Novel access to HEDM polyazanes

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Overview

High Energy Density Materials

Key parameters promoting propulsion : I_{sp} and **density**

- **Specific impulse (Isp)** allows to compare propulsion performance of propellants

$$I_{sp} = \frac{F}{q_w \cdot g_0} \ (s)$$

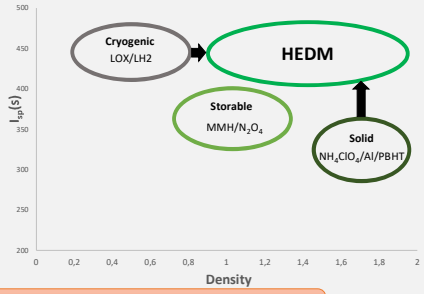
F thrust (N)
q_w gas ejection mass flow rate in kg/s
g Earth's gravitational acceleration (9,81 N/kg)

- **Density allows access to launcher scale optimisations**
  High density → Smaller propellants tanks
  → Lower weight launcher

Current liquid rocket propellants used in most launchers (for main stage)
Liquid oxygen/liquid hydrogen (LOX/LH2)

O_2/H_2 (cryogenic) :
High Isp
Poor density

PBHT/PA/Al (solid) :
High density
Poor I_{sp}



Create new compounds with both excellent I_{sp} and high density : **HEDM**

Why polynitrogen compounds ?

$$I_{sp} = \frac{F}{q_m \cdot g_0} \propto \sqrt{\frac{T_0}{M_0}}$$

ΔH_f (standard enthalpy of formation)
Ejected gas : N_2, H_2

Increasing T_0

- **N-N to N≡N** energetically favourable (gain of 60% compared to C-C to C≡C)
- ↗ **N-N bonds → ↗ ΔH_f**

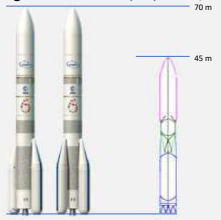
Minimise M_0

- **N_2** no toxic gas and inert
- **H_2** : small molar mass (I_{sp} ↗)

Maximize number of N-N bonds

Theoretical calculations :
- High Density
- Ring strain → high I_{sp}
- Polynitrogen compounds (with **N≥3**) → high I_{sp} (**>400 s**)

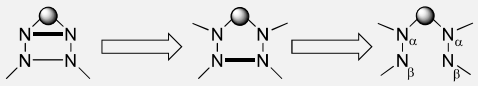
By using HEDM as monopropellant, we could :
- reduce launcher size (single stage)
- reduce costs (oxidant not requested)
- be more competitive



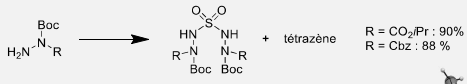
Simplified technology

Strategy

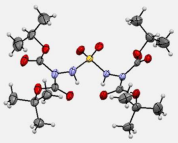
Tetrazetidine precursor with a sulfonyl linker



❖ Condensation of a protected hydrazine on a sulfonyl linker



R = CO_2*i*Pr : 90%
R = Cbz : 88 %



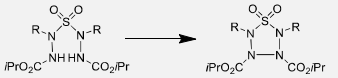
- High yields / First sulfonyl linker
- Selective double protection of the β position

❖ Selective protection of the α position

Entry	R_1	R_2	Yield
1	Cbz	Me	50%
2	CO_2*i*Pr	Me	92%
3	CO_2*i*Pr	Bn	90%
4	CO_2*i*Pr	Cbz	73%

➢ R_1 and R_2 insensitive in the Boc deprotection conditions (acidic conditions)
➢ High yields with R = CO_2*i*Pr

❖ Cyclization after Boc deprotection



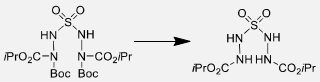
R = Me : 67%
R = Bn : 10%
R = Cbz : 0%

➢ With this strategy, R_2 choice limited to stable groups in acidic conditions

Other way

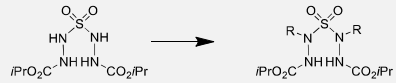
A new strategy enabling a wide variety of the R_2 groups

❖ Early Boc deprotection before N_α protection



- Hydrophilic product (theoretical logP : - 0,18)
- Hypothesis : Proton in alpha more acid than beta
- Access to other protective groups

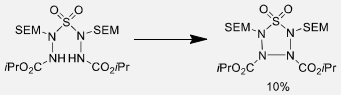
❖ Wide variety of protective groups in the α position



R = Me : 60%
R = SEM : 70%
R = BOM : 50%

✓ Very fast reaction with high yield
✓ Stable at room temperature

❖ Cyclization



10%

- Optimization of conditions according to protective groups

Conclusion

- Stable polynitrogen structures has been synthesized
- Further works on cyclization of these structures toward the tetrazetidine HEDMs
- Final HEDM would be obtained by removing protecting groups on these rings