

## Progress in the Development of Energetic Materials

# Inensitive Replacements for RDX

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## The Challenge

### RDX Replacements should:

- be less sensitive than RDX

$$E_{\text{impact}} = 7 \text{ J}, F_{\text{friction}} = 120 \text{ N}$$

- show an equal or higher performance

$$D_{\text{det}} = > 9000 \text{ m s}^{-1}, P_{\text{C-J}} > 350 \text{ kbar}$$

- be less toxic
- be easily available



BAM drophammer



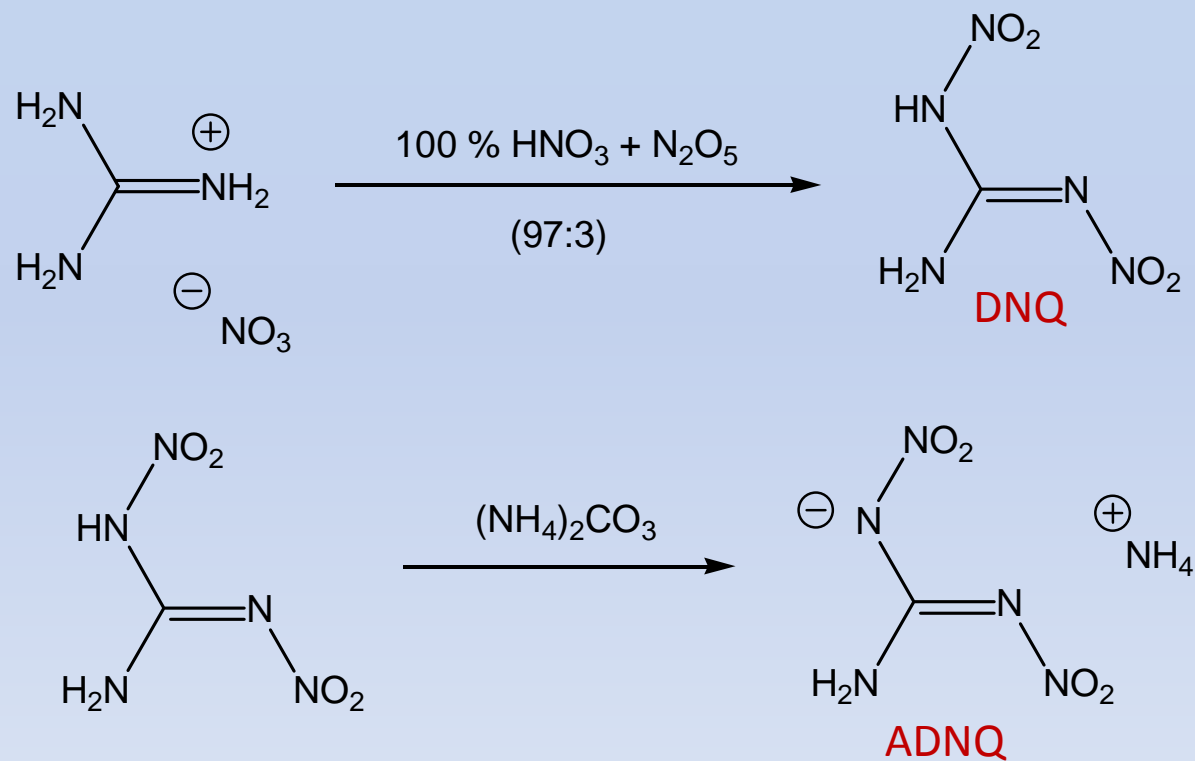
BAM friction tester

## Possible Candidates

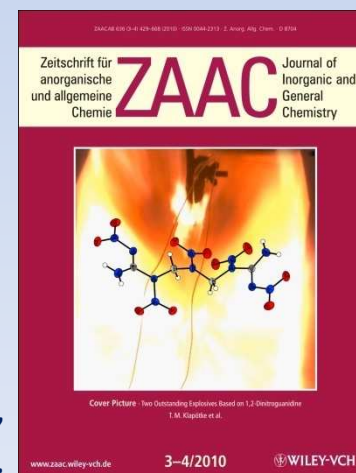
1. Ammonium dinitroguanidine (ADNQ)
2. Amino-nitro-guanidine (ANG)
3. Diaminouronium nitrate (DAUNO<sub>3</sub>)
4. Diamino-oxadiazolium 5-aminotetrazolate
5. Triaminoguanidinium dinitriminoazatriazolate

# Ammonium dinitroguanidine (ADNQ)

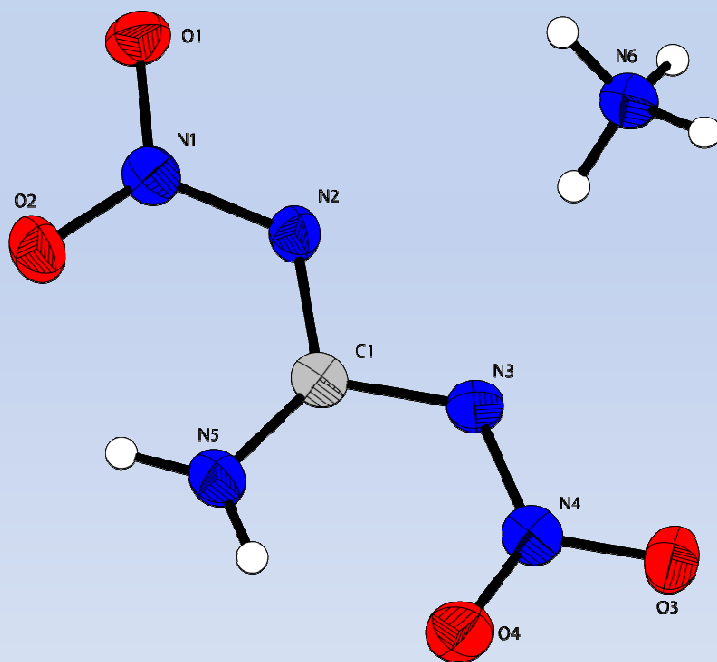
## Synthesis



T. Altenburg, T. M. Klapötke, A. Penger, J. Stierstorfer,  
*Z. Anorg. Allg. Chem.* **2010**, 636, 463-471.

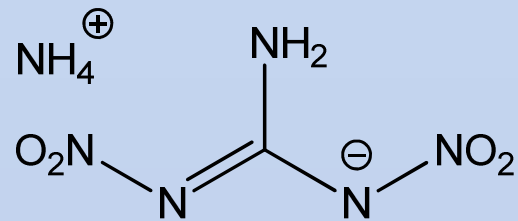


## Structure and energetic properties



$$\rho = 1.735 \text{ g cm}^{-3}$$

	ADNQ	RDX
Formula	$\text{CH}_6\text{N}_6\text{O}_4$	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$
FW / $\text{g mol}^{-1}$	166.09	222.12
IS / J	10	7
FS / N	252	120
ESD / J	0.4	0.1 - 0.2
N / %	50.60	37.8
$\Omega$ / %	-9.63	-21.6
$T_{\text{Dec.}} / ^\circ\text{C}$	197	210
$\rho / \text{g cm}^{-3}$	1.735	1.80
$\Delta_f H_m^\circ / \text{kJ mol}^{-1}$	-1.5	70
$\Delta_f U^\circ / \text{kJ kg}^{-1}$	81.0	417
<b>EXPLO5 values:</b>		
$-\Delta_{\text{Ex}} U^\circ / \text{kJ kg}^{-1}$	5193	6038
$T_{\text{det}} / \text{K}$	3828	4368
$P_{\text{CJ}} / \text{kbar}$	327	341
$V_{\text{Det.}} / \text{m s}^{-1}$	9066	8906
$V_o / \text{L kg}^{-1}$	934	793



ADNQ



Sensitivities, Performance.

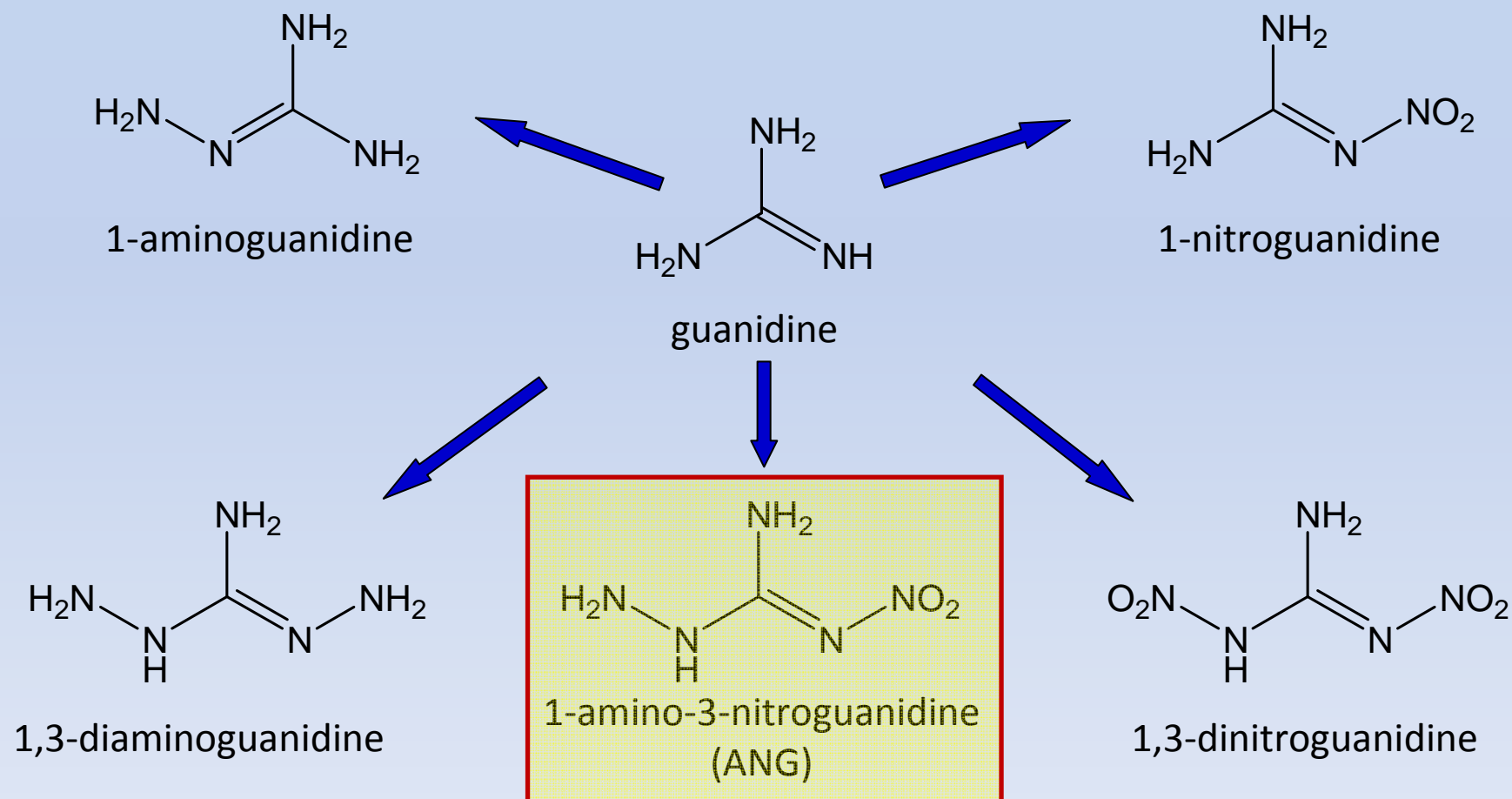


Stability in water, Synthesis

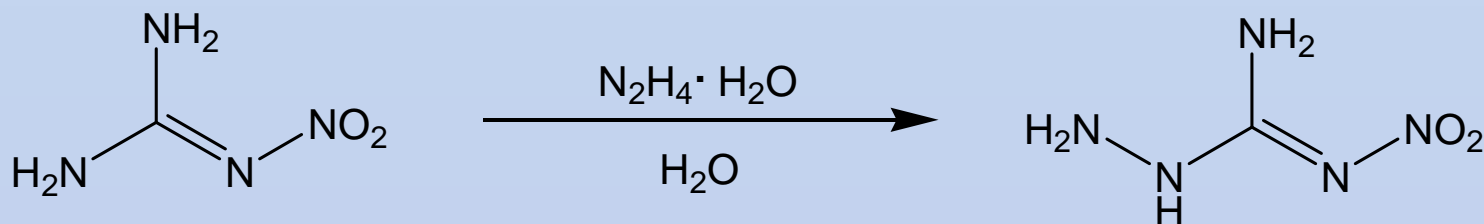
# 3-Amino-1-nitro-guanidine (ANG)



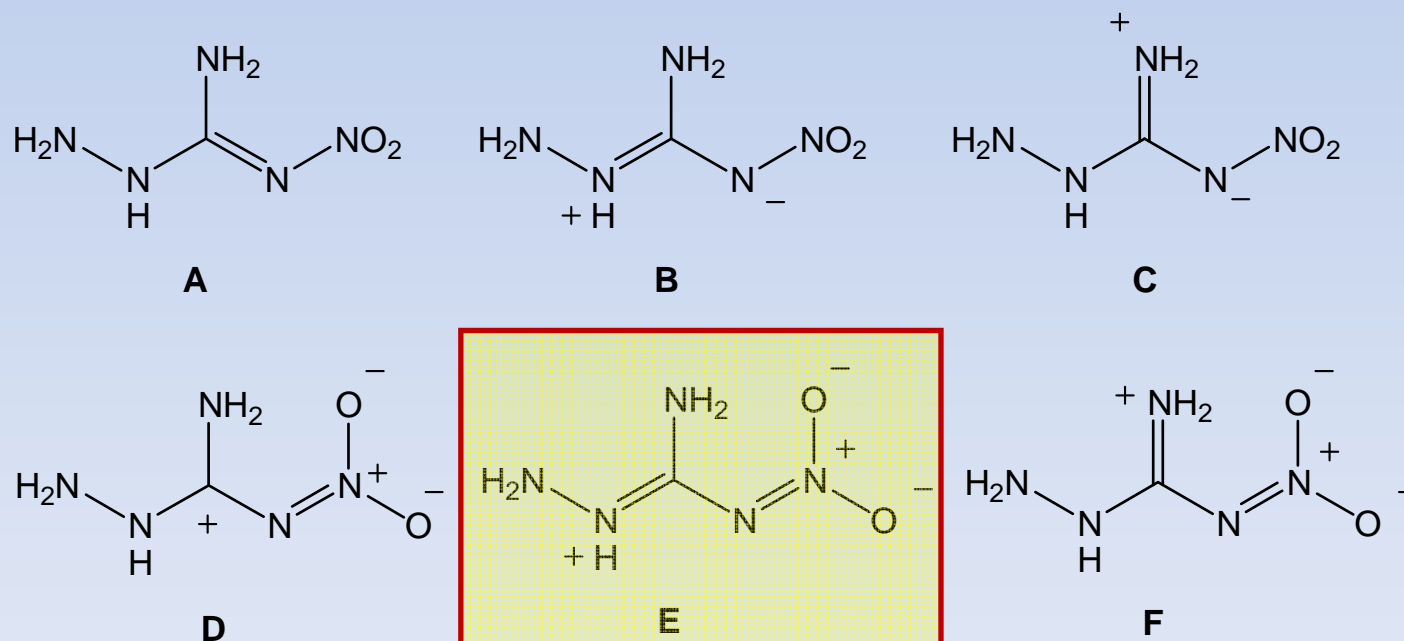
## Guanidine chemistry



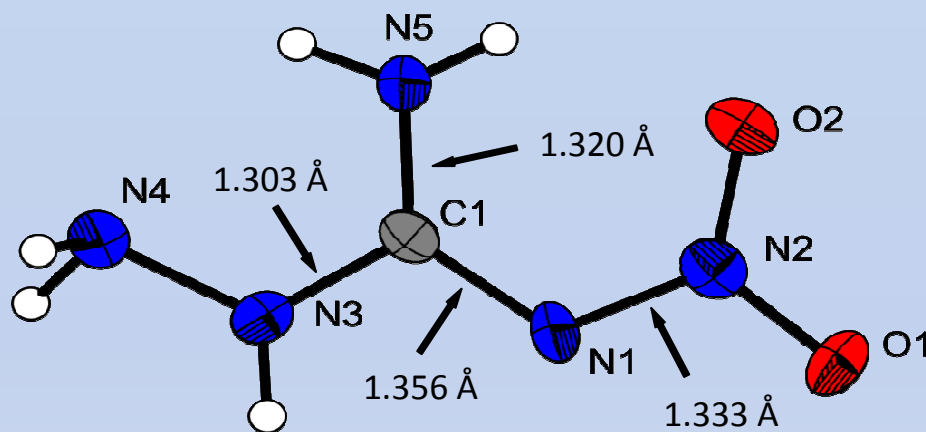
## ANG – Synthesis



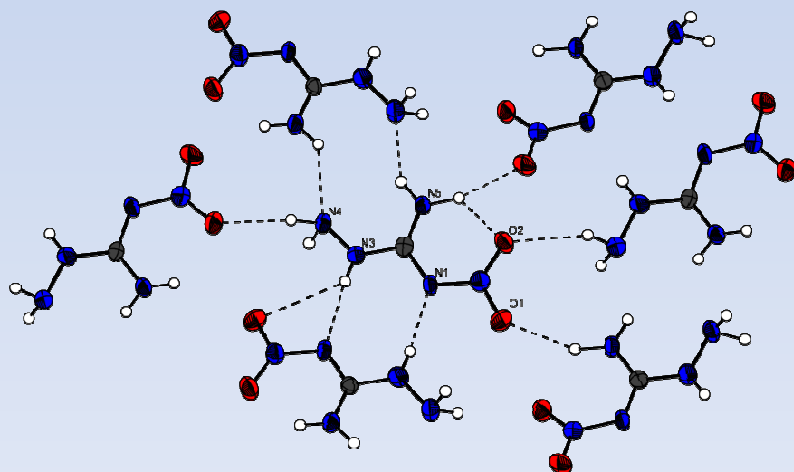
J. A. Castillo-Mendez, B. T. Golding, *Synthesis* **2004**, *10*, 1655-1663.



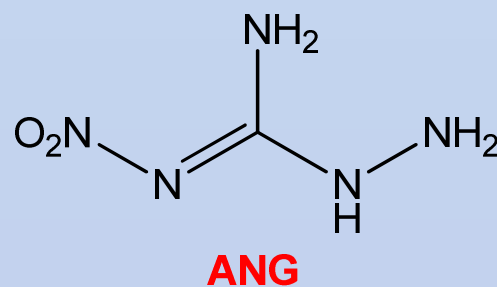
## Structure and energetic properties



$$\rho = 1.767 \text{ g cm}^{-3}$$



	ANG	RDX
Formula	CH <sub>5</sub> N <sub>5</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
FW / g mol <sup>-1</sup>	119.08	222.12
IS / J	20	7
FS / N	144	120
ESD / J	0.15	0.1 - 0.2
N / %	58.81	37.8
Ω / %	-33.6	-21.6
T <sub>Dec.</sub> / °C	184	210
ρ / g cm <sup>-3</sup>	1.767	1.80
Δ <sub>f</sub> H <sub>m</sub> <sup>o</sup> / kJ mol <sup>-1</sup>	77	70
Δ <sub>f</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	770	417
<b>EXPLO5 values:</b>		
-Δ <sub>Ex</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	4934	6038
T <sub>det</sub> / K	3436	4368
P <sub>Cl</sub> / kbar	323	341
V <sub>Det.</sub> / m s <sup>-1</sup>	8977	8906
V <sub>o</sub> / L kg <sup>-1</sup>	890	793



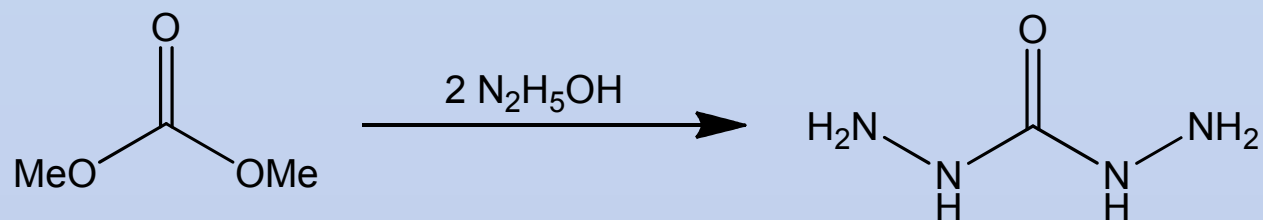
Facile and cheap synthesis, Sensitivities.



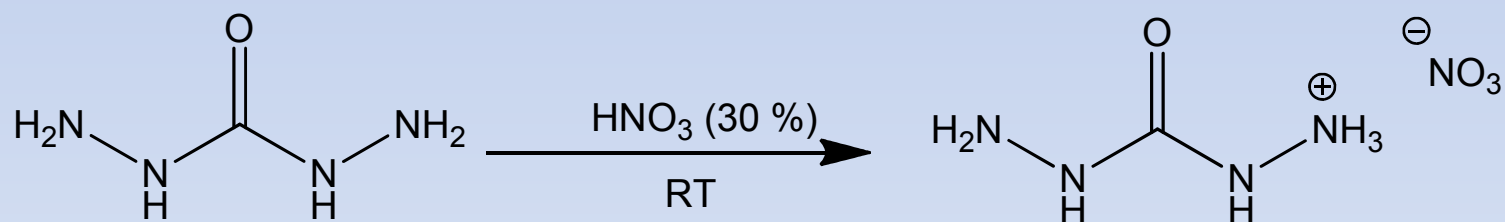
Compatibilities?

# Diaminouronium nitrate (DAU-NO<sub>3</sub>)

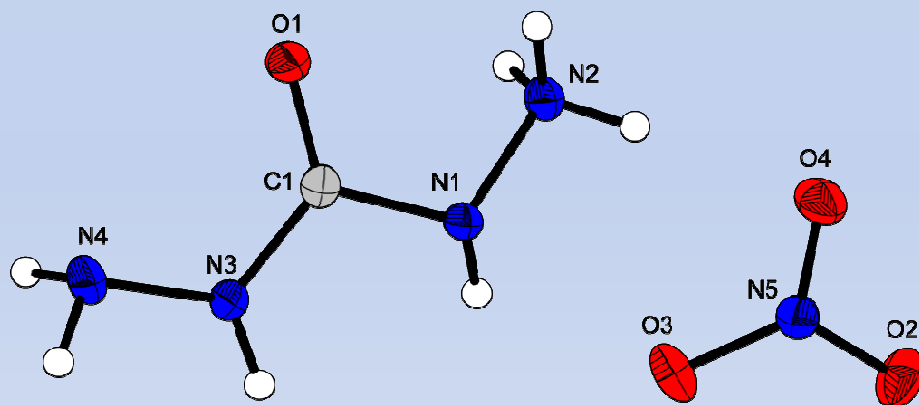
## Synthesis



DAU

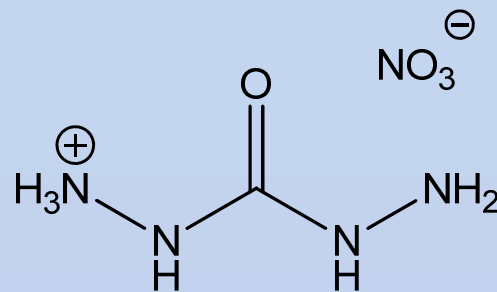
DAUNO<sub>3</sub>

## Structure and energetic properties



$$\rho = 1.785 \text{ g cm}^{-3}$$

	DAUNO <sub>3</sub>	RDX
Formula	CH <sub>7</sub> N <sub>5</sub> O <sub>4</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
FW / g mol <sup>-1</sup>	153.10	222.12
IS / J	9	7
FS / N	288	120
ESD / J	0.6	0.1 - 0.2
N / %	45.74	37.8
Ω / %	-15.67	-21.6
T <sub>Dec.</sub> / °C	242	210
ρ / g cm <sup>-3</sup>	1.782	1.80
Δ <sub>f</sub> H <sub>m</sub> <sup>o</sup> / kJ mol <sup>-1</sup>	-180	70
Δ <sub>f</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	-1048	417
<b>EXPLO5 values:</b>		
-Δ <sub>Ex</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	5014	6038
T <sub>det</sub> / K	3480	4368
P <sub>Cl</sub> / kbar	317	341
V <sub>Det.</sub> / m s <sup>-1</sup>	8829	8906
V <sub>o</sub> / L kg <sup>-1</sup>	925	793

**DAUNO<sub>3</sub>**

Synthesis, Sensitivities, Thermal stability.



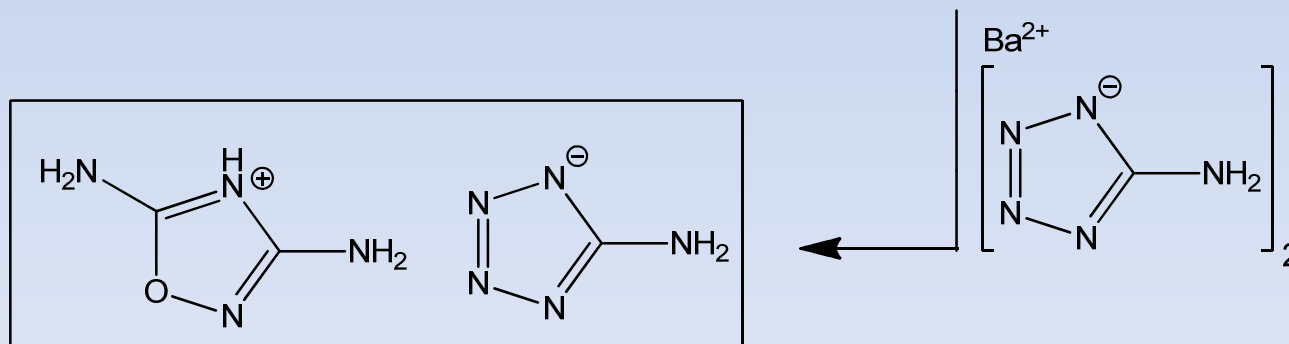
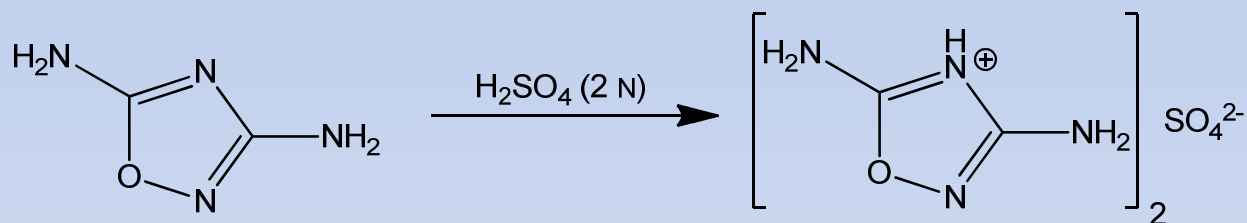
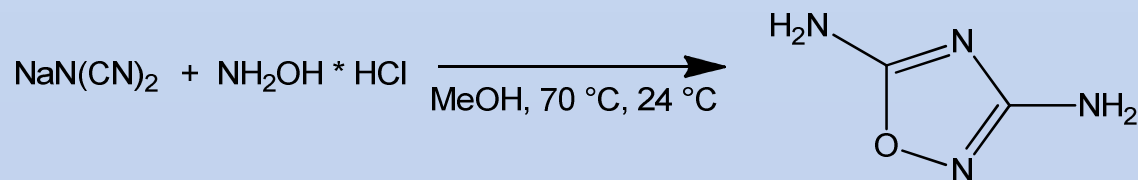
Performance



# Diamino-oxadiazolium 5-aminotetrazolate

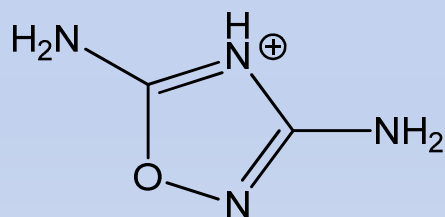
## (DAODH-AT)

## Synthesis



**DAODH-AT**

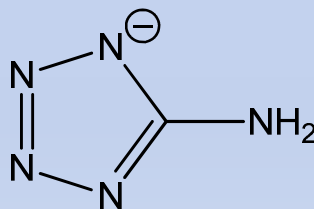
## Energetic properties



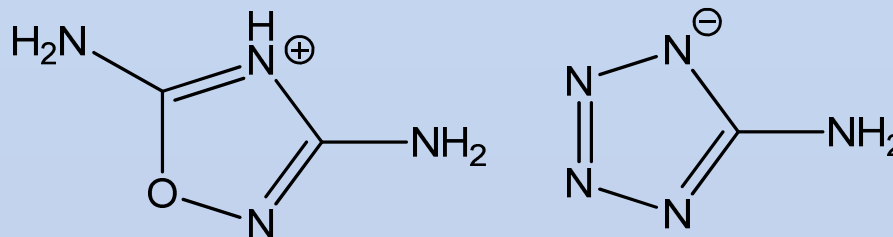
DAODH-AT

$$\rho = 1.76 \text{ g cm}^{-3}$$

(gas-pycnometry)



	DAODH-AT	RDX
Formula	C <sub>3</sub> H <sub>7</sub> N <sub>9</sub> O	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
FW / g mol <sup>-1</sup>	185.15	222.12
IS / J	>40	7
FS / N	>360	120
ESD / J	1.0	0.1 - 0.2
N / %	68.09	37.8
Ω / %	-73.45	-21.6
T <sub>Dec.</sub> / °C	170	210
ρ / g cm <sup>-3</sup>	1.76	1.80
Δ <sub>f</sub> H <sub>m</sub> <sup>o</sup> / kJ mol <sup>-1</sup>	680	70
Δ <sub>f</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	4034	417
<b>EXPLO5 values:</b>		
-Δ <sub>Ex</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	4034	6038
T <sub>det</sub> / K	3719	4368
P <sub>CJ</sub> / kbar	348	341
V <sub>Det.</sub> / m s <sup>-1</sup>	9382	8906
V <sub>o</sub> / L kg <sup>-1</sup>	802	793



DAODH-AT



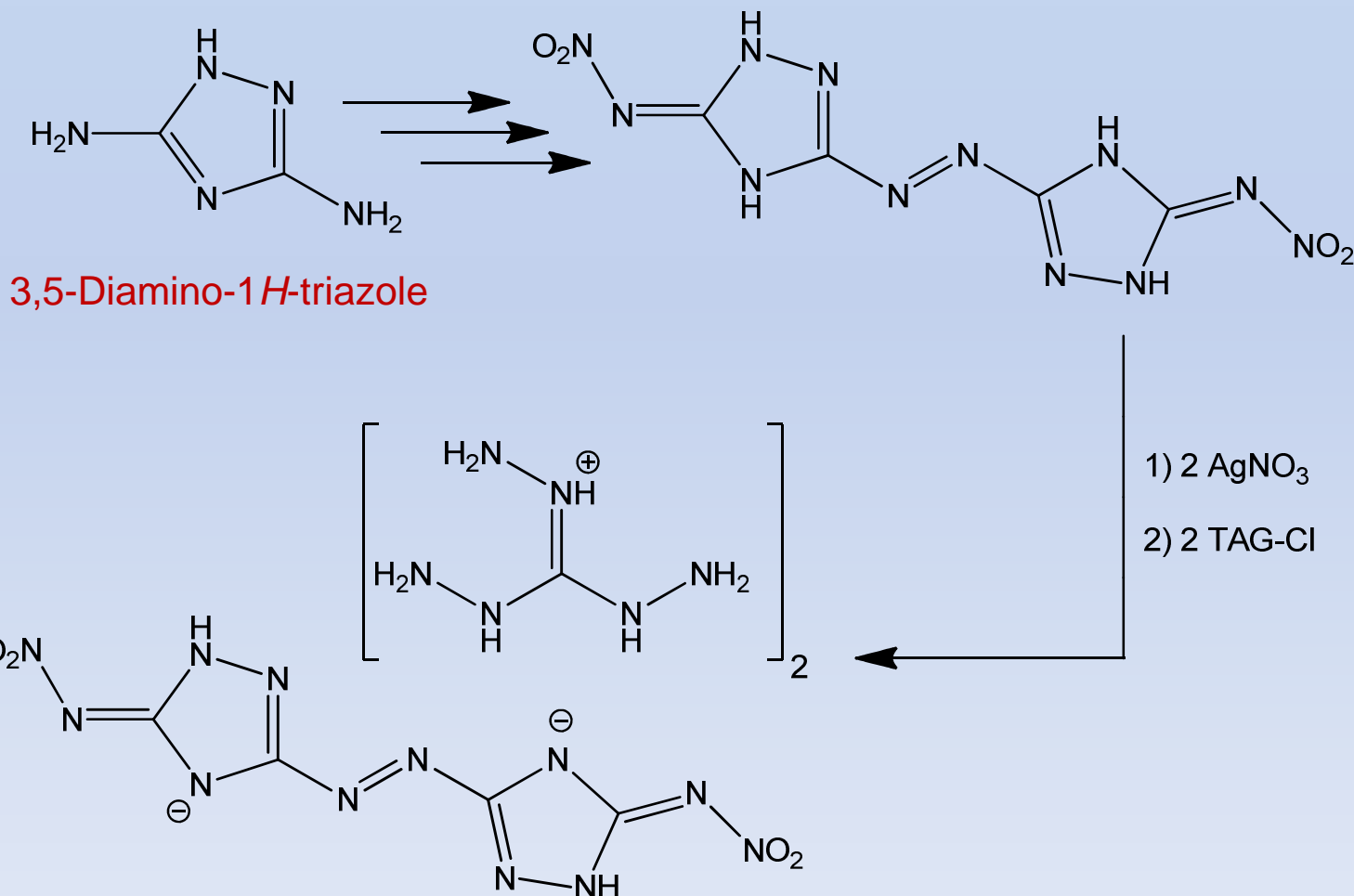
Performance, Insensitivity.



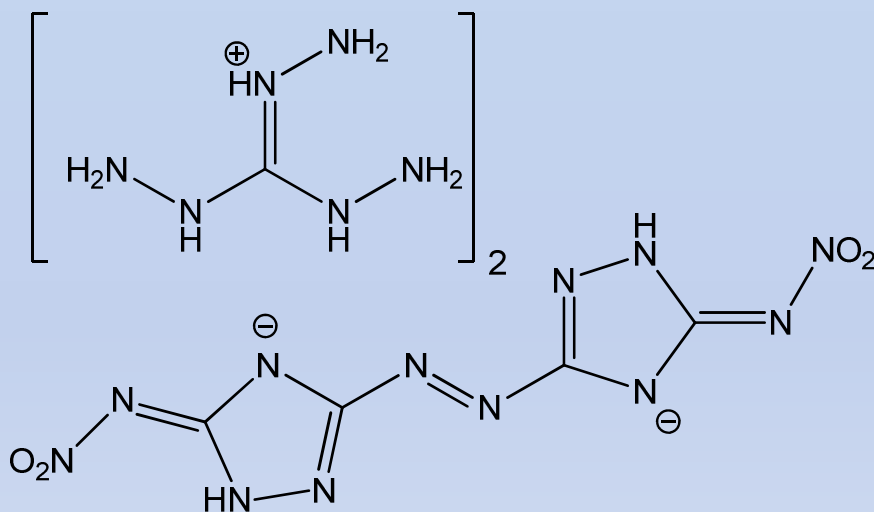
Thermal stability, Initiability?

# Triaminoguanidinium dinitriminoazatriazolate (TAG<sub>2</sub>-DNAAT)

## Synthesis



## Energetic properties

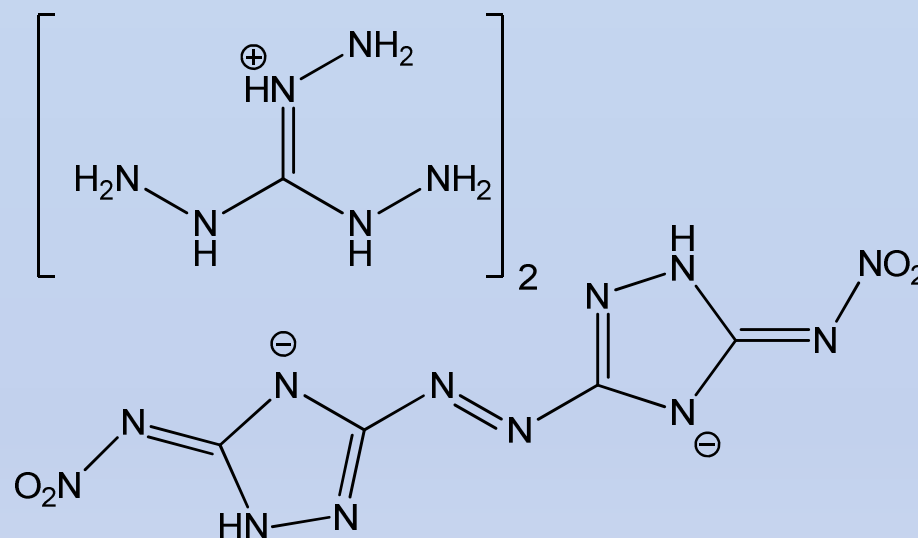
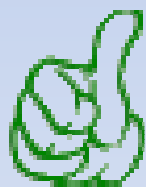


**TAG<sub>2</sub>-DNAAT**

$$\rho = 1.70 \text{ g cm}^{-3}$$

(gas-pycnometry)

	TAG <sub>2</sub> -DNAAT	RD <sub>X</sub>
Formula	C <sub>6</sub> H <sub>20</sub> N <sub>24</sub> O <sub>4</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
FW / g mol <sup>-1</sup>	492.38	222.12
IS / J	>40	7
FS / N	>360	120
ESD / J	1.0	0.1 - 0.2
N / %	69.27	37.8
Ω / %	58.49	-21.6
T <sub>Dec.</sub> / °C	212	210
ρ / g cm <sup>-3</sup>	1.70 (est.)	1.80
Δ <sub>f</sub> H <sub>m</sub> <sup>o</sup> / kJ mol <sup>-1</sup>	260	70
Δ <sub>f</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	2332	417
<b>EXPLO5 values:</b>		
-Δ <sub>Ex</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	4681	6038
T <sub>det</sub> / K	3213	4368
P <sub>CJ</sub> / kbar	300	341
V <sub>Det.</sub> / m s <sup>-1</sup>	8890	8906
V <sub>o</sub> / L kg <sup>-1</sup>	352	793

**TAG<sub>2</sub>-DNAAT**

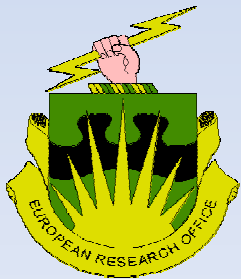
Insensitivity, Thermal stability.



Performance, Synthesis.



# The Group and our Partners



## Energetic Materials Research

	RDX	ADNQ	ANG	DAUNO <sub>3</sub>	DAODH-AT	TAG <sub>2</sub> -DNAAT
Formula	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	CH <sub>6</sub> N <sub>6</sub> O <sub>4</sub>	CH <sub>5</sub> N <sub>5</sub> O <sub>2</sub>	CH <sub>7</sub> N <sub>5</sub> O <sub>4</sub>	C <sub>3</sub> H <sub>7</sub> N <sub>9</sub> O	C <sub>6</sub> H <sub>20</sub> N <sub>24</sub> O <sub>4</sub>
FW <sup>a</sup> / g mol <sup>-1</sup>	222.12	166.09	119.08	153.10	185.15	492.38
IS <sup>b</sup> / J	7	10	20	9	>40	>40
FS <sup>c</sup> / N	120	252	144	288	>360	>360
ESD <sup>d</sup> / J	0.1 - 0.2	0.4	0.15	0.6	1.0	1.0
N <sup>e</sup> / %	37.8	50.60	58.81	45.74	68.09	69.27
Ω <sup>f</sup> / %	-21.6	-9.63	-33.6	-15.67	-73.45	58.49
T <sub>Dec.</sub> <sup>g</sup> / °C	210	197	184	242	170	212
ρ <sup>h</sup> / g cm <sup>-3</sup>	1.80	1.735	1.767	1.782	1.76	1.70 (est.)
Δ <sub>f</sub> H <sub>m</sub> <sup>o</sup> / kJ mol <sup>-1</sup>	70	-1.5	77	-180	680	260
Δ <sub>f</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	417	81.0	770	-1048	4034	2332
<b>EXPLOS values:</b>						
-Δ <sub>Ex</sub> U <sup>o</sup> / kJ kg <sup>-1</sup>	6038	5193	4934	5014	4034	4681
T <sub>det</sub> <sup>l</sup> / K	4368	3828	3436	3480	3719	3213
P <sub>CJ</sub> <sup>m</sup> / kbar	341	327	323	317	348	300
V <sub>Det.</sub> <sup>n</sup> / m s <sup>-1</sup>	8906	9066	8977	8829	9382	8890
V <sub>a</sub> <sup>q</sup> / L kg <sup>-1</sup>	793	934	890	925	802	352

<sup>a</sup> formula weight; <sup>b</sup> impact sensitivity (BAM drophammer, method: 1 of 6); <sup>c</sup> impact sensitivity (BAM friction tester, method: 1 of 6); <sup>d</sup> electrical spark sensitivity (OZM small scale electrical discharge device); <sup>e</sup> nitrogen content; <sup>f</sup> oxygen balance; <sup>g</sup> temperature of decomposition; <sup>h</sup> X-ray density; <sup>i</sup> heat of formation; <sup>j</sup> energy of formation; <sup>k</sup> energy of explosion; <sup>l</sup> explosion temperature; <sup>m</sup> detonation pressure (Chapman-Jouguet); <sup>n</sup> detonation velocity; <sup>q</sup> volume of explosion gases.