# Preliminary study of the reactivity of a primal carbon cluster towards ammonia in space

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# Introduction

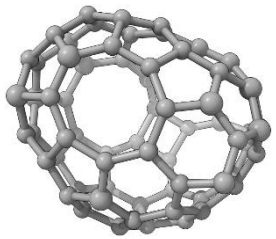
- Amination of a primal carbon cluster in space
  - Maximum number of cumulative barrierless aminations
  - Simulation of the first amination with a barrier
  - Spontaneous side reactions

  - Characterization of the processes, including reasons for the chemistry

  - First study of its kind

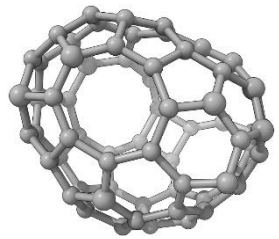
cost
EUROPEAN COOPERATION
IN SCIENCE & TECHNOLOGY

BULGARIAN
SCIENCE
FUND

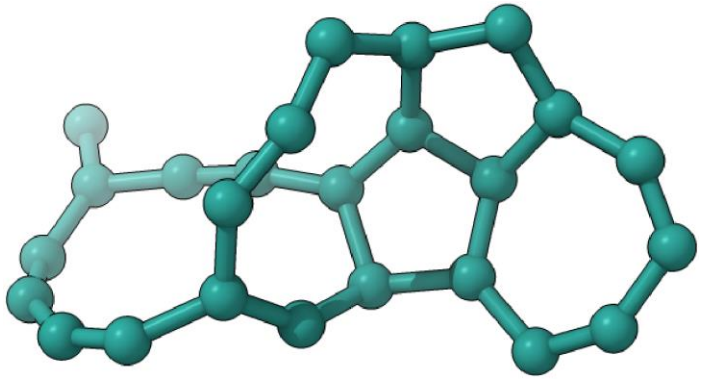


# Methods

- Methods
  - SCF
    - DFTB2
  - Simulation
    - Born-Oppenheimer Molecular Dynamics
      - Statistical nature
      - NVP, 400K, 20ps
    - Born-Oppenheimer Molecular Metadynamics
      - Reaction guidance
      - NVT, 400K, 20ps

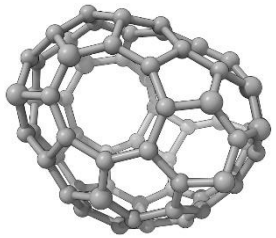


# Carbon cluster

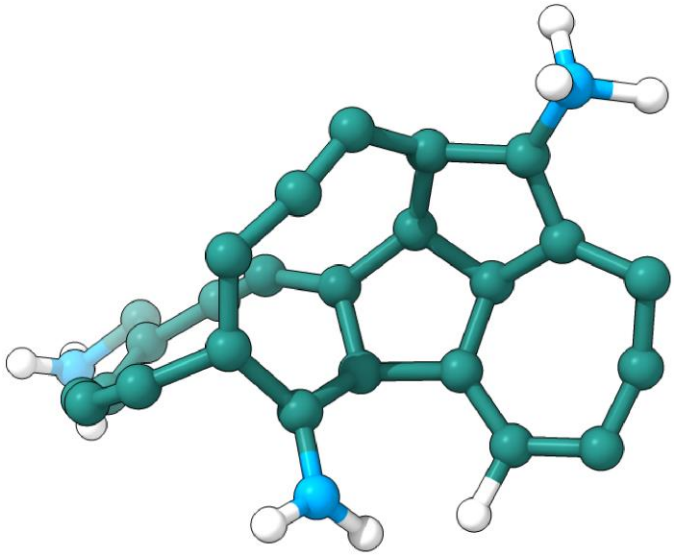


C25

- Product of spontaneous stabilization of a non-covalent aggregate or 25 randomly positioned atoms
- Additional stabilization with 20ps NVT dynamics at 400K
- High-energy
- Experimental data for amorphous carbon and hydrocarbon structures in space [1,2]



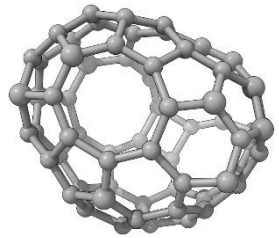
# Barrierless amination



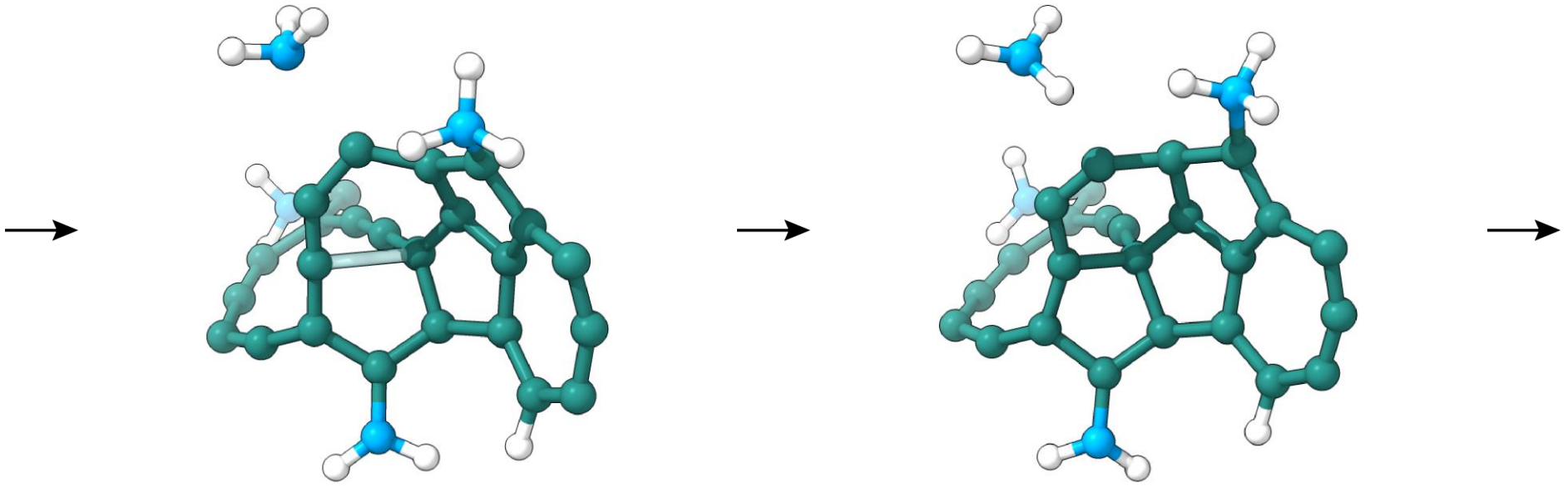
Carbon
Nitrogen

$C_{25}H(NH_3)_2NH_2$

- The cumulative amination is a self-inhibiting process
  - $:NH_3$ is a nucleophile, while the charge in the C-frame is (-)
- Cumulative barrierless amination occurs at most three times



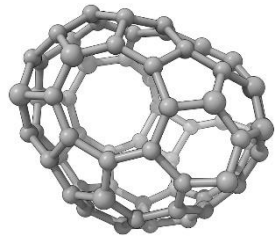
# Guided amination



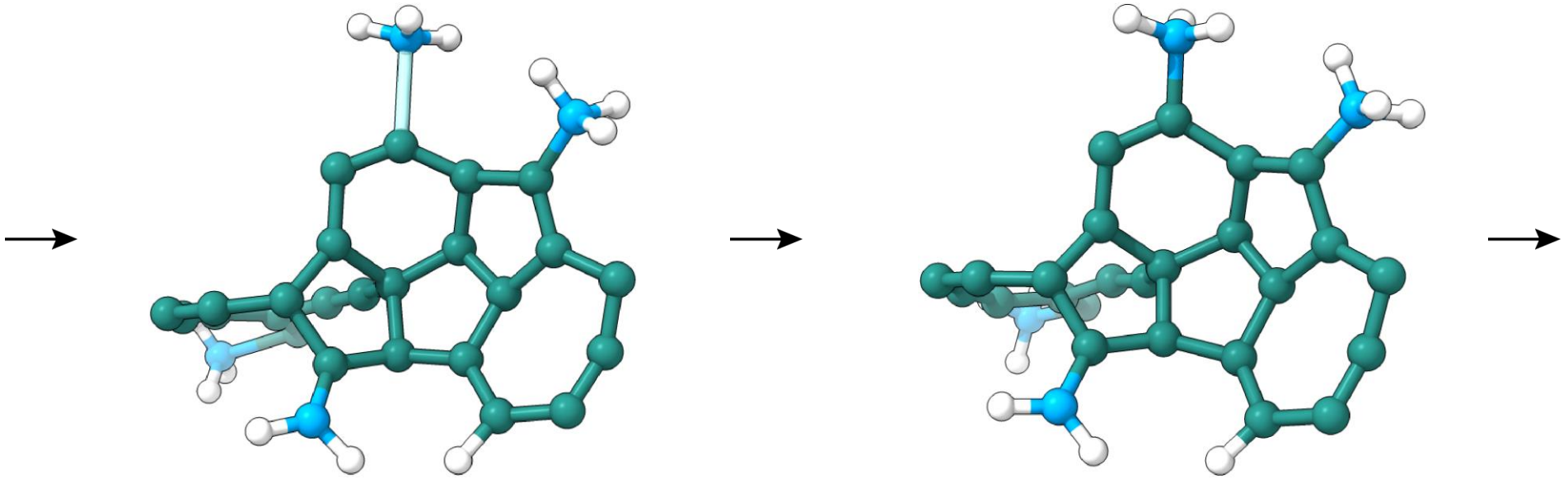
Transition State

iC25

- Stabilization due to a spontaneous reaction
  - Intramolecular cyclization



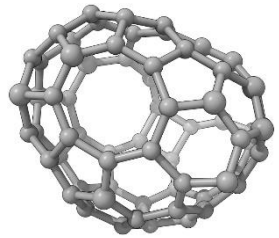
# Guided amination



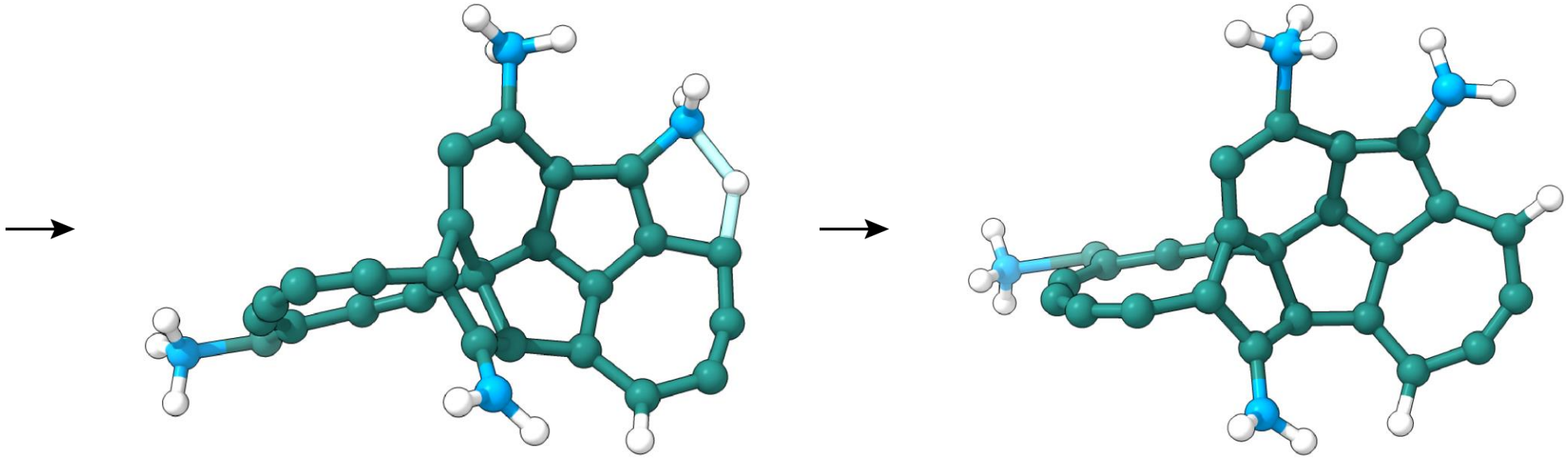
Transition State

$C_{25}H(NH_3)_3NH_2$

- Amination step: three (+) charges at N atoms and three (-) charges at C atoms



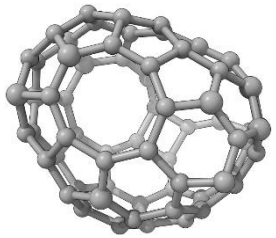
# Guided amination



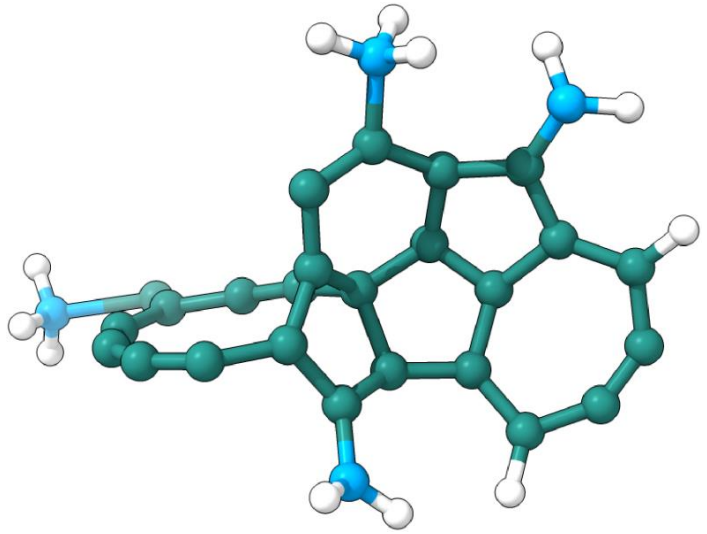
Transition State

$C_{25}H_2(NH_3)_2(NH_2)_2$

- Reduced number of (+) charges at N atoms
- Negation of opposite charges in the molecule
- $n_N$ - $\pi_{CC}$ conjugation between the N atom and a π-electronic system

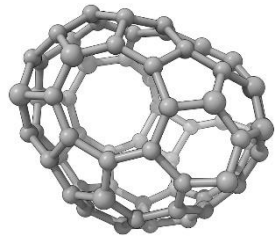


# Final product

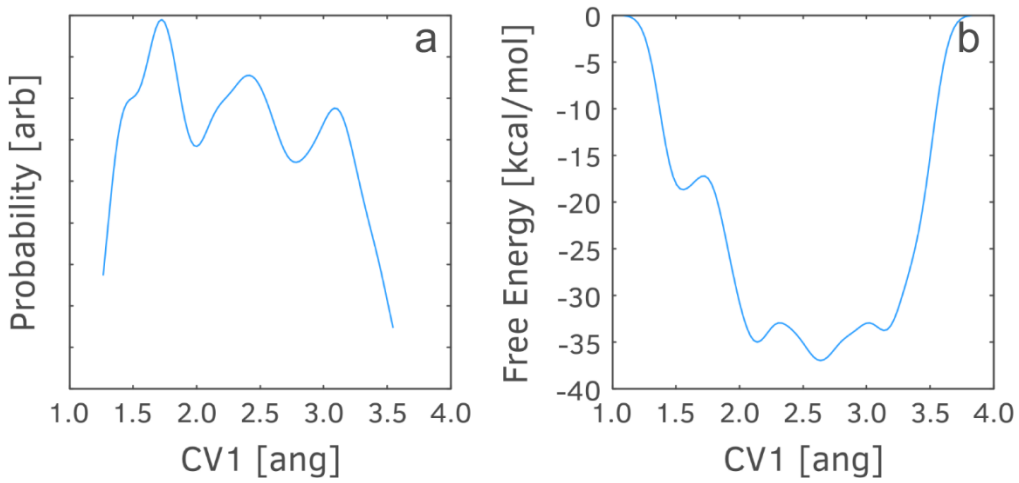


$C_{25}H_2(NH_3)_2(NH_2)_2$

- Acyclic conjugated fragment with 8 π-electrons
- Cyclic conjugated fragment of condensed rings with 16 π-electrons
- All amino groups are substituents to fragments with conjugated π-density

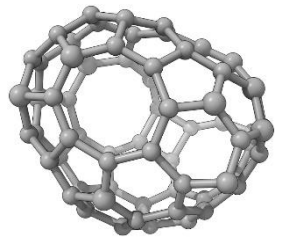


# Metadynamics trajectory



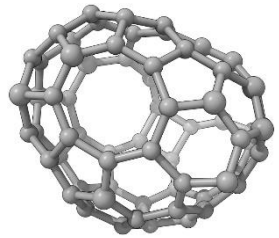

Barrier of the forward reaction 20 kcal/mol
Barrier of the reverse reaction 1.5 kcal/mol

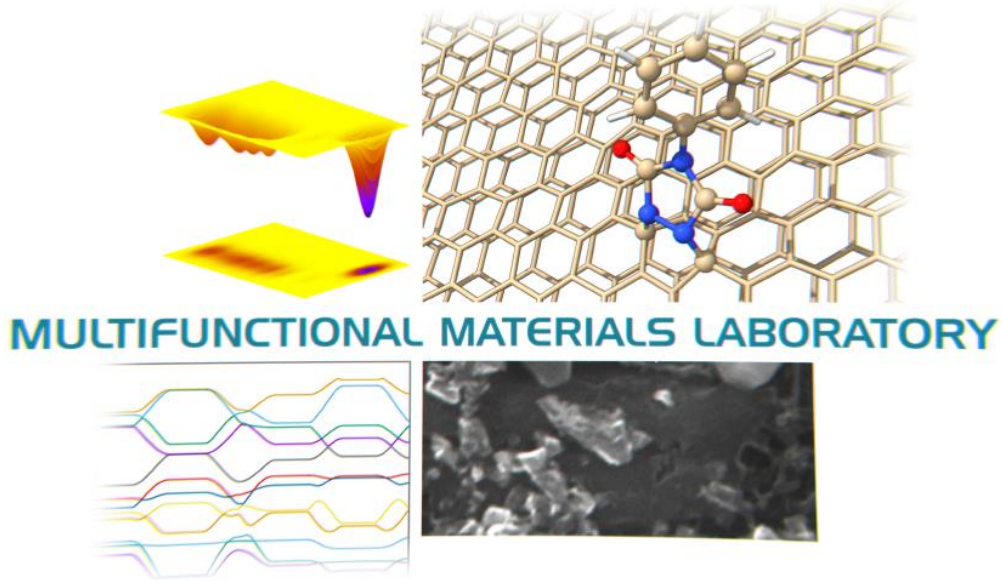
- Highly endothermic process
- The reagents are prevalent in the trajectory



# Conclusions

- The cumulative amination is a self-inhibiting process
- Spontaneous barrierless amination occurs at most three times
- Primal carbon clusters are highly reactive
- The fourth ammonia addition:
  - The reaction has a barrier
  - Highly endothermic
  - The reverse reaction is highly prefered
- Spontaneous stabilization:
  - Intramolecular cyclization of the C-frame
  - Hydrogen transfer



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# Референции


- [1] Amorphous carbon grains and PAH molecules in space.
  - Blanco, A.; Borghesi, A.; Fonti, S.; Orofino, V.; Bussoletti, E.; Colangeli, L.; *Memorie della Societa Astronomica Italiana*, **1987**, Vol. 58, p. 315-319.
- [2] The evolution of amorphous hydrocarbons in the ISM: dust modelling from a new vantage point.
  - Jones, A. P.; Fanciullo, L.; Köhler, M.; Verstraete, L.; Guillet, V.; Bocchio, M.; Ysard, N.; *Astronomy and Astrophysics*, **2013**, Vol. 558, A. N. A62.