Synthesis of Advanced Energetic Materials- The Path Forward

University of Maryland College Park

April 3-5 2011

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outlook

- **Developpement of known materials / tools and methods**
  - Routes to CL20
  - Morphology (CL20, ADN)
- **New ingredients**
  - Compromise perfo-sensitivity
  - Research of new curing systems
  - HEM-HEDM
  - Nanos in formulation
- **New processes**
  - continuous processes, micro
  - Tests of high pressure and/or CO_2
- **Modelling**
  - QSPR sensitivity
  - Toxicology

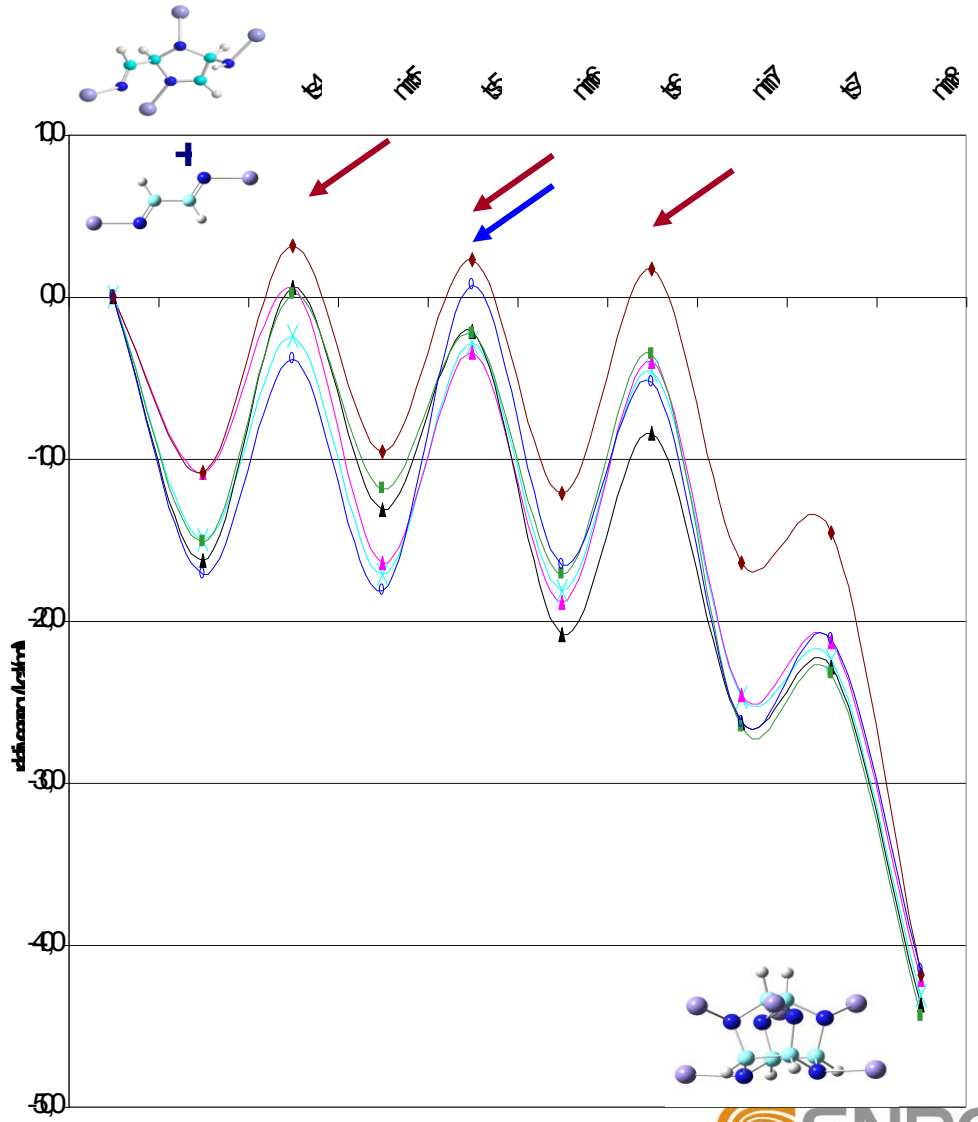
Routes to CL20

❑Background on new IW cages

- Calibration semiempirical – ab initio shows PM3 allows reliable comparison of substituant effects.
- QM description of the cyclisation mechanism.
- Computation of activation barrier for several amines.
- CL20 in 2 steps achievable with selected amines

Routes to CL20 (computational)

- benzyl, 2-Cl-benzyl : Reference substituants leading to cage (Nielsen).
- R3, R4 : « bad » candidates as demonstrated by experi-ments and computations.
- R5 : « good » candidate as shown by experiments and computations.
- R6 : « promising » candidate.



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Routes to CL20

❑ Results:

- 6 new cages with amines previously rejected

(Chem. Eur. J. 2006, 12, 3339-3344 and EP 1 479 683 A1).

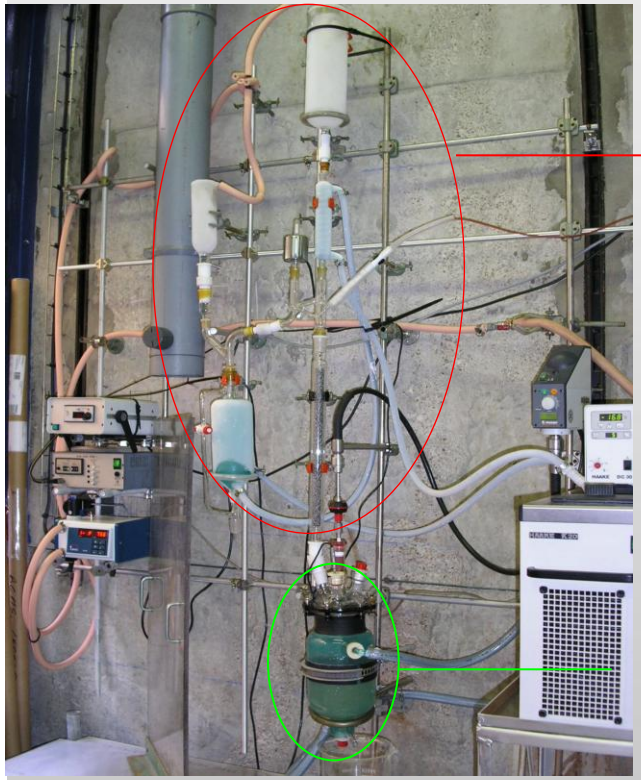
❑ To be continued

- Improvement of nitration yield
- Tailor the competition nitration vs decomposition

Morphology

Mechanical parameters

(Re, Fr, N_P, N_{QP}, V_p…)



Distillation process

Reactor

Hydrodynamics

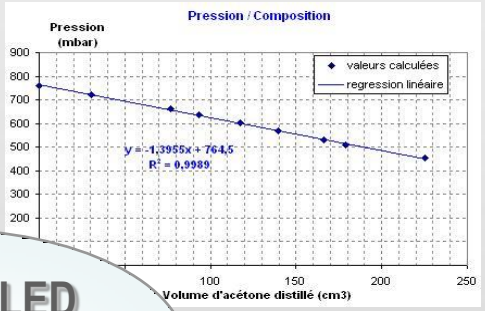
Propeller design

Optimized design of laboratory process

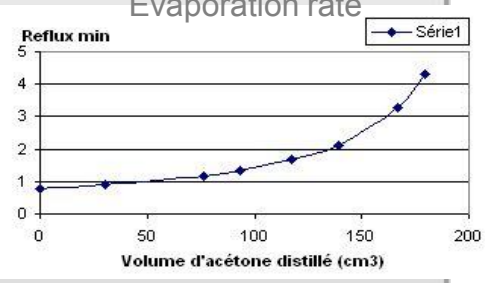
Process parameters

(evaporation & stirring rates, nucléis…)

Sursaturation control

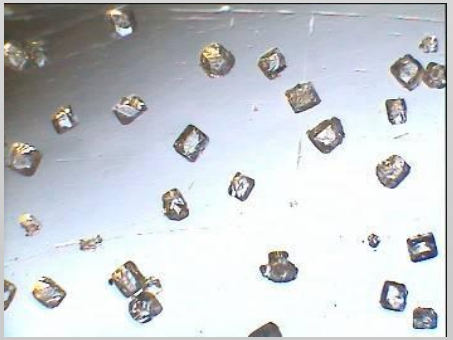


Evaporation rate



CONTROLLED CRYSTALLIZATION

Nucleis (weight and size controlled)



Stirring and temperature optimization

Shape processing

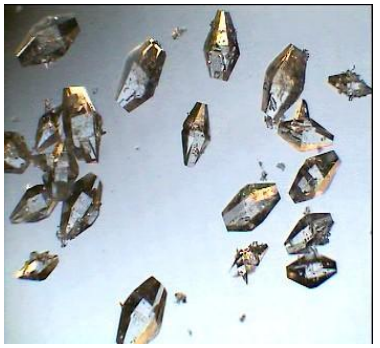
❑ CL20 mastering of particle size and morphology

By varying process parameters

Bad evaporation rate

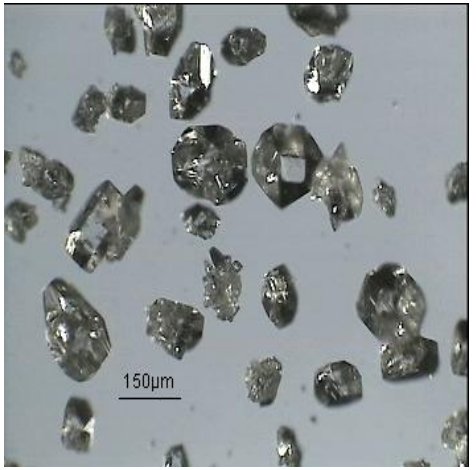
Good evaporation rate

Bad stirring rate



Good evaporation rate

Good stirring rate



Improved aspect ratio

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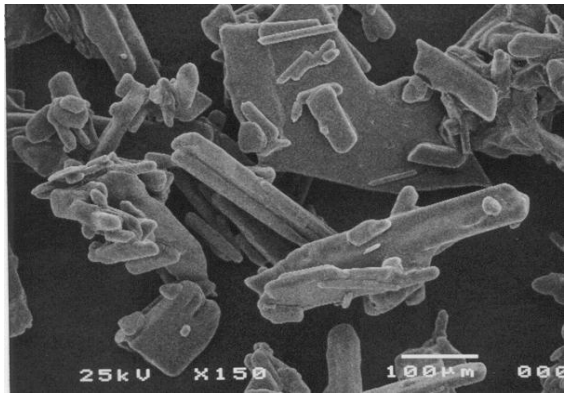
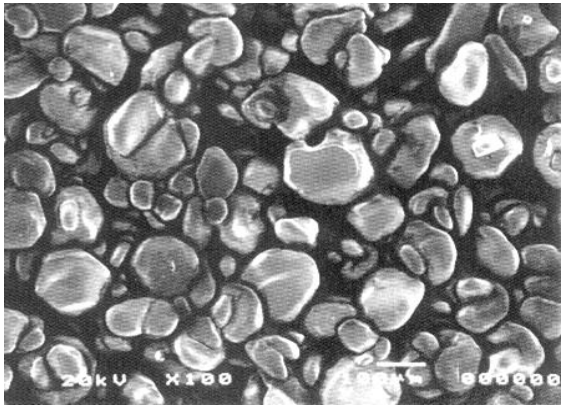
Shape processing

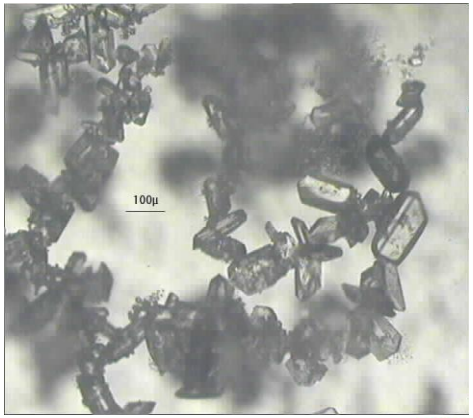
❑ ADN crystallization

Shape improvement by crystallization

Crude Eurenco-Bofors ADN







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New ingredients

- Look for a compromise performance – sensitivity

Outside of nitramines:

furazanes

pyrazoles

- New curing systems

Future ingredients may not be so chemically inert than nitramines (specially if sensitivity is related to hydrogen bonding)

- High energy materials
- nanos

Furazanes

❑ Furazane features (bibliographic data and computations)

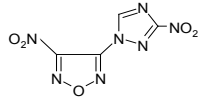
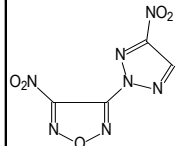
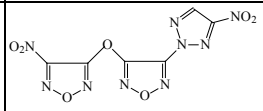
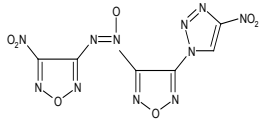
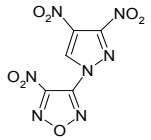
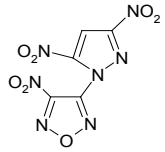
- High thermal stability due to aromaticity
- High heat of formation (aromaticity)
- 1.8 < density < 2
- Good predicted performances in explosive and propellant
- More powerful than nitramines (including CL20 sometimes)
- Sensitivity reported: good to unsuitable (only few furazanes tested)

Validation of the range of sensitivity and stability on models compounds produced at ZIOC(*) ⇨ engage research work

*: N. Makhova and A. Sheremetev (contract with SNPE)

Synthetized furazanes

Analytical data and safety elementary characterizations

Exemple	1	3	4	5	6	7
Formula						
NMR ^{1}H (ppm)	9,47	8,60	8,56	9,72	9,62 (s, CH)	8,49 (s, CH)
NMR ^{13}C (ppm)	146,1, 150,6, 156,5 (t), 165,1 (large)	134,7 (CH), 145,2 (Q), 153,4 (t, C-NO_2, J_{C-N} =19,7 Hz), 1 56,3 (C-NO_2, large)	134,3 (CH), 143,6, 151,2, 153,9, 154,6, 155,4	154,9, 153,6, 152,1, 149,9, 148,3, 126,4	130,2,137,3,147,4,151,1,156,3	105,4,147,0,148,7,157,0,157,9
NMR ^{14}N (ppm)	343,5, 351,9	340,4 (NO_2), 349,3 (NO_2)	349,3, 341,3, 311,1	353,7, 341,2, 310,4	343,6, 352,6	353,4, 348,3, 343,2, 310,6
MS	IE : 227 ($M^{+\cdot}$), IC^+ (CH_4) : 228 (MH^+)	IE : 227, 181 ($M-NO_2$)$^+$; IC^+ : 228 (MH)$^+$; IC^- : 226 ($M-H$)$^-$	IE : 311 (M)$^{+\cdot}$, IC^+ (NH_3) : 311, Infusion liquide : 312 (MH)$^+$, 324 ($MHNa^+$)	IC^+ (CH_4) 340 (MH)$^+$, 329, 368	IE : 271 (25) [M] $^{+\cdot}$	IC^+ (CH_4) : 272 (100) [MH]$^+$, 300 (13) [$M+C_2H_5$]$^+$, 312 (5) [$M+C_3H_5$]$^+$
impact	5.1 J	13 J	> 3 J	1 J	> 3.16 J	> 3.16 J
friction	353 N	> 353 N	> 353 N	30 N	> 353 N	> 353 N
Spark	> 726 mJ	> 726 mJ	> 726 mJ	< 51 mJ	> 104 mJ	> 104 mJ
Thermal stability	223 °C (onset dec)	mp= 50.3 °C; bp = 215 °C	mp = 80.9 °C bp = 189 °C	mp = 150 °C dec = 191 °C (onset)	mp = 98 °C bp = 276 °C	mp = 144.8 °C bp = 239 °C

Performances

From computed physical and thermodynamic values

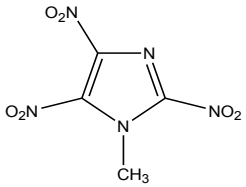
Molecule	Enthalpy of formation (kcal/mol)	density	Detonation energy (V/Vo= 2)*	Smokeless propellant Filler/GAP (85/15) Is (s)	Smokeless propellant Filler/HTPE (85/15) Is (s)
HMX	20,1	1,908	100% HMX	260,4	249,9
CL20 ε	91,5	2,04	120% HMX	268,0	260,1
1	123,3	1,884	102% HMX	264,6	253,8
3	158,5	1,884	111% HMX	276,3	267,2
4	209,4	1,921	112% HMX	273,2	263,2
5	272,4	1,954	120% HMX	278,7	269,4
6	124,1	1,934	110% HMX	270,5	261,8
7	124,1	1,936	110% HMX	270,5	261,8

Furazanes conclusion

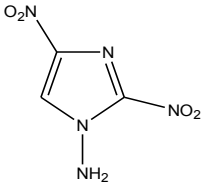
- This family shows promising
- Measurements of d and ΔHf in progress
- Current work to examine deeper the properties for formulations
- Development requires control of the whole synthetic route (from inert starting material up to the end product)

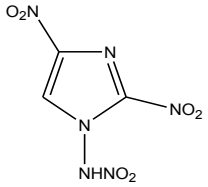
Motivation to explore pyrazoles

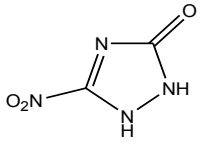
New energetic compounds with moderate sensitivity that appeared in recent years are based on triazoles and imidazoles



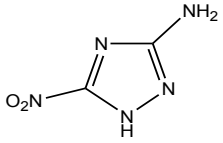
MTNI



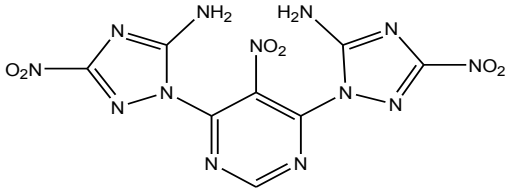




NTO



ANTA



DANTNP

Regarding energy content, the pyrazole ring seems effective

name	pyrrole	1H-imidazole	1H-pyrazole	1H-1,2,4-triazole	1H-tetrazole
structure					
Heat of formation (kcal/mol)[i]	15.1 (liquid)	11.9 – 13.97	25.2 – 27.7	25.79 – 27.03	56.4 – 56.6
Heat of formation (kcal/kg)	225.07	174.8 – 205.2	370.2 – 406.9	373.4 – 391.3	805.1 – 808.0

⇨Synthesis and measurements on highly nitrated pyrazoles is desirable (Work under Fr-Sw TA)

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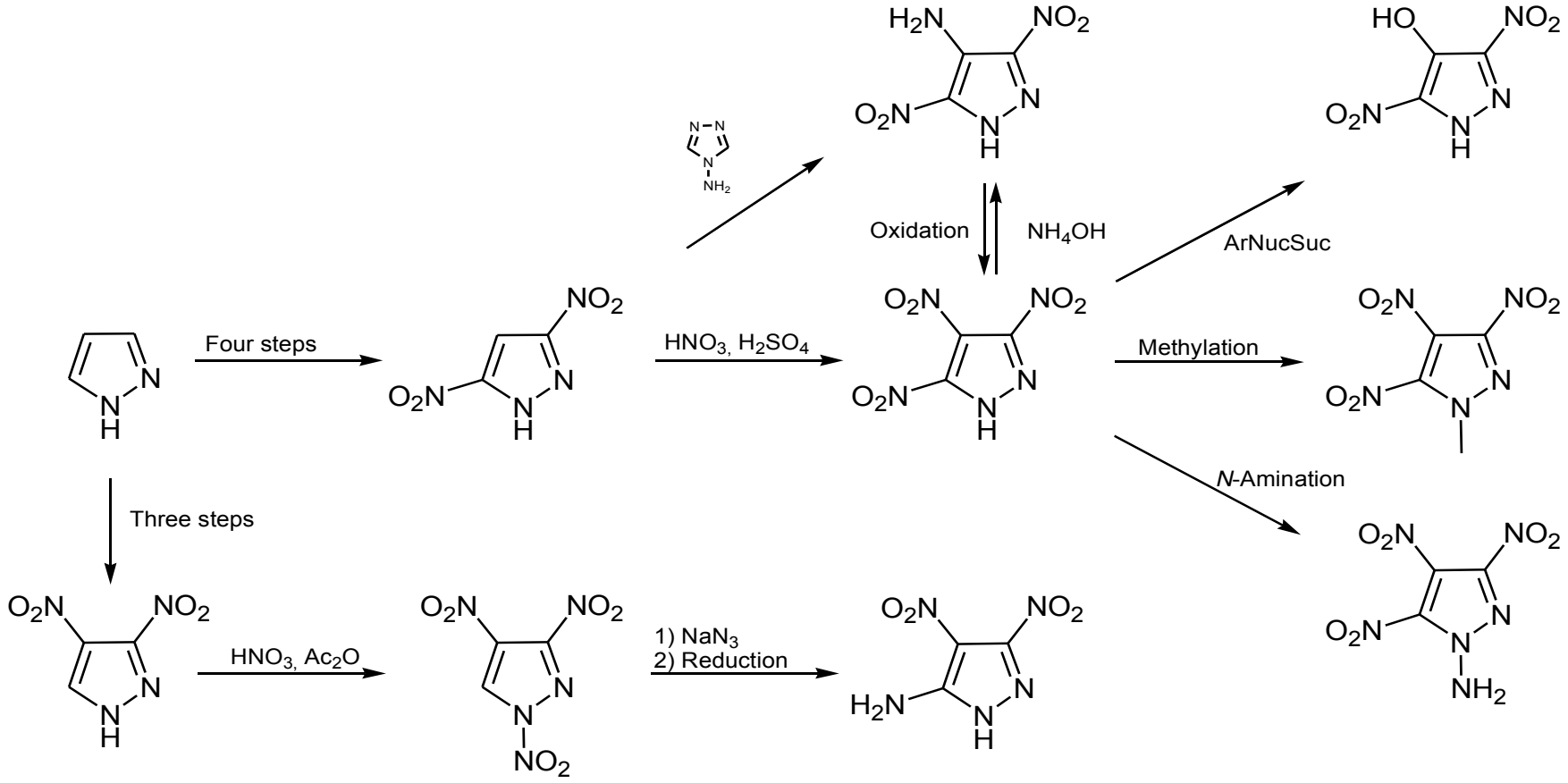
Syntheses

- 5 compounds have been synthesized according to the following routes



G. Jacob, N. Latypov, P. Goede, S. Ek, G. Hervé NTREM 2009 (Pardubice)

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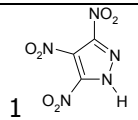
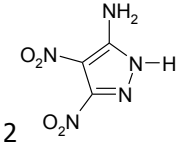
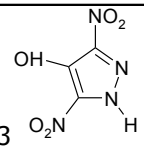
Sensitivity

❑ Sensitivities and thermal behavior

compound	sensitivity			Thermal stability (DSC)
	impact	friction	spark	
NTO	22 J	> 353 N	> 784 mJ	286°C (dec.)
HMX	4 J	125 N	> 726 mJ	287°C (dec.)
 1	17 J	92 N	> 784 mJ	188°C (m.p.) 258°C (dec.)
 2	> 50.1 J	> 353 N	> 784 mJ	189°C (m.p) 218°C (dec.)
 3	4.9	183	> 784 mJ	195°C (dec.)

Calculated performances

Molecule	Enthalpy of formation (kcal/mol)	Density	Detonation Velocity (m/s) E/EHMX (V/Vo= 2)*	Specific impulse 70/1 (s) *
HMX	20.1	1.908	9321 100%	253.8
RDX	16.7	1.823	9008 92%	254.3
NTO	-25.7	1.910	8544 72%	/
CL20	92	2.04	10053 120%	261.5
1	34.1 (exp.)	1.867	9253 96%	261.9
2	14.4 (litt.) 7.6 (this work)	1.872	8640 82%	230.1
3	-3.6 (calc.)	1.92	8901 90%	241.9
5	60.76 (calc.)	1.90	9682 109 %	264.9

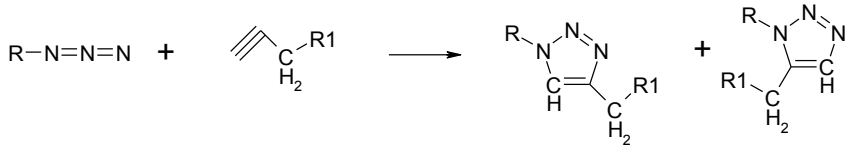
***: 70% mass in plasticized GAP**

Pyrazoles status

- **The exploration of the chemistry of pyrazoles has been successful and resulted in the preparation of five compounds.**
  - Trinitropyrazole has been used as a versatile synthetic scaffold.
- **The results of our calculations and the preliminary characterization of these compounds show their potential as new ingredients with high performance and low sensitivity in both explosives and propellant formulations.**
  - Good balance of properties compared to other new energetic materials
- **The continuation of this work is the scale-up of the synthesis in order to fully characterize these promising materials.**
  - Feasible synthesis compared to other new energetic materials
  - Limitation of the number of steps

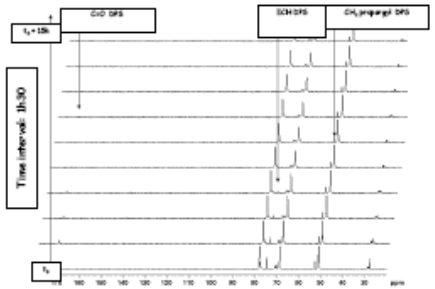
Curing systems

❑ New curing systems

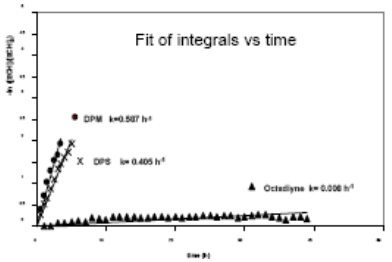


- Application of this chemistry to energetic materials may solve difficulties encountered when curing new energetic fillers bearing nucleophilic groups with isocyanates
- Setup of a methodology to follow the crosslinking reaction into the NMR probe

One spectra every 30 minutes during curing.
Polymerization at 50°C in the NMR probe.



On the terminal ^{13}C signal of acetylenic groups.
Best fit obtained with 1rst order law.



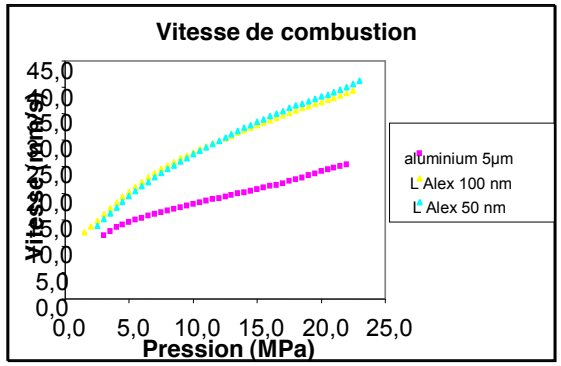
❑ Information collected

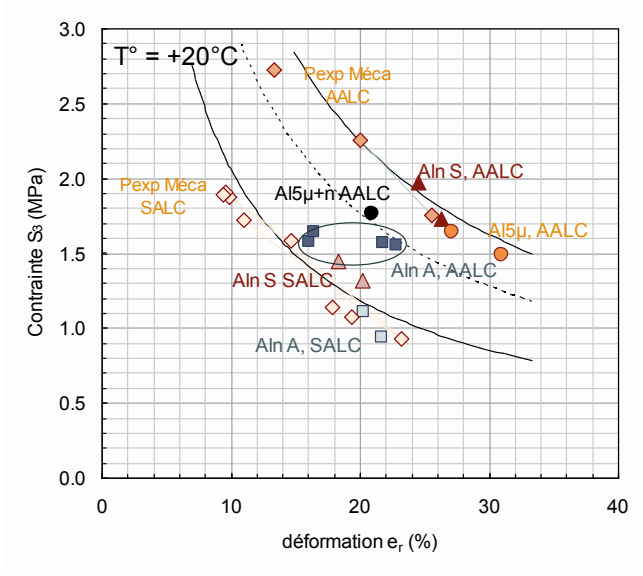
- Reactivity of different propargyls groups
- 1rst order reaction indicating close reactivity of the N_3 groups of GAP

⇨3D structure of the network to be examined

❑ n-Al evaluation in propellants

- 50 and 100 nm commercial grades (palmitic acid passivated)
- Faisabilty of propellants (viscous paste but still usable)
- Safety tests : pass
- Positive effect on burning rate and MP





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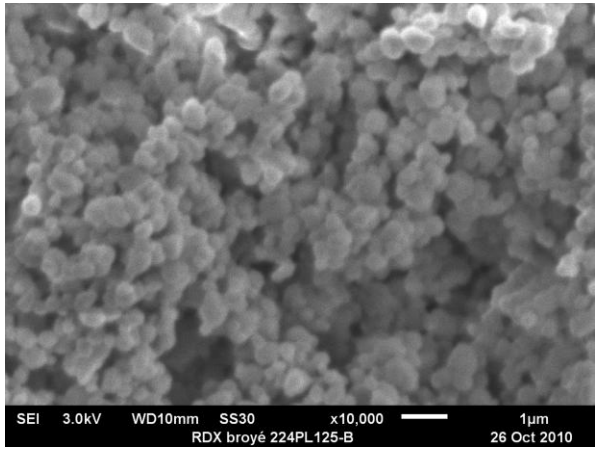
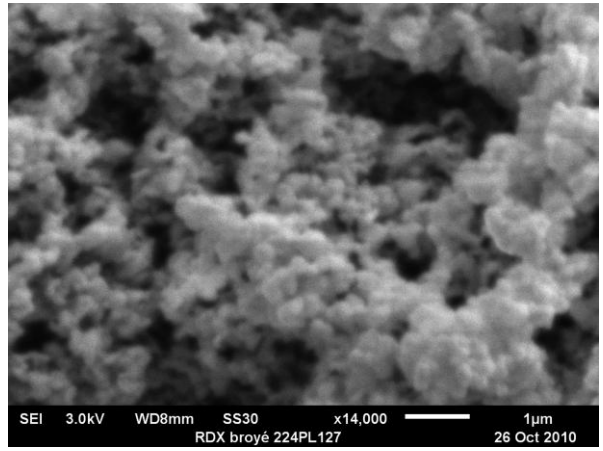
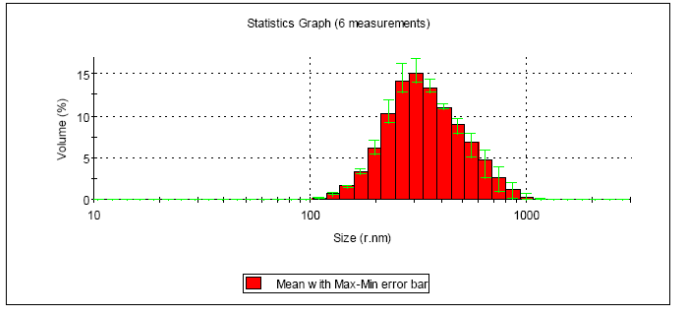
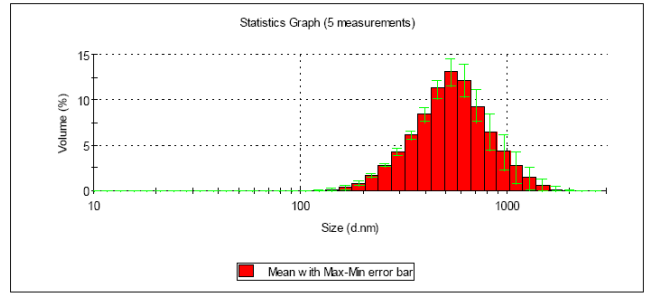
nanos

- n-RDX preparation (for explosives)
- Grinding in organic medium produces









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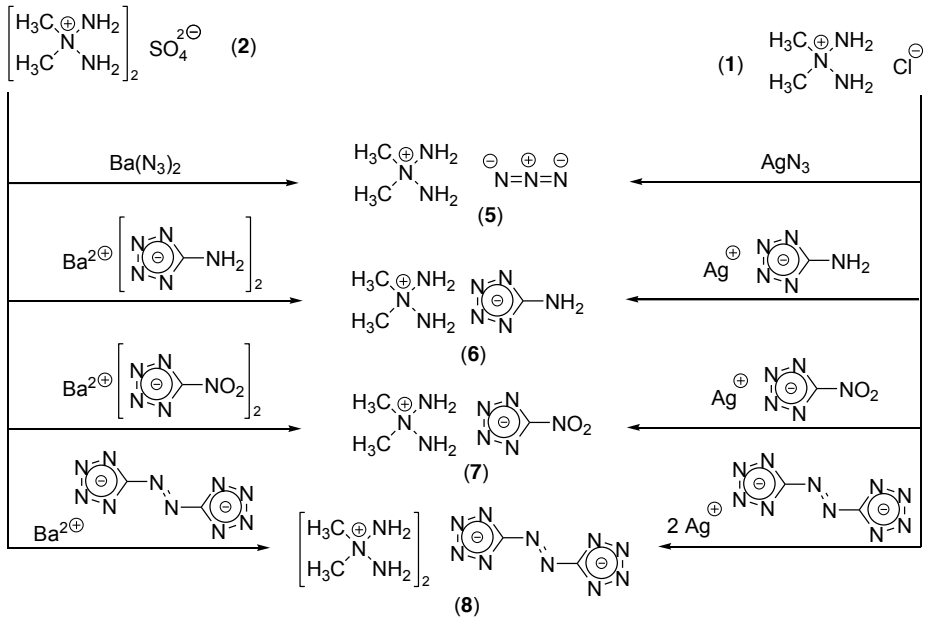
HEM-HEDM

- **Setup of a joint laboratory (SME-CNRS-CNES-University Lyon) with former "Laboratoire Hydrazines et Procédés" into "Hydrazines et Composés Energétiques Polyazotés "**

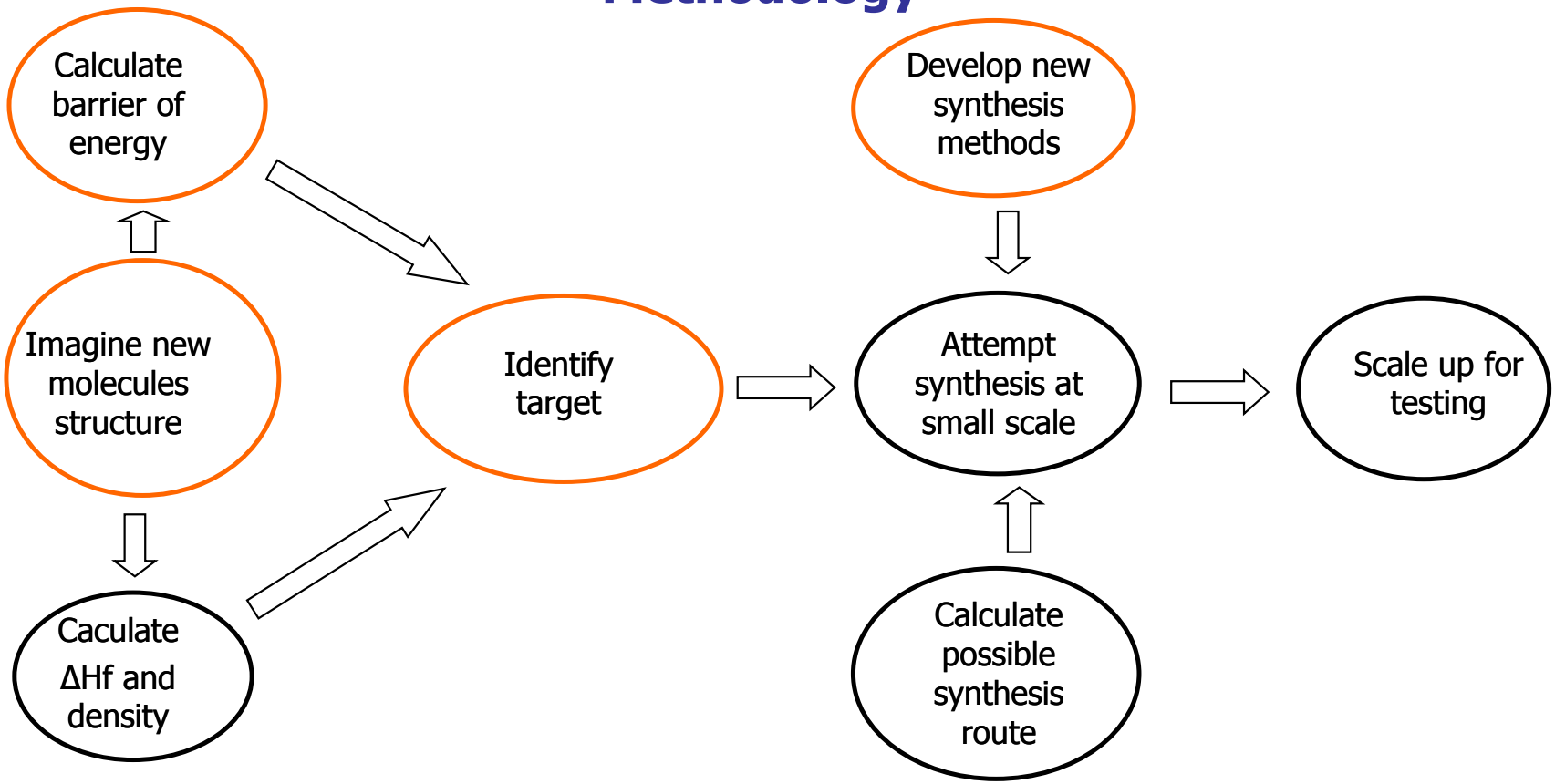
  - **Objectives:**
    - continue hydrazines development (processes, new grades)
    - benefit from knowledge in hydrazines to prepare new high nitrogen derivatives
    - Converge to N-HEDM



V. Forquet, C. Darwich, C. Miró Sabaté, H. Delalu NTREM 2010 Pardubice

Nitrogen HEDM

Methodology



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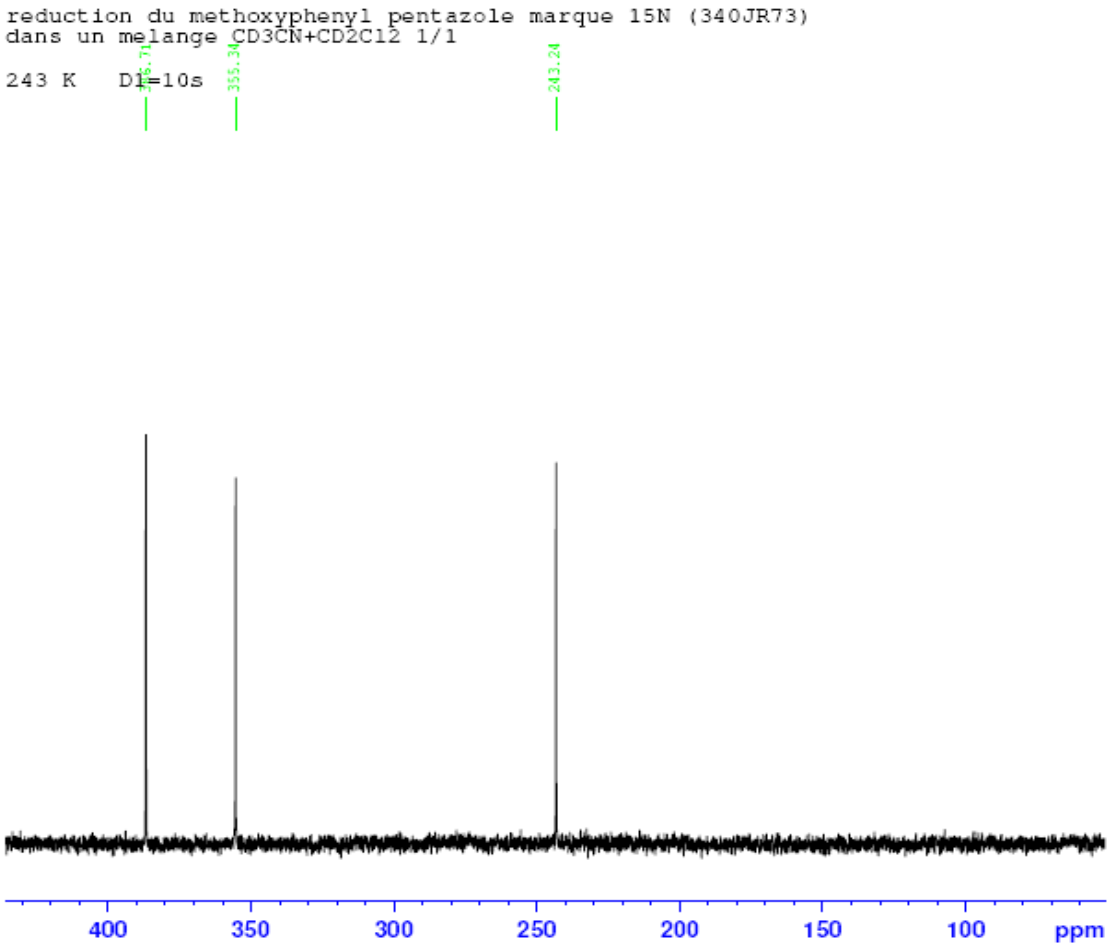
❑ CRB work in progress on HEDM (Fr-Sw TA with FOI):

- implementation of a program for design of targets
- computation of properties and stability (quantum mechanics)
- design of synthetic routes (computation of intermediates energies)
- implementation of specific lab equipments (safety concerns)
- Preparation of precursors (for CRB focused on pentazole)

Preparation of p-methoxyphenylpentazole as a precursor : High purity shown by ^{15}N NMR (route via organic nitrite , ^{15}N marked azide)



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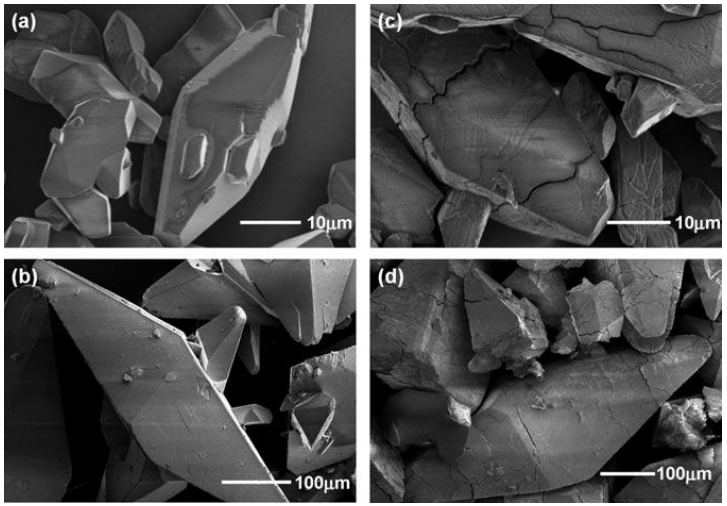
Emerging processes

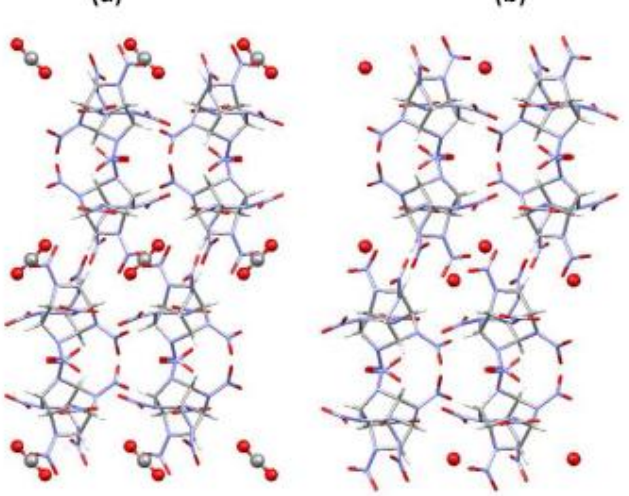
❑ Continuous / micro reactions

- **Work just started**
  - to handle low volume production of sensitive materials
- **future applications**
  - uses in lab to explore new domains of reactions, screen reaction conditions …and then transfer to industrial scale
  - High throughout flow synthesis (screening compounds) ??
  - Integrate into EM manufacture
- **Main difficulties**
  - Handling of solids
  - Isolation and purification of product
- **Main issue**
  - Optimizing production tools

❑ Trials with high pressure / CO_2

- Evidence of a new inclusion complex between CO_2 and CL20
- Complete transformation of ε-CL20 at 80°C-15MPa (crit. Pt = 31°C-7.4MPa)
- Occurs from the solid with cracks formation and change of conformation





of ε-CL20 at 150 K,[26] α-CL20–0.5 CO_2 at 150 K and α-CL20–0.25 H_2O at 293 K.[15]

	ε-CL20	α-CL20–CO_2	α-CL20–H_2O
space group	*P*21/*n*	*Pbca*	*Pbca*
a [Å]	8.800(1)	9.6895(6)	9.485(2)
b [Å]	12.499(1)	13.210(1)	13.225(4)
c [Å]	13.299(1)	23.515(2)	23.673(3)
β [°]	106.62	90	90
V [Å^3]	1401.7	3010.0	2969.5
ρ_{calcd}	2.076	2.031	1.980

S. Saint Martin et al. , Chem. Eur. J. 2010,16, 13473-13478

Modelling

❑ Sensitivity

Multi levels contributions

molecule

- Composition (quality and quantity of EG)
- *Intra*molecular bonding
- Energy (ΔH°_{f}) of the molecule
- EP of the molecule

crystal

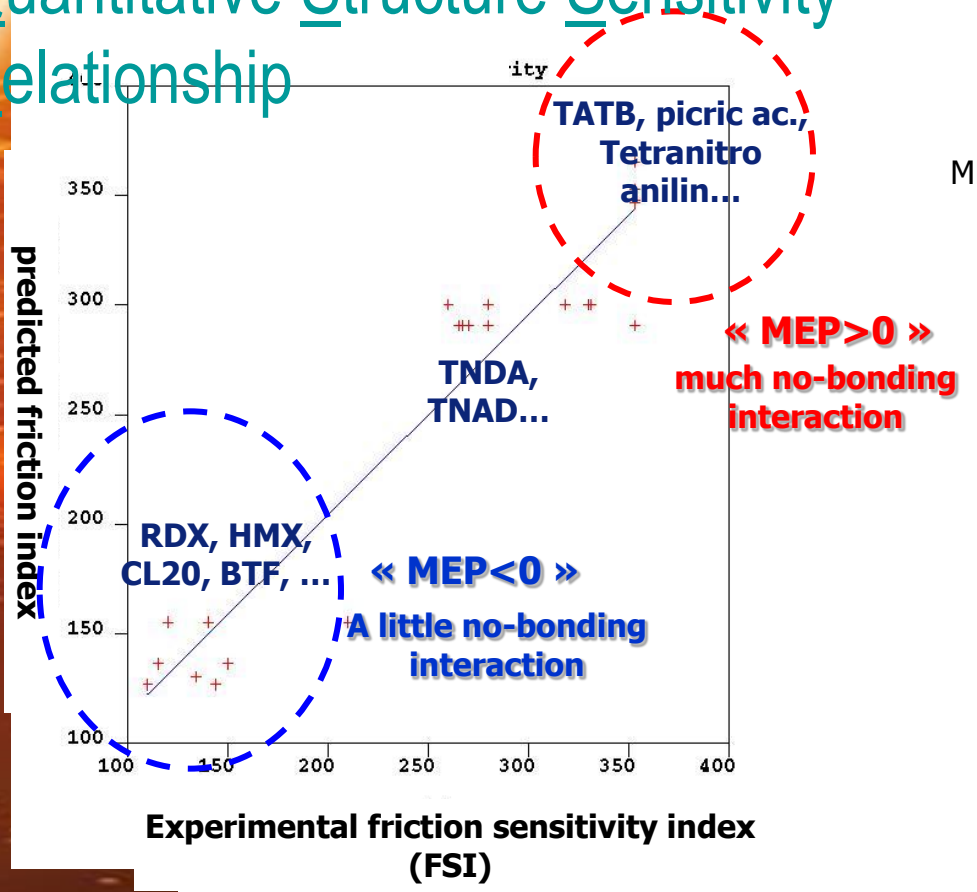
- *Inter*molecular (no)bonding
- Energy and MEP of the crystal
- Defects, adsorbats and nanostructuration (“Hot spot” -microscopic concept)
- Shape and crystal packing (density)

material

- Interaction with the surrounding matter (polymer)
- “Hot spot” (macroscopic concept)

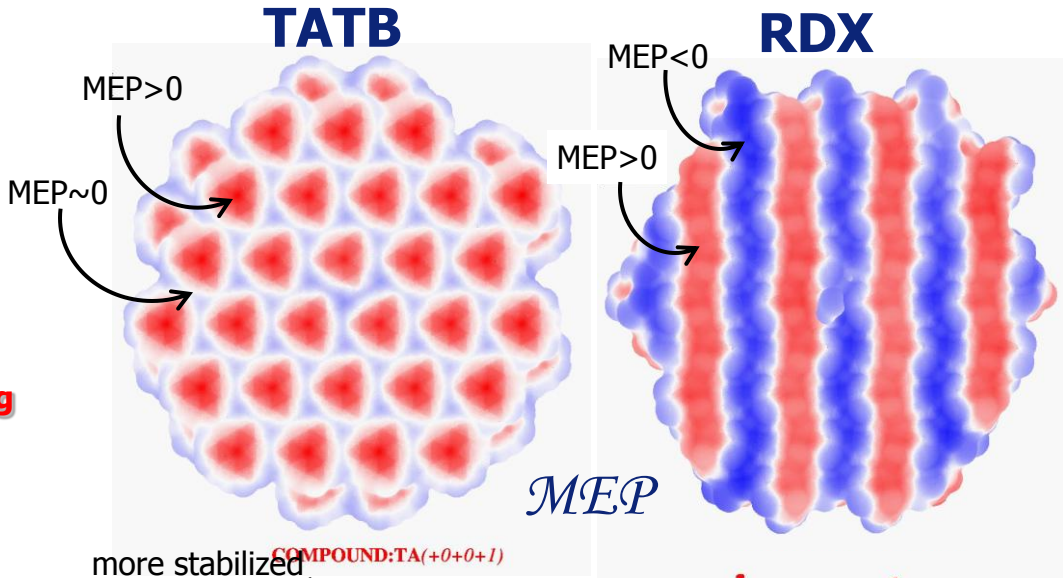
ISF best model & starting point

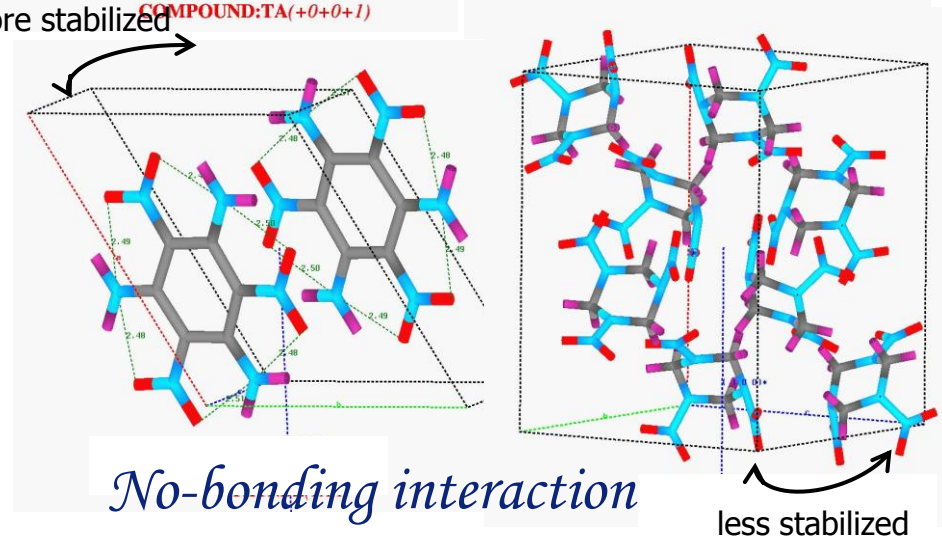
Quantitative Structure Sensitivity Relationship



ISF=f(MEP, no-bonding interaction)

r^2=0.911 , 3 variables, 22 observables





G. Jacob, S. Benazet Propellants Expl. Pyr. 2003

modeling

❑ To be developed:

- **Sensitivity based on the molecular structure (guideline for screening)**
  - With several tests
- **Interaction with the formulation (to know the sensitivity of the material)**
- **Toxicology (as guideline if reliable)**
  - Complexity of practical evaluation of figures
- **Tools for fast screening of large number of candidates**

- **Modeling of the process lines (to fit production decrease)**
  - Forecast benefit by looking in pharma