Strategies in the Development of Potential Replacements for RDX

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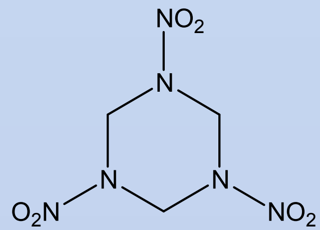
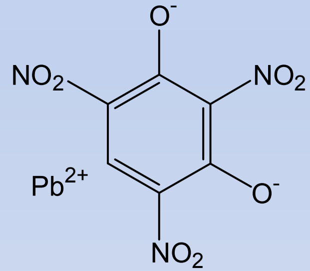
Main Topics

- RDX Replacements - HEDM
- Lead-free Primary Explosives
- High Oxidizers - HEDO
- Nitrogen-Rich Propellants
- Energetic Polymers
- Non-Polluting Pyrotechnical Compositions
- High-performance MTV-Flares
- Advanced NIR illuminants



Hexogen (RDX)

$Pb(N_3)_2$



lead azide **lead styphnate**

RDX Replacements

• Performance	D > 8800 m/s
• Sensitivity	IS > 7J, FS > 120 N
• Thermal Stability	> 180 °C
• Price and Yield	better than CL-20
• Compatibility	TNT, RDX, DNAN, binder
• Long-term stability	> 48 h at 75 °C
• Toxicity	< RDX
• Solubility (H_2O)	as low as possible

Sensitivity Parameters

●	Impact	BAM drop hammer
●	Friction	BAM friction tester
●	Electrostatic (ESD)	OZM ESD apparatus
●	Thermal	DSC, RADEX (TSC), FCO, Koenen test, hot plate, …
●	Shock	GAP @ DIEHL (Roethenbach)

Performance Parameters

●	Detonation velocity (VoD)	EXPLO5.04, optical fiber method
●	Detonation pressure, p_{C-J}	EXPLO5.04
●	Heat of explosion, Q_{ex}	EXPLO5.04, bomb calorimetry
●	Volume of detonation gases, V_0	EXPLO5.04
●	Burn rate	high speed video
●	Performance	SSRT (Indian Head) (2011)

Strategies in the Development of Potential
Replacements for RDX

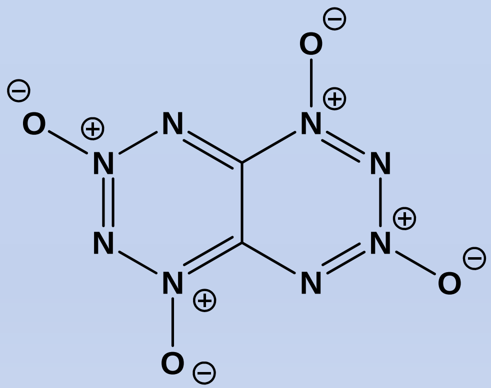
Outline

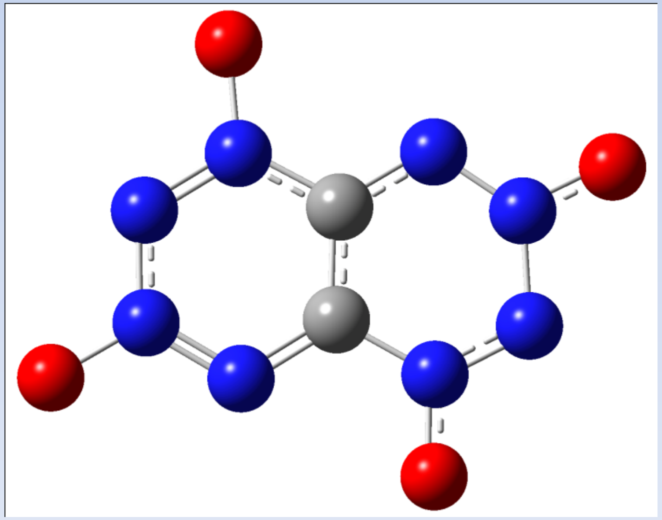
I. The Introduction of N-oxides

II. The Amide Moiety in Energetics

Holy Grail in N-Oxide Chemistry

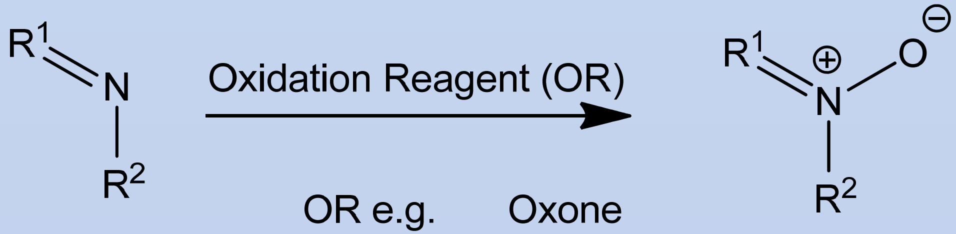
TTTO





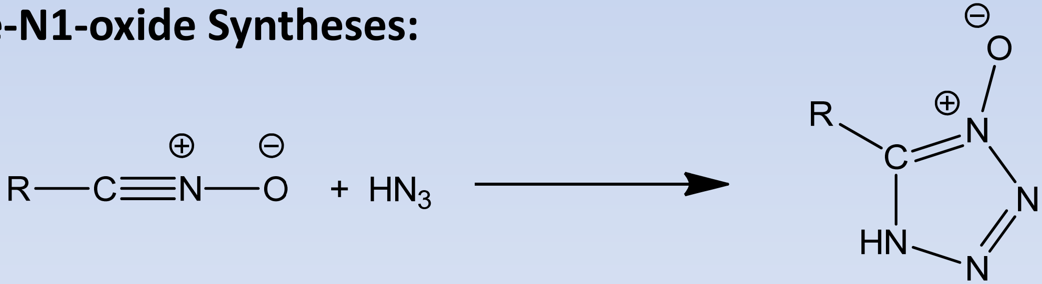
	TTTO	TTTO	TTTO
Formula	$C_2N_8O_4$	$C_2N_8O_4$	$C_2N_8O_4$
FW [g mol^{-1}]	200.0	200.0	200.0
IS [J]	?	?	?
FS [N]	?	?	?
ESD-test [J]	?	?	?
N [%]	56.01	56.01	56.01
Ω [%]	0	0	0
$T_{dec.}$ [°C]	?	?	?
Density [g cm^{-3}]	2.0	2.05	2.1
$\Delta_f H_m°$ / kJ mol^{-1}	213	213	213
$\Delta_f U°$ / kJ kg^{-1}	4521	4521	4521
$-\Delta_E U°$ [kJ kg^{-1}]	7850	7871	7894
T_E [K]	6228	6195	6164
$p_{C\text{-}J}$ [kbar]	501	527	554
D [m s^{-1}]	9885	10044	10203
Gas vol. [L kg^{-1}]	679	678	677

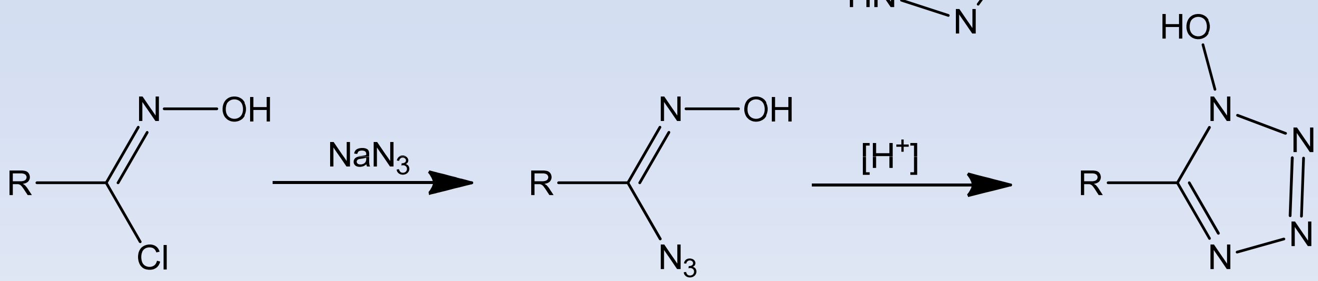
The Introduction of N-oxides



OR e.g.
Oxone
MCPBA
H_2O_2/H_2SO_4
$H_2O_2/F_3C\text{-}COOH$
Ozone
HO-F*CH_3CN ($F_2+H_2O+CH_3CN$)

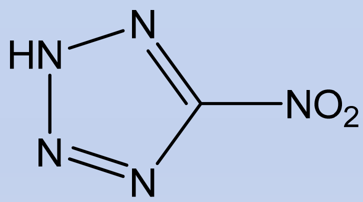
Tetrazole-N1-oxide Syntheses:

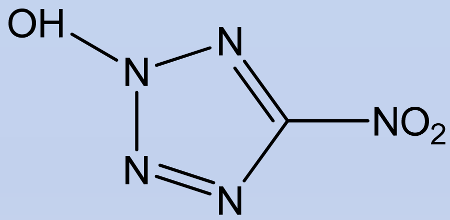
A)


B)


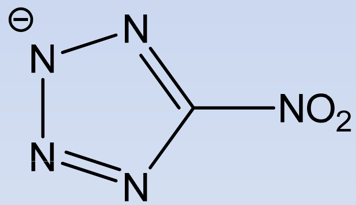
5-Nitrotetrazole (NT) vs. 5-Nitrotetrazole-N-oxide (NTX)

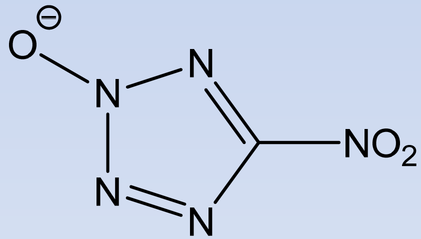
neutral:





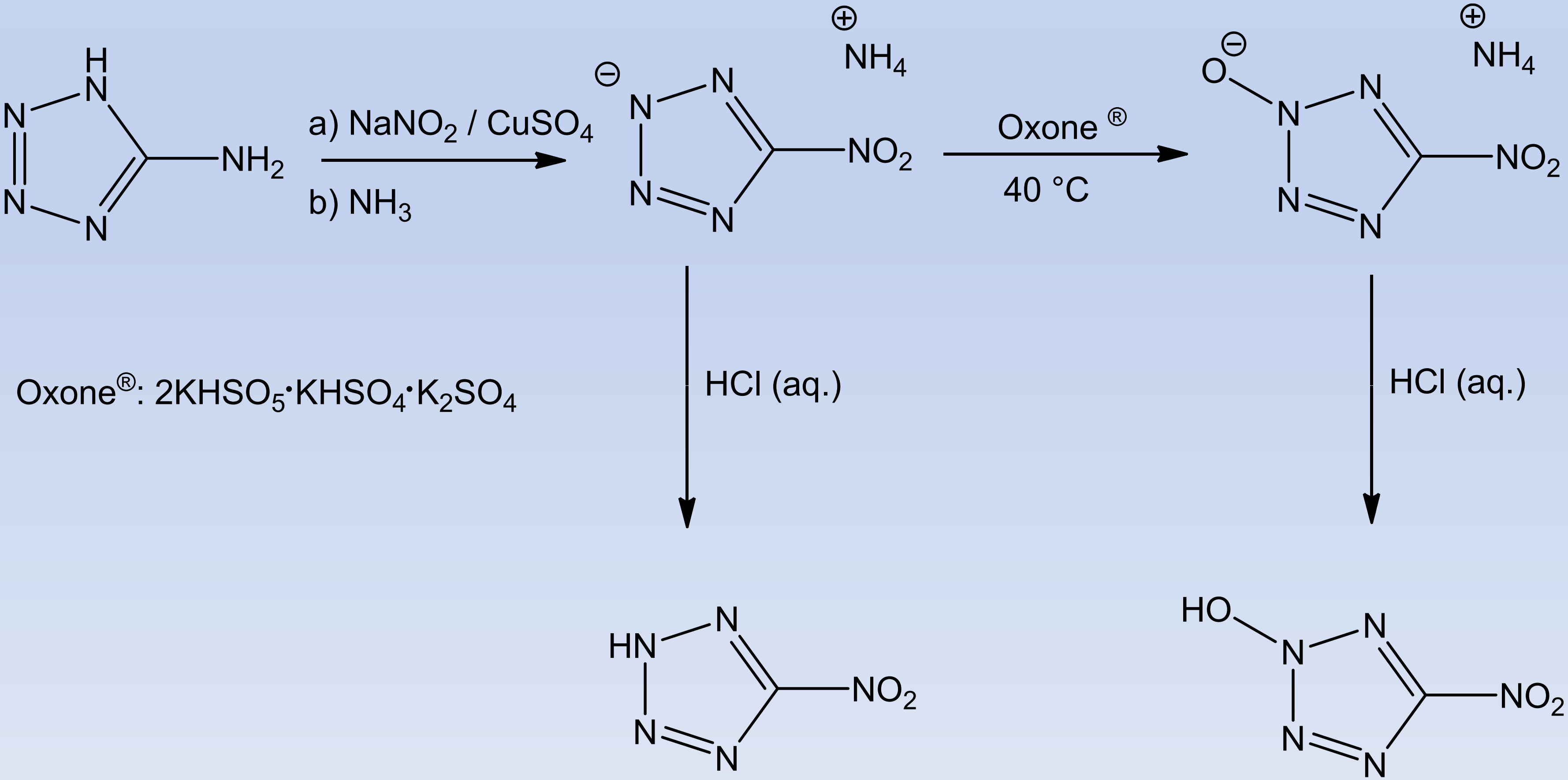
anionic:





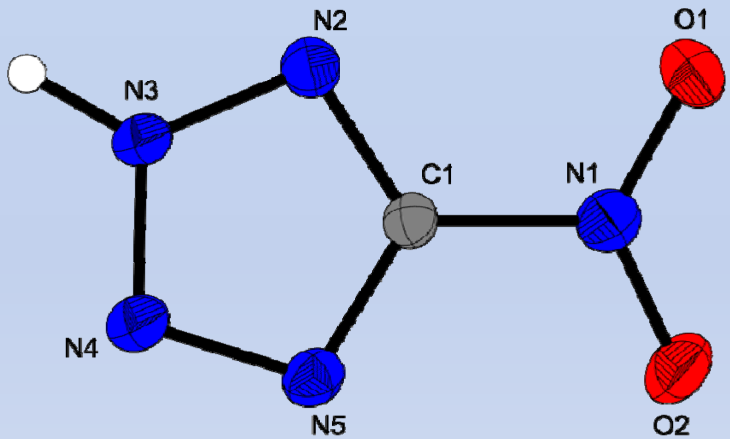
5-Nitrotetrazole (NT) vs. 5-Nitrotetrazole-N-oxide (NTX)

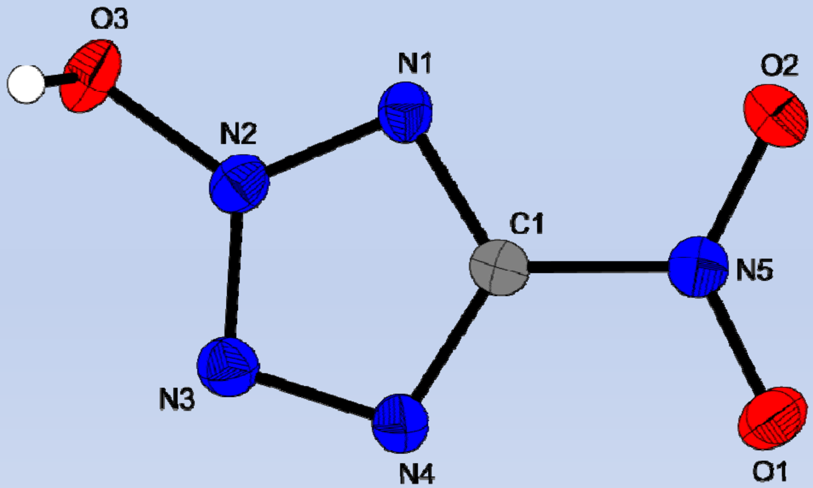
Synthesis:



Oxone®: $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$

5-Nitrotetrazole (NT) vs. 5-Nitro-2-hydroxytetrazole (NTX)





1.90 g cm^{-3}

ΔH_f = 279 kJ mol^{-1}
D = 9184 m s^{-1}

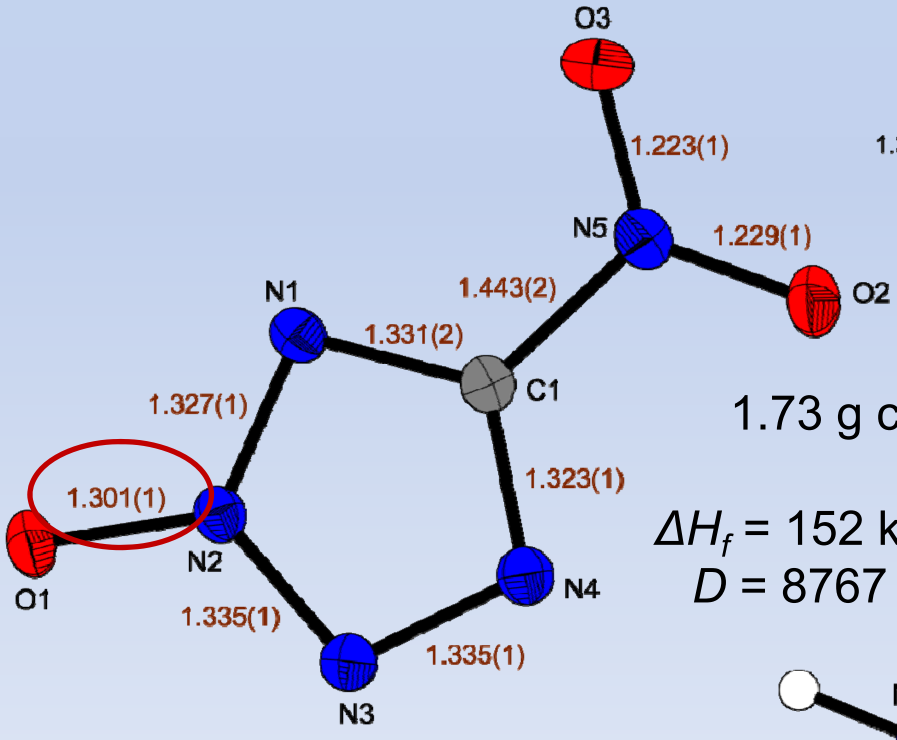
1.94 g cm^{-3}

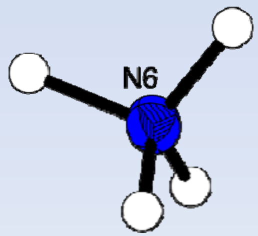
ΔH_f = 269 kJ mol^{-1}
D = 9186 m s^{-1}

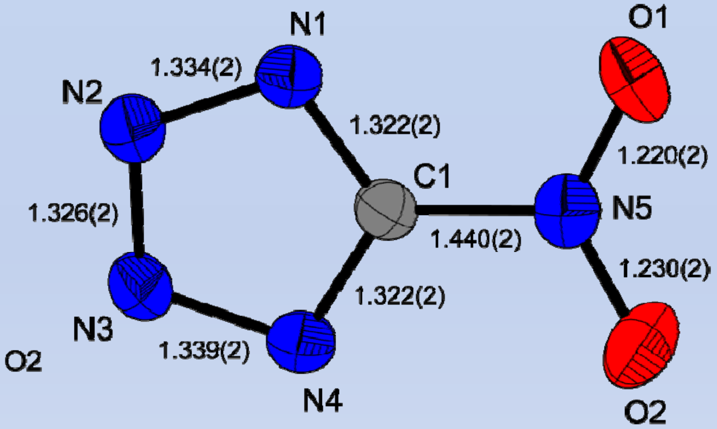
T. M. Klapötke, C. M. Sabaté, J. Stierstorfer, *New J. Chem.* **2009**, *33*, 136-147.

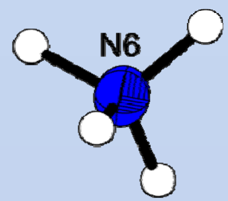
M. Göbel, K. Karaghiosoff, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *J. Am. Chem. Soc.* **2010**,132, 17216-17226.

Ammonium 5-Nitrotetrazolate (NT) vs. Ammonium 5-Nitrotetrazolate-N-oxide (NTX)









1.73 g cm^{-3}

ΔH_f = 152 kJ mol^{-1}
D = 8767 m s^{-1}

1.64 g cm^{-3}

ΔH_f = 172 kJ mol^{-1}
D = 8327 m s^{-1}

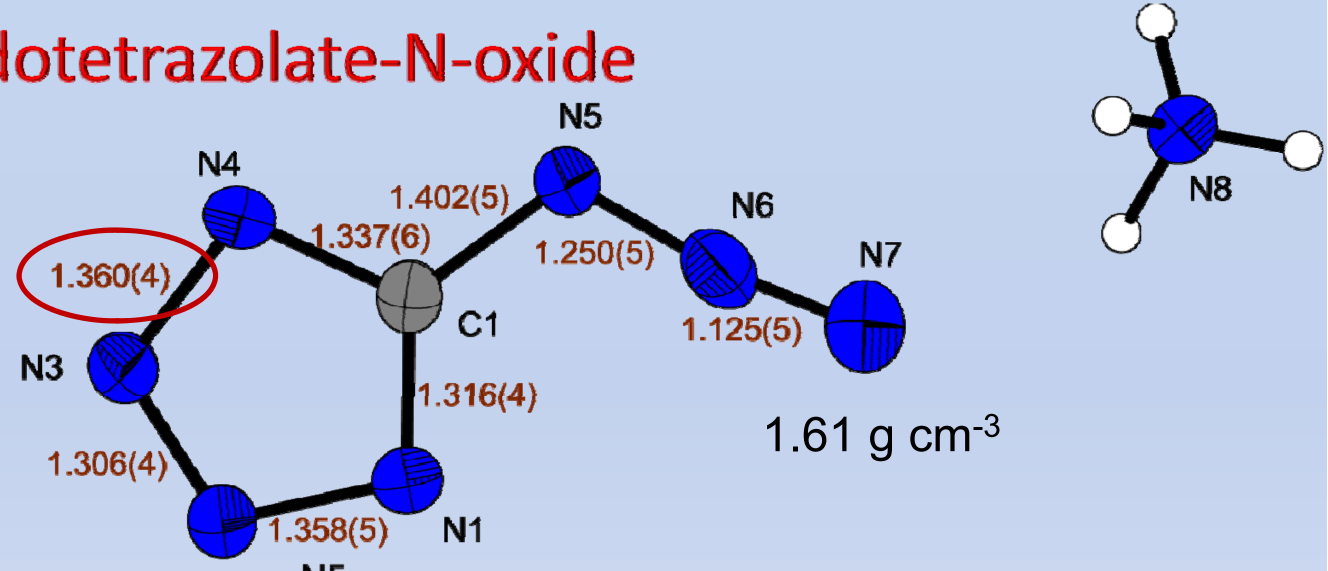
Standard N-O bond length: 145 pm

M. Göbel, K. Karaghiosoff, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *J. Am. Chem. Soc* **2010**,132, 17216-17226.

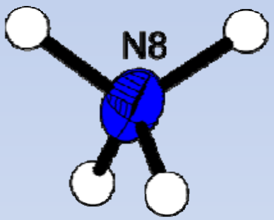
Comparison of 5-Nitrotetrazole (NT) vs. 5-Nitrotetrazole-N-oxide (NTX)

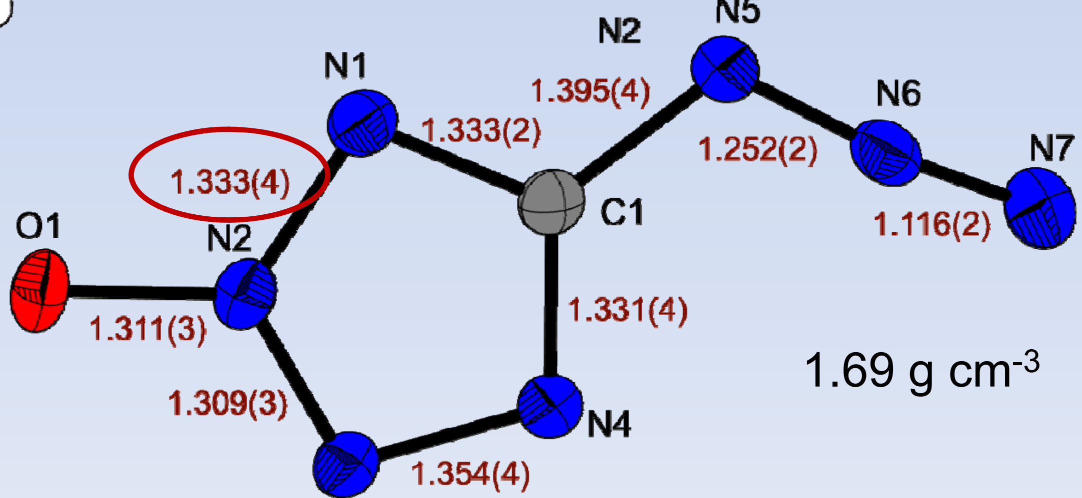
- Heats of formation lower for NTX compared with NT salts. ☹
- Densities for NTX higher than NT salts. ☺
- Performances higher for NTX salts (400 to 1000 m s^{-1} higher). ☺
- Thermal stabilities slightly lowered when compared to NT salts. ☹
- Explosive sensitivities generally lower than NT salts. ☺

Ammonium 5-Azidotetrazolate vs. Ammonium 5-Azidotetrazolate-N-oxide



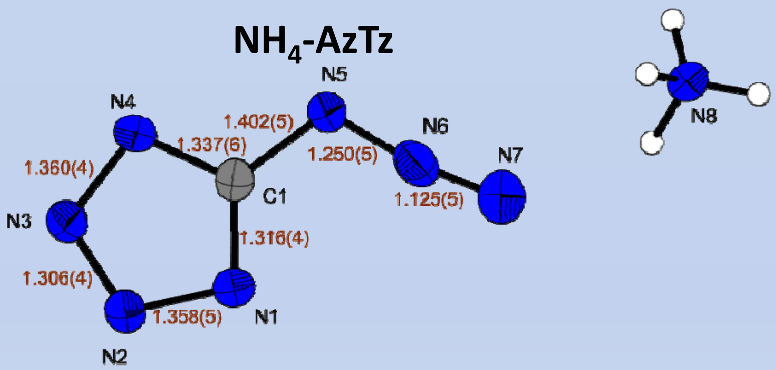
1.61 g cm^{-3}

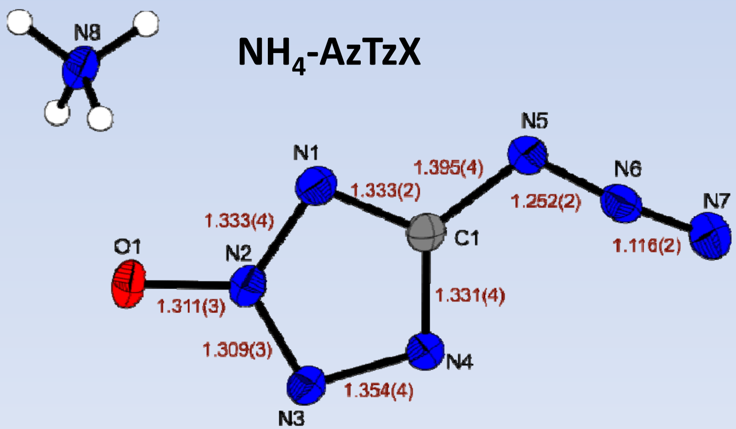




1.69 g cm^{-3}

T. M. Klapötke, J. Stierstorfer, *J. Am. Chem. Soc.* **2009**, *131,* 1122–1134.

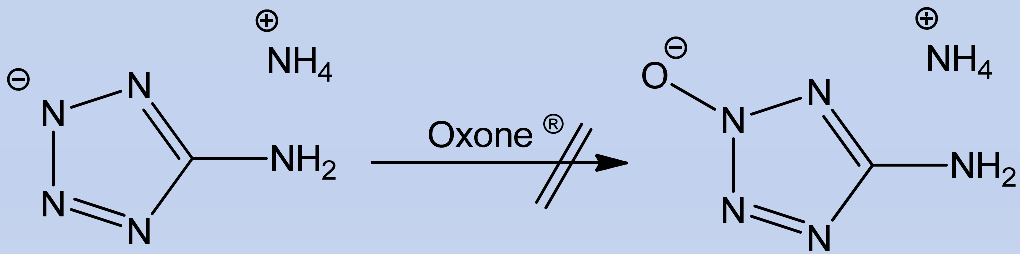




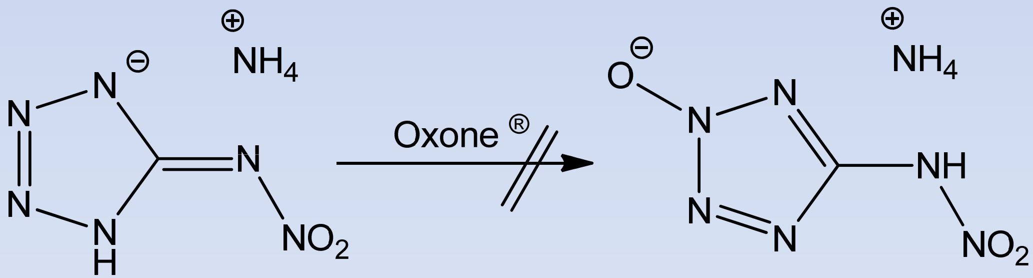
	NH_4-AzTz	NH_4-AzTzX
Formula	$[NH_4][CN_7]$	$[NH_4][CN_7O]$
FW [g mol^{-1}]	128.12	144.13
IS [J]	< 1	1
FS [N]	5	10
ESD-test [J]	10	30
N [%]	87.48	77.76
Ω [%]	-50.0	-33.31
$T_{dec.}$ [°C]	157	151
Density [g cm^{-3}]	1.61	1.69
$\Delta_f H_m°$ / kJ mol^{-1}	540	534
$\Delta_f U°$ / kJ kg^{-1}	4336	3817
$-\Delta_E U°$ [kJ kg^{-1}]	4765	5667
T_E [K]	3382	3960
p_{C-J} [kbar]	273	325
D [m s^{-1}]	8471	8930
Gas vol. [L kg^{-1}]	819	830

Limits of N-oxidation

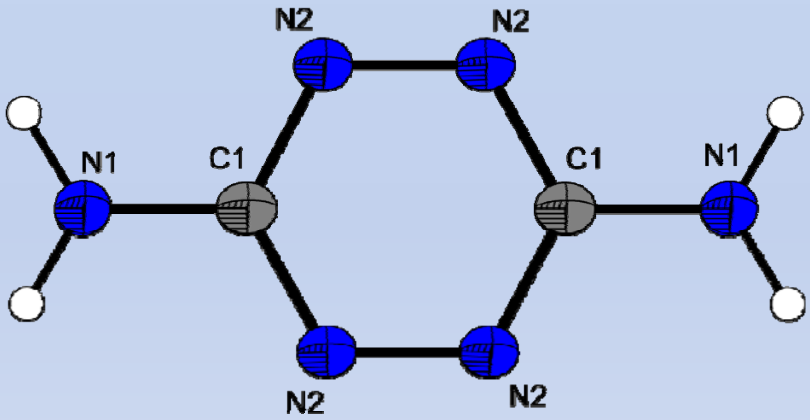
5-Aminotetrazole:



5-Nitriminotetrazole:

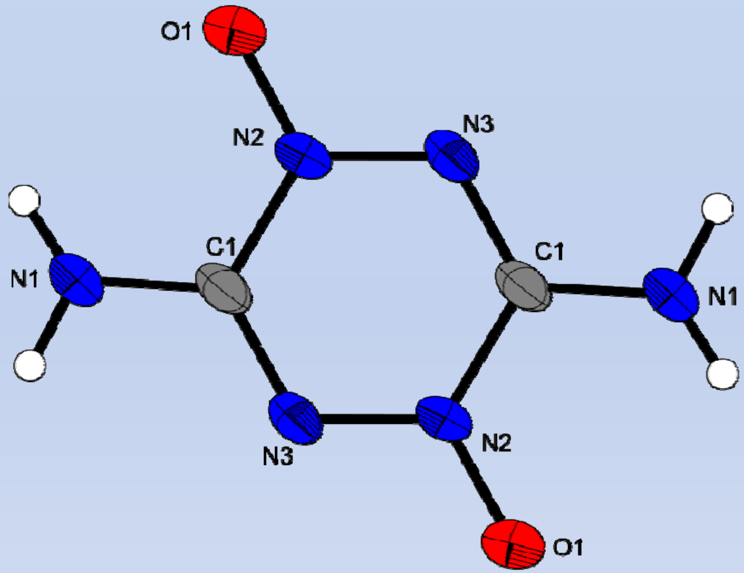


Diaminotetrazine vs. Diaminotetrazine-di-N-oxide



1.624 g cm^{-3}

ΔH_f = 311 kJ mol^{-1}
D = 7662 m s^{-1}

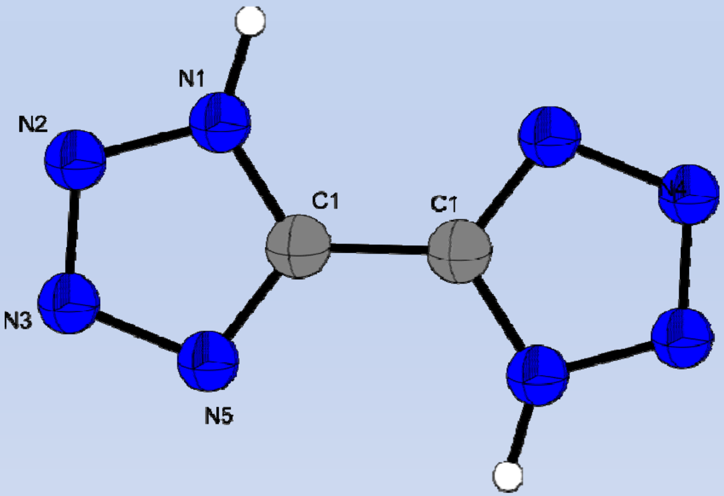


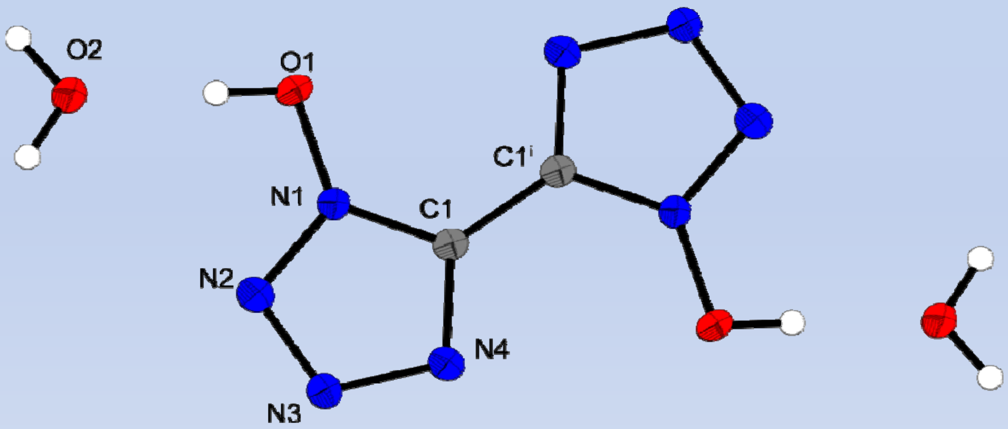
1.875 g cm^{-3}

ΔH_f = 251 kJ mol^{-1}
D = 8991 m s^{-1}
T_{dec} = 213°C

M.D. Coburn, M. A. Hiskey, K.-Y. Lee, D. G. Ott, M. M. Stinecipher, J. Heterocyclic Chem. 1993, 30, 1593.

5,5-Bistetrazole vs. 5,5-Bis-1-hydroxytetrazole dihydrate





1.738 g cm^{-3}
T_{dec} = 252°C

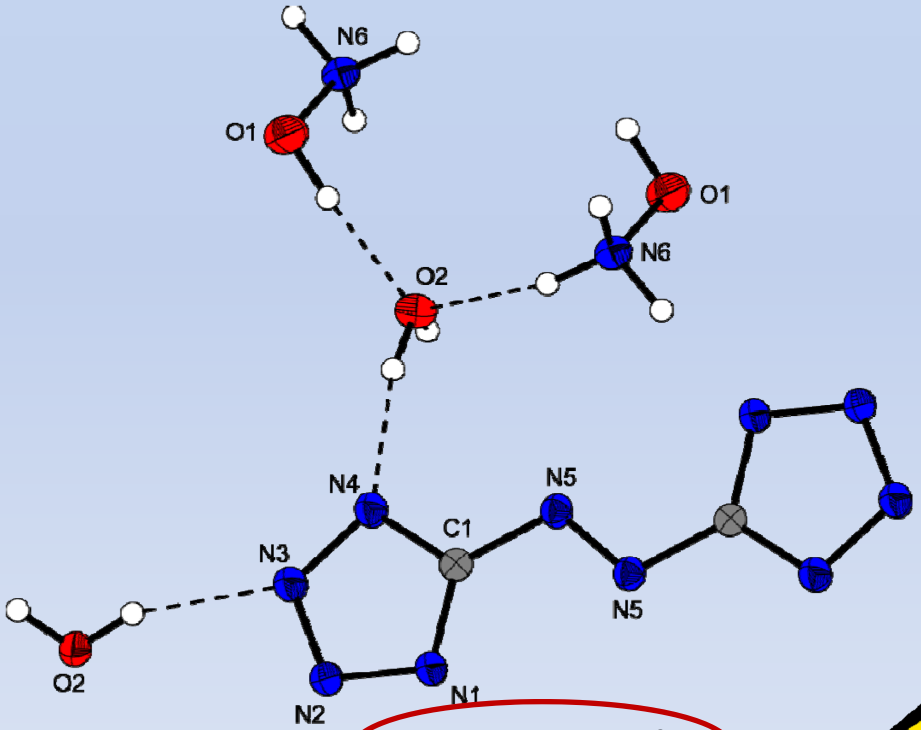
ΔH$_f$ = 564 kJ mol^{-1}
D = 8224 m s^{-1}

1.811 g cm^{-3}
T_{dec} = 214°C

ΔH$_f$ = 114 kJ mol^{-1}
D = 8763 m s^{-1}

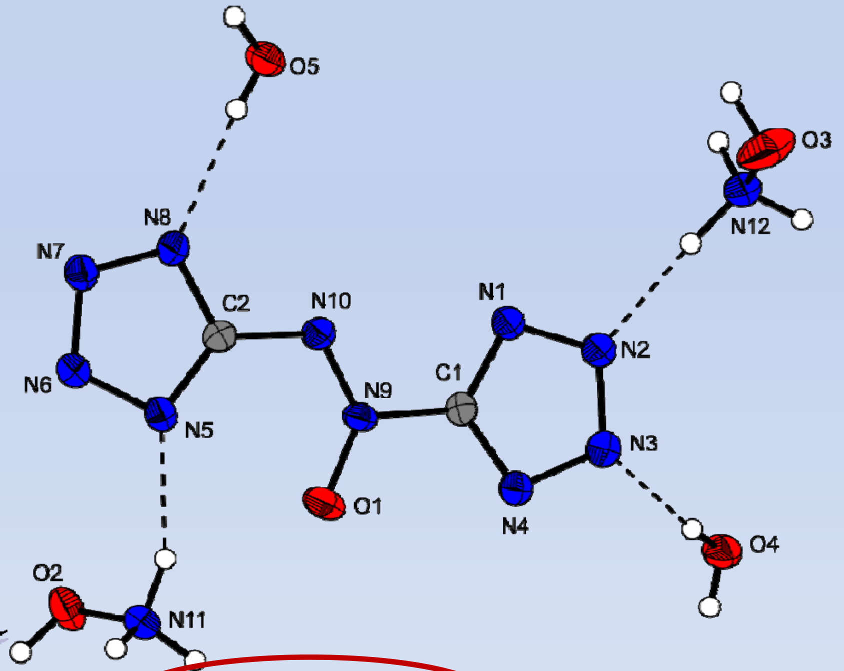
P. J. Steel, *J. Chem. Cryst.* **1996**, *26*, 399-402.

Hydroxylammonium 5,5‘-Azotetrazolate vs. Hydroxylammonium 5,5‘-Azoxy-tetrazolate



1.615 g cm^{-3}

ΔH_f = 156 kJ mol^{-1}
D = 8295 m s^{-1}

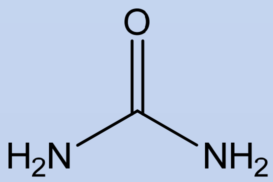


1.596 g cm^{-3}

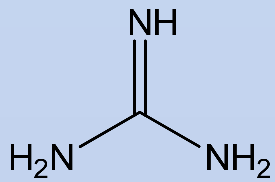
ΔH_f = 132 kJ mol^{-1}
D = 8294 m s^{-1}

II. The Amide Moiety in Energetics

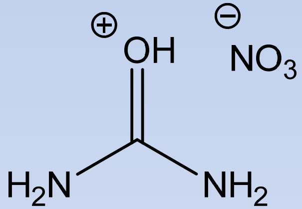
The Amide Moiety in Energetics



ρ = **1.32 g cm^{-3}**

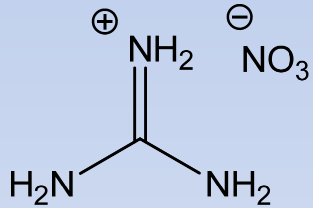


ρ = **1.29 g cm^{-3}**

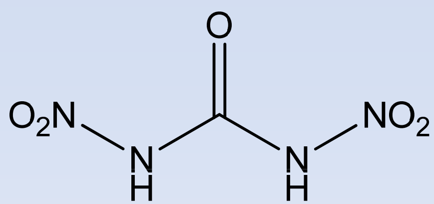


ρ = **1.68 g cm^{-3}**

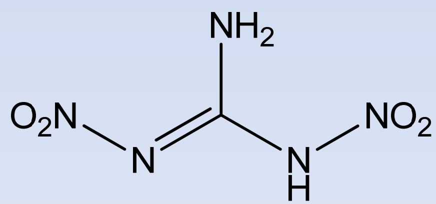
Densities



ρ = **1.41 g cm^{-3}**

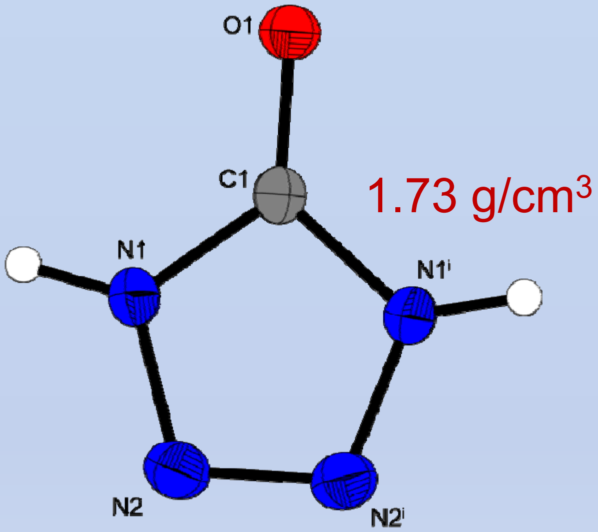


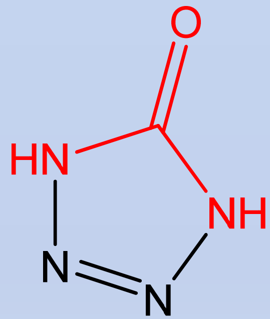
ρ = **2.01 g cm^{-3}**

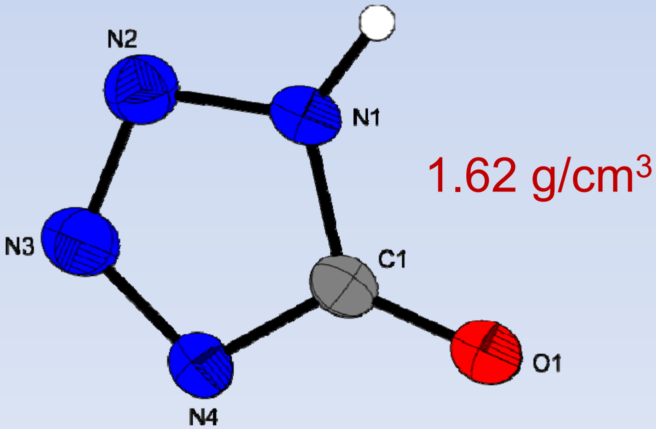


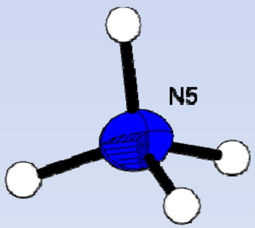
ρ = **1.88 g cm^{-3}**

5-Oxotetrazole



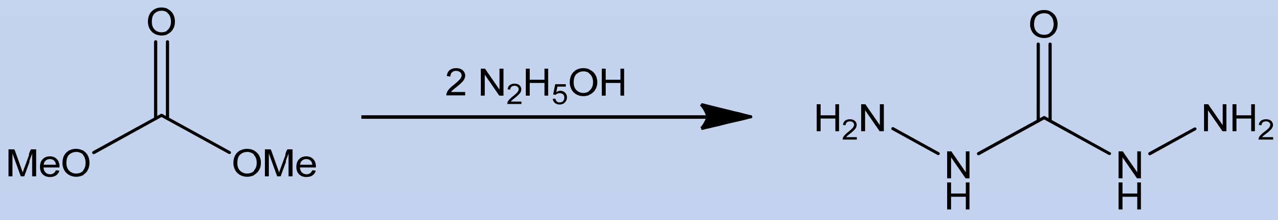




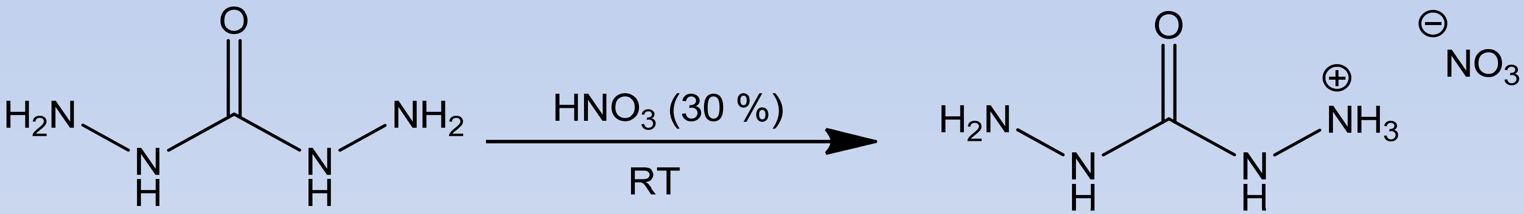


	H_2OTz	NH_4HOTz
Formula	CH_2N_4O	CH_5N_5O
FW [g mol^{-1}]	86.05	103.08
Impact sensitivity [J]	>40	>40
Friction sensitivity [N]	360	>360
ESD-test [J]	0.6	1.5
N [%]	65.11	67.94
Ω [%]	-37.18	-54.32
$T_{dec.}$ [°C]	239	205
Density [g cm^{-3}]	1.699	1.618
$\Delta_f H°$ / kJ mol^{-1}	-2.2	101.1
$\Delta_f U°$ / kJ kg^{-1}	74	1112.5
$-\Delta_E U°$ [kJ kg^{-1}]	2850	3851
T_E [K]	2544	2703
$p_{C\text{-}J}$ [kbar]	204	224
D [m s^{-1}]	7356	7902
Gas vol. [L kg^{-1}]	779	872

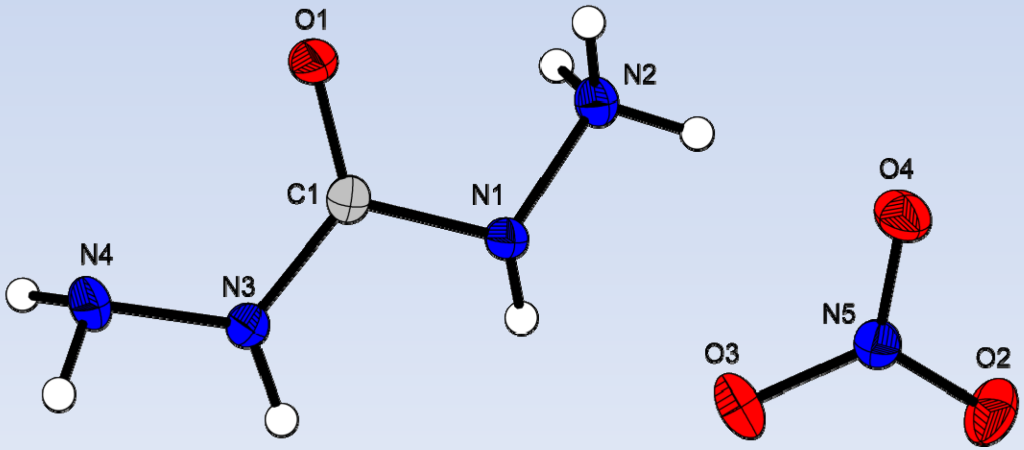
Diaminouronium Nitrate



Diaminourea



Diaminouronium Nitrate



N. Fischer, T.M. Klapötke, J. Stierstorfer, Propellants, Explosives, Pyrotech. **2011**, in press.

Diaminouronium Nitrate

	$DAU\text{-}NO_3$	RDX
IS / J	10	7
FS / N	288	120
ESD / J	0.6	0.15
N / %	45.74	37.8
Ω / %	-15.67	–21.6
$T_{Dec.}$ / °C	242	210
ρ / g cm^{-3}	1.782	1.80
$\Delta_f H_m°$ / kJ mol^{-1}	-180	70
EXPLO5 values:		
$-\Delta_{Ex}U°$ / kJ kg^{-1}	5048	6125
T_{det} / K	3397	4236
P_{CJ} / kbar	335	349
$V_{Det.}$ / m s^{-1}	8903	8748
V_o / L kg^{-1}	910	739

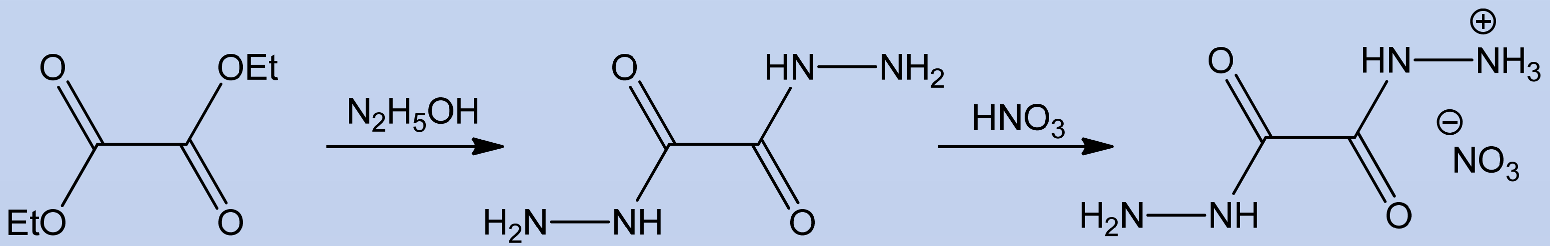
N. Fischer, T.M. Klapötke, J. Stierstorfer, Propellants, Explosives, Pyrotech. **2011**, in press.

Hot Plate Test: secondary explosive

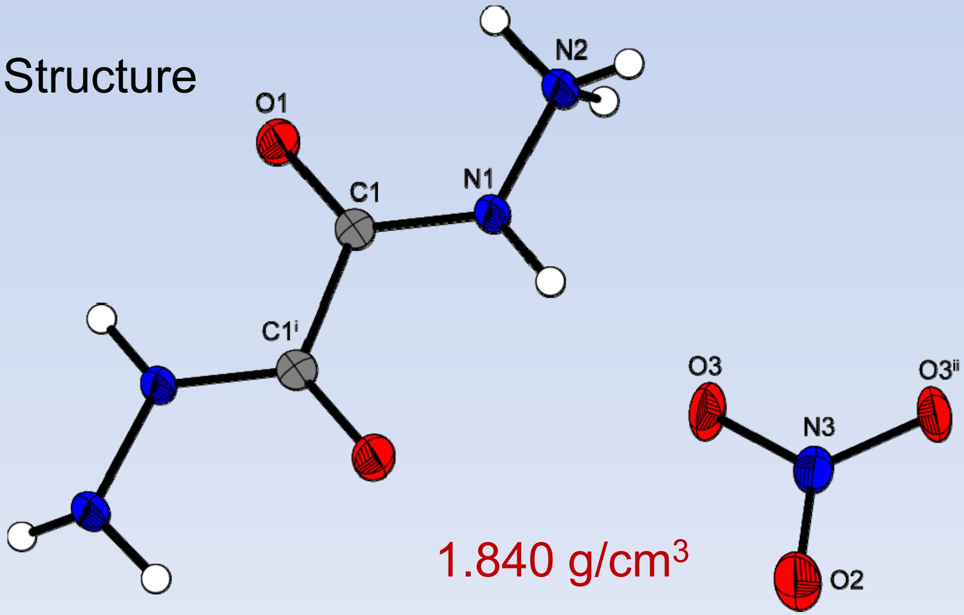
Hot Plate Test: primary explosive

Oxalylhydrazide and its Nitrate Salt

Synthesis



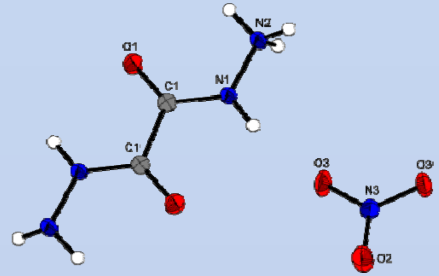
X-ray Structure



1.840 g/cm^3

Dennis Fischer, MSc thesis, LMU Munich, **2010**.

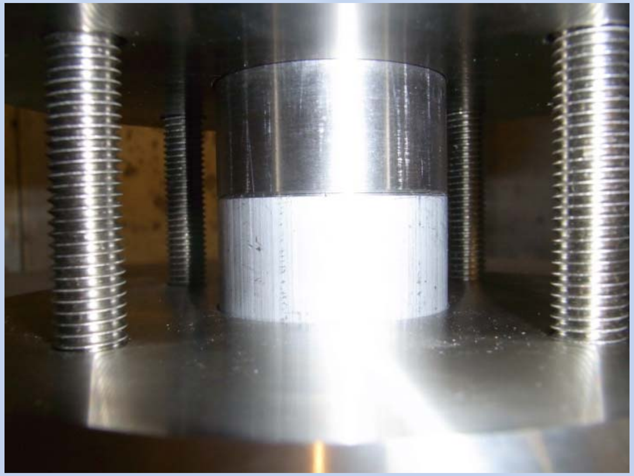
Oxalylhydrazinium Nitrate



Energetic Properties

	$OxahyNO_3$		
Formula	$C_2H_7N_5O_5$	$\Delta_f H°$ / kJ mol^{-1}	-299
Molecular Mass [g mol^{-1}]	181.11	$\Delta_f U°$ / kJ kg^{-1}	-1536
Impact sensitivity [J]	11		
Friction sensitivity [N]	>360	*calculated values using EXPLO5:* V 5.04 (V 5.03)	
ESD-test [J]	0.3	$-\Delta_E U°$ [kJ kg^{-1}]	4661 (4634)
N [%]	38.67	T_E [K]	3275 (3367)
Ω [%]	-22.1	p_{C-J} [kbar]^l	325 (313)
$T_{dec.}$ [°C]	273	D [m s^{-1}]^m	8655 (8665)
Density [g cm^{-3}]	1.84	Gas vol. [L kg^{-1}]^n	827 (849)

Overall synthetic costs on lab scale: 10 times lower than RDX !!!


	PETN	RDX	HMX	CL20	TKX50
Formula	$C_5H_8N_4O_{12}$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_6H_6N_{12}O_{12}$	
Molecular Mass [g mol^{-1}]	316.1	222.1	296.2	438.2	ca. 200 – 250
IS [J] [a]	4	7.5	7	4	20
FS [N] [b]	80	120	112	48	120
ESD-test [J] [c]	0.1	0.2	0.2	-	0.1
N [%] [d]	17.72	37.8	37.8	38.3	59.3
Ω [%] [e]	-10.12	-21.6	-21.6	-11.0	-27.1
$T_{dec.}$ [°C] [f]	150	210	285	195	221
Density [g cm^{-3}] [g]	1.778	1.820	1.905	2.038	1.915
$\Delta_f U°$ / kJ kg^{-1} [h]	-1611	417	353	982	2010
$-\Delta_E U°$ [kJ kg^{-1}] [i]	6190	6125	6063	6473	6029
T_E [K] [j]	4306	4236	4117	4654	3957
$p_{C\text{-}J}$ [kbar] [k]	320	348	392	446	425
D [m s^{-1}] [l]	8320	8748	9058	9342	9687
Gas vol. [L kg^{-1}] [m]	688	739	734	669	846

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