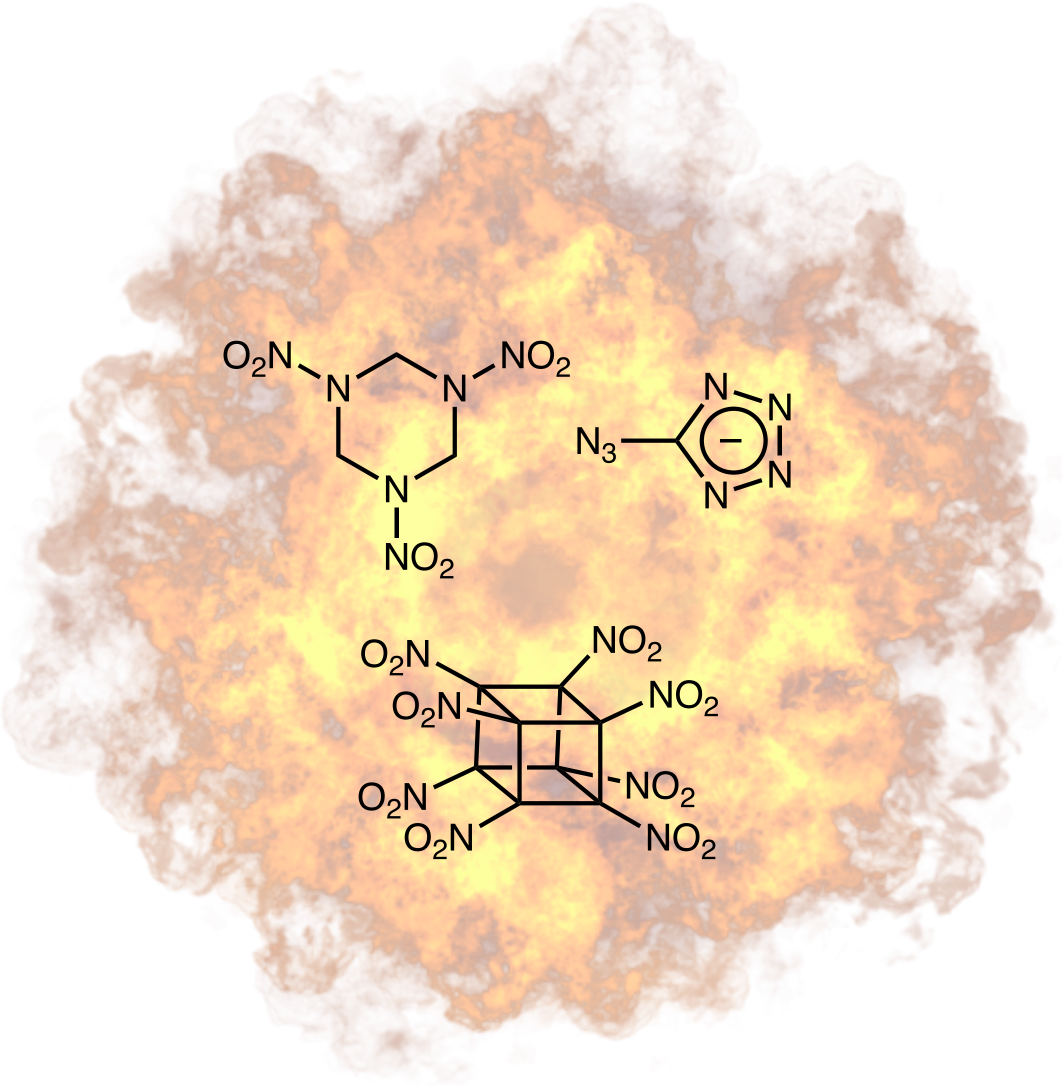
High Energy Materials



Vlad Bacauanu

MacMillan Research Group

Group Meeting

July 25th, 2019

What Are High Energy Materials?

high energy material (HEM) → *compound that stores chemical energy and which upon stimulation undergoes rapid decomposition with release of energy and gas*

explosives

propellants

pyrotechnics

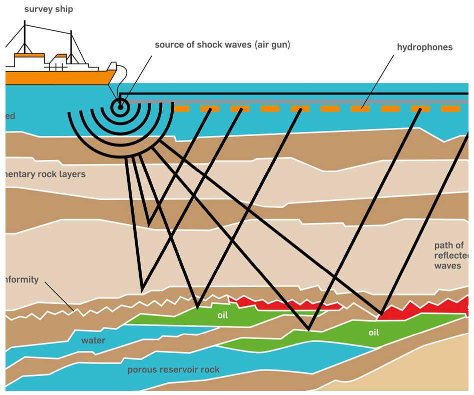
Applications of High Energy Materials

The obvious – military applications

Civil and scientific applications

mining

civil engineering



oil industry

space exploration

High Energy Materials – Outline

Generals aspects of high energy materials

Very brief history

Fundamental properties

Decomposition via deflagration or detonation

Primary vs secondary explosives

Oxygen balance

Synthesis of high energy materials

Safety precautions in HEM labs

Explosophore functional groups

Examples of synthetic approaches

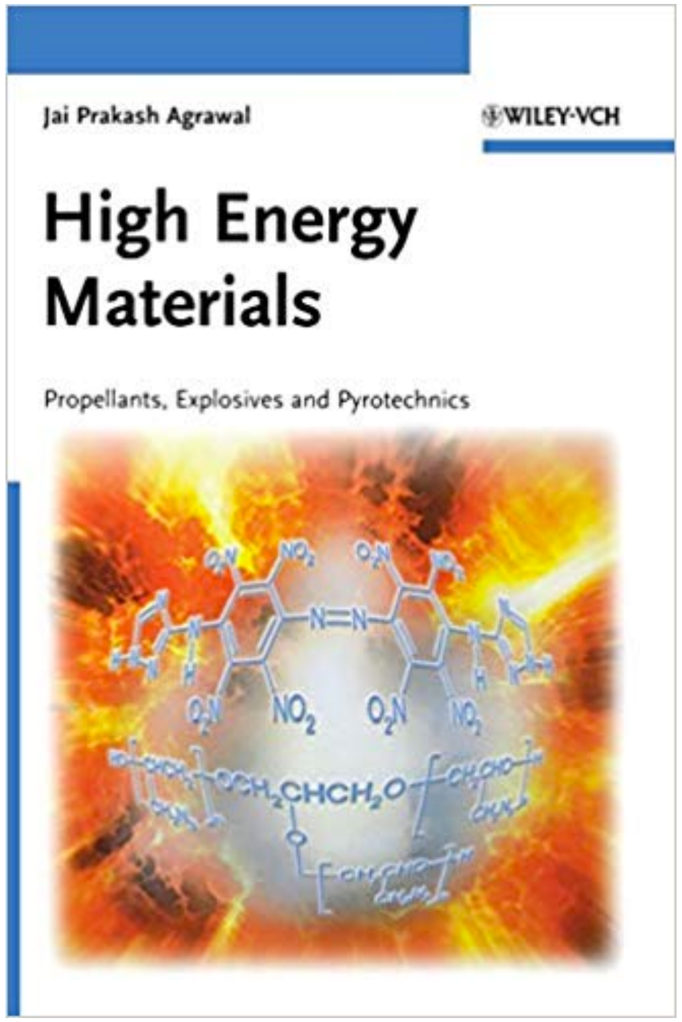
Recent avenues within the field

Nitrogen-rich molecules

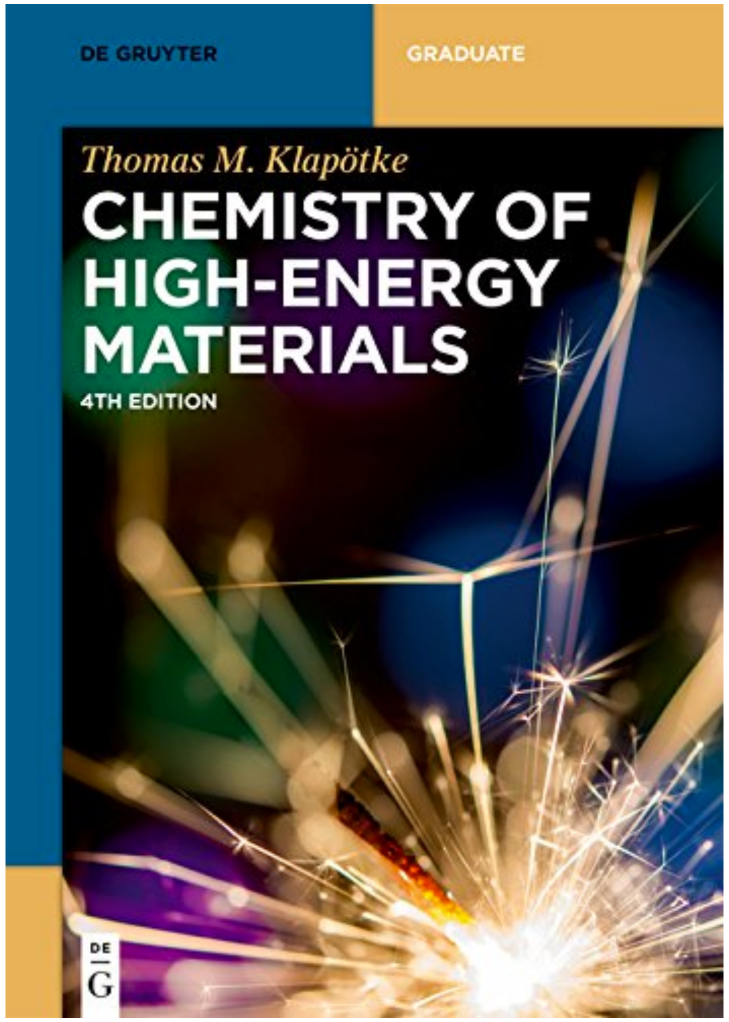
Strained energetic materials: HNIW and ONC

Exploring stereochemistry of materials

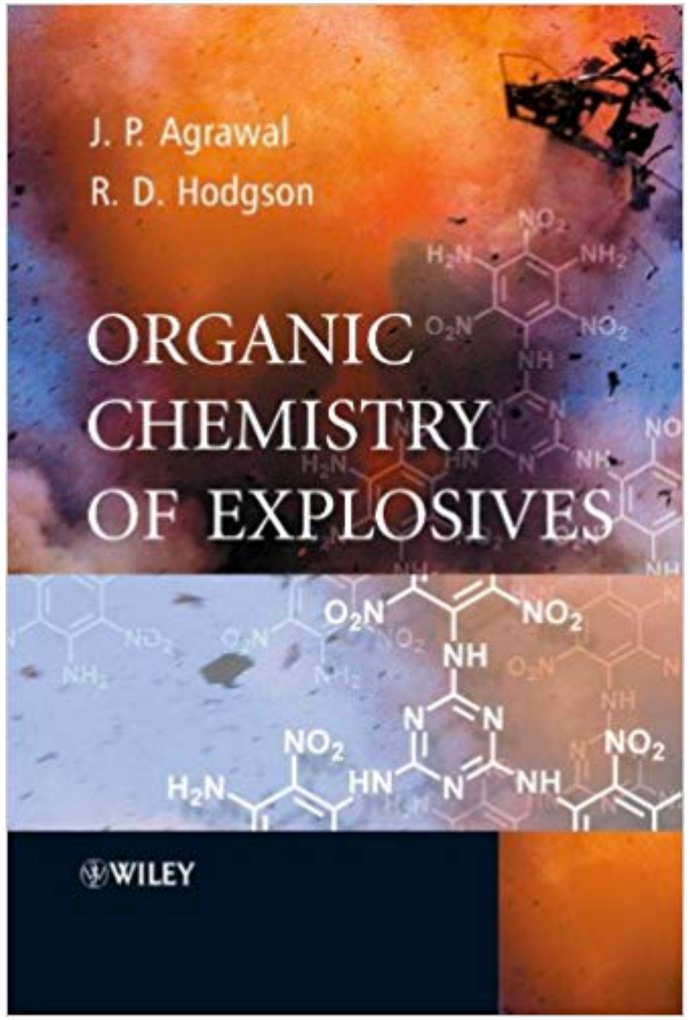
Book References for High Energy Materials



High Energy Materials
Jai P. Agrawal
1st ed. (2010)

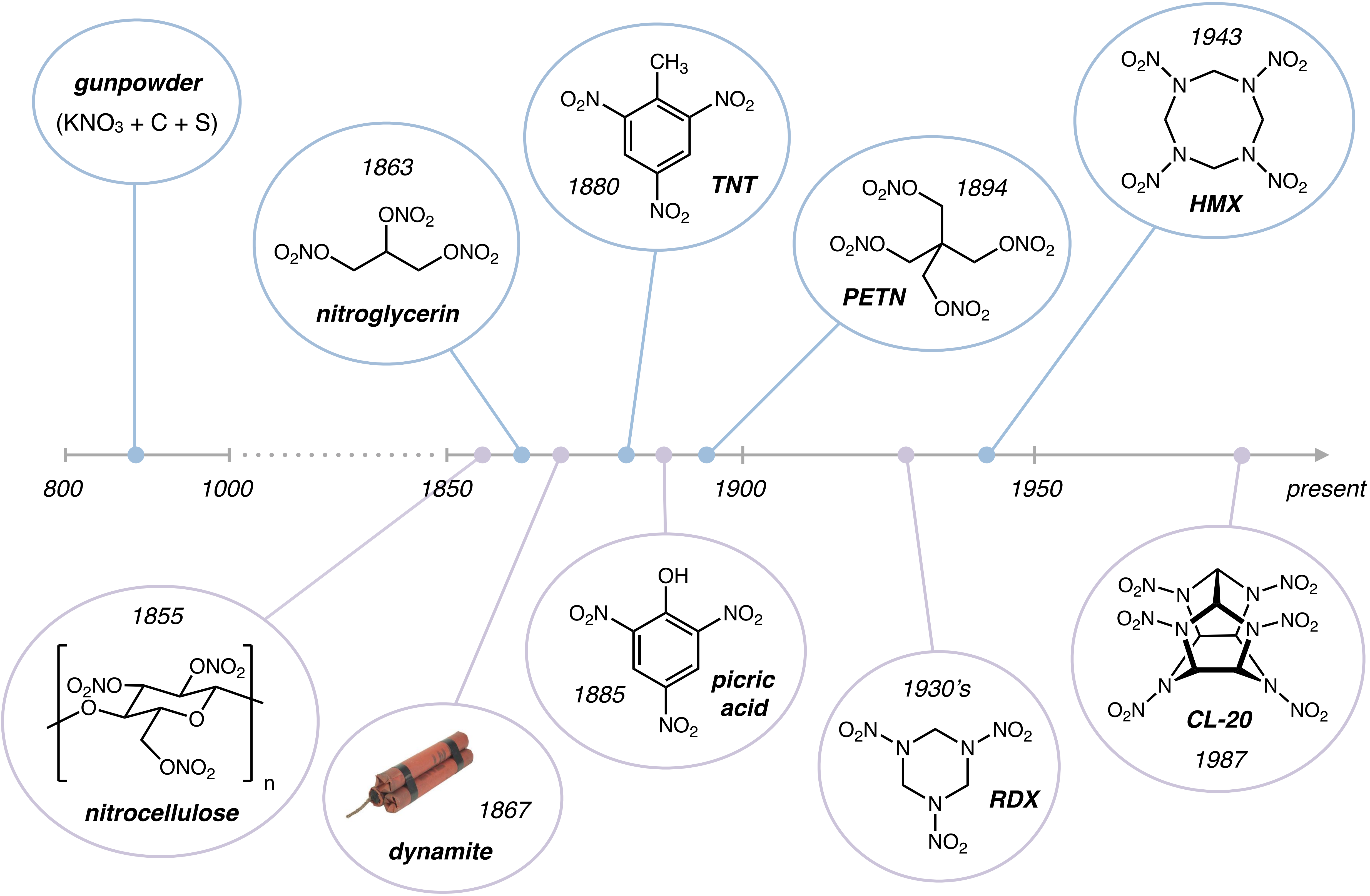


Chemistry of High-Energy Materials
Thomas M. Klapötke
4th ed. (2017)



Organic Chemistry of Explosives
Jai P. Agrawal & Robert D. Hodgson
1st ed. (2007)

History of Development of High Energy Materials



Fundamental Properties of High Energy Materials

heat of formation (ΔH_f)

$$C + H_2 + N_2 + O_2 \xrightarrow{\Delta H_f} \text{explosive}$$

heat of explosion (Q)

$$\text{explosive} \xrightarrow{Q} \text{explosion products } (CO_2, CO, H_2O, N_2, \text{etc.})$$

density of material (ρ)

volume of gases released (V)

velocity of detonation (VOD)

speed with which detonation wave propagates

detonation pressure (DP)

peak pressure in detonation wave

explosive power = Q** x **V

"ability of explosive to do useful work"

brisance ~ ρ** x **VOD^2

shattering power of an explosive

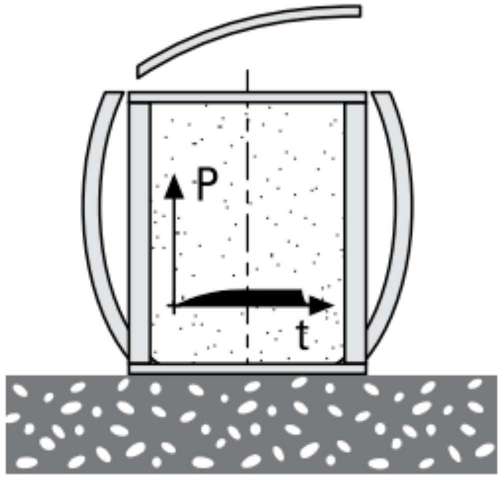
specific impulse (I_{sp})

total impulse delivered by a unit of propellant

sensitivity

to **heat**, shock, friction, electrical discharge, etc.

Deflagration vs. Detonation in High Energy Materials



Deflagration – propellants

very rapid burning

subsonic propagation wave

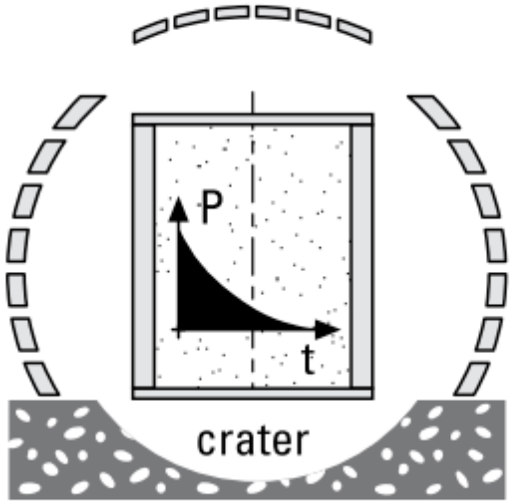
controlled, regular process

**deflagration
to
detonation**

transition

(always for explosives;

avoid for propellants)



Detonation – explosives

extremely rapid decomposition

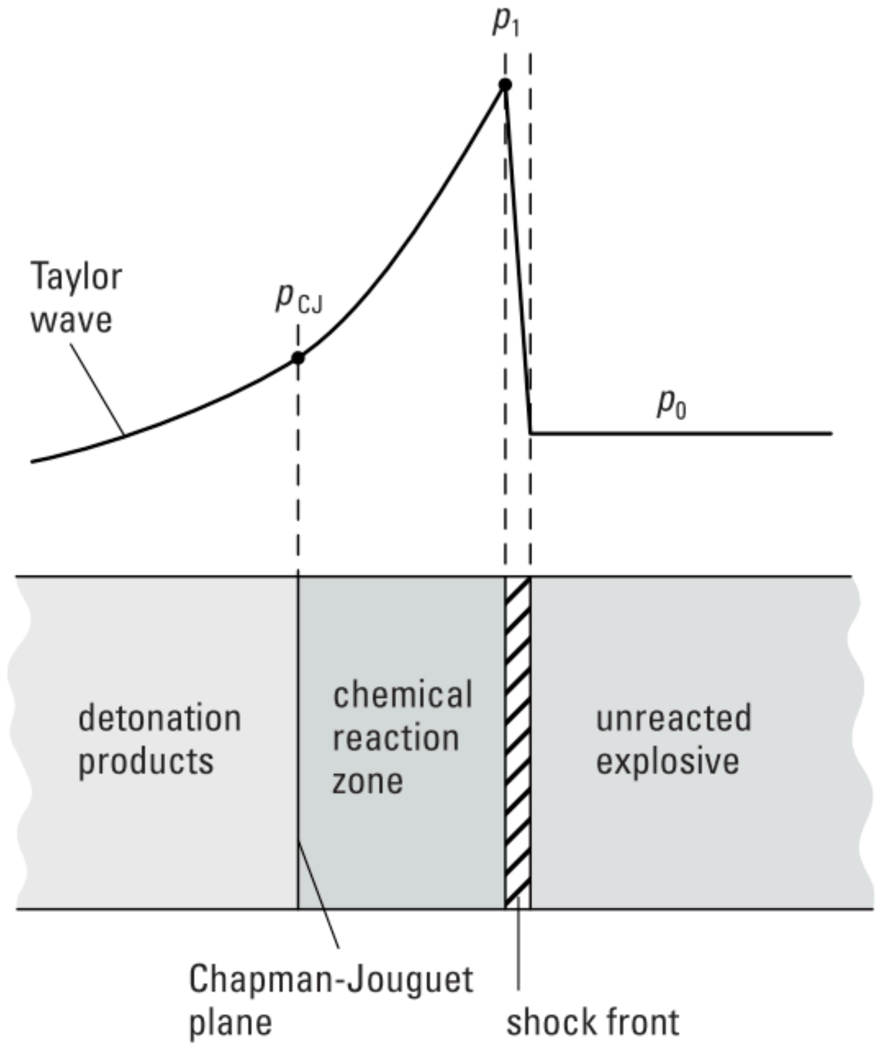
supersonic propagation wave

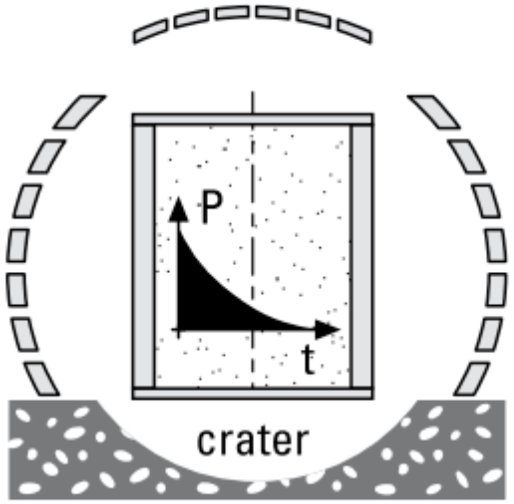
uncontrollable past initiation

Tab. 1.5: Reaction types of an energetic material with $Q_{ex} = 1000$ kcal kg^{-1}.

reaction type	**reaction speed / m s^{-1}**	**mass flow / m^3 s^{-1}**	**gaseous products / m^3 s^{-1}**	**reaction time / s m^{-3}**
Combustion	10^{-3}–10^{-2}	10^{-3}–10^{-2}	1–10	10^{2}–10^{3}
Deflagration	10^{2}	10^{2}	10^{5}	10^{-2}
Detonation	10^{4}	10^{4}	10^{7}	10^{-4}

Deflagration vs. Detonation in High Energy Materials





Detonation – explosives

extremely rapid decomposition

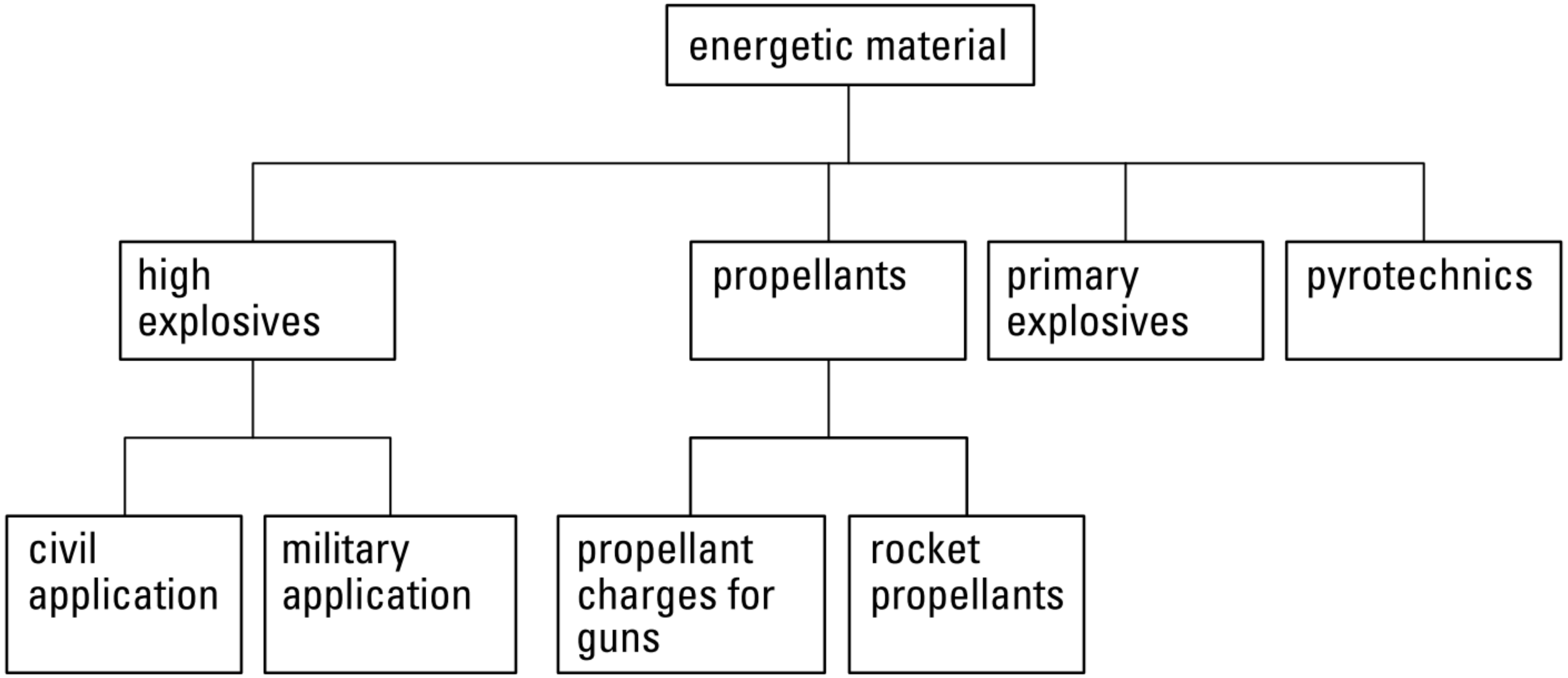
supersonic propagation wave

uncontrollable past initiation

how does a detonation wave propagate?

hot gases released → high pressure shock front → material is compressed → material heats up → material decomposes with release of gas

Classification of High Energy Materials



energetic material

high explosives

propellants

primary explosives

pyrotechnics

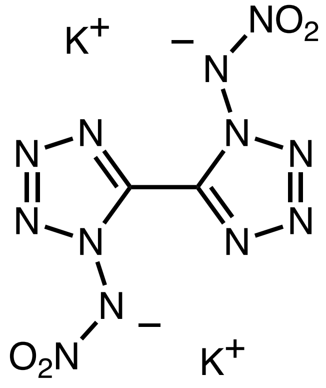
civil application

military application

propellant charges for guns

rocket propellants

$Hg(CNO)_2$ $Pb(N_3)_2$



Primary explosives

very sensitive to stimuli

rapid detonation

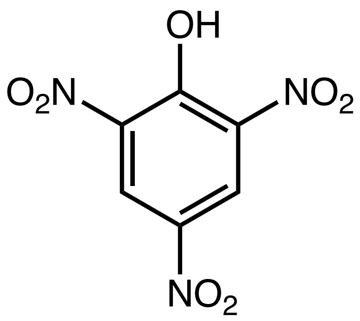
inititate decomposition of 2° explosive or propellant

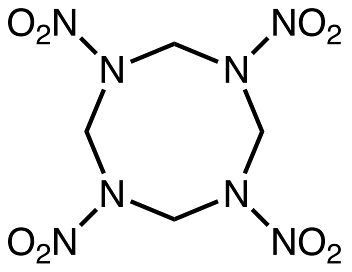
Secondary (high) explosives

relatively insensitive

high performance

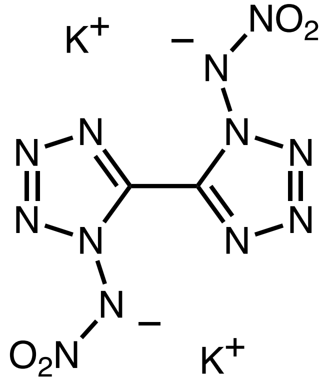
main load of explosive ensemble





Classification of High Energy Materials

$Hg(CNO)_2$ $Pb(N_3)_2$



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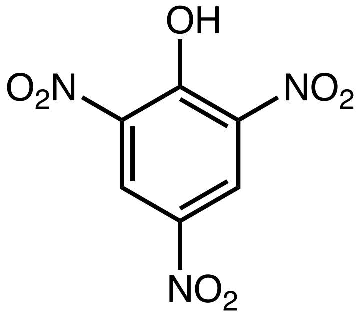
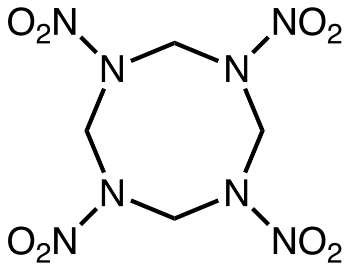
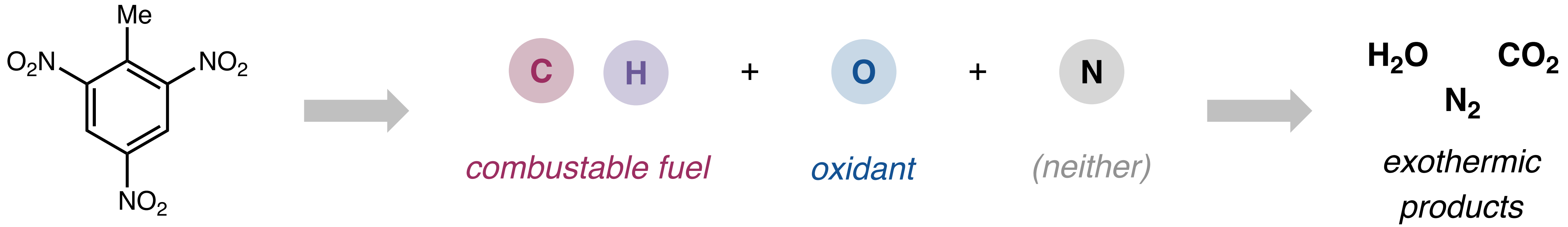




	typical primary explosives	**$Pb(N_3)_2$**	**typical secondary explosives**	**RDX**
sensitivity data				
impact sensitivity / J	≤ 4	2.5–4	≥ 4	7.4
friction sensitivity / N	≤ 10	< 1	≥ 50	120
ESD / J	0.002–0.020	0.005	≥ 0.1	0.2
performance data				
detonation velocity / m s^{-1}	3500–5500	4600–5100	6500–9000	8750
detonation pressure / kbar		343	210–390	347
heat of explosion / kJ kg^{-1}	1000–2000	1639	5000–6000	5277 ($H_2O(g)$)

Traditional Approach To Explosives Design



combustable fuel

oxidant

(neither)

exothermic products

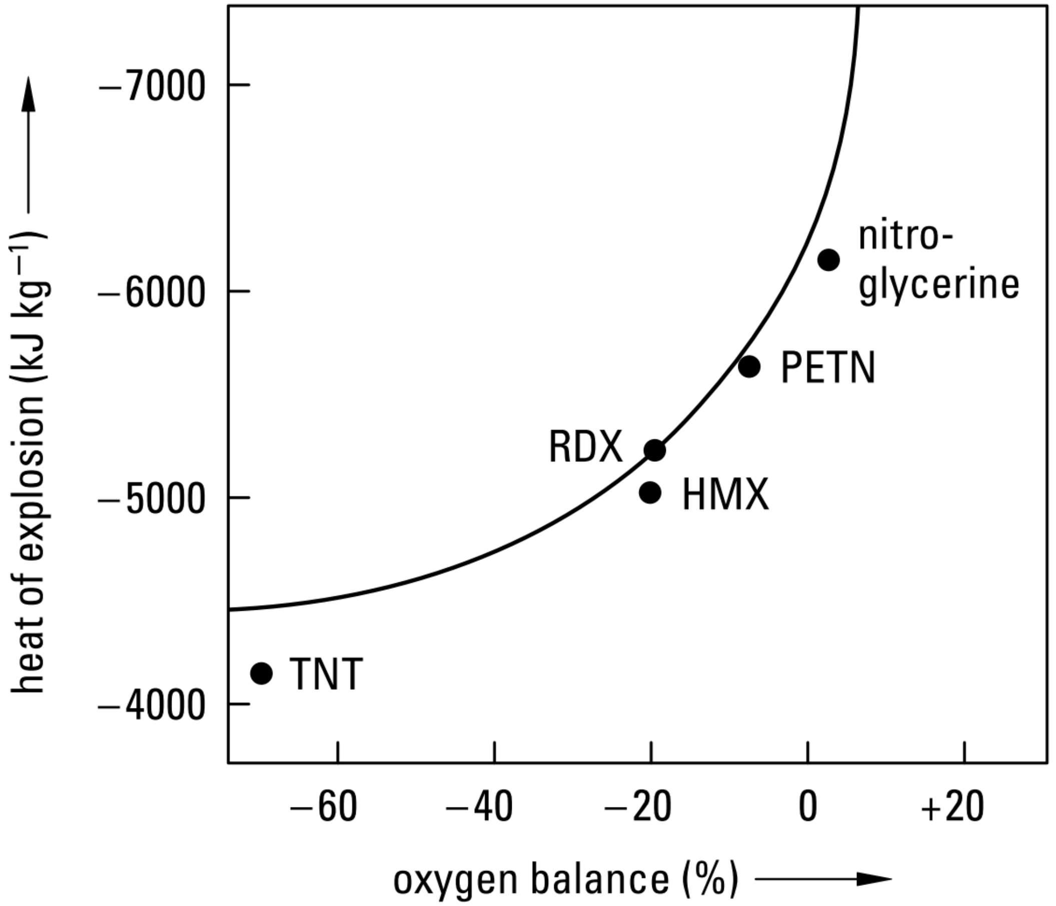
an explosive is a mixture of fuel and oxidant – balancing the two is ideal

Ω oxygen balance

for generic $C_aH_bN_cO_d$

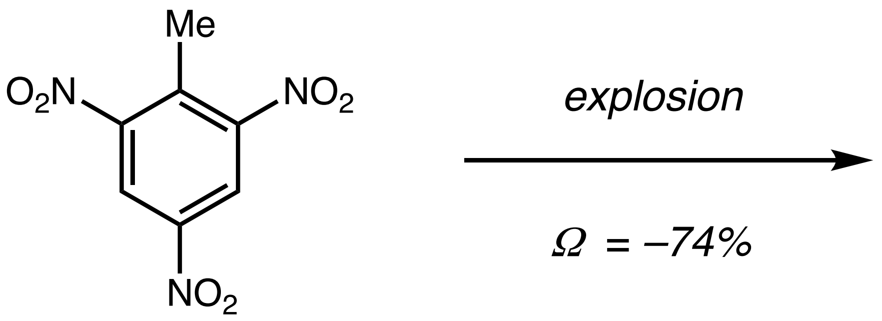
$$\Omega = \Omega_{CO2} = \frac{(d - 2a - b/2) \times 1600}{M}$$

$$\Omega_{CO} = \frac{(d - a - b/2) \times 1600}{M}$$



Importance of Having Good Oxygen Balance for Secondary Explosives

How is oxygen balance important?



1 CO_2
3 CO **3 C**

\+

1 H_2O
1.5 H_2

\+

1.5 N_2

incomplete oxidation of C,H backbone

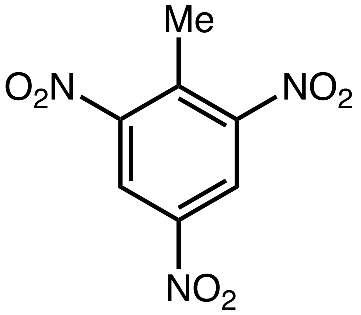
wasted potential energy of the fuel

enthalpy of formation

$$\Delta H_{f,\mathrm{CO2}} \ll \Delta H_{f,\mathrm{CO}} < \Delta H_{f,\mathrm{C}} = 0$$

$$\Delta H_{f,\mathrm{H2O}} < \Delta H_{f,\mathrm{H2}} = 0$$

Ideal explosion for TNT

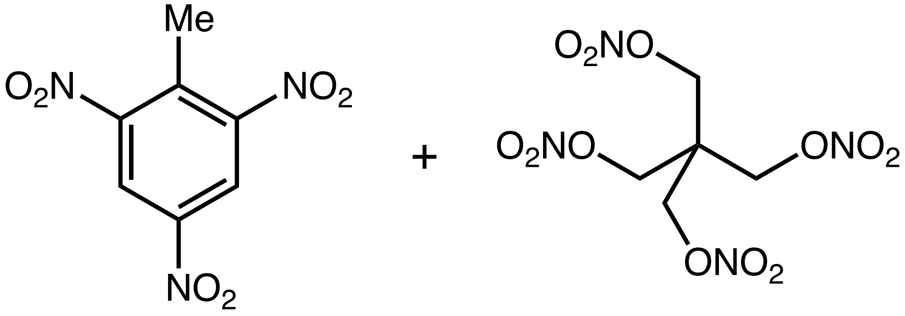


\+ 5.25 O_2

oxidizer deficit

7 CO_2 + 2.5 H_2O + 1.5 N_2

How do I fix my bad OB?

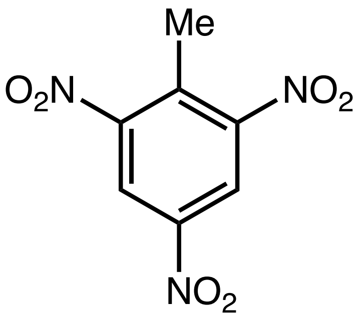


bad Ω

good Ω

issues overcome by formulation with others HEMs

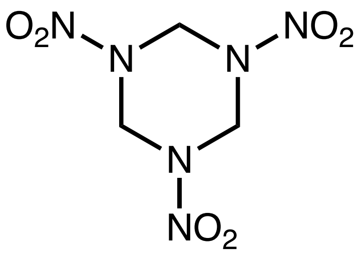
Most Commonly Used Explosives in Military



TNT

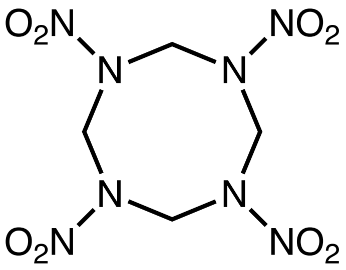
trinitrotoluene (1880)

stable, cheap, melt-castable



RDX

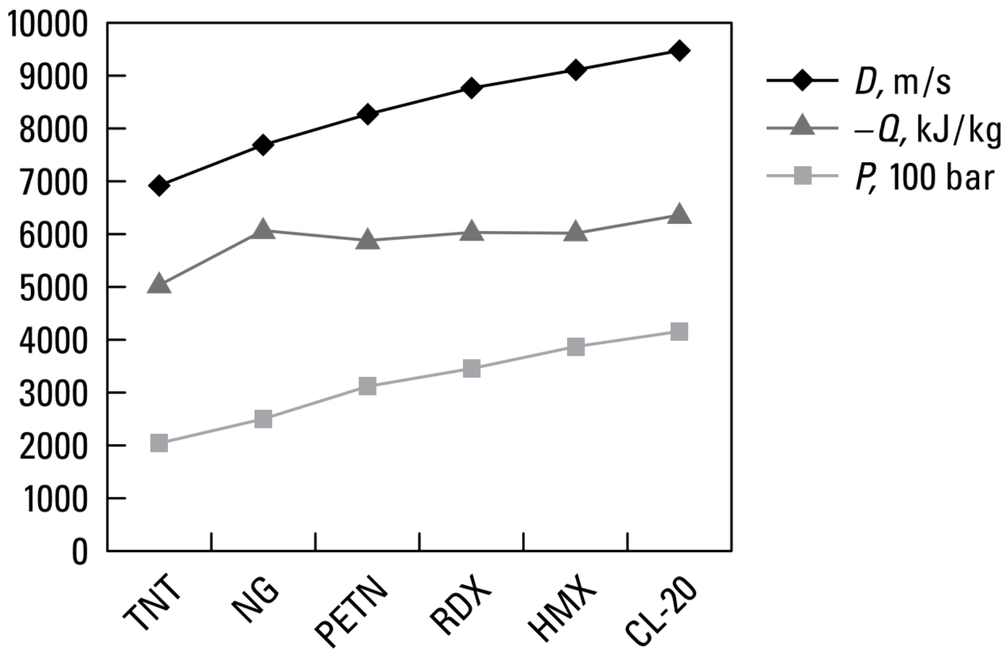
research department explosive (1930's)



HMX

high melting explosive (1943)

stable, more expensive, very powerful



next generation
high-performance explosive?

⬇

organic synthesis!

Safety Precautions for High Energy Materials

Safety precautions in HEM labs

first synthesis on 250 mg scale or less

keep distance from experiments (tongs, clamps)

protective equipment must be used

protective gloves

Kevlar wrist protectors

full-visor face shield

ear protectors

protective leather or Kevlar jacket

Student in the Klapötke group

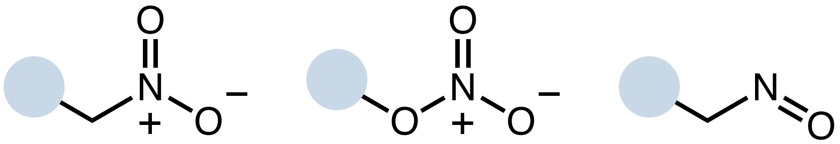
Safety is not a joke – refusing to follow the safety guidelines gets you fired!

Kemsley, J. *Chem. Eng. News* **2008**, *86*, 22

Explosophores – Common Functional Groups in HEM

V. Plets' theory of explosophores (1953) — several common functional groups in explosives

nitro, nitrate, and nitroso

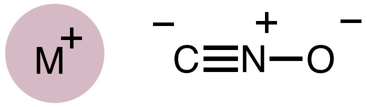


azo and azide

N-haloamino

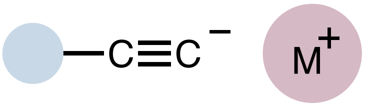
chlorate and perchlorate

fulminates



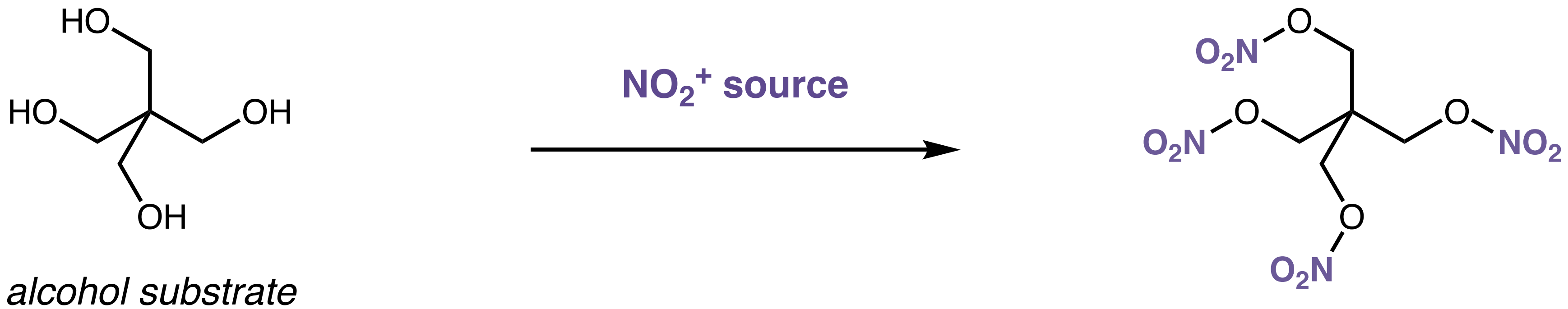
peroxide and ozonide

metal acetylides



Synthesis of Nitrate Esters and Nitramines

Direct nitration of alcohols



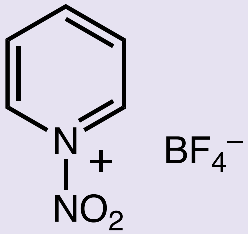
alcohol substrate

100% HNO_3

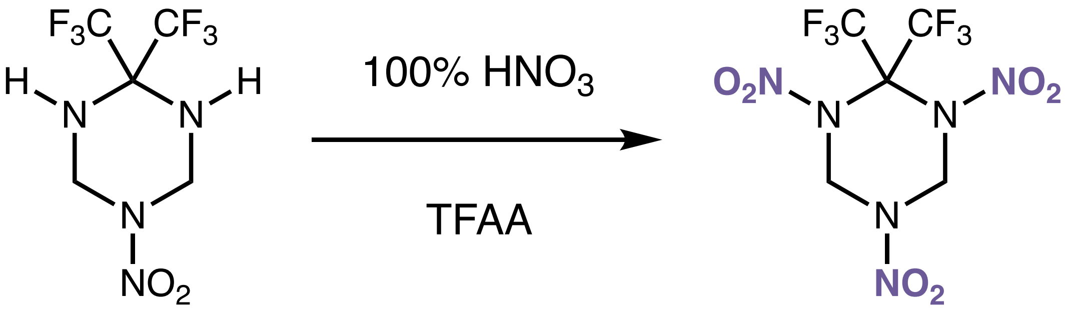
conc. HNO_3
w/ conc. H_2SO_4

N_2O_5
$[NO_2]^+ [NO_3]^-$

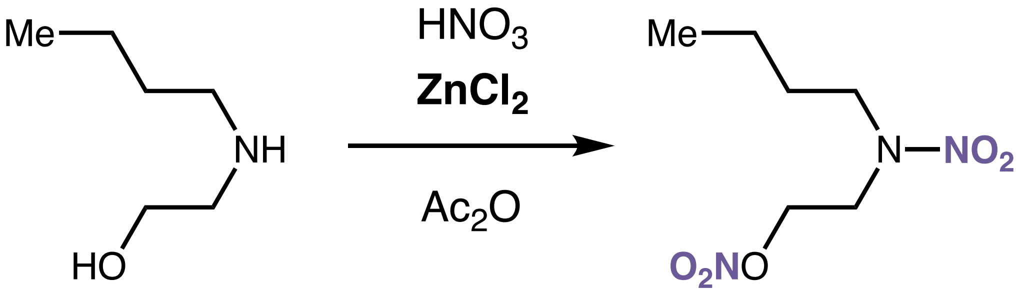
NO_2BF_4



Direct nitration of amines



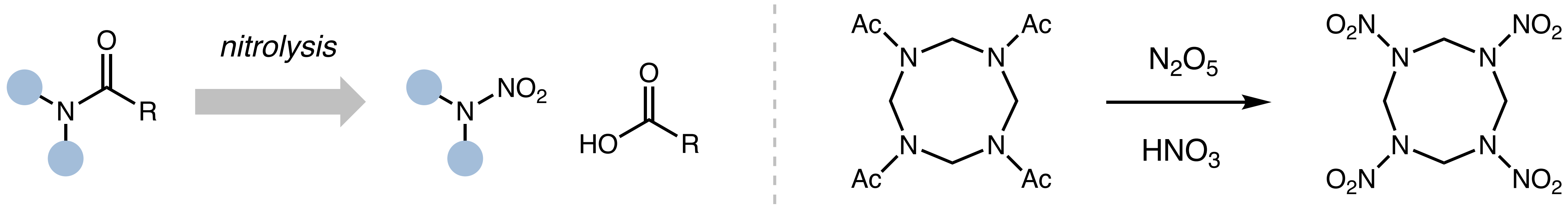
acidic conditions work best for non-basic amines



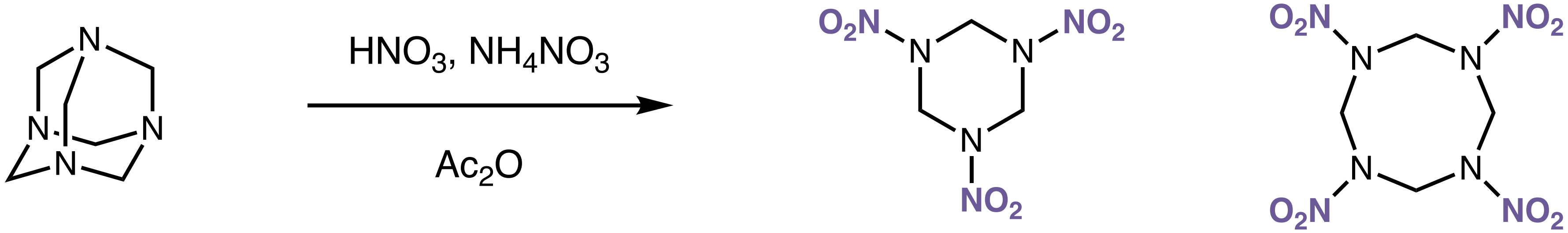
proceeds via N-chloro intermediate (from AcOCl)

Synthesis of Nitrate Esters and Nitramines

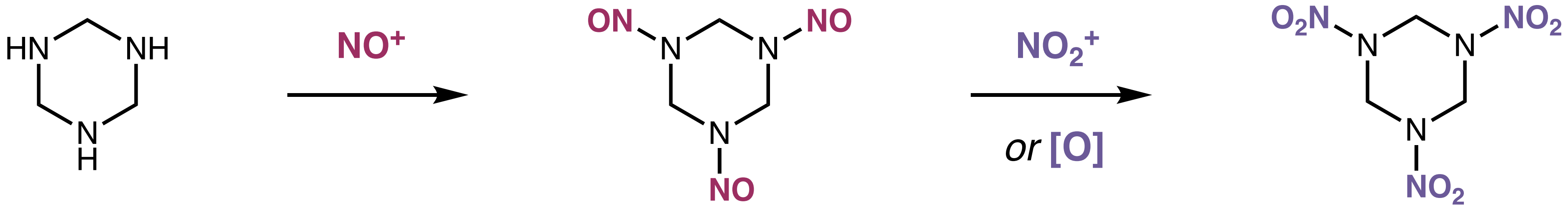
Tertiary amides undergo nitrolysis readily to form nitramines



N-alkyl bonds can also undergo nitrolysis to form nitramine products

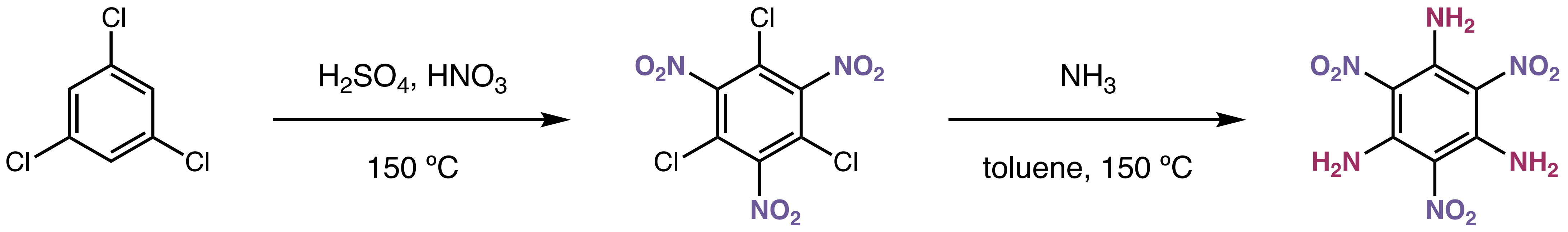


Nitrosation followed by oxidation or exchange nitration is also a viable strategy



Synthesis of Aromatic and Aliphatic C–NO_2 Compounds

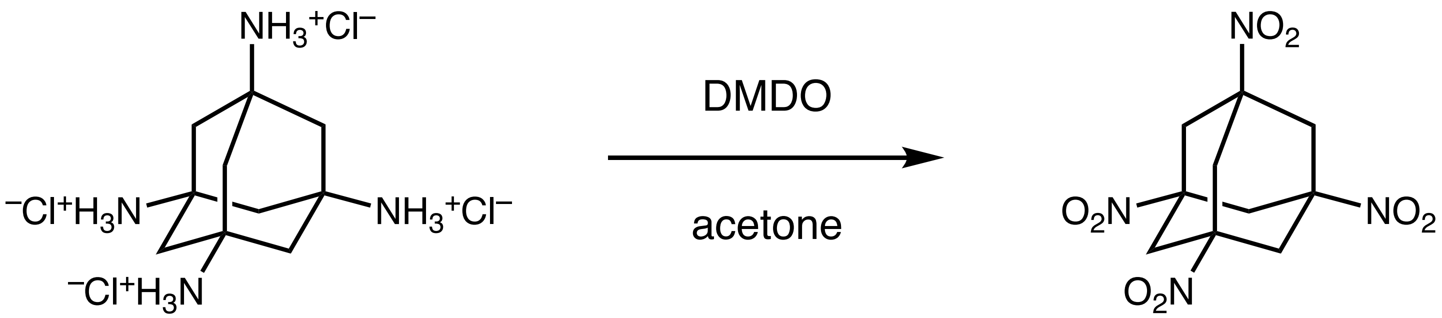
Aromatic C–NO_2 products



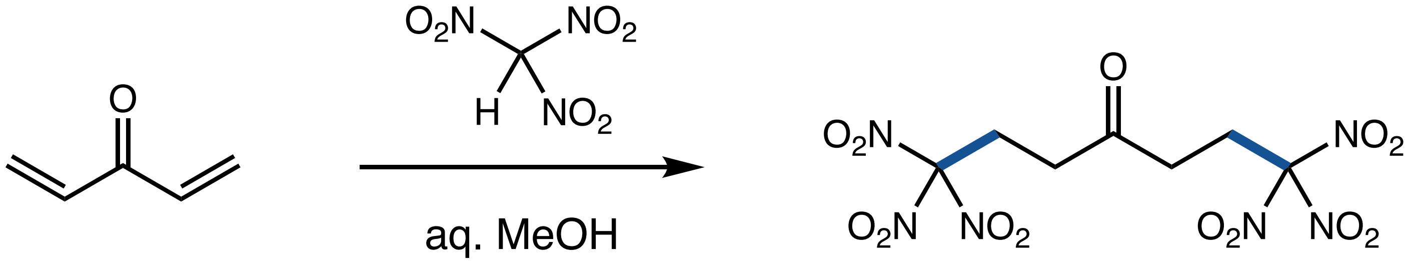
electrophilic aromatic substitution is a staple

subsequent S_NAr is facile and enabling

Aliphatic C–NO_2 products

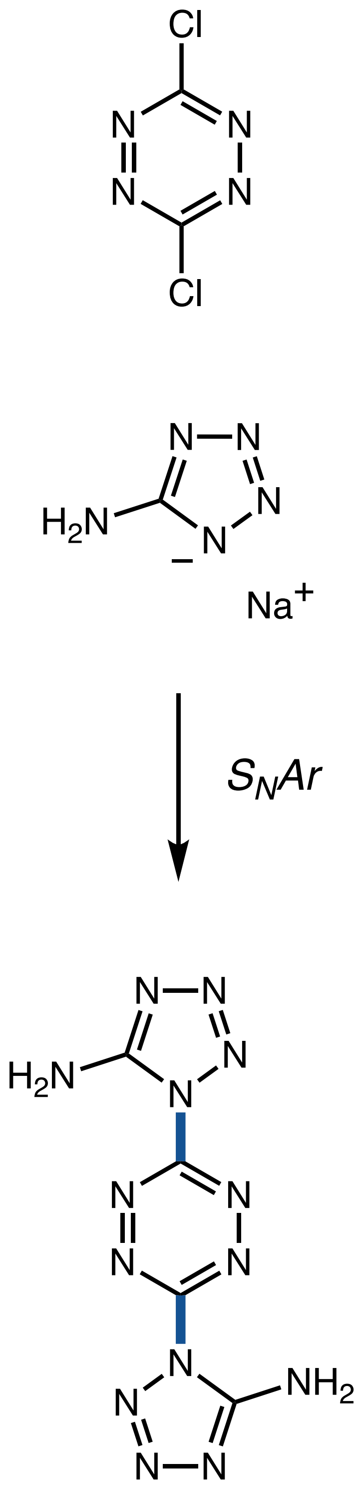


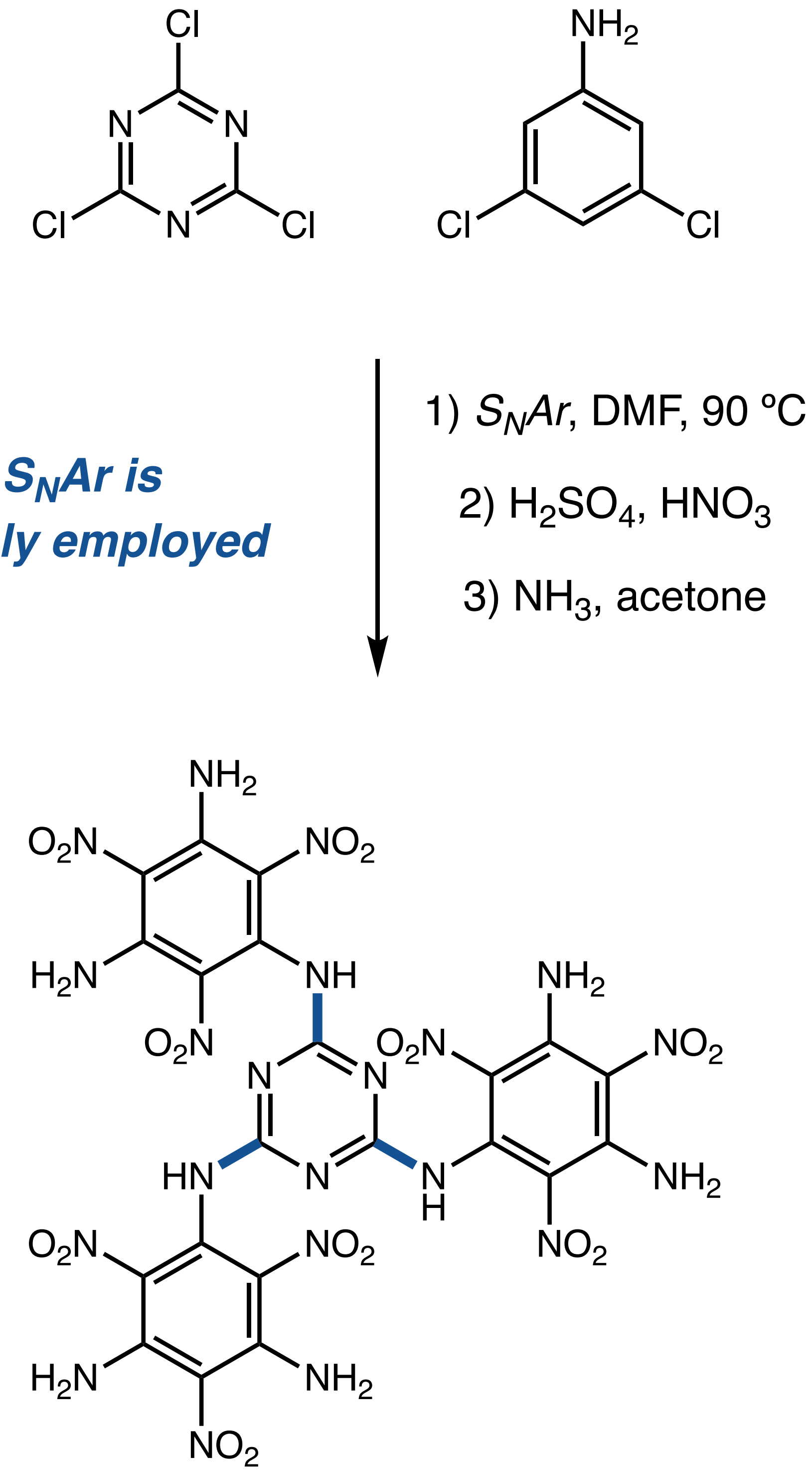
oxidation of amines with various reagents



additions of nitro nucleophiles

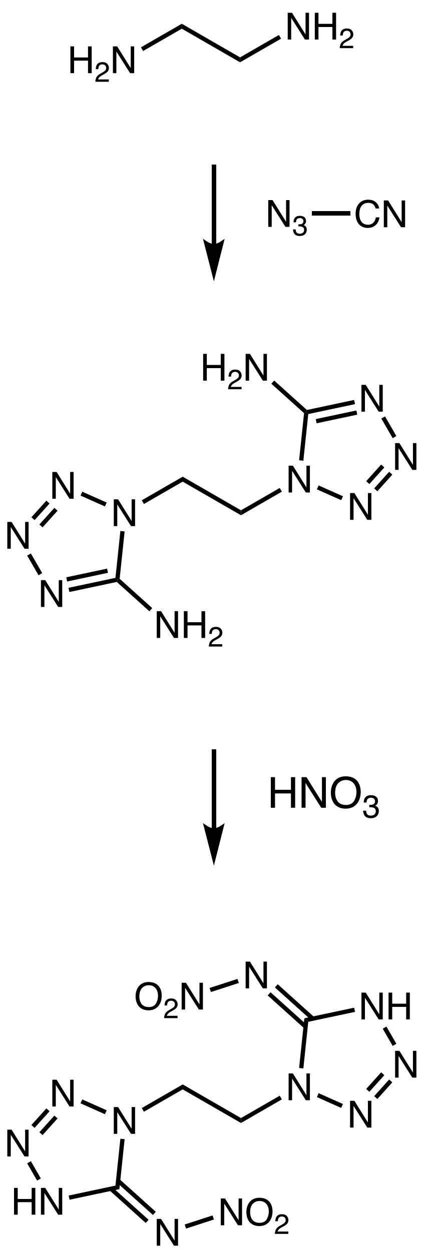
Synthesis of Nitrogen-Rich Compounds for HEM Development





***S$_N$Ar* is widely employed**

cyanogen azide for tetrazole synthesis



Design of Novel Energetic Materials

Higher performance materials

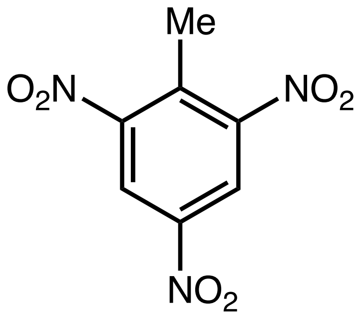
increased heat of explosion

higher detonation pressure

higher detonation velocity

maximize energy of material (per unit volume)

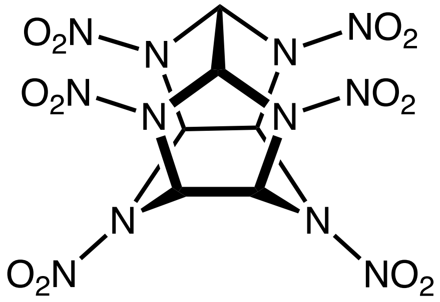
Oxidation of C,H backbone



energy from “combustion”

traditional approach

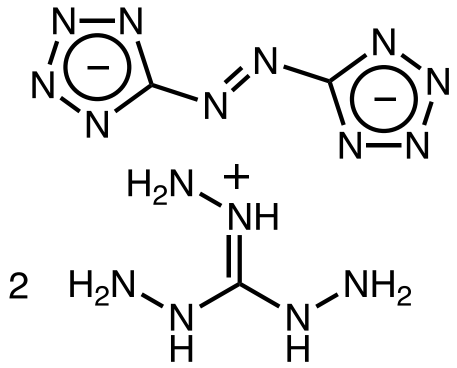
Inherent strain



strain release – extra energy

newer approach

Nitrogen-rich molecules

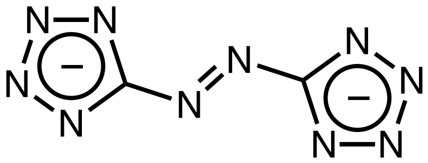


energy from formation of N_2

newer approach

Nitrogen-Rich Molecules as High Energy Materials

Nitrogen-rich molecules



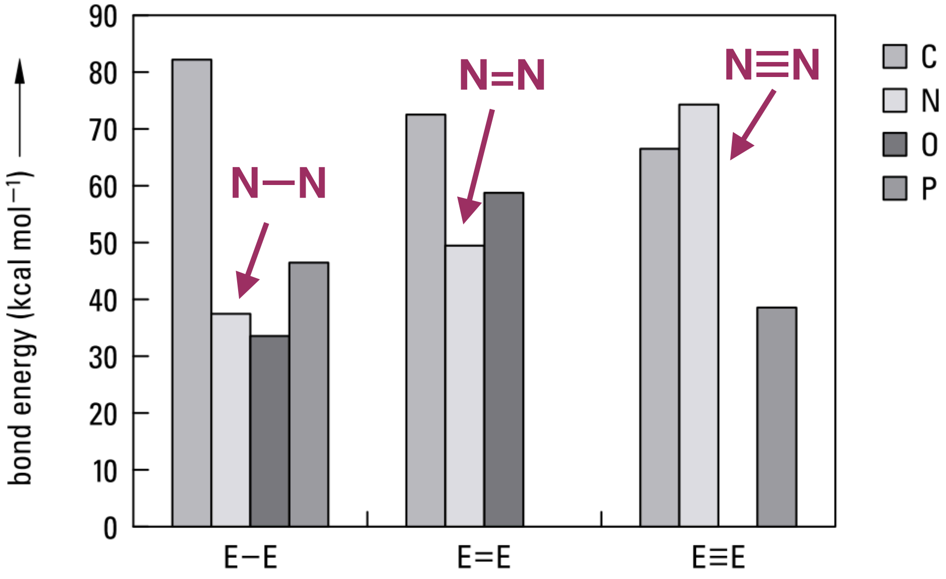
good performance (*Q*, *VOD*, *P*)

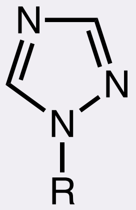
candidates for “green” HEM

N-rich propellants lead to less erosion

very endothermic compounds (ΔH_f >> 0)

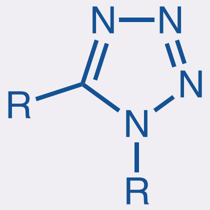
BDEs normalized by bond order





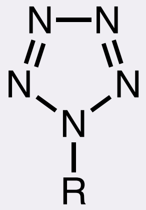
stable

not endothermic enough



relatively stable

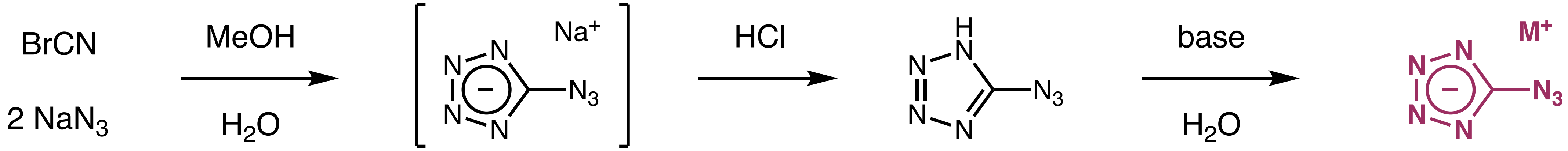
high energy



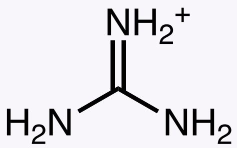
too unstable

high energy

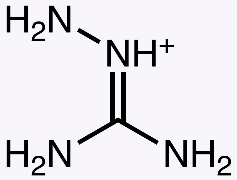
Synthesis of Family of Azidotetrazolate Salts



several counterions were installed

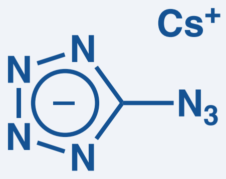


$H_2N{-}NH_3^+$ NH_4^+



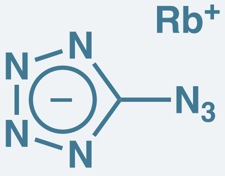
Li^+ Na^+ K^+

Cs^+ Ca^{2+}



$CsCN_7$

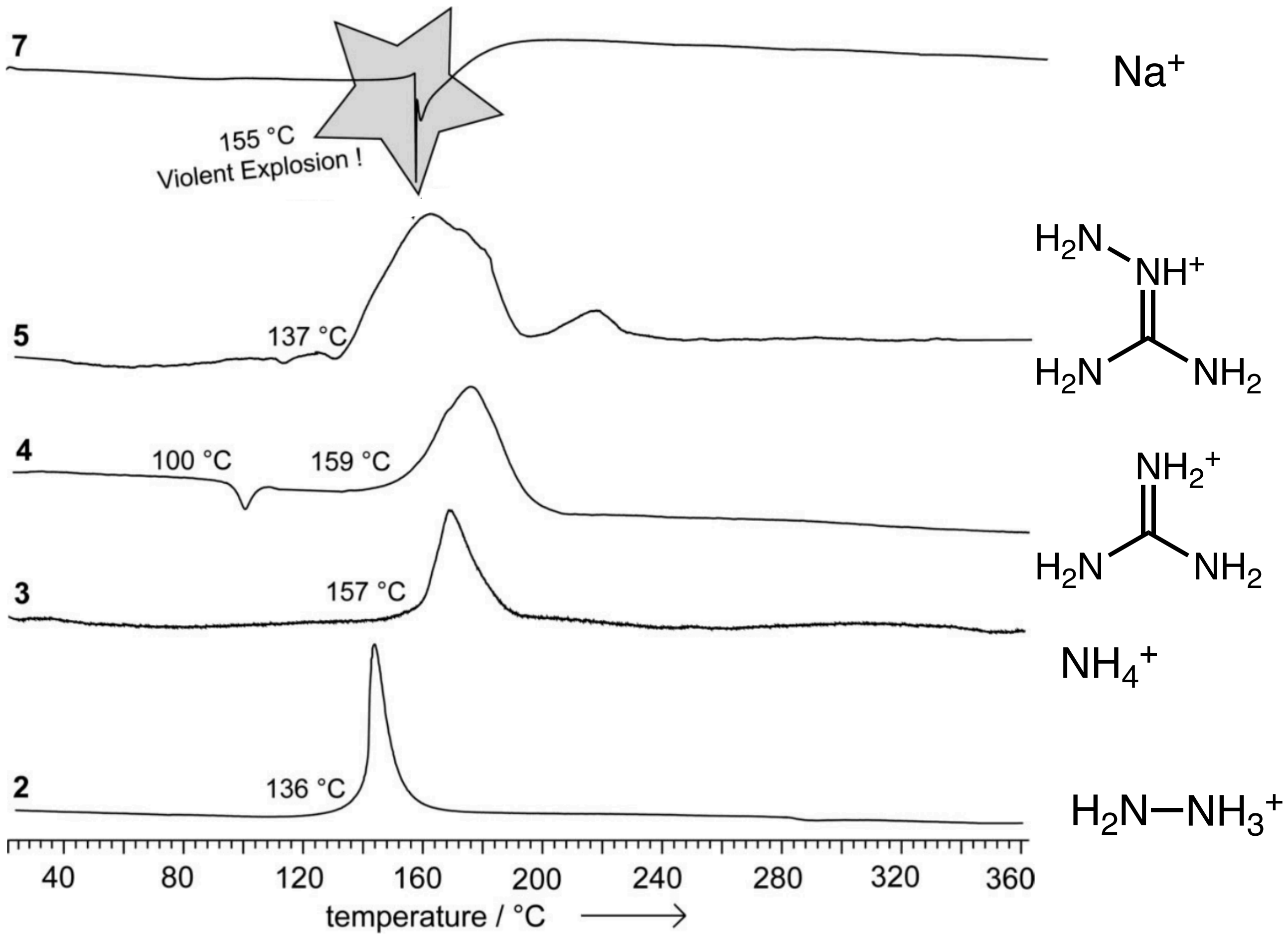
“The aqueous solution was left for crystallization on a watch glass, and “fortunately” three single crystals could be isolated […] A few hours later the whole preparation exploded spontaneously.”



“Synthesis of rubidinium 5-azidotetrazole has been tried a few times. However, we never could observe any solid material, and the reaction mixture (left undisturbed in an explosive case and in the dark) detonated spontaneously for each preparation”

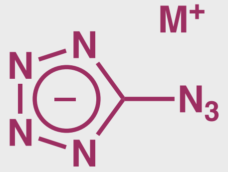
Klapotke, T. M.; Stierstorfer, J. *J. Am. Chem. Soc.* **2009**, *131*, 1122

Properties of Azidoterazolates



*"In the measurement of **7** a violent explosion destroyed the setup."*

Differential scanning calorimetry (DSC)



"The compounds decompose/explode violently, most of them without melting."

some experimental measurements hindered by sensitivity

thermodynamic parameters derived computationally instead

Table 8. Solid State Enthalpies ($\Delta_f H^\circ$) and Energies of Formation ($\Delta_f U^\circ$)

	$\Delta_f H^\circ$(s) / kcal mol^{-1}	$\Delta_f H^\circ$(s) / kJ mol^{-1}	Δn	$\Delta_f U^\circ$(s) / kcal mol^{-1}	M / g mol^{-1}	$\Delta_f U^\circ$(s) / kJ kg^{-1}
$[N_2H_5][CN_7]$	+168.1	+703.8	−7	+172.2	143.1	+5034.8
$[NH_4][CN_7]$	+129.9	+543.9	−6	+133.5	128.1	+4360.4
$[AG][CN_7]$	+153.5	+642.7	−9	158.8	185.2	+3587.6

Klapotke, T. M.; Stierstorfer, J. *J. Am. Chem. Soc.* **2009**, *131*, 1122

Properties of Azidoterazolates

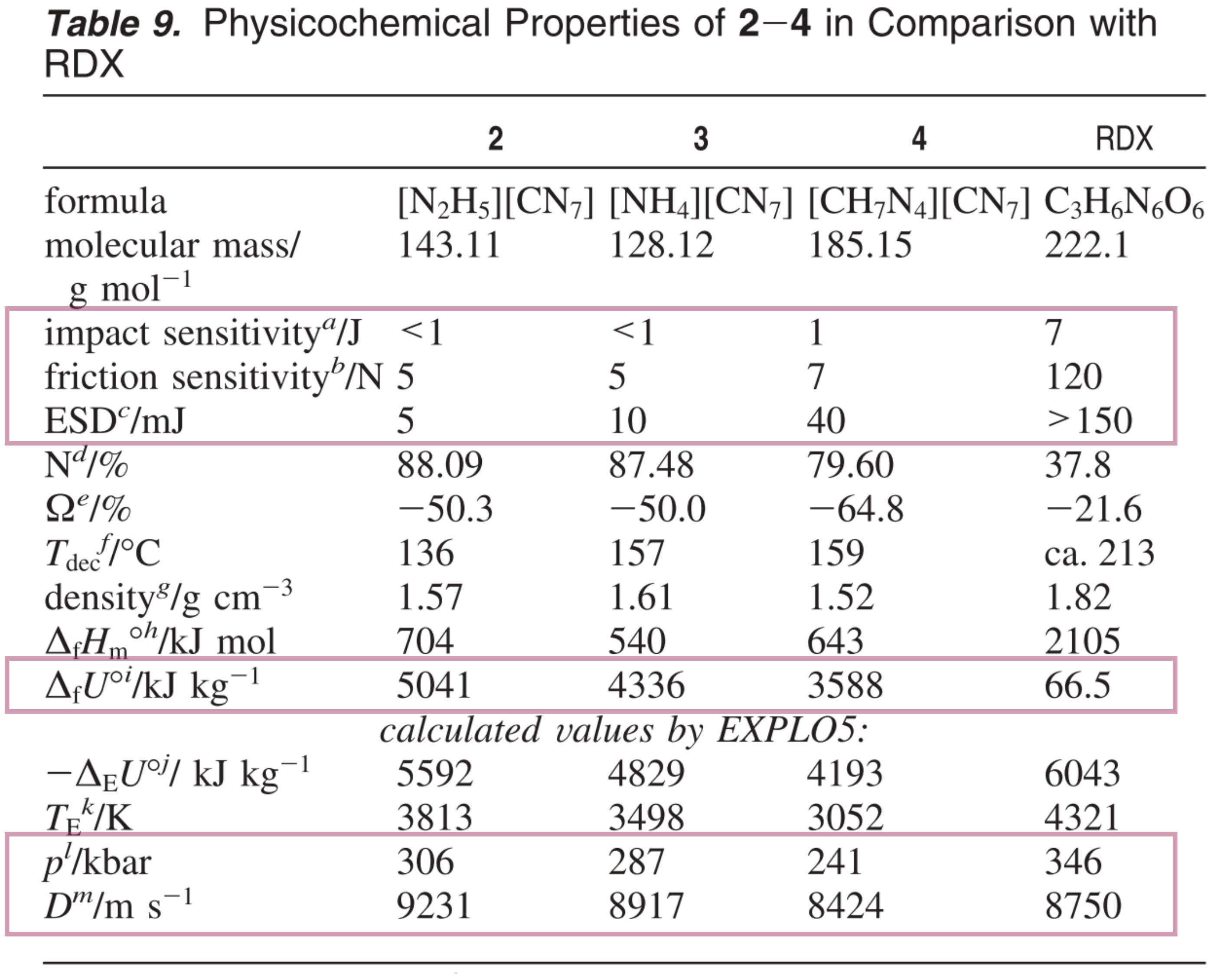


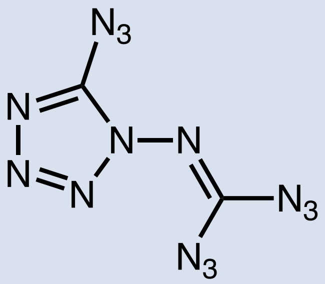
Table 9. Physicochemical Properties of **2**−**4** in Comparison with RDX

	2	**3**	**4**	RDX
formula	$[N_2H_5][CN_7]$	$[NH_4][CN_7]$	$[CH_7N_4][CN_7]$	$C_3H_6N_6O_6$
molecular mass/g mol^{-1}	143.11	128.12	185.15	222.1
impact sensitivity[a]/J	<1	<1	1	7
friction sensitivity[b]/N	5	5	7	120
ESD[c]/mJ	5	10	40	>150
N[d]/%	88.09	87.48	79.60	37.8
Ω[e]/%	−50.3	−50.0	−64.8	−21.6
T_{dec}[f]/°C	136	157	159	ca. 213
density[g]/g cm^{-3}	1.57	1.61	1.52	1.82
$\Delta_f H_m^{\circ}$[h]/kJ mol	704	540	643	2105
$\Delta_f U^{\circ}$[i]/kJ kg^{-1}	5041	4336	3588	66.5
calculated values by EXPLO5:				
$-\Delta_E U^{\circ}$[j]/ kJ kg^{-1}	5592	4829	4193	6043
T_E[k]/K	3813	3498	3052	4321
p[l]/kbar	306	287	241	346
D[m]/m s^{-1}	9231	8917	8424	8750

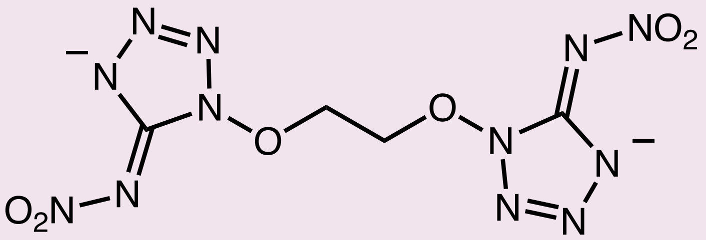
"probably too sensitive for practical applications"

Klapotke, T. M.; Stierstorfer, J. *J. Am. Chem. Soc.* **2009**, *131*, 1122

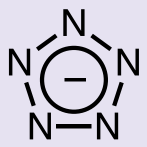
Other Publications on Highly Nitrogenous Compounds



Klapötke *Angew. Chem. Int. Ed.* **2011**, *50*, 4227



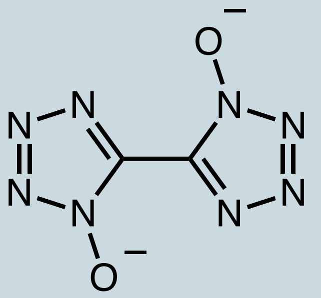
Shreeve *J. Am. Chem. Soc.* **2011**, *132*, 15081



isolated as

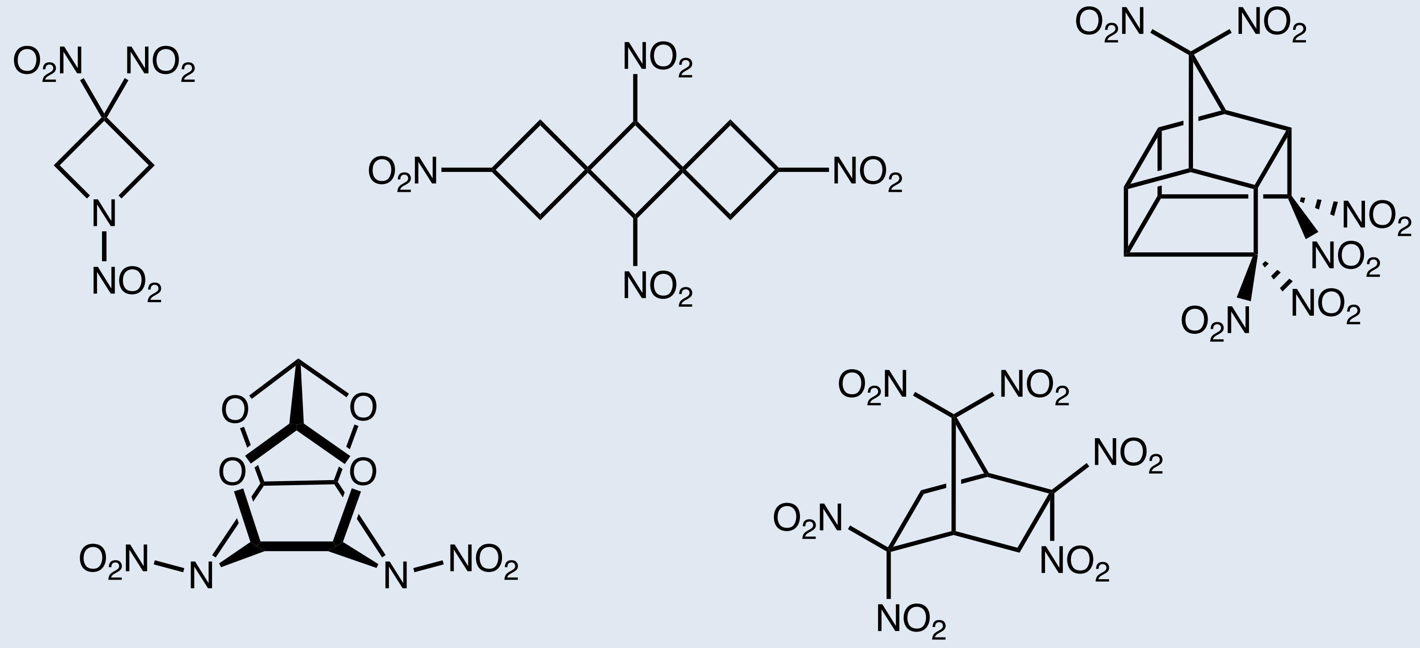
$(N_5)_6(H_3O)_3(NH_4)_4Cl$

Hu & Lu *Science* **2017**, *355*, 374



Klapötke *J. Mater. Chem.* **2012**, *22*, 20418

Development of Strain and Caged Molecules for High Energy Materials



Strained and caged structures

---

high crystal density

additional energy as strain

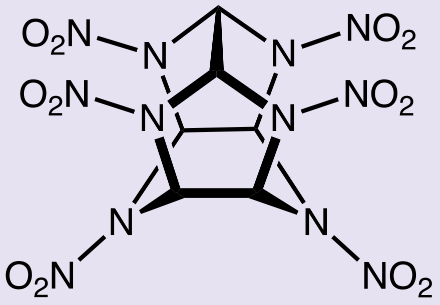
very high energy density!

2,4,6,8,10,12-hexanitro-
2,4,6,8,10,12-hexaazaisowurtzitane

---

synthesized in 1987
at Naval Air Warfare Center

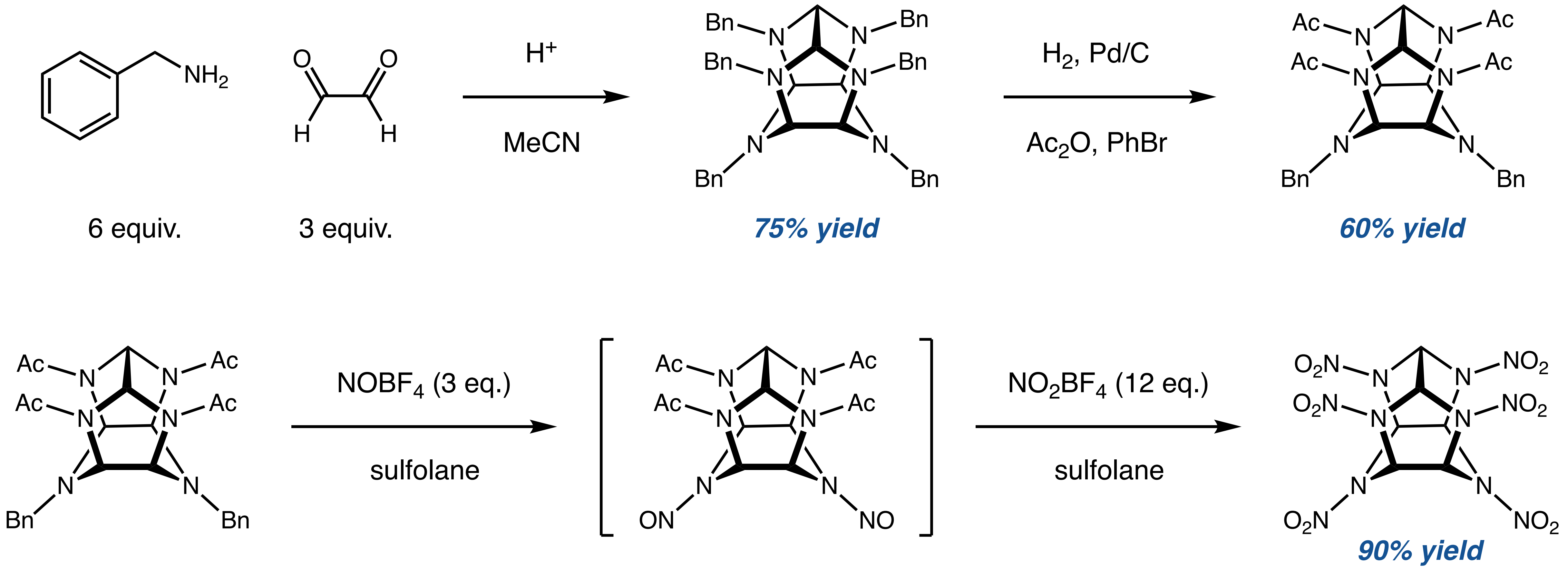
already produced on 100 kg scale

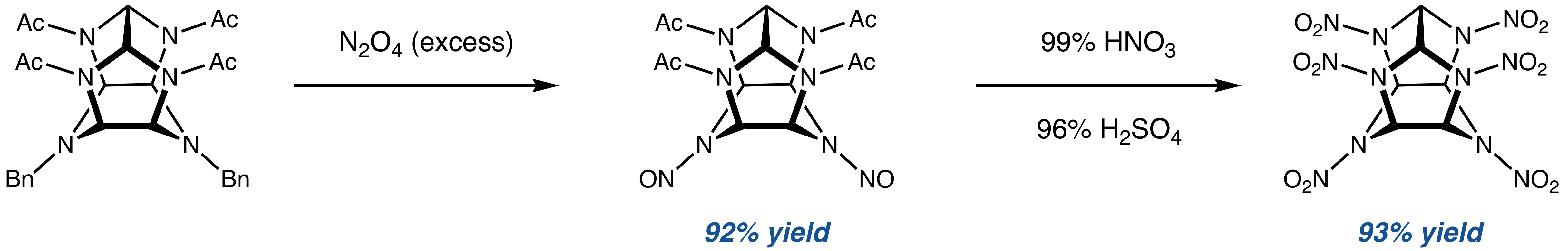


HNIW (CL–20)

density	2.04 g/mL
enthalpy of formation	100 kcal/mol
detonation velocity	9400 m/s
decomp T	228 ºC

Syntheses of HNIW

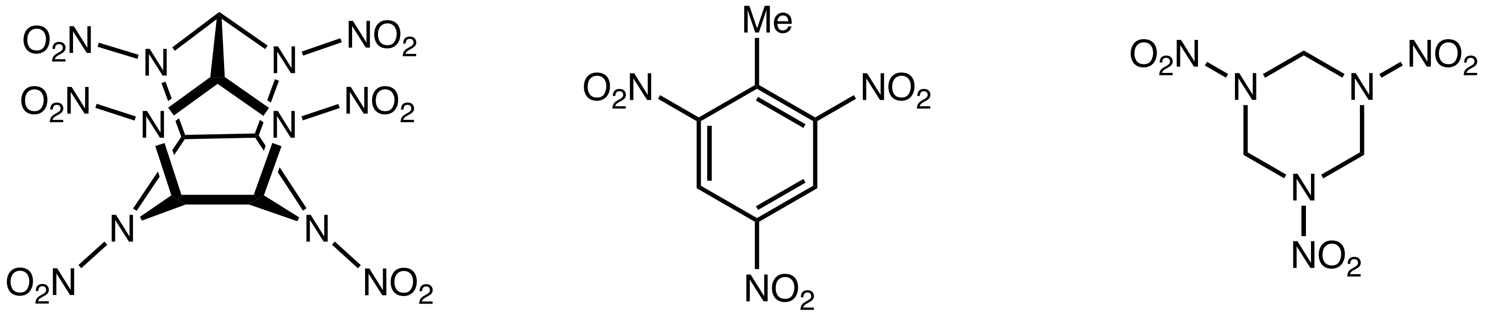




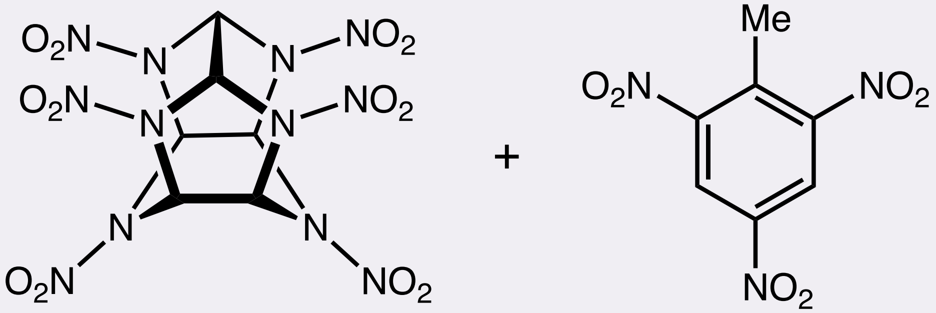
Nielsen, A. T. *et al.* *Tetrahedron* **1998**, *54*, 11793

Co-Crystallization of HNIW with TNT

Disadvantage of HNIW: sensitivity



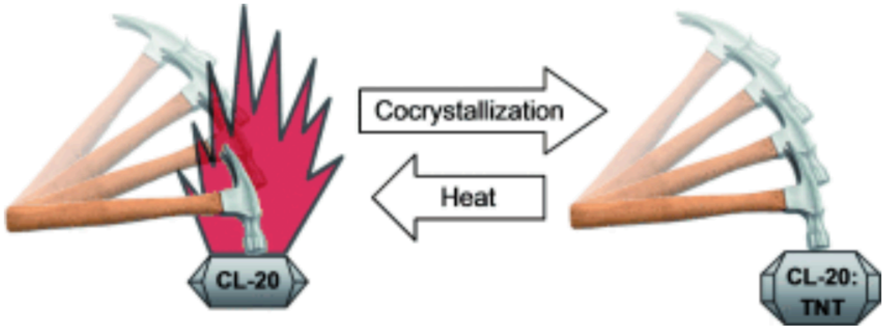
impact sensitivity:	***4 J***	***15 J***	***7.5 J***
friction sensitivity:	***48 N***	***> 353 N***	***120 N***



HNIW:TNT 1:1 cocrystal

density drops by 5–10%

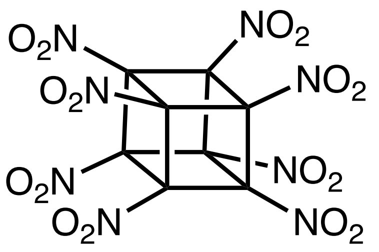
sensitivity improved two fold!



Bolton, O.; Matzger, A. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 8960

Octanitrocubane – Idealistic Dream or Tangible Reality?

Octanitrocubane



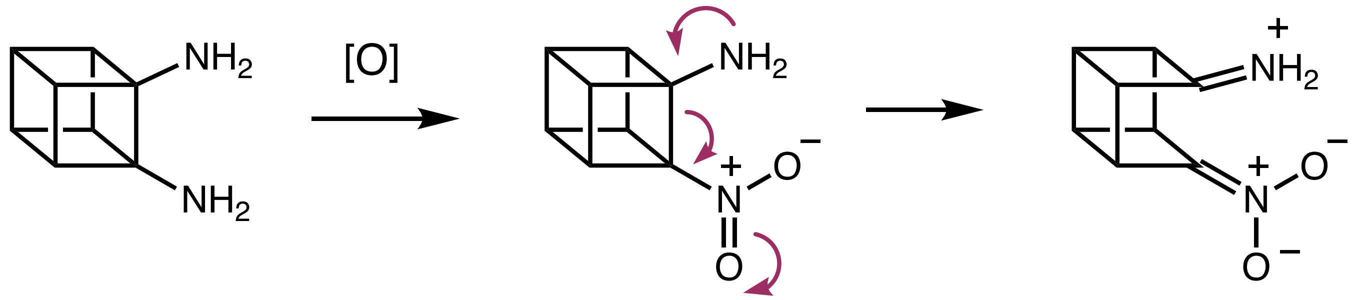
predicted properties

high energy

high density

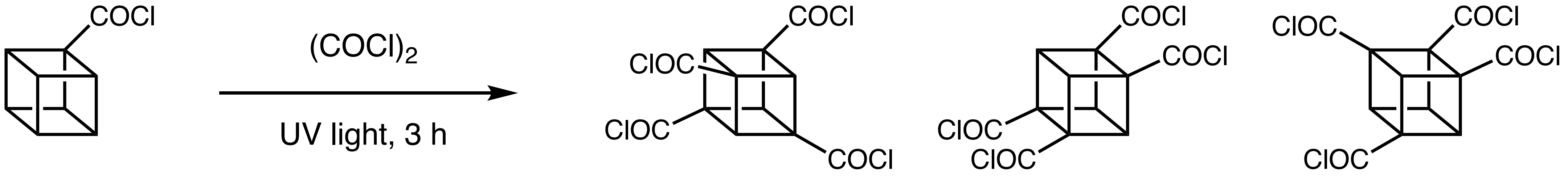
kinetically stable

Caveat in synthesis



push-pull intermediates will lead to opening of the cube → **must avoid 1,2-diamino precursors**

Synthesis of a 1,3,5,7-substituted precursor



Kharasch-Brown reaction

70% selectivity

31% yield (recrystalization)

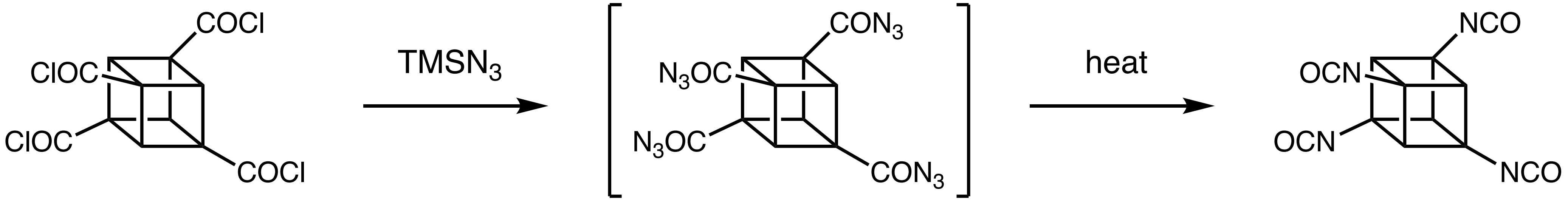
8% selectivity

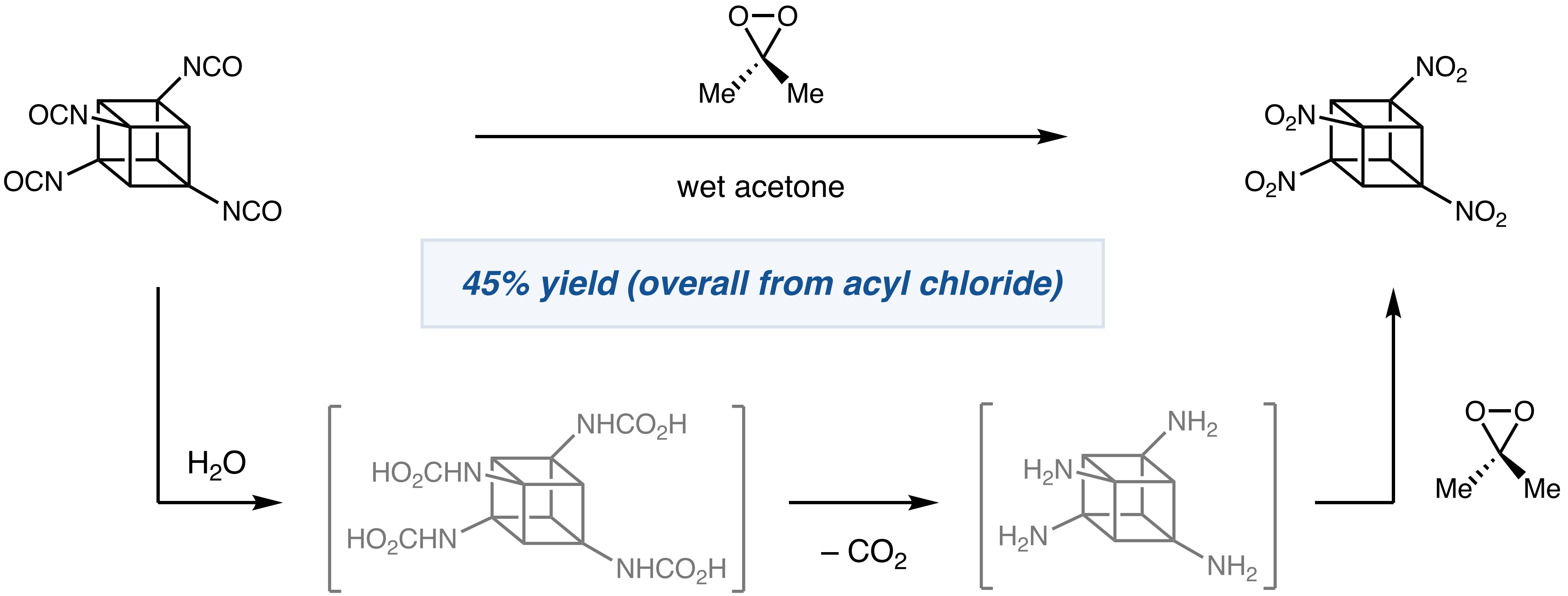
22% selectivity

undesired regioisomers

Lukin, K. A.; Li, J.; Eaton, P. E.; Kanomata, N.; Hain, J.; Punzalan, E.; Gilardi, R. *J. Am. Chem. Soc.* **1997**, *119*, 9591

Synthesis of Tetranitrocubane

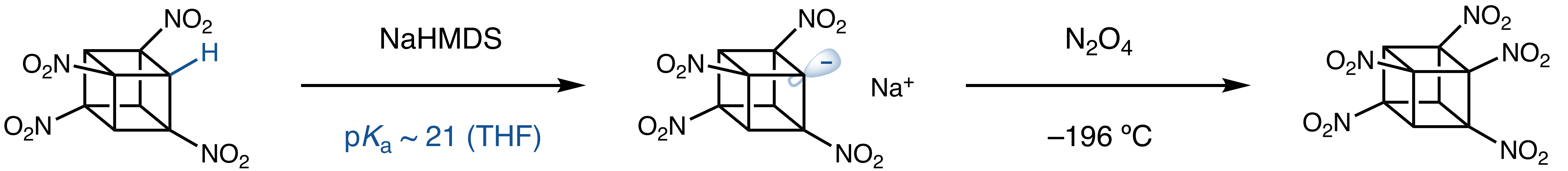




45% yield (overall from acyl chloride)

Lukin, K. A.; Li, J.; Eaton, P. E.; Kanomata, N.; Hain, J.; Punzalan, E.; Gilardi, R. *J. Am. Chem. Soc.* **1997**, *119*, 9591

Synthesis of More Highly Substituted Nitrocubanes



NaHMDS

$pK_a \sim 21$ (THF)

N_2O_4

–196 °C

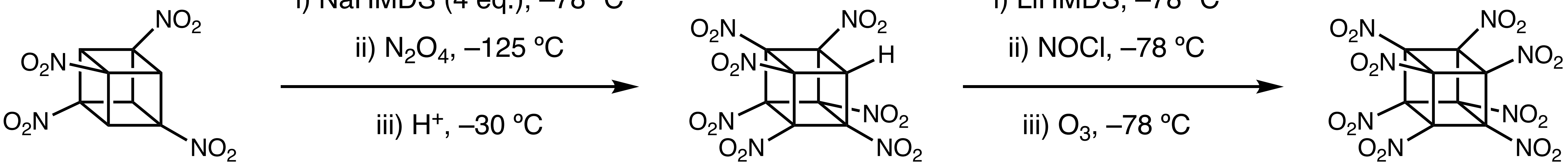
density = 1.81 g/mL
stable up to 300 °C

> *"Despite the predictions of naysayers, pentanitrocubane is stable […], showing no obvious shock sensitivity or special thermal sensitivity."*

40% yield
(chromatography)

Lukin, K. A.; Li, J.; Eaton, P. E.; Kanomata, N.; Hain, J.; Punzalan, E.; Gilardi, R. *J. Am. Chem. Soc.* **1997**, *119*, 9591

Synthesis of octanitrocubane is achieved in 2000



i) NaHMDS (4 eq.), –78 °C
ii) N_2O_4, –125 °C
iii) H^+, –30 °C

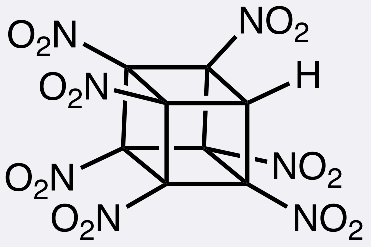
74% yield

i) LiHMDS, –78 °C
ii) NOCl, –78 °C
iii) O_3, –78 °C

~50% yield

Zhang, M.-X.; Eaton, P. E.; Gilardi, R. *Angew. Chem. Int. Ed.* **2000**, *39*, 401

Properties of Heptanitrocubane and Octanitrocubane



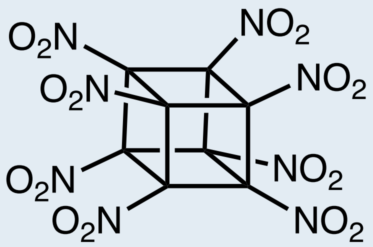
heptanitrocubane

“Beautiful, colorless, solvent-free crystals formed when its solution in fuming nitric acid was diluted with sulfuric acid.”

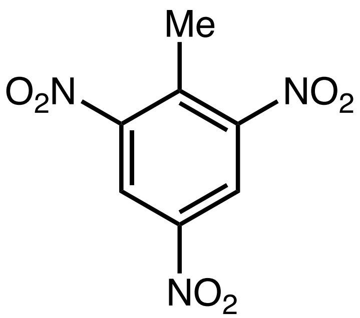
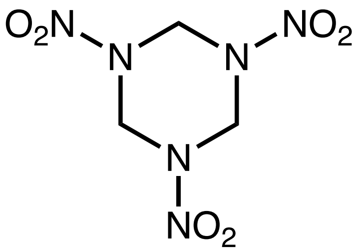
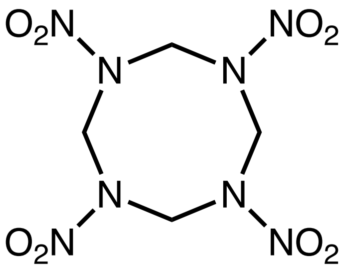
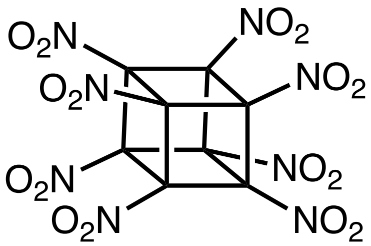
stable up to 200 °C

perfect oxygen balance

“smokefree” detonation

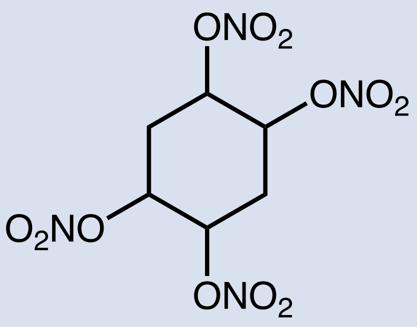


octanitrocubane

predicted or measured properties	 TNT	 RDX	 HMX	 octanitrocubane
density	1.6 g/mL	1.8 g/mL	1.9 g/mL	**2.0 g/mL**
oxygen balance	–74%	–22%	–22%	**0%**
detonation velocity	7000 m/s	8800 m/s	9100 m/s	**10100 m/s**
detonation pressure	190 kbar	338 kbar	390 kbar	**500 kbar**

Zhang, M.-X.; Eaton, P. E.; Gilardi, R. *Angew. Chem. Int. Ed.* **2000**, *39*, 401

New Avenues in HEM Development – Stereo- and Regiochemistry?



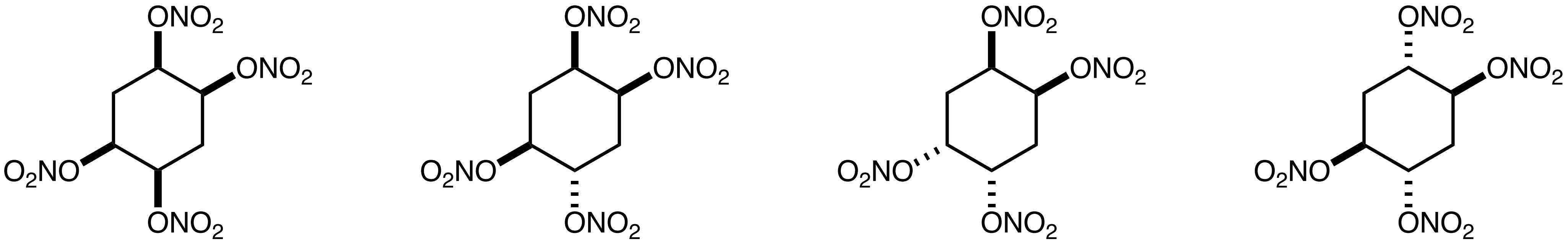
generic candidate

computation

desirable properties predicted
(ΔH_f, density, detonation pressure detonation velocity, etc.)

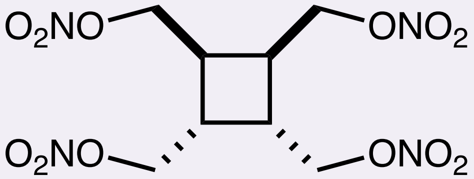
synthesize candidate

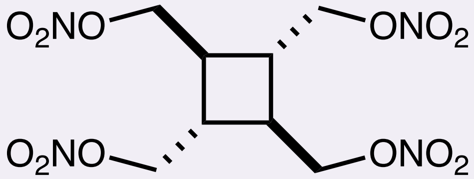
Stereochemistry – traditionally ignored aspect within HEM design

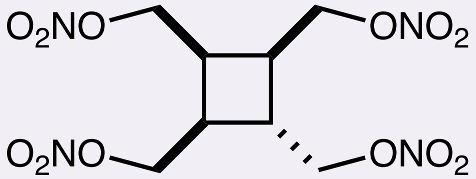


Baran, P. S. *et al. ChemRxiv* **2019** DOI 10.26434/chemrxiv.8521955

New Avenues in HEM Development – Stereo- and Regiochemistry?

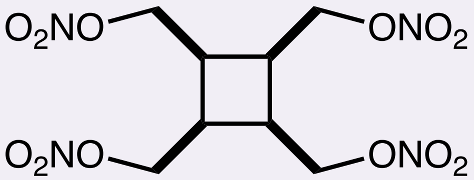


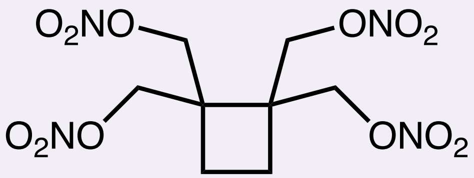


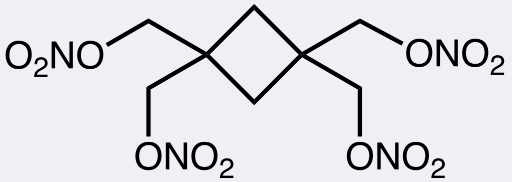


similar detonation velocities: 7500 m/s

similar detonation pressures: 23 GPa





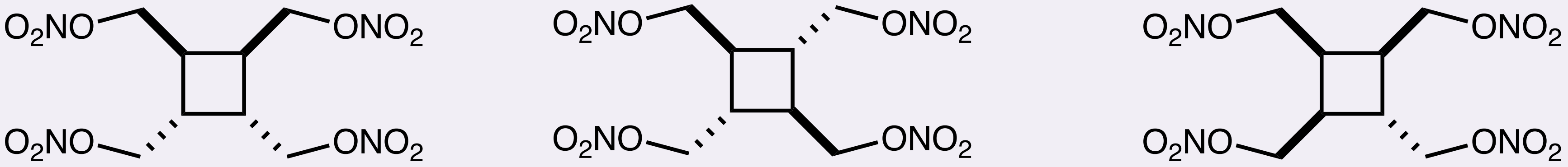


similar specific impulse: 240 s

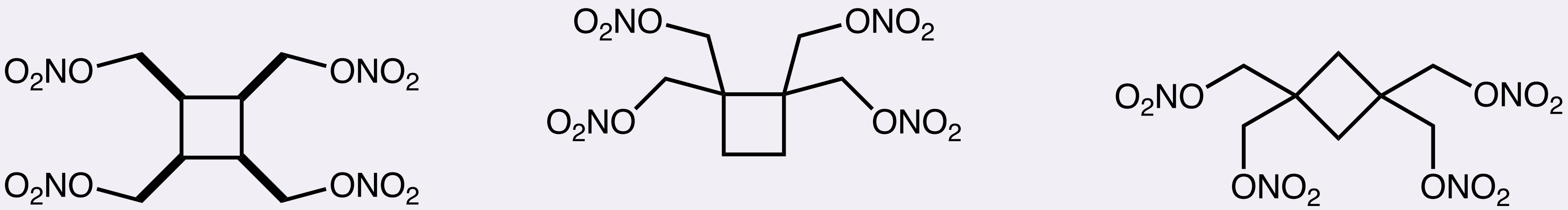
similar enthalpy of formation: –500 kJ/mol

Baran, P. S. *et al. ChemRxiv* **2019** DOI 10.26434/chemrxiv.8521955

New Avenues in HEM Development – Stereo- and Regiochemistry?



melting T	**106**	48	**< –40**	*(ºC)*
decomp T	199	200	187	*(ºC)*

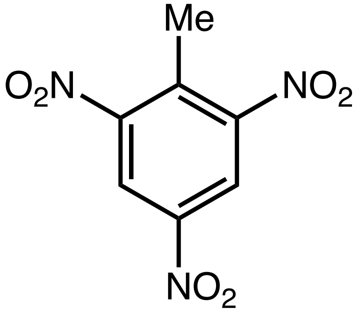
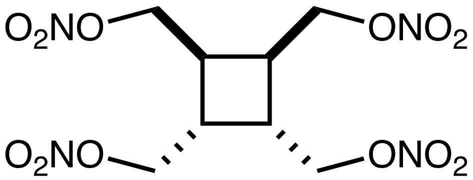
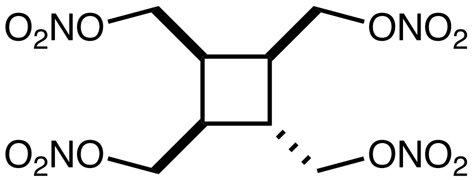
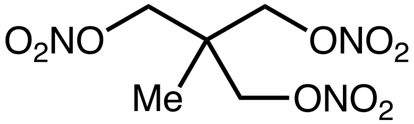


melting T	**101**	**86**	147	*(ºC)*
decomp T	194	193	196	*(ºC)*

Range of melting points across family of stereo- and regioisomers

Baran, P. S. *et al.* *ChemRxiv* **2019** DOI 10.26434/chemrxiv.8521955

New Avenues in HEM Development – Stereo- and Regiochemistry?

predicted or measured properties				
	melt-castable explosive	*candidate*	*candidate*	*propellant plasticizer*
melting T (ºC)	**80**	**106**	**< –40**	**–3**
decomp T (ºC)	**295**	**199**	187	182
density (g/mL)	1.65	1.64	1.54	1.27
detonation velocity (m/s)	6950	7438	7577	7050
detonation pressure (GPa)	19.3	24.5	24.5	23.7
specific impulse (s)	—	241	240	247

Baran, P. S. *et al. ChemRxiv* **2019** DOI 10.26434/chemrxiv.8521955

High Energy Materials – Outline

Generals aspects of high energy materials

- Very brief history
- Fundamental properties
- Decomposition via deflagration or detonation
- Primary vs secondary explosives
- Oxygen balance

Synthesis of high energy materials

- Safety precautions in HEM labs
- Explosophore functional groups
- Examples of synthetic approaches

Recent avenues within the field

- Nitrogen-rich molecules
- Strained energetic materials: HNIW and ONC
- Exploring stereochemistry of materials