong Xue – postdoctoral fellow
Dr. Takashi Abe – postdoctoral fellow
Dr. Guo-Hong Tao – postdoctoral fellow
Dr. Yangen Huang – postdoctoral fellow
Dr. Young-Hyuk Joo – postdoctoral fellow
Dr. Haixiang Gao – postdoctoral fellow
Dr. Yong Guo – postdoctoral fellow
Dr. Yanqiang Zhang – postdoctoral fellow

VI. Publications

Ye, C.; Shreeve, J. M. "Rapid and Accurate Estimation of Densities of Room Temperature Ionic Liquids and Salts," *J. Phys. Chem. A*, **2007**, *111*, 1456-1461.

Xue, H.; Gao, H.; Twamley, B.; Shreeve, J. M. "Energetic Salts of 3-Nitro-1,2,4-triazole-5-one (NTO), 5-Nitroaminotetrazole and Other Nitro-substituted Azoles," *Chemistry of Materials*, **2007**, *19*, 1731-1739.

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Xue, H.; Gao, H.; Shreeve, J. M. "Energetic Monomer and Polymer Salts from 1-Vinyl-1, 2, 4-triazole Derivatives," *Journal of Polymer Science Part A: Polymer Chemistry*, **2008**, 46, 2414-2421.

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Joo, Y.-H.; Shreeve, J. M. "Functionalized Tetrazoles from Cyanogen Azide with Secondary Amines," *European Journal of Organic Chemistry*, **2009**, 3573-3578.

Abe, T.; Tao, G.-H.; Joo, Y.-H.; Shreeve, J. M. "5-(1,2,3-Triazol-1-yl)-tetrazoles derivatives of an azido-tetrazole *via* click chemistry," *Chemistry – A European Journal*, **2009**, *15*, 4102-4110.

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Tao, G.-H.; Joo, Y.-H.; Twamley, B.; Shreeve, J. M. "A thermally stable nitrogen-rich energetic material - 3,4,5-triamino-1-tetrazolyl-1,2,4-triazole (TATT)," *Journal of Materials Chemistry*, **2009**, *19*, 5850-5854.

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Report

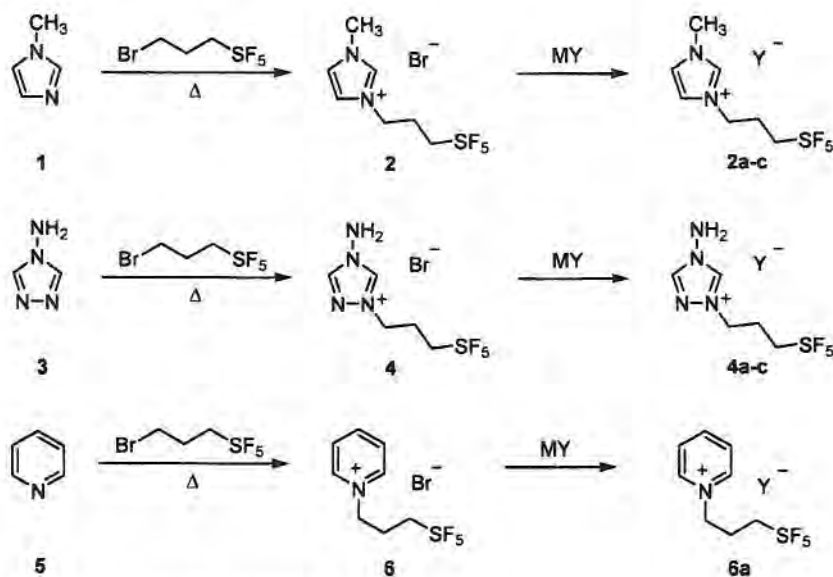
III. Work Accomplished

Pentafluorosulfanyl-containing (SF_5) salts

A. Pentafluorosulfanyl (SF_5)-containing energetic salts

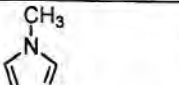
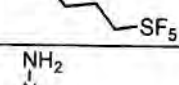
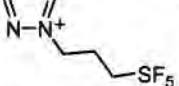
New quaternary salts of pentafluorosulfanyl-substituted (SF_5) N-methylimidazole (1), 4-amino-1-2-4-triazole (3) or pyridine (5) were prepared and characterized. Most of the salts exhibit good thermal stabilities and low melting points placing them in the ionic liquid class. Their densities range between 1.4 and 1.8 g/cm^3 . The standard enthalpies of formation for the new salts were calculated by the use of computationally feasible DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on densities of salts.

Pentafluorosulfanyl liquids



$\text{MY} = \text{AgNO}_3, \text{AgClO}_4, \text{NH}_4\text{N}(\text{NO}_2)_2, \text{K}(\text{SF}_5\text{NNO}_2)$

Structure and Properties of SF₅-containing Salts

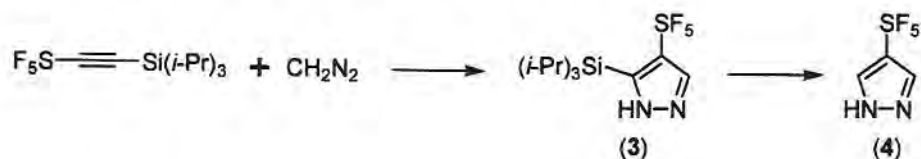
Cation	Anion	No.	T_m/T_g (°C)	T_d (°C)	d (g cm ⁻³)	$\Delta_c U_m^\circ$ (kJ mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ mol ⁻¹)
	Br	2	90.5	—	—	—	—
	NO ₃	2a	-33.7	172.3	1.54	3494.2	-306.0
	ClO ₄	2b	-68.0	247.1	1.46	3354.1	87.1
	[N(NO ₂) ₂]	2c	-50.7	201.7	1.52	3050.3	-328.9
	Br	4	101.3	—	—	—	—
	NO ₃	4a	58.6	145.8	1.43	2777.5	-313.1
	ClO ₄	4b	50.7	242.7	1.41	3042.1	533.5
	[N(NO ₂) ₂]	4c	84.8	160.9	1.44	2797.4	223.0
	[SF ₅ NNO ₂]	4d	-20.6	188.2	1.82	4703.8	513.6
	Br	6	95.4	—	—	—	—
	[N(NO ₂) ₂]	6a	11.0	182.3	1.47	3408.1	-89.8

Gao, H.; Ye, C.; Winter, R. W.; Gard, G. L.; Sitzmann, M. E.; Shreeve, J. M. "Pentafluorosulfanyl (SF₅)-Containing Energetic Salts," *European Journal of Inorganic Chemistry* **2006**, 3221-3226

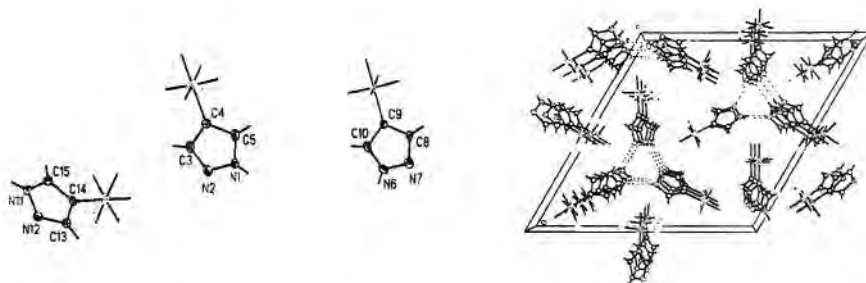
B. Synthesis of pentafluorosulfanyl (SF₅)-pyrazole and 1,2,3-triazole and their derivatives as energetic materials by click chemistry

1-Pentafluorosulfanyl acetylene and its derivatives react with azide or diazomethane giving rise to an SF₅-substituted 1,2,3-triazole or pyrazole. The SF₅ group increases density remarkably and as a result enhances the detonation performance of the energetic materials relative to the CF₃ group.

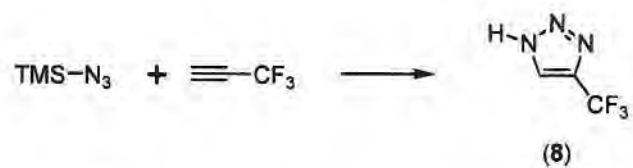
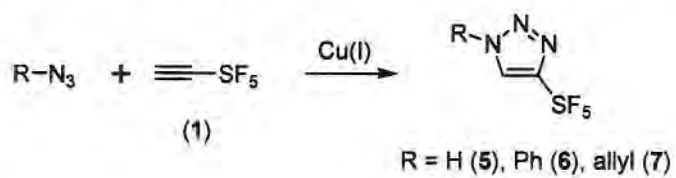
Synthesis of 4-SF₅-pyrazole



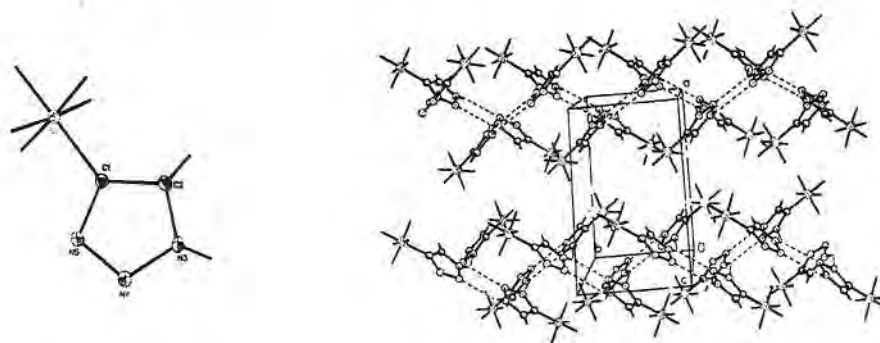
4-Pentafluorosulfanyl-pyrazole

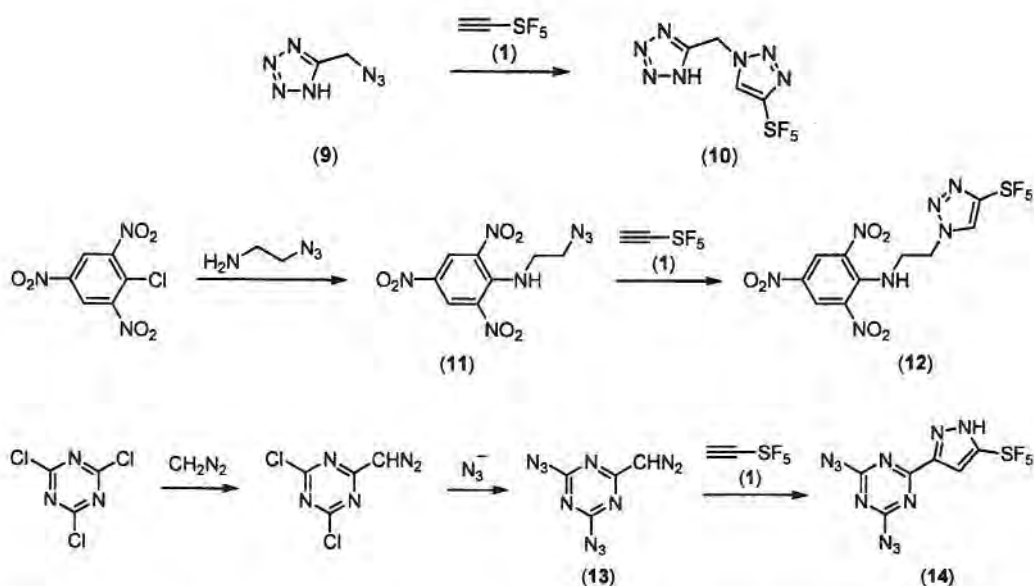


Synthesis of 4-SF₅-1,2,3-triazole and 4-CF₃-1,2,3-triazole



4-Pentafluorosulfanyl-1,2,3-triazole





Compd	T_m^a (°C)	T_d^a (°C)	Density (g cm ⁻³)		$\Delta_f H_m^\circ$ (kJ mol ⁻¹)	P^d (GPa)	D^d (m s ⁻¹)
			Exp. ^b	Calcd. ^c			
4 pyr	141	— ^e	1.83	2.00	-882.97	10.48	5487
5 SF₅	99	— ^e	2.08	2.07	-773.78	19.24	6945
8 CF₃	83	— ^e	1.79	1.83	-465.22	14.11	6518
10	132	238	1.89	1.90	-425.27	20.88	7107
12	176	313	1.80	1.82	-717.19	19.55	6931
14	128	223	1.85	1.88	-21.57	20.41	7464

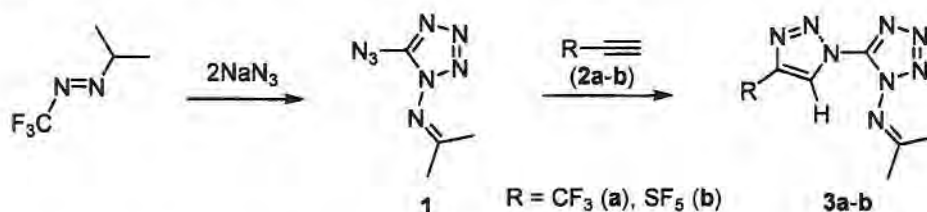
^a DSC under nitrogen gas, 10 °C/min. ^b gas pycnometer. ^c Ye, C.; Shreeve, J. M. *J. Phys. Chem. A* **2007**, *111*, 1456-1461. ^d calculated. ^e sublimes 170 °C.

Ye, C.; Gard, G. L.; Winter, R. W.; Syvret, R. G.; Twamley, B.; Shreeve, J. M.
 "Synthesis of pentafluorosulfanyl (SF₅)-pyrazole and 1,2,3-triazole and their derivatives
 as energetic materials by click chemistry," *Organic Letters*, **2007**, *9*, 3841-3843.

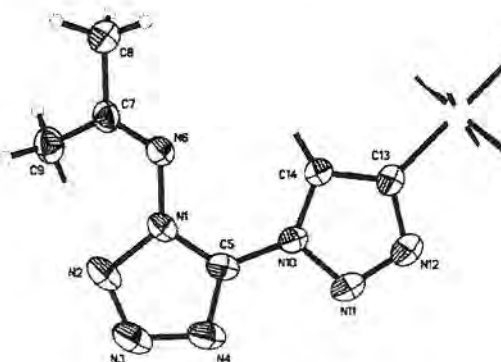
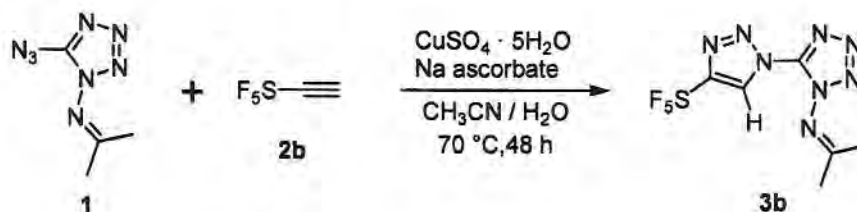
C. 5-(1,2,3-Triazol-1-yl)-tetrazoles derivatives of an azido-tetrazole via click chemistry

N-C bonded (non-bridged) 5-(1,2,3-triazol-1-yl)-tetrazoles were synthesized by the Cu(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition click reaction using 5-azido-*N*-(propan-2-ylidene)-1*H*-tetrazole (1). For example, the click reaction of 1 in the presence of CuSO₄·5H₂O and Na ascorbate at 65–70 °C for 48 h in CH₃CN/H₂O co-solvent was found to be limited only to that with terminal alkynes having electron-withdrawing groups, CF₃C≡CH (**2a**) and SF₅C≡CH (**2b**), giving rise to *iso*-propylidene-[5-(4-trifluoromethyl-1,2,3-triazol-1-yl)-tetrazol-1-yl]-amine (**3a**) and *iso*-propylidene-[5-(4-pentafluorosulfanyl-1,2,3-triazol-1-yl)-tetrazol-1-yl]-amine

(**3b**) in 47% and 66% yields, respectively. When carried out under conditions using CuI and 2,6-lutidine as catalysts at 0 °C for 13 h in CHCl₃, the click reaction was versatile toward alkynes even those having electron-donating groups. Properties of new products were determined and compared with those of **1**. Heats of formation, detonation pressures, detonation velocities and impact sensitivities are reported for these new 5-(1,2,3-triazol-1-yl)-tetrazoles.



Compd	T_m (°C)	T_d (°C)	Density (g cm ⁻³)	$\Delta_f H_m^\circ$ (kJ mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ g ⁻¹)	P (GPa)	D (m s ⁻¹)	IS (J)
1	67	149	1.36	730.5	4.39	16.45	7251	—
3a	64	162	1.44	-37.9	-0.15	11.75	6160	40
3b	76	162	1.64	-315.9	-0.99	16.23	6777	35



Abe, T.; Tao, G.-H.; Joo, Y.-H.; Winter, R. W.; Gard, G. L.; Shreeve, J. M. "5-(1,2,3-Triazol-1-yl)-tetrazoles derivatives of an azido-tetrazole via click chemistry," *Chemistry – A European Journal*, **2009**, *15*, 9897-9904.

Conclusion – SF₅

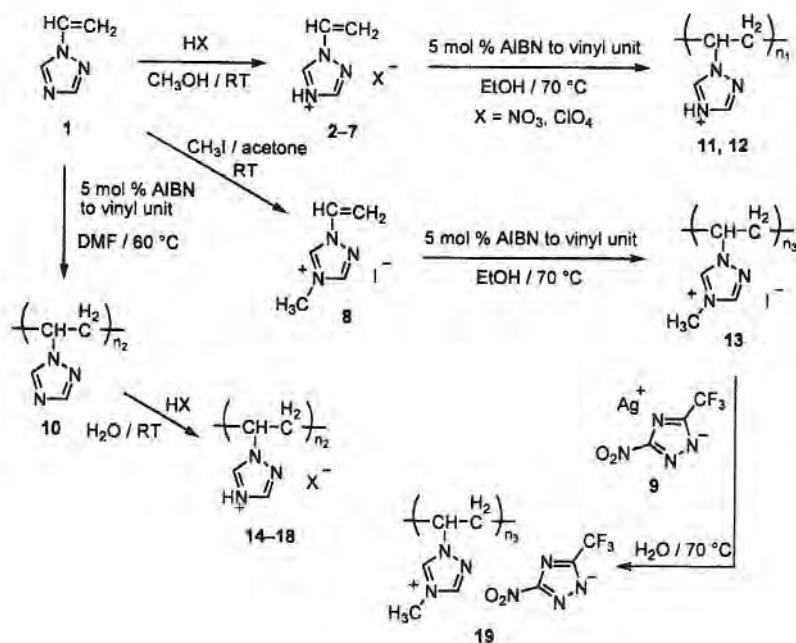
The SF₅ group increases density remarkably and thus enhances the detonation performance of energetic materials relative to the CF₃ group. SF₅-containing materials exhibit detonation properties similar to TNT. Thermal and hydrolytic stabilities are acceptable.

Energetic polymer salts

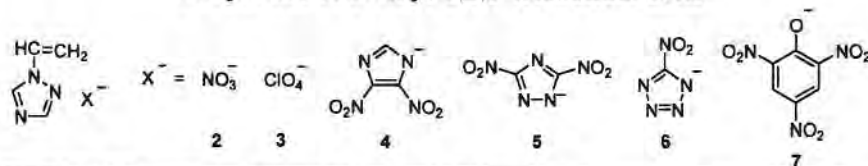
A. Energetic monomer and polymer salts from 1-vinyl-1, 2, 4-triazole derivatives

Energetic polymers salts from 1-vinyl-1, 2, 4-triazole derivatives have been synthesized via free radical polymerization of 1-vinyl-1, 2, 4-triazolium monomer salts or by protonation of poly (1-vinyl-1, 2, 4-triazole) with inorganic or organic acids. Standard enthalpies of formation of the new monomer salts were calculated using the computationally feasible DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on densities of salts. Compared with the monomer salts, the polymer salts have good thermal properties with high densities > 1.5 g cm⁻³.

Energetic polymer salts from 1-vinyl-1,2,4-triazole derivatives



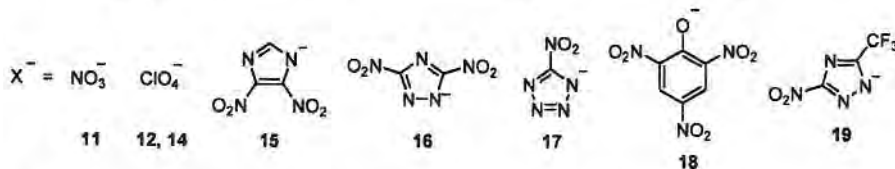
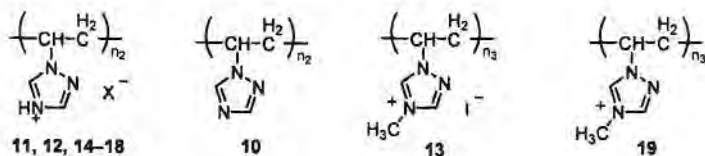
Properties of 1-vinyl-1,2,3-triazolium salts



Compd	T_m^a °C	T_d^b °C	d^c g cm ⁻³	OB ^d %	$\Delta_f H_a^{oe,f}$ kJ mol ⁻¹	$\Delta_f H_L^{og}$ kJ mol ⁻¹	$\Delta_f H^{oh}$ kJ mol ⁻¹ , kJ g ⁻¹	P^i GPa	D^j m s ⁻¹
2	119	119	1.50	-81	-307.9	528.2	62.5, 0.40	17.85	7099
3	102	106	1.61	-53	-277.8	508.8	111.9, 0.57	24.38	7243
4	76	166	1.57	-85	-103.2	473.2	322.1, 1.28	18.65	7168
5	69	132	1.58	-69	-41.2	473.0	384, 1.51	20.44	7358
6	63	152	1.44	-84	112.8	485.1	526.2, 2.51	16.66	7035
7	118	161	1.61	-84	-108.5	446.8	446.8, 343.2	19.99	7136

^a Melting point. ^b Thermal degradation. ^c Density, gas pycnometer, 25 °C. ^d OB (%) is oxygen balance, for C_aH_bN_cO_d: OB (%) = 1600(d-2a-b/2)/MW, MW = molecular weight of salt. ^e Molar enthalpy of formation of cation, 898.5 kJ mol⁻¹. ^f Molar enthalpy of formation of anion. ^g Lattice energy. ^h Molar enthalpy of formation of salt. ⁱ Detonation pressure. ^j Detonation velocity. All detonation values given in ij columns were calculated using Cheetah 4.0.

Properties of Polymer Salts



Compd	Y ^a %	Subst ^b %	M ^c g mol ⁻¹	M _w /M _n ^c	T _g (T _m) ^d °C	T _d ^e °C	d ^f g cm ⁻³
10	88		25900	2.39	146	354	1.28
11	80	70	15200	1.60	118	204	1.72
12	84	69	30300	1.83	185	258	1.78
13	87	100			181(253)	>400	—
14	90	92	44500	1.56	186	248	1.53
15	85	83			81	175	1.57
16	82	76			141	203	1.56
17	81	73	55800	1.43	114	181	1.52

18	65	48			142	242	1.72
19	85	100			88	209	1.54

^a Weight yield. ^b Molar degree of substitution of anions based on elemental analysis. ^c Determined by GPC. ^d Phase transition temperature/melting point. ^e Thermal degradation. ^f Density, gas pycnometer, 25 °C.

Xue, H.; Gao, H.; Shreeve, J. M. "Energetic Monomer and Polymer Salts from 1-Vinyl-1, 2, 4-triazole Derivatives," *Journal of Polymer Science Part A: Polymer Chemistry*, **2008**, *46*, 2414-2421.

Conclusions – 1-Vinyl-1,2,4-Triazole Derivatives

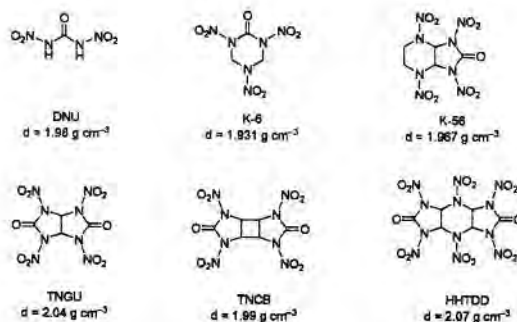
Polymer salts of N-vinyl triazolium monomeric salts were prepared by polymerization of the N-vinyl-1,2,4-triazolium monomer or by protonation of poly(1-vinyl-1,2,4-triazole with inorganic or organic acids. Polymer salts exhibit higher thermal stabilities and higher densities than their monomer precursors.

Dense high nitrogen molecular and ionic materials

A. Structure and synthesis of energetic salts of N, N'-dinitrourea (DNU)

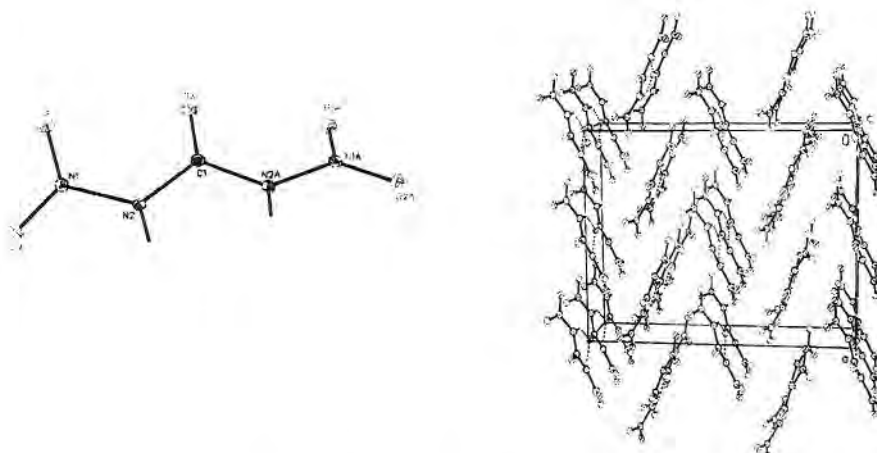
The structure of dinitrourea (DNU) as determined by X-ray single crystal diffraction is orthorhombic; space group: Fdd2; $a = 12.0015(9)$, $b = 17.6425(13)$, $c = 4.5555(4)$; $\alpha = \beta = \gamma = 90^\circ$; $V = 964.57 \text{ \AA}^3$, $Z = 8$, $T = 90 \text{ K}$; $d = 2.067 \text{ g cm}^{-3}$. The heat of formation ($\Delta_f H^\circ_{298}$) of DNU in the gas phase was calculated to be $24.88 \text{ kJ mol}^{-1}$ by using the G3MP2 method based on isodesmic reactions. Eleven mono organic salts of DNU were prepared in acetonitrile and characterized via NMR spectra, elemental analyses, and DSC. Derivatives of 1,2,4-triazolium salts of DNU exhibit densities ranging from $1.75\text{-}1.86 \text{ g cm}^{-3}$ and detonation properties comparable with those of RDX and HMX.

N,N'-Dinitrourea

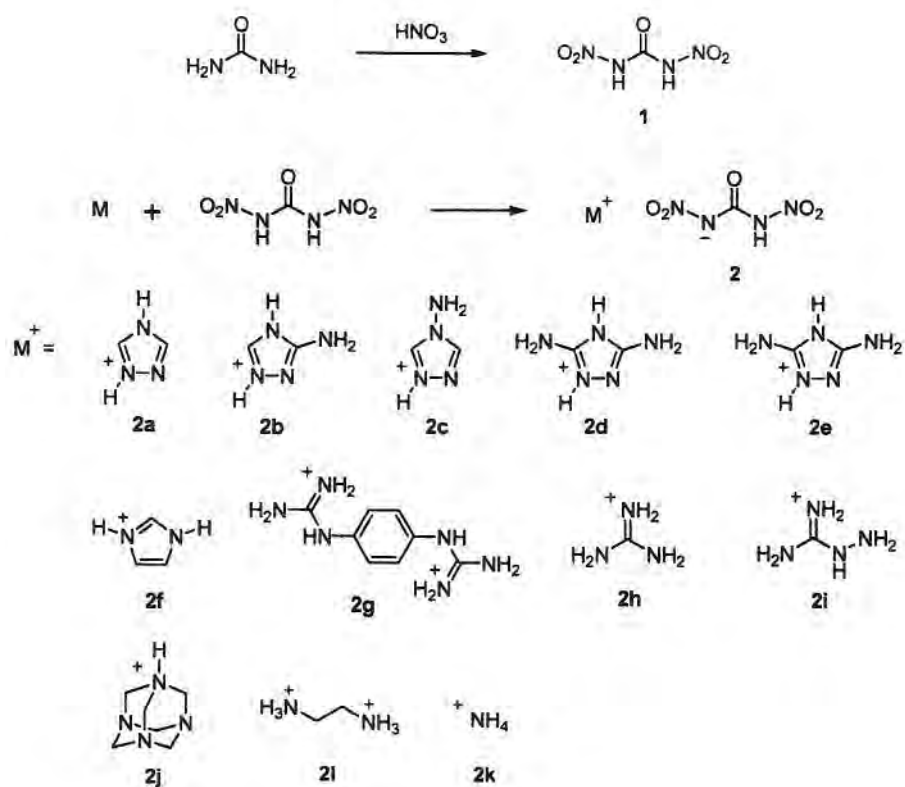


Structures of some explosive candidates containing a DNU fragment.

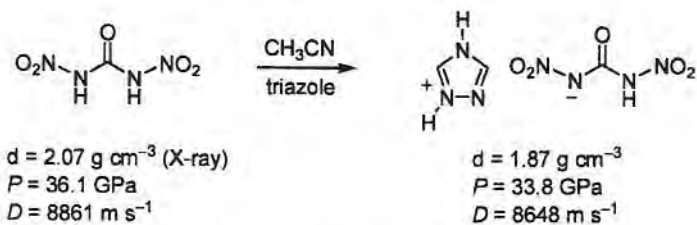
N,N'-Dinitrourea



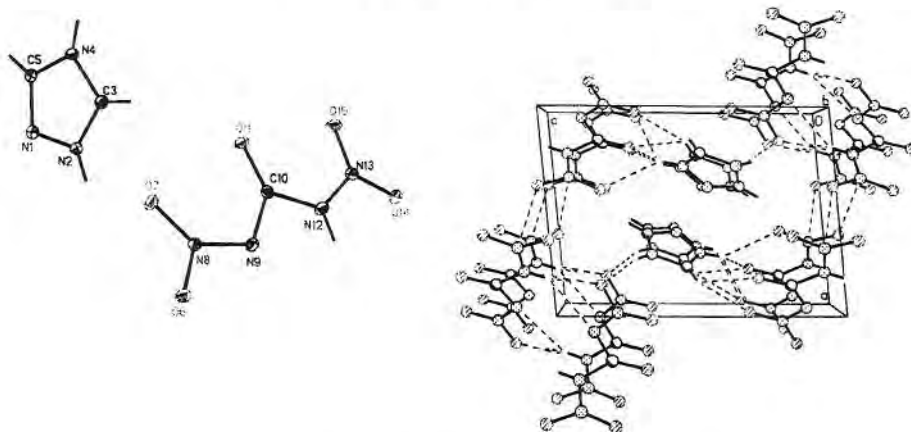
Mono Salts of *N,N'*-Dinitrourea



Synthesis of 1,2,4-triazolium dinitrourea



1,2,4-Triazolium Dinitrourea



Properties of dinitrourea monoanion salts

Cation	T_m °C	d g cm ⁻³	$\Delta_f H^\circ$ kJ mol ⁻¹	P GPa	D m s ⁻¹
	90	1.98	-58.8	36.1	8861
	122	1.83	127.6	33.8	8648
	148	1.80	101.2	32.2	8568
	110	1.86	240.2	36.4	8905
	157	1.85	70.3	35.1	8881

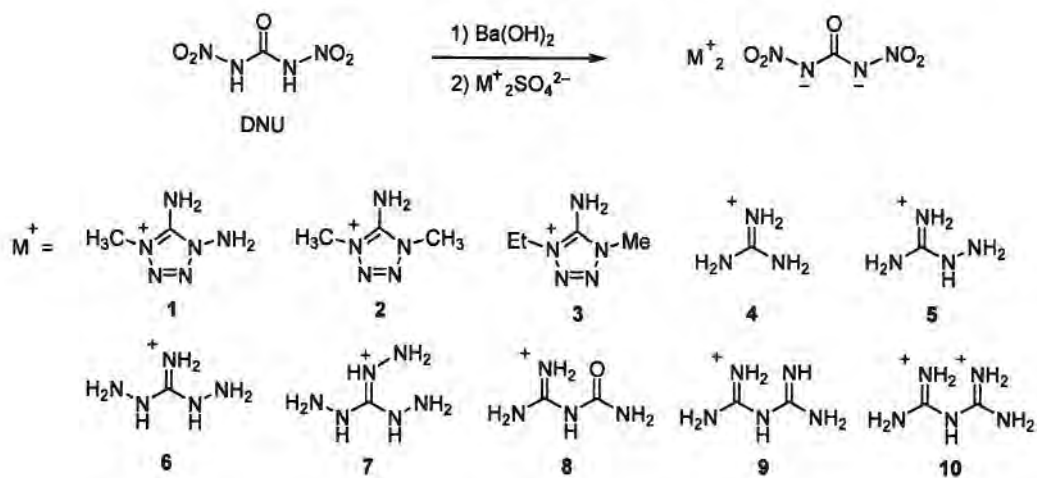
	182	1.75	198.2	31.0	8609
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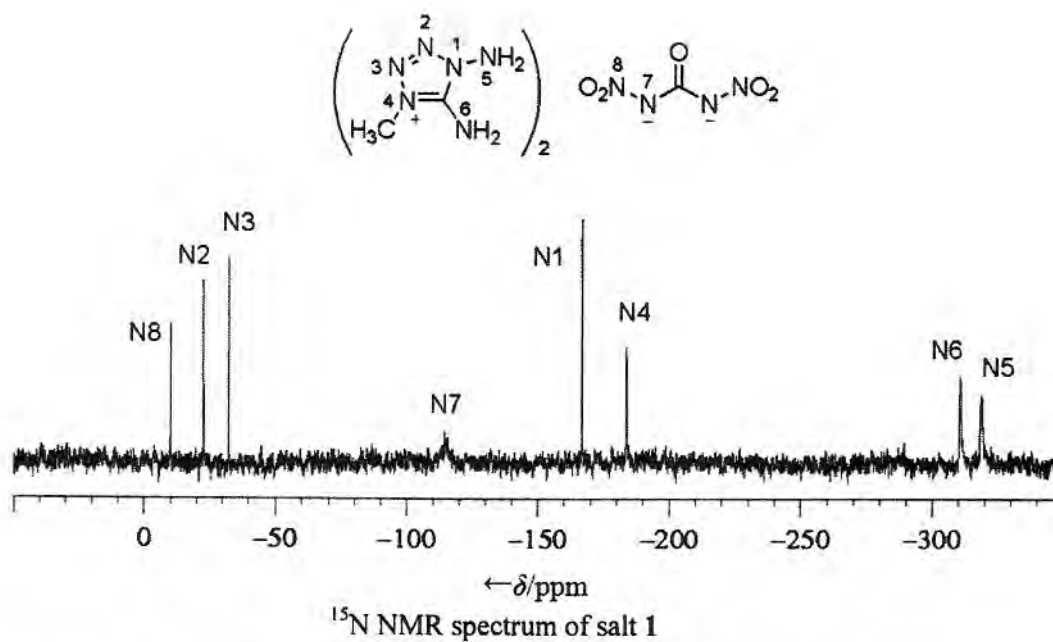
Ye, C.; Gao, H.; Twamley, B.; Shreeve, J. M. "Structure and Synthesis of Energetic Salts of N, N'-dinitrourea (DNU)," *New Journal of Chemistry*, **2008**, 32, 317 – 322.

B. Impact insensitive dianionic dinitrourea salts: The $\text{CN}_4\text{O}_5^{2-}$ anion paired with nitrogen-rich cations

Having examined the energetic properties of dinitrourea (DNU) as a monoanion, this study was extended to the syntheses and characterization of ten DNU dianionic salts by the metathesis of tetrazolium and guanidinium sulfates with *in situ*-generated barium DNU in aqueous solution. These materials are impact insensitive. They were fully characterized by NMR, elemental analysis, IR, DSC and TGA. Bis(guanylguanidinium) DNU dianionic salt (**9**) crystallizes in the triclinic space group *P*-1. The detonation pressure (*P*) values calculated for these salts range from 19.59 to 29.10 GPa, and the detonation velocities (*vD*) from 7521 to 8908 m/s, which make them competitive energetic materials. The chlorine-free DNU dianionic salts are green, and the straightforward synthesis process avoids the use of costly silver salts. The DNU dianion compares very favorably with dinitramide as a novel oxidative species.

Synthesis of dianionic DNU energetic salts

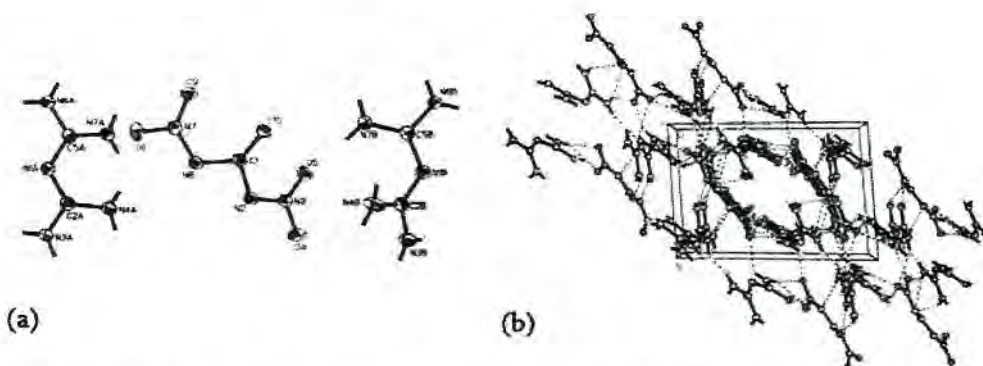




Physical properties and thermochemical values of energetic salts based on DNU dianion

Salt	cation	T_d °C	d g cm ⁻³	OB %	$\Delta_f H^\circ$ kJ mol ⁻¹ (kJ g ⁻¹)	P GPa	D m s ⁻¹
1		120	1.62	-29.6	791.2 (2.09)	26.8	8457
4		134	1.66	-23.9	-208 (-0.77)	25.8	8457
5		111	1.63	-26.8	48 (0.16)	28.0	8752
6		139	1.56	-29.2	333 (1.01)	26.7	8582
7		139	1.57	-31.3	572 (1.60)	29.1	8908
8		171	1.74	-22.6	-520 (-1.47)	25.6	8345
9		119	1.56	-36.3	57 (0.16)	20.1	8563

Molecular structure of 9



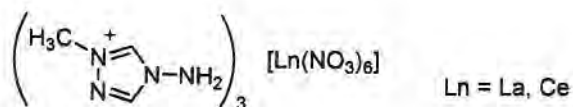
Gao, Y.; Tao, G.-H.; Joo, Y.-H.; Twamley, B.; Parrish, D. A.; Shreeve, J. M. "Impact Insensitive Dianionic Dinitrourea Salts: The $\text{CN}_4\text{O}_5^{2-}$ Anion Paired with Nitrogen-Rich Cations," *Energy & Fuels*, **2009**, *23*, 4567-4574.

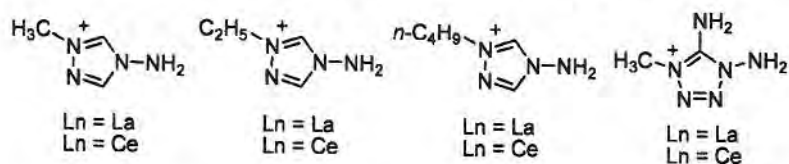
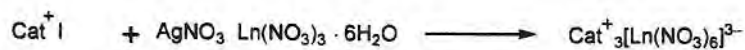
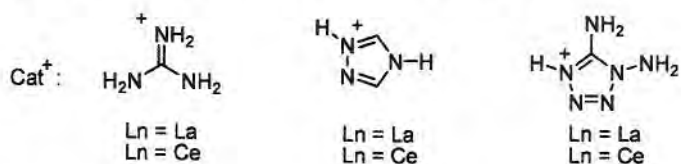
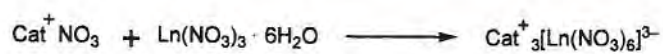
Conclusions – DNU Mono- and Di-anion salts

DNU dianion salts are impact insensitive (>40 J). They exhibit reasonable physical properties, such as relatively high densities (1.51 to 1.67 g/cm³). Their calculated detonation velocities (7521 to 8909 m/s) and detonation pressures (19.6 to 29.1 kJ/mol) are comparable to those of TNT, TATB, and ADN. Given the ready preparation of DNU and lower impact sensitivity of the salts, they could be potential alternatives to costly dinitramide salts ($\text{M}^+\text{N}(\text{NO}_2)_2^-$). Monodinitrourea salts also have low decomposition temperatures, but display higher densities, heats of formation, and detonation pressures and velocities.

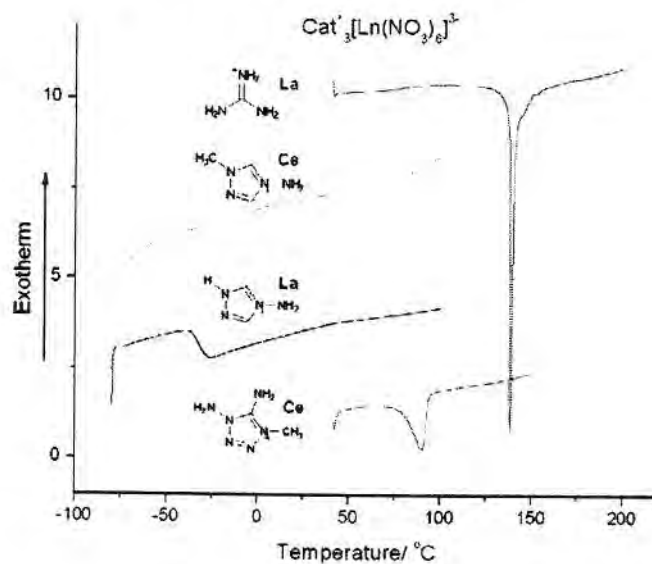
C. Energetic ionic liquids based on anionic rare earth nitrate complexes

Energetic ionic liquids based on anionic rare earth nitrate complexes, $\text{Cat}^+_3[\text{Ln}(\text{NO}_3)_6]^{3-}$, where Cat^+ is guanidinium, 4-aminotriazolium, 4-amino-1-methyltriazolium, 4-amino-1-ethyltriazolium, 4-amino-1-butyltriazolium, 1,5-diaminotetrazolium, and 1,5-diamino-4-methyltetrazolium, were prepared. The hexanitrate lanthanum (cerium) salts with the latter two cations are the first CO-balanced energetic ionic liquids that are hydrolytically and air stable with impact sensitivities of ~ 27 J. For environmental considerations, these ionic liquids were obtained by a simple method using nitrate-containing precursors. All salts are fully characterized by IR, NMR, elemental analysis, thermal stability, phase behavior, density, and water content determinations. Based on theoretical calculations, these new compounds have potential as propellants.

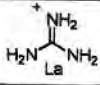
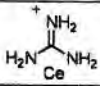
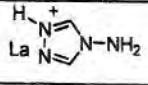
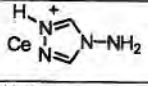
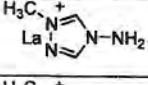
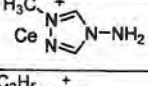
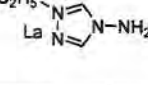
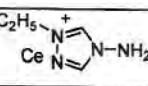
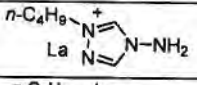
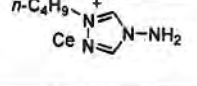
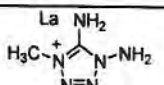
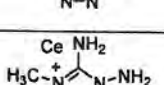
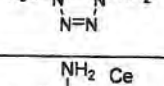




DSC Scans for Rare Earth Salts



Properties of rare earth salts

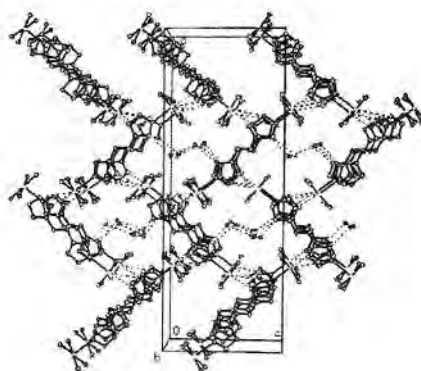
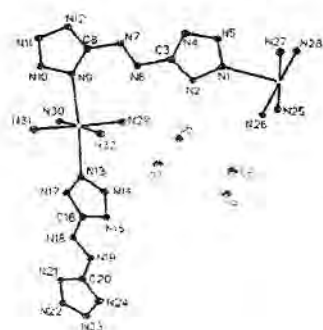
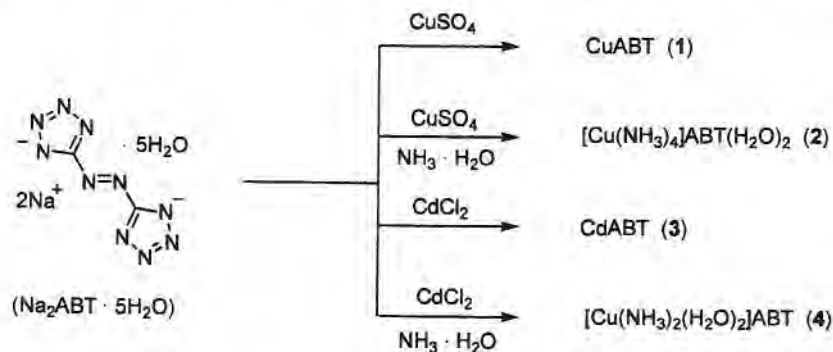
Ionic liquid	T_m °C	T_d °C	d g cm ⁻³	OB %	$\Delta_f H^\circ$ kJ mol ⁻¹ , kJ g ⁻¹
	119	119	1.50	-81	62.5, 0.40
	102	106	1.61	-53	111.9, 0.57
	76	166	1.57	-85	322.1, 1.28
	69	132	1.58	-69	384, 1.51
	63	152	1.44	-84	526.2, 2.51
	118	161	1.61	-84	446.8, 343.2
	119	119	1.50	-81	62.5, 0.40
	102	106	1.61	-53	111.9, 0.57
	76	166	1.57	-85	322.1, 1.28
	69	132	1.58	-69	384, 1.51
	63	152	1.44	-84	526.2, 2.51
	118	161	1.61	-84	446.8, 343.2
	118	161	1.61	-84	446.8, 343.2

Tao, G. -H.; Huang, Y.; Boatz, J. A.; Shreeve, J. M. "Energetic Ionic Liquids based on Anionic Rare Earth Nitrate Complexes," *Chemistry – A European Journal*, 2008, 14, 11167-11173.

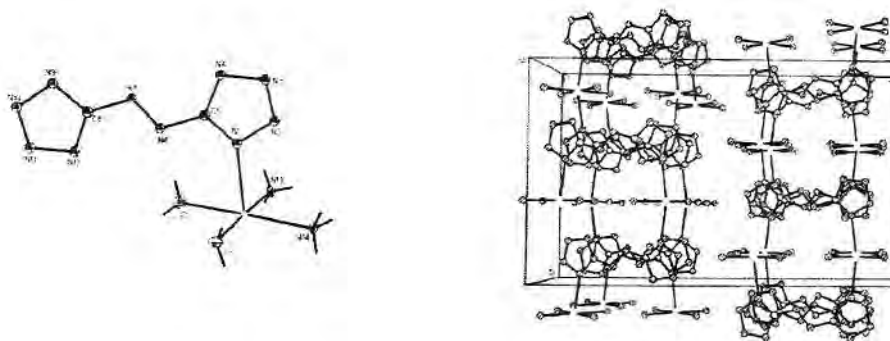
D. Energetic nitrogen-rich Cu(II) and Cd(II) 5,5'-azobis(tetrazolate) complexes

Copper(II) and cadmium(II) complexes of 5,5'-azobis(tetrazolate) (ABT) were synthesized at ambient temperature. The anhydrous copper(II) and cadmium(II) salts (1) and (3) are very sensitive. The energetic copper(II) and cadmium(II) ABT coordination complexes, tetraammine copper 5,5'-azobis(tetrazolate) dihydrate $[\text{Cu}(\text{NH}_3)_4]\text{ABT}(\text{H}_2\text{O})_2$ (2) and diammine dihydrate cadmium 5,5'-azobis(tetrazolate) $[\text{Cd}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{ABT}$ (4) were prepared and then structured by single crystal X-ray diffraction. Their vibrational spectra (IR) were measured and compared with the calculated frequencies. Thermal stabilities were obtained from DSC measurements and sensitivity towards impact was determined by BAM standards. The energies of combustion of 2 and 4 were based on oxygen bomb calorimetry values and were used to calculate the corresponding heats of formation.

Nitrogen-rich Cu(II) and Cd(II) 5,5'-azobis(tetrazolate) complexes



Compound 2



Compound 4

Properties of azobis(tetrazolate) complexes

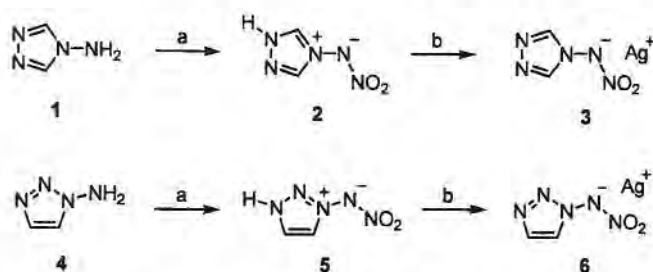
Compound	1	2	3	4
Mw (g mol ⁻¹)	227.6	663.7	276.5	346.6
T _d (°C)	217	189	239	213
d (g cm ⁻³)	2.10	1.75	2.59	2.11
N (%)	61.5	59.1	50.7	48.5
IS (J)	<3	28	<3	25
ΔH _f (kJ g ⁻¹)		-4.49		-5.17

Tao, G.-H.; Twamley, B.; Shreeve, J. M. "Energetic Nitrogen-rich Cu(II) and Cd(II) 5,5'-Azobis(tetrazolate) Complexes," *Inorganic Chemistry*, **2009**, *48*, 9918-9923.

E. Nitroamino triazoles: nitrogen-rich precursors of stable energetic salts

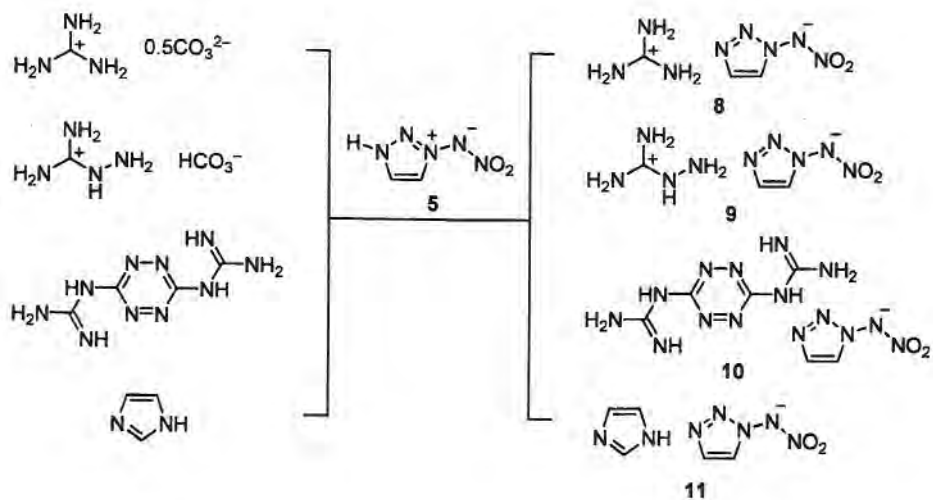
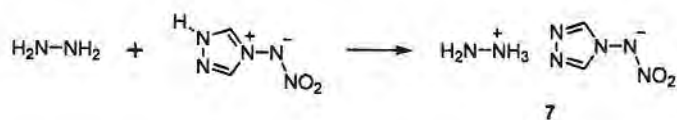
1-Nitroamino-1,2,3-triazole, **5**, was synthesized and its zwitterionic structure was established using single crystal X-ray diffraction. The calculated detonation properties for 4-nitroamino-1,2,4-triazole, **2**, (*P* 33.4 GPa, *vD* 8793 m/s) and 1-nitroamino-1,2,3-triazole, **5**, (*P* 33.0 GPa, *vD* 8743 m/s) are comparable with RDX. A new family of energetic salts **7-21** based either on the 1-nitroamino-1,2,3-triazolate or the 4-nitroamino-1,2,4-triazolate anion were prepared and characterized via vibrational spectroscopy (IR), multinuclear NMR spectra, elemental analyses, density, TGA and DSC. The heats of formation (Δ_fH°₂₉₈) and detonation properties for these stable salts were calculated using Gaussian 03 and Cheetah 4.0, respectively. Comparison of the properties of the 1,2,3- and 1,2,4-triazolate salts indicates that while the 1,2,4-derivatives are more stable thermally, the 1,2,3-analogues invariably have higher heats of formation. In contrast to its salts, 1-nitroamino-1,2,3-triazole, **5**, is extremely shock sensitive with an impact sensitivity of <1J.

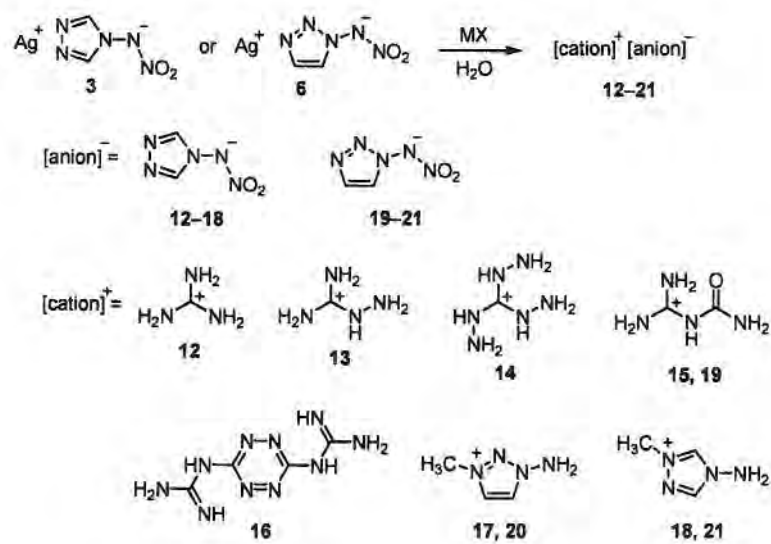
Syntheses of nitroaminotriazoles and their silver salts



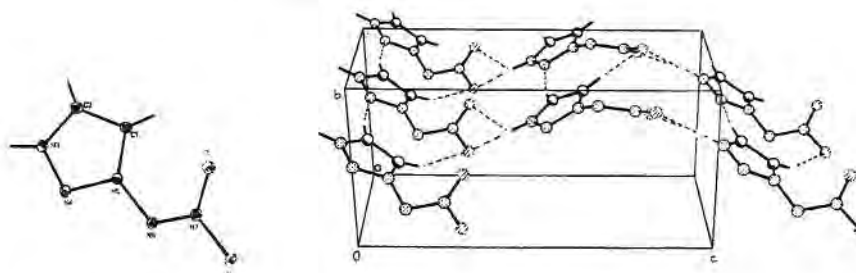
a = 95% H_2SO_4 , 70% HNO_3 , 0 °C, 30 min, r. t. 2h.
b = 1) NaOH , H_2O , r. t., 2) AgNO_3 .

Salts of nitroamino salts by metathesis reactions

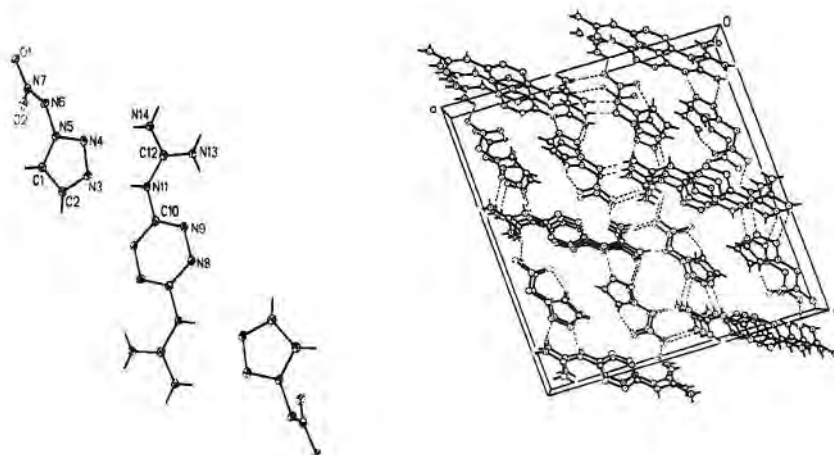




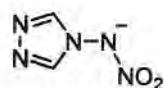
1-Nitroamino-1,2,3-triazole (5)



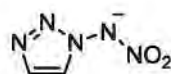
3,6-Diguanidino-1,2,4,5-tetrazinium 1-nitroamino-1,2,3-triazolate (10)



Comparison of 1,2,4- and 1,2,3-nitroaminotriazoles



12, 13, 16–18



9–11, 20, 21

Salt	T_m^a °C	T_d^b °C	d^c g cm ⁻³	$\Delta_f H_c^{od}$ kJ mol ⁻¹	$\Delta_f H_a^{od}$ kJ mol ⁻¹	$\Delta_f H_L^{od}$ kJ mol ⁻¹	$\Delta_f H^{od}$ kJ mol ⁻¹ , kJ g ⁻¹	P^e GPa	D^f m s ⁻¹
2	172	180	1.82	–	–	–	340.1, 2.64	33.4	8793
5	–	105	1.80	–	–	–	367.0, 2.84	33.0	8743
13	138	220	1.50	667.4	141.5	500.0	308.9, 1.52	22.0	8011
9	71	187	1.50	667.4	195.5	494.5	368.4, 1.81	20.9	7783
16	–	211	1.58	1903.6	141.5	1396.6	790.0, 1.74	20.2	7506
10	–	226	1.62	1903.6	195.5	1406.2	888.3, 1.96	21.2	7765
18	138	213	1.54	895.6	141.5	483.7	553.4, 2.44	21.4	7487
21	92	192	1.63	895.6	195.5	490.9	600.2, 2.64	22.7	7957
17	–33	206	1.47	963.2	141.5	477.9	626.8, 2.76	20.0	7663
20	–45	195	1.43	963.2	195.5	474.6	684.2, 3.01	19.2	7532
12	184	240	1.48	566.7	141.5	502.8	205.4, 1.09	19.7	7700
11	86	147	1.51	711.5	195.5	499.3	407.7, 2.07	18.6	7403

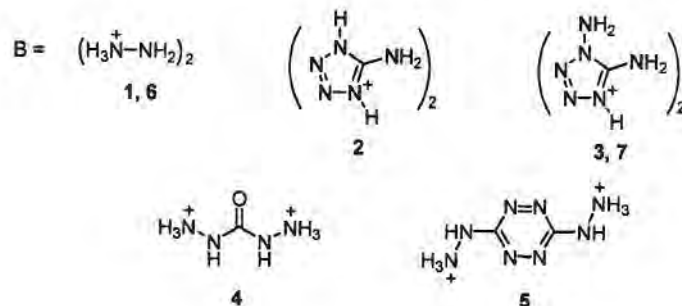
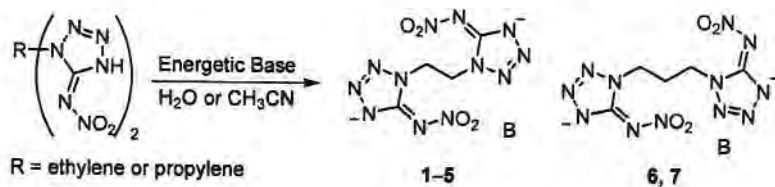
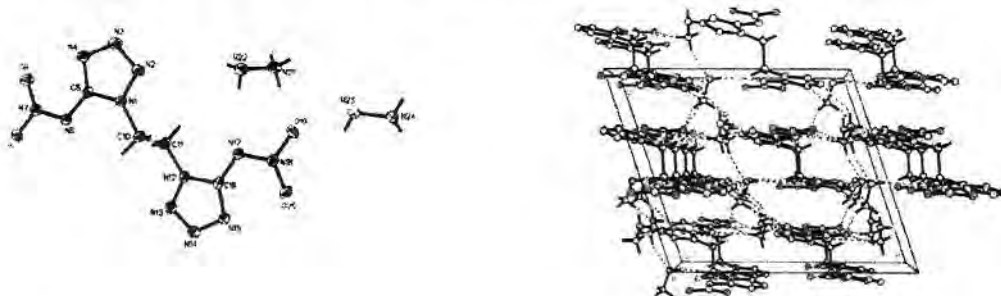
^a Melting point, (°C). ^b Decomposition temperature (°C). ^c Density (g cm⁻³). ^d By Gaussian 3.0. ^e Detonation pressure (GPa). ^f Detonation velocity (m s⁻¹) (Cheetah 5.0)

Huang, Y.; Gao, H.; Twamley, B.; Shreeve, J. M. "Nitroamino Triazoles: Nitrogen-Rich Precursors of Stable Energetic Salts," *Eur. J. Inorg. Chem.*, **2008**, 2560-2568.

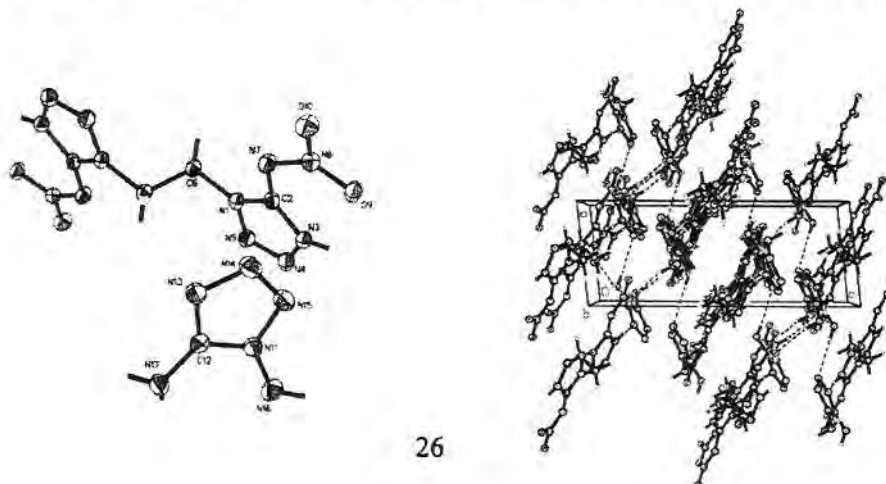
F. Energetic ethylene and propylene-bridged bis(nitroiminotetrazolate) salts

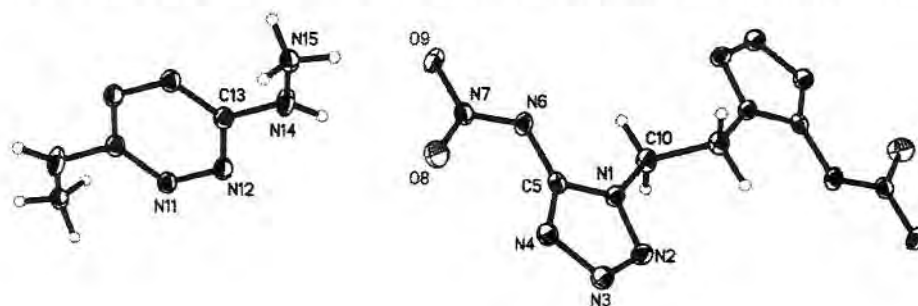
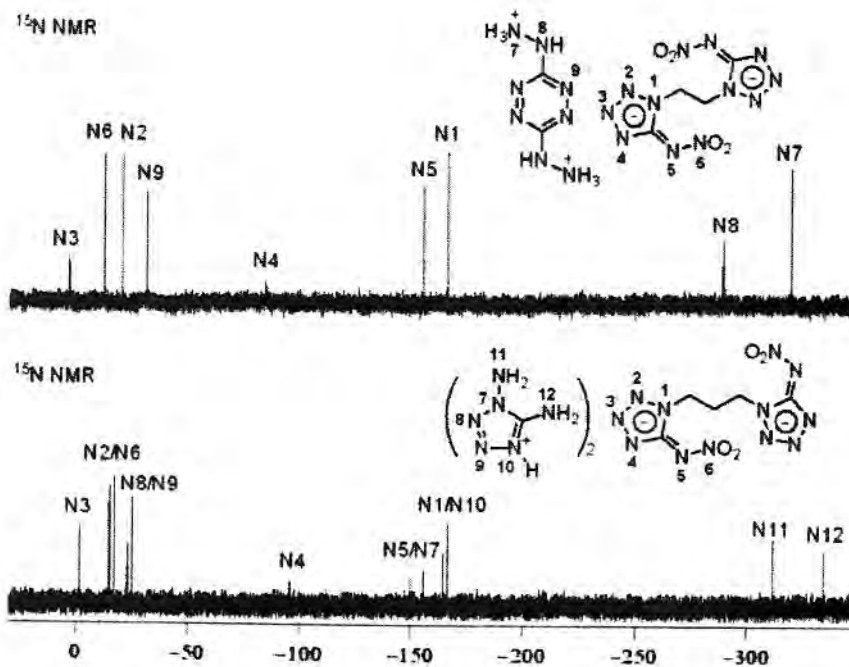
The synthesis and detonation properties of high energy density materials with ethylene- and propylene bis(nitroiminotetrazolate) as the anions are reported; all salts were fully characterized by IR, and ¹H, ¹³C and ¹⁵N NMR spectroscopy as well as elemental analyses. In addition, the heats of formation ($\Delta_f H_f$) were calculated with the Gaussian 3.0 suite of programs. By using the experimental values for the densities of the nitroiminotetrazolate salts, the detonation pressures (P) and velocities (D) were calculated using Cheetah 5.0.

Energetic salts of nitroiminotetrazoles

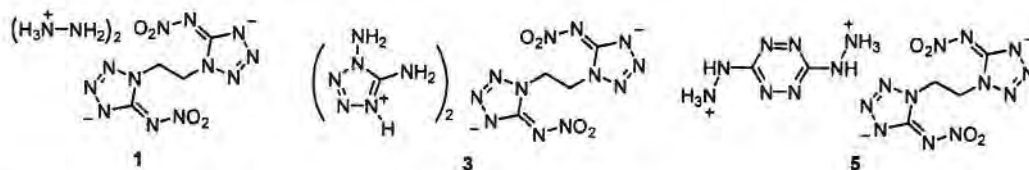
Dihydrazinium salt of 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (**1**)

Bis(1,5-diaminotetrazolium) salt of 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (3)



3,6-Dihydrazinyl-1,2,4,5-tetrazine salt of 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (**5**)¹⁵N NMR spectra of **5** and **7**

Physical properties of nitroiminotetrazolate salts compared with TNT, RDX, and HMX



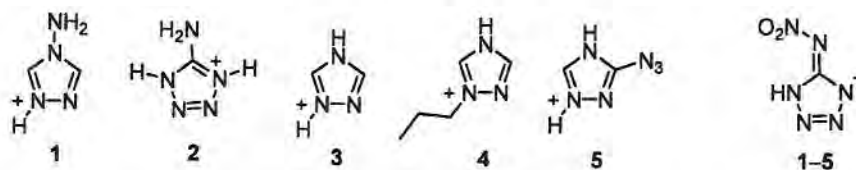
compd	T_m °C	d g cm ⁻³	$\Delta_f H^\circ$ kJ mol ⁻¹ , kJ g ⁻¹	P GPa	D m s ⁻¹	IS J	OB %
1	223	1.73	1067.2, 3.05	35.27	9478	10	-50.2
2	196, d	1.69	1610.5, 3.53	29.56	8756	15	-49.1
3	174	1.70	1767.6, 3.63	31.22	8990	10	-49.3
4	203, d	1.72	1093.5, 2.91	31.98	8957	10	-46.8
5	203, d	1.82	1231.3, 2.87	34.25	9303	15	-52.3
6	123	1.62	1055.3, 2.90	29.33	8846	15	-61.5
7		1.66	1728.1, 3.45	28.83	8742	10	-57.6
TNT	81	1.65	-67, -0.30	19.50	6881	15	-74.0
RDX	230, d	1.82	92.6, 0.42	35.17	8977	7.4	-21.6
HMX	287, d	1.91	104.8, 0.354	39.63	9320	7.4	-21.6
I-8	194	1.86	1038.3, 3.63	38.19	9329	10	-39.1

Joo, Y.-H.; Shreeve, J. M. "Energetic Ethylene and Propylene-Bridged Bis(nitroiminotetrazolate) Salts," *Chemistry – A European Journal*, **2009**, *15*, 3198-3203.

G. Energetic salts of 3-nitro-1,2,4-triazole-5-one (NTO), 5-nitroaminotetrazole and other nitro-substituted azoles

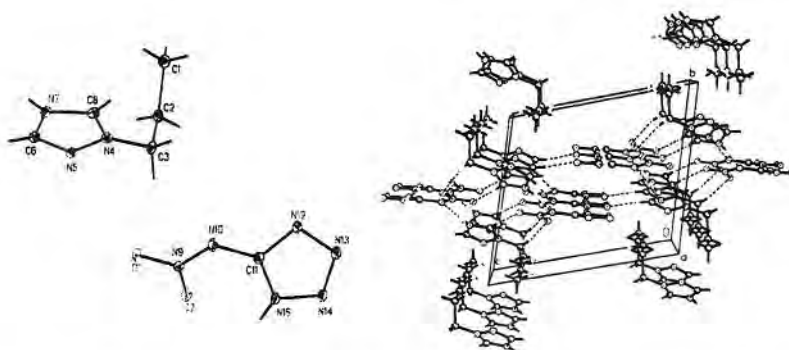
Energetic salts comprised of substituted 1,2,4-triazolium and tetrazolium cations and 3-nitro-1,2,4-triazolate-5-one (NTO), 5-nitroimino-tetrazolate, 3-nitro-5-trifluoromethyl-1,2,4-triazolate, 3,5-dinitro-1,2,4-triazolate, 4,5-dinitro-imidazolate, 3,5-dinitro-pyrazolate, and 5-nitro-tetrazolate anions were synthesized and characterized. The structure of 1-propyl-1,2,4-triazolium 5-nitroimino-tetrazolate (**4**) was confirmed by X-ray analysis. Standard enthalpies of formation were calculated using the computationally feasible DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on densities of salts. Cheetah 4.0 was used to calculate detonation properties. Salts **4** and **5** fall into the ionic liquid class (mp <100 °C).

5-Nitroimino-tetrazolates



compd	T_m/T °C	T_d °C	d g cm ⁻³	OB %	N %	$\Delta_f H^\circ$ kJ g ⁻¹	P GPa	D m s ⁻¹	I _{sp} s
1	143	184	1.72	-52	65.4	2.06	27.0	8506	218.9
2	165	165	1.63	-33	71.6	2.27	25.5	8276	229.0
3	177	177	1.74	-52	63.3	1.65	26.0	8334	208.7
4	69	122	1.48	-103	52.3				
5	89	135	1.68	-40	70.0	2.89	25.9	8230	233.5
6 ^a			1.65	-27		0.57	27.1	8536	219.2
NTO			1.93	-25		-0.78	33.4	8655	210.5
			2.06	-12		1.94	48.5	10358	257.6

1-Propyl-1, 2, 4-triazolium 5-nitroimino-tetrazolate (4)

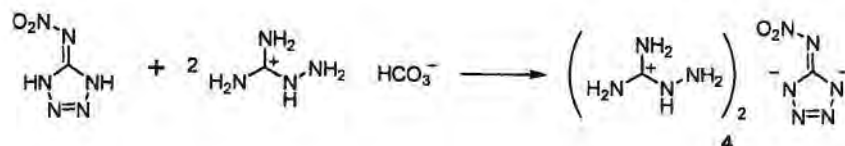
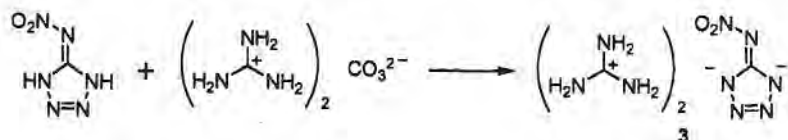
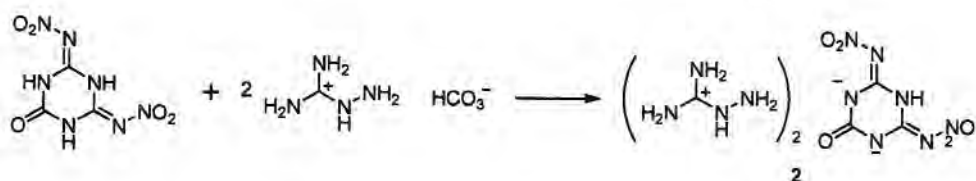
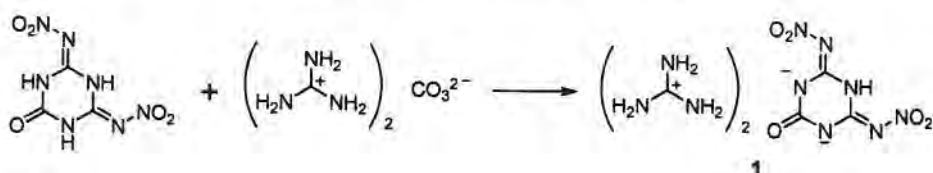


Xue, H.; Gao, H.; Twamley, B.; Shreeve, J. M. "Energetic Salts of 3-Nitro-1,2,4-triazole-5-one (NTO), 5-Nitroaminotetrazole and Other Nitro-substituted Azoles," *Chemistry of Materials*, **2007**, *19*, 1731-1739.

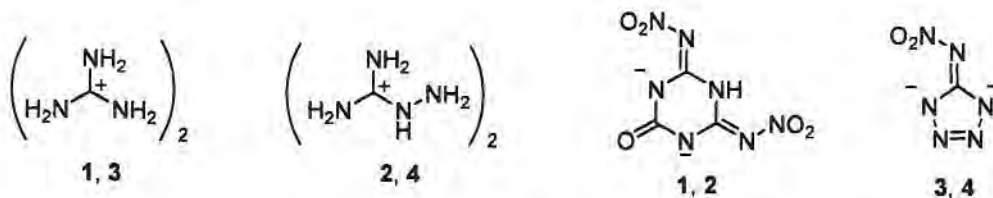
H. The synthesis of di(aminoguanidine) 5-nitroimino-tetrazolate; some diprotic or monoprotic acids as precursors of energetic salts

Syntheses of salts with 4,6-bis(nitroimino)-1,3,5-triazinan-2-one (DNAM), 3,5-dinitro-1,2,4-cyclopentanetrione (DDCP), 3-nitroimino-triazolate, and 5-nitroimino-tetrazolate as anions led to moderately dense nitro-containing energetic salts which are thermally stable to $> 200\text{ }^{\circ}\text{C}$ (TGA). Di(aminoguanidine) 5-nitroiminotetrazolate **4** crystallizes in the monoclinic space group $P2(1)/c$ with an essentially planar 5-nitroiminotetrazolate dianion. Based on experimental and calculated densities, and theoretical calculations carried out using the Gaussian 03 suite of programs, all of the salts have calculated detonation pressures and velocities that exceed that of 2,4,6-trinitrotoluene (TNT) and a few approach that of triaminotrinitro benzene (TATB).

Dianionic 5-nitroimino salts



Properties of dianionic nitroiminotetrazole salts



Salt	d^a g cm ⁻³	T_d^b °C	$\Delta_f H_L^\circ$ kJ mol ⁻¹	$\Delta_f H_c^\circ$ kJ mol ⁻¹	$\Delta_f H_a^\circ$ kJ mol ⁻¹	$\Delta_f H^\circ$ kJ mol ⁻¹ , kJ g ⁻¹	P^c GPa	D^d m s ⁻¹	I_{sp}^e °C
1	1.63	289	1247.6	575.9	214.8	119.0, 0.35	22.6	7959	204
2	1.69	211	1224.3	667.4	214.8	325.4, 0.89	27.1	8571	214
3	1.65	244	1403.5	575.9	338.7	87.0, 0.35	24.0	8533	187
4	1.65	217	1344.7	667.4	338.7	328.9, 1.18	27.2	8993	204

^a density; ^b decomposition temperature; ^c detonation pressure; ^d detonation velocity; ^e specific impulse.

Gao, H.; Huang, Y.; Ye, C.; Twamley, B.; Shreeve, J. M. "The Synthesis of Di(aminoguanidine) 5-nitroimino-tetrazolate; Some Diprotic or Monoprotic Acids as Precursors of Energetic Salts," *Chemistry – A European Journal*, **2008**, *14*, 5596-5603.

Summary – Nitroamino/imino salts

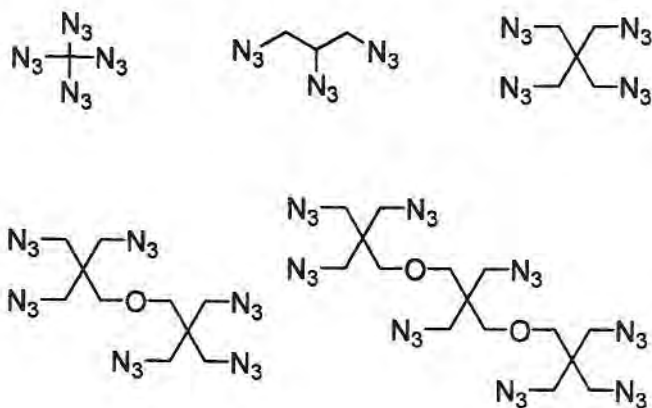
All of dicationic nitroimino salts exhibit higher thermochemical values than their monocationic analogues - heats of formation, detonation pressures and velocities, and specific impulse. Nitroimino tetrazoles are considerably more energetic than their nitroimino triazole counterparts; however, the triazoles are more stable thermally. In general, thermal stability of a salt is enhanced over the parent compound. Comparison of 1-nitroamino-1,2,3-triazolates and 4-nitroamino-1,2,4-triazolates with common cations shows that the 1,2,4-triazolates in general are more stable thermally, and the 1,2,3-analogues invariably have higher heats of formation

I. 1,3-Diazido-2-(azidomethyl)-2-propylammonium salts

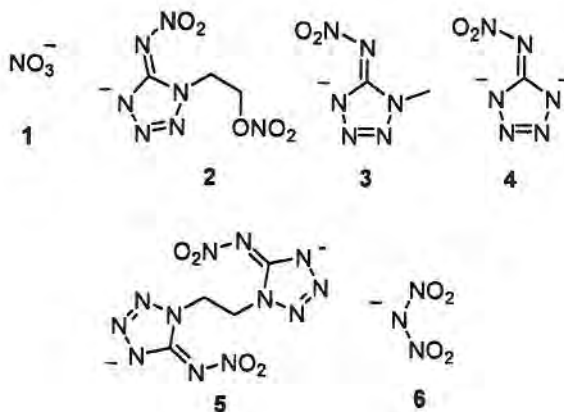
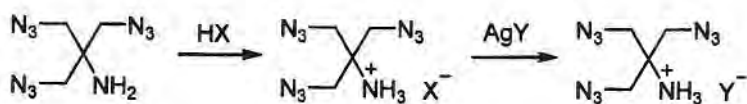
New energetic inorganic materials comprised of 1,3-diazido-2-(azidomethyl)-2-propylammonium salts have been fully characterized by IR, ¹H, ¹³C, and ¹⁵N NMR spectroscopy, and elemental analyses as well as single crystal X-ray diffraction. In addition, the heats of formation, and detonation pressures and velocities were calculated.

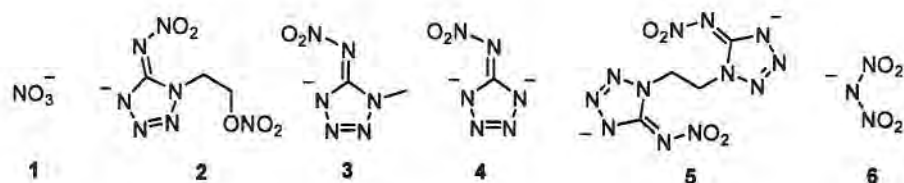
1,3-Diazido-2-(azidomethyl)-2-propylammonium salts

Polyazides

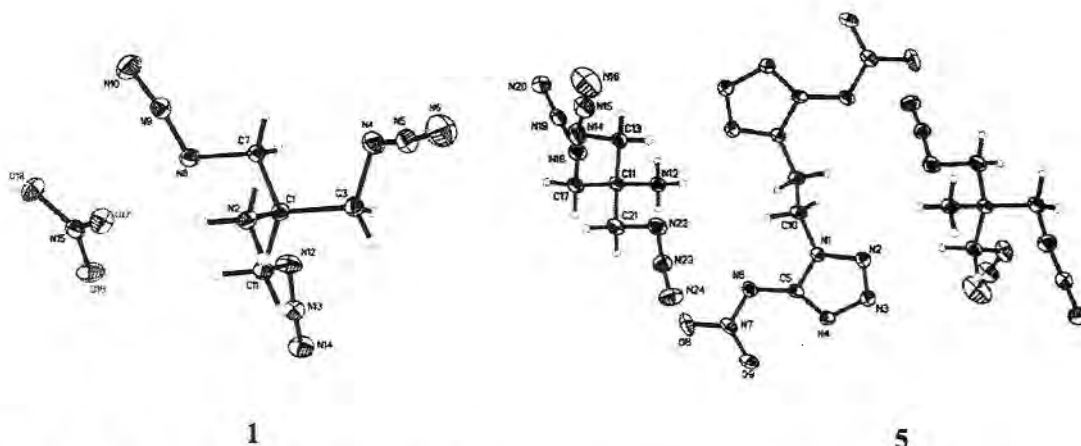


Energetic ammonium salts





Anion	T_m °C	density g cm ⁻³	$\Delta_f H^\circ$ kJ g ⁻¹	P GPa	D m s ⁻¹	IS J
1	204 d	1.58	2.94	25.47	8241	5
2	171 d	1.45	3.18	24.59	7737	30
3	98	1.53	4.15	24.22	8160	7.5
4	111	1.53	4.59	24.64	8246	10
5	186	1.60	4.31	26.45	8429	5
6	178 d	1.49	3.10	25.03	7917	20
RDX	230 d	1.82	0.42	35.17	8977	7.4



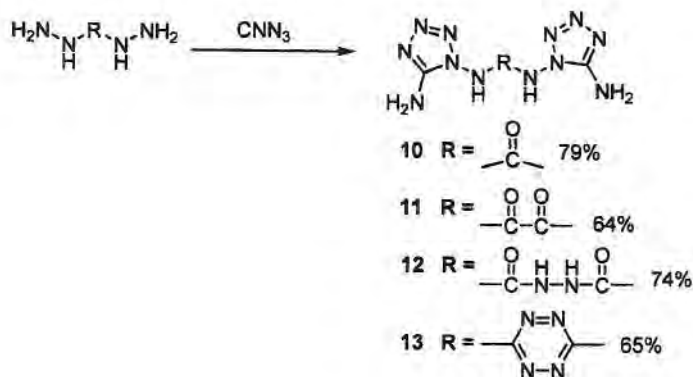
Joo, Y.-H.; Shreeve, J. M. "1,3-Diazido-2-(azidomethyl)-2-propylammonium salts," *Inorganic Chemistry*, **2009**, 48, 8431-8438.

J. Carbonyl and oxalyl bridged bis(1,5-Diaminotetrazole)-based energetic salts

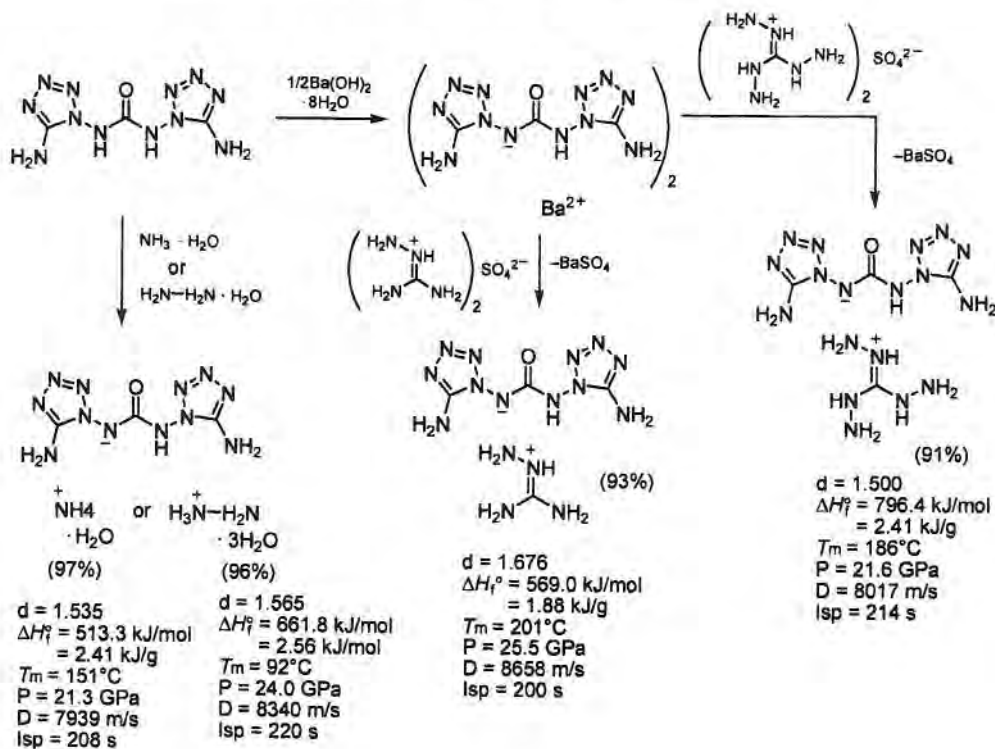
High density energetic salts containing nitrogen rich cations and carbonyl- or oxalylbis(diamino-tetrazole) anions, which were obtained from cyanogen azide and hydrazine, were readily synthesized. In every case, a new family of energetic salts were characterized by vibrational spectroscopy, multinuclear (¹H, ¹³C, ¹⁵N) NMR, elemental analyses, density, differential scanning calorimetry and impact sensitivity. Compound 12 was structured by single crystal X-ray diffraction. The densities, determined by a gas pycnometer, range between 1.50 and 1.68 g cm⁻³. The heats of formation and detonation

properties for these stable salts were calculated by using Gaussian 03 and Cheetah 5.0, respectively.

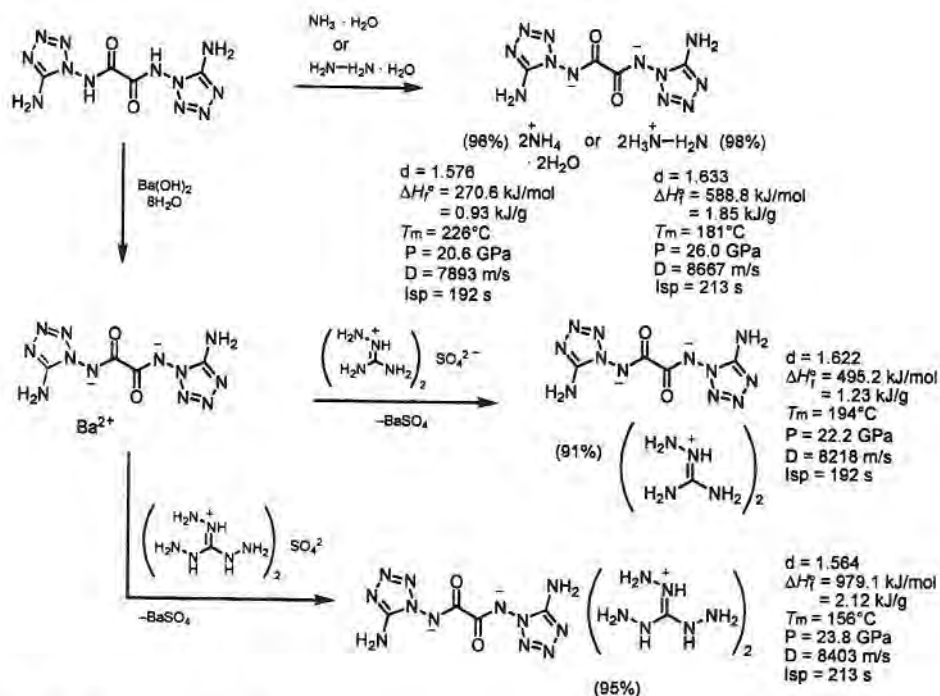
Disubstituted diaminotetrazoles



Reactions of N',N''-bis(5-amino-1H-tetrazol-1-yl)urea (10)



Reactions of N',N''-bis(5-amino-1H-tetrazol-1-yl)oxalamide (11)



Joo, Y.-H.; Twamley, B.; Shreeve, J. M. "Carbonyl and Oxalyl Bridged Bis(1,5-Diaminotetrazole)-Based Energetic Salts," *Chemistry – A European Journal*, **2009**, *15*, 9097-9104.

Summary

The SF_5 group increases density remarkably and thus enhances the detonation performance of energetic materials relative to the CF_3 group. SF_5 -containing materials exhibit detonation properties similar to TNT. Thermal and hydrolytic stabilities are acceptable.

Anion and cation with high nitrogen content enhances the density and therefore detonation characteristics.

Polymer salts of *N*-vinyl triazolium monomeric salts were prepared by polymerization of the *N*-vinyl-1,2,4-triazolium monomer or by protonation of poly(1-vinyl-1,2,4-triazole) with inorganic or organic acids. Polymer salts exhibit higher thermal stabilities and densities than their monomer precursors.

With water as a solvent, a straightforward approach to highly energetic salts – good thermal stabilities/moderate densities – was found.

All of the dicationic nitroimino salts exhibit higher heats of formation, detonation pressures and velocities, and specific impulse values than their monocationic analogues.

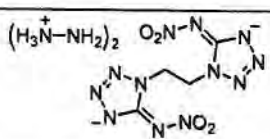
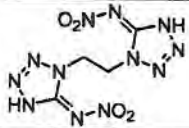
Nitroimino tetrazoles are considerably more energetic than their nitroimino triazole counterparts; however, the triazoles are more stable thermally.

In general, thermal stability of a salt is enhanced over the parent compound.

Comparison of 1-nitroamino-1,2,3-triazolates and 4-nitroamino-1,2,4-triazolates with common cations shows that the 1,2,4-triazolates in general are more stable thermally, and the 1,2,3-analogues invariably have higher heats of formation.

VI. Compounds worthy of further study

Compounds worthy of further study.

Compounds	T_m °C	density g cm ⁻³	$\Delta_f H^\circ$ kJ g ⁻¹	P GPa	D m s ⁻¹	IS J
	223	1.73	3.05	35.3	9478	10
	194	1.86	3.63	38.2	9329	10
TNT	81	1.65	-0.30	19.5	6881	15
RDX	230 dec.	1.82	0.42	35.2	8977	7.4
HMX	230 dec.	1.91	0.35	39.6	9320	7.4

Joo, Y.-H.; Shreeve, J. M. "Energetic Ethylene and Propylene-Bridged Bis(nitroiminotetrazolate) Salts," *Chemistry – A European Journal*, **2009**, *15*, 3198-3203;
 Joo, Y.-H.; Shreeve, J. M. "Energetic Mono-, Di-, and Trisubstituted Nitroiminotetrazoles," *Angew. Chem. Int. Ed.* **2009**, *48*, 564-567.

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