Механизъм на образуване на фулерено-подобни наночастици от агрегати на въглеродни атоми в космоса

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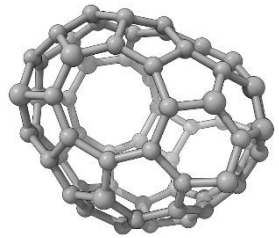
Проф. Теодор И. Миленов

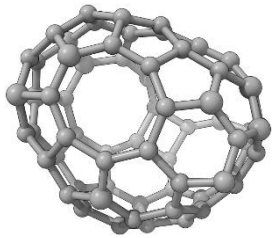
Въведение

- Произход на първичните въглеродни клъстери и наночастици в космоса
  - Пре-реакционни атомни агрегати
    - Размер
    - Междуатомна ориентация
    - Плътност
  - Характеризация на клъстерите
    - Структурни мотиви
    - Хибридизация
  - Реакции между клъстери и малки молекули
    - Хидрогениране
    - Аминиране
  - Формиране на фулерено-подобни наночастици
    - Механизми
    - ИЧ спектър + сравнение с известни фулерени



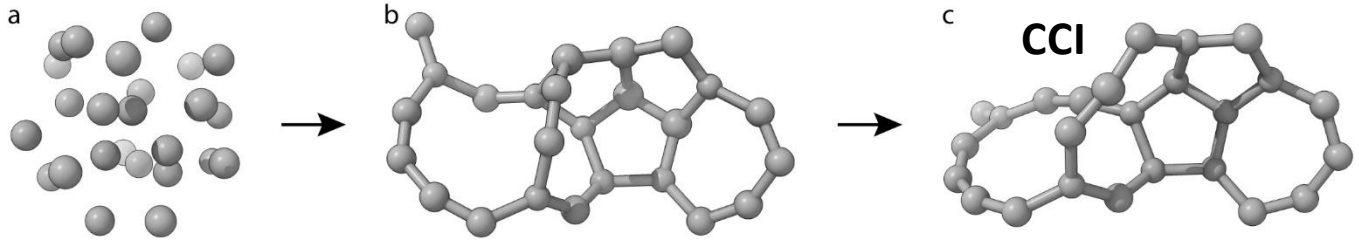
Методи

- Методи
  - DFTB2
  - Динамика
  - Метадинамика
- Изчислителни стъпки
  - Клъстери
    1. Оптимизация
    2. Динамика: NPT, 400K, 20ps
    3. Оптимизация
    4. Метадинамика: NVT, 400K
    5. Оптимизация
    6. ИЧ спектър
  - Наночастици със затворена клетка
    - Постъпкова Метадинамика



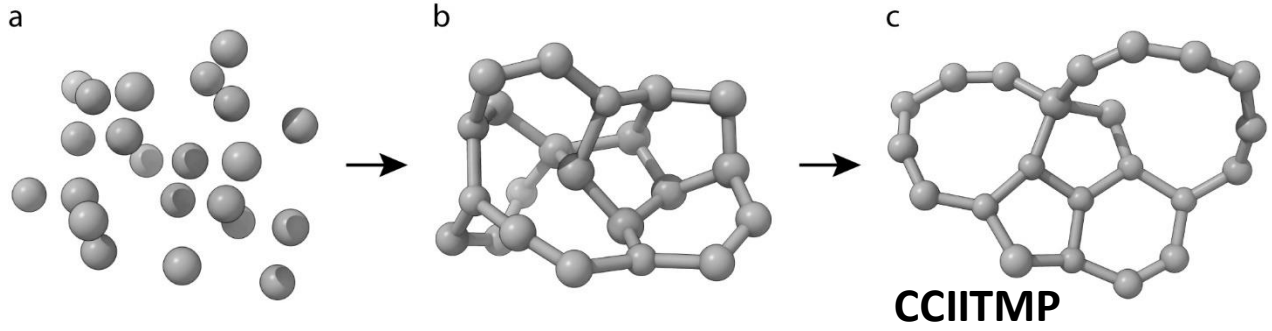
Клъстери

Висока плътност
Случайна ориентация



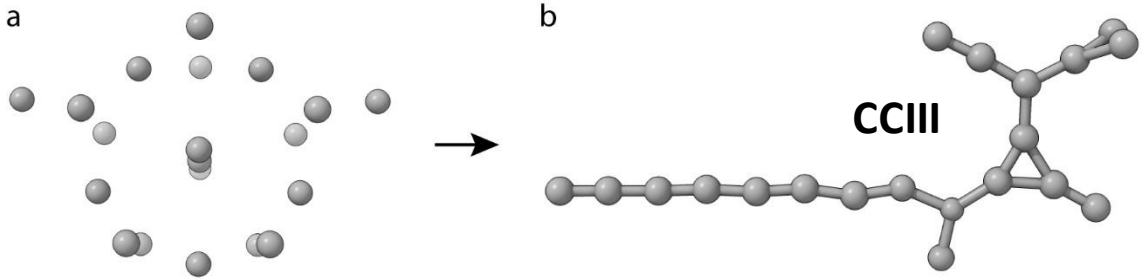
Оплетена полициклична
Главно sp^2
Градивен блок за затворена клетка

Висока плътност
Тетраедрична ориентация



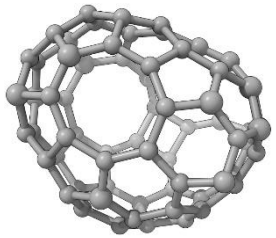
Оплетена полициклична
Главно sp^2
Градивен блок за затворена клетка

Ниска плътност
Случайна ориентация



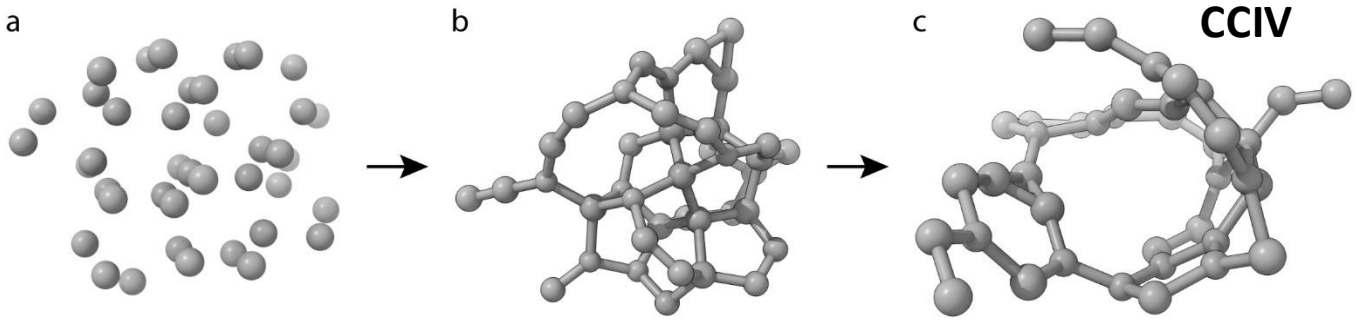
Разклонена линейна
3-атомни пръстени
sp и sp^2, по равно; *[3]*

Открити аморфни C и HC молекули в космоса [1,2]

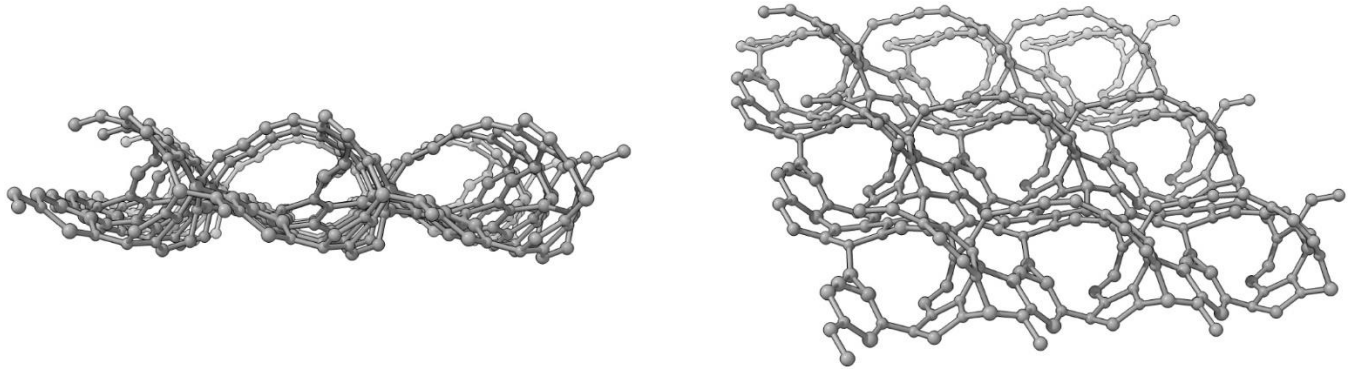


Полимер

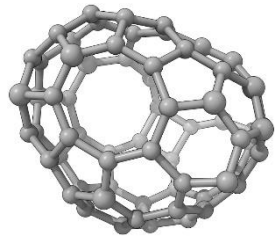
PBC за полимеризация
Висока плътност
Тетраедрична ориентация



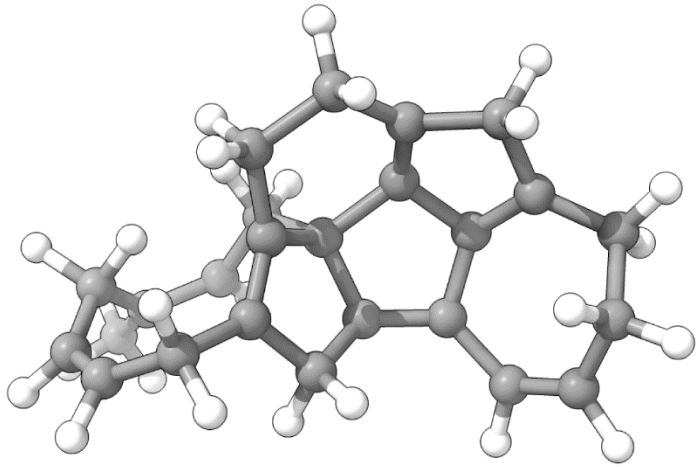
1D порест полимер
Главно sp^2
Наподобява CNTs



Няколко-клетъчен изглед

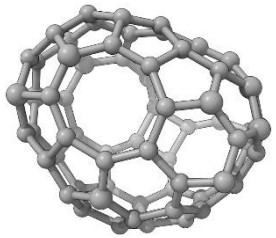


Присъединително хидрогениране

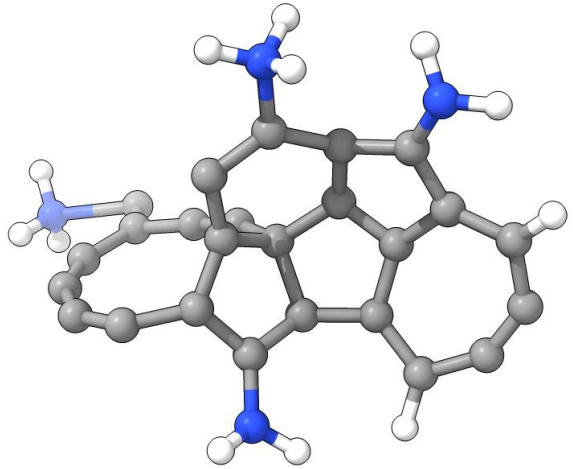


$C_{25}H_{26}$

- 3 механизма
- Допълнителни реакции: вътрешномолекулна циклизация
- Висока реактивоспособност на С-клъстера

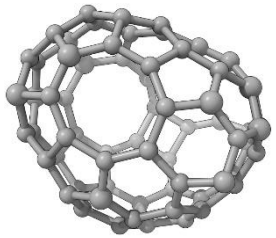


Присъединително аминиране



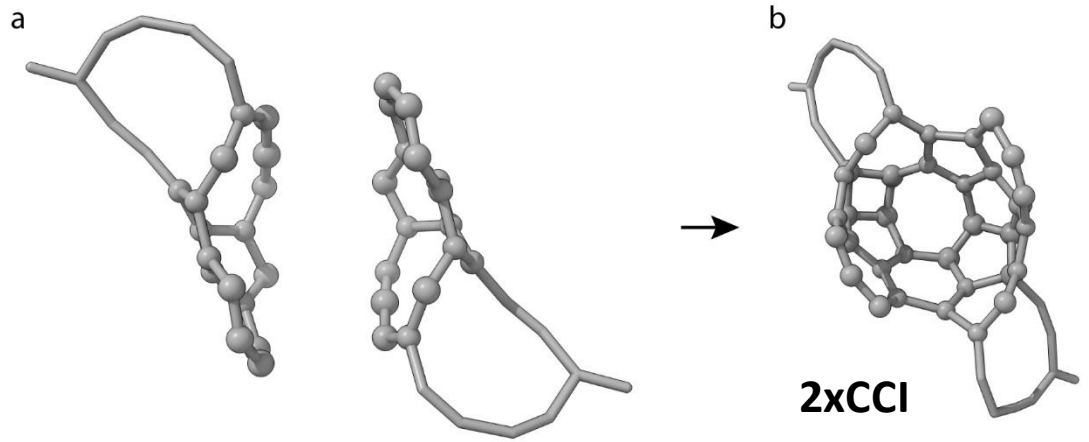
$C_{25}H_2(NH_3)_2(NH_2)_2$

- 1 механизъм
- Допълнителни спонтанни реакции: H-трансфер и вътрешномолекулна циклизация
- Аминиране – автоинхибиращ се процес, но първоначално (трикратно) е безбариерен
- Висока реактивоспособност на C-клъстера
- Четвърто аминиране – бариерно, ендотермично, силно нестабилен продукт



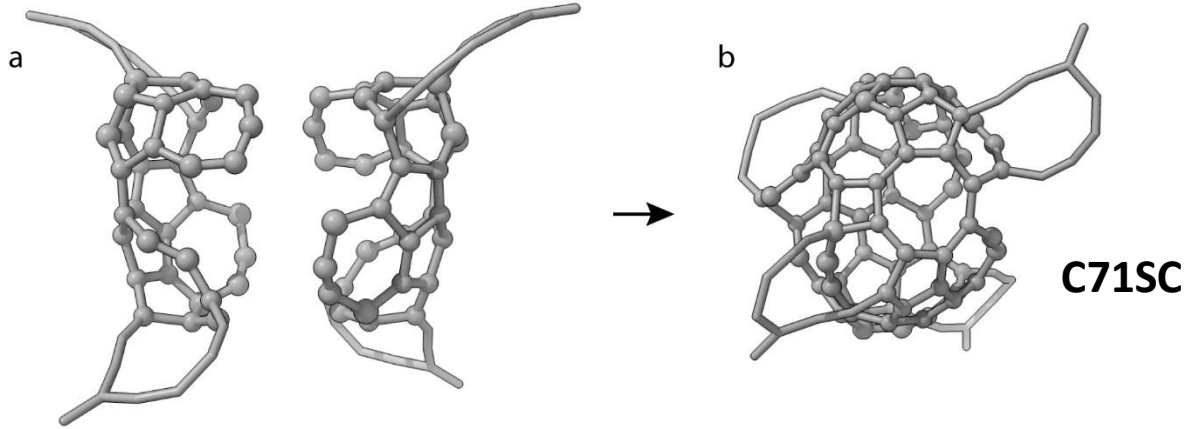
Насочени симулации на асемблиране

2 x CCl

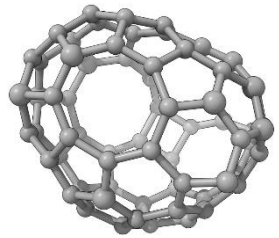


Полу-сферични

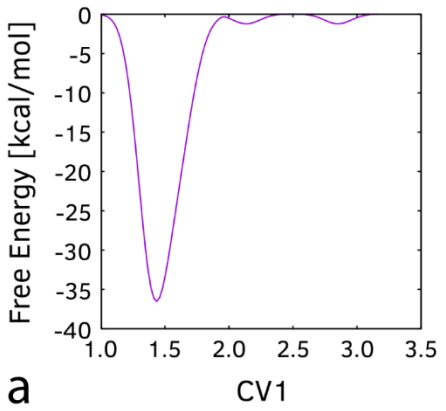
2 x 2xCCl

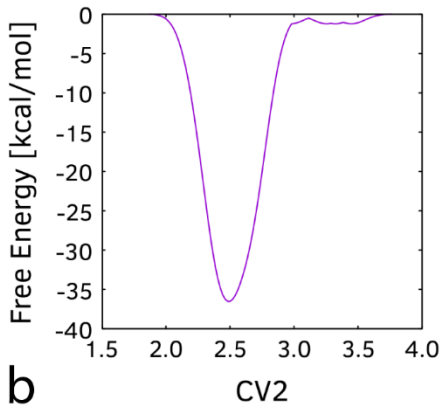


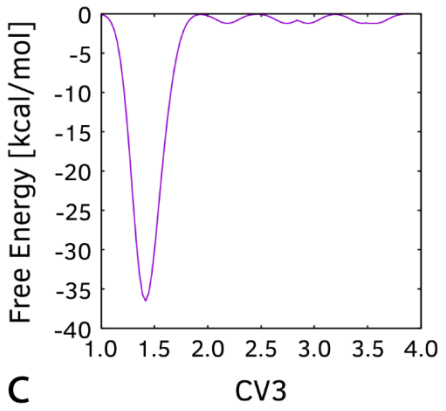
Сфероидни /
Затворена клетка

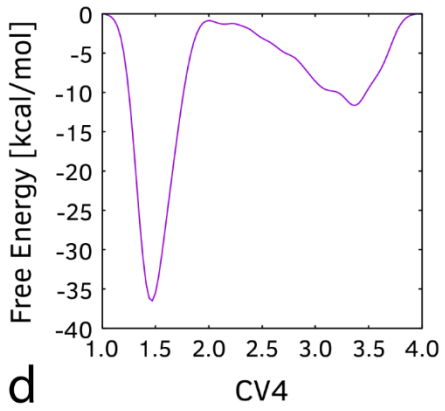


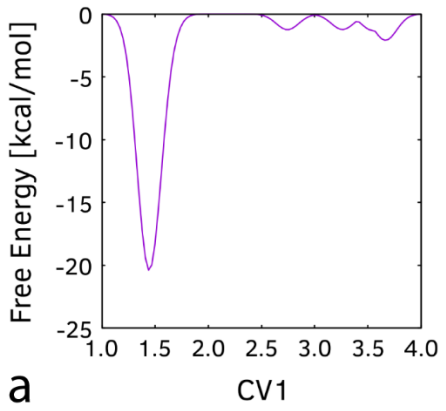
Енергетични профили на асемблиране

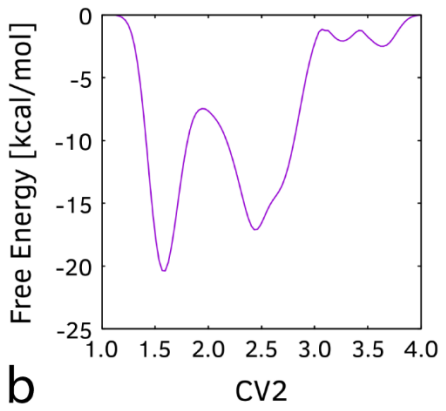


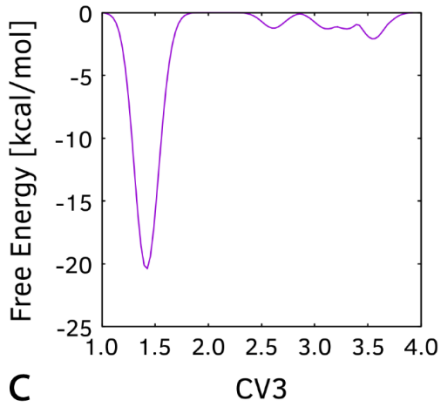


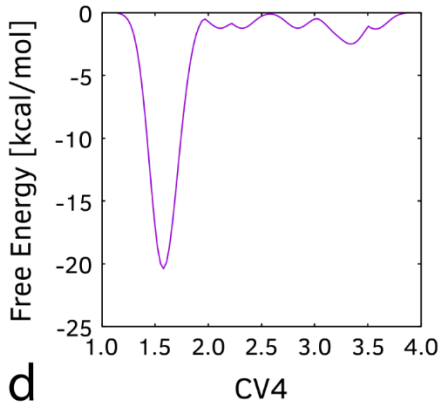






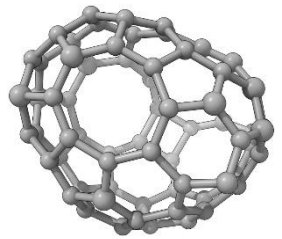




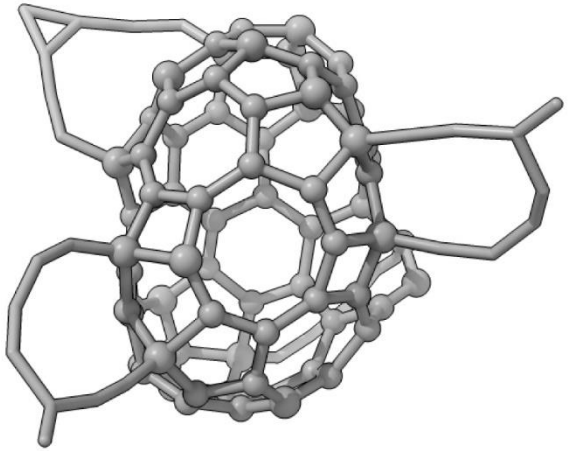


CCl + CCl -> 2xCCl

2xCCl + 2xCCl -> 2x2CCl

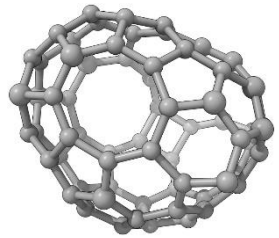


Насочена симулация на закърпване



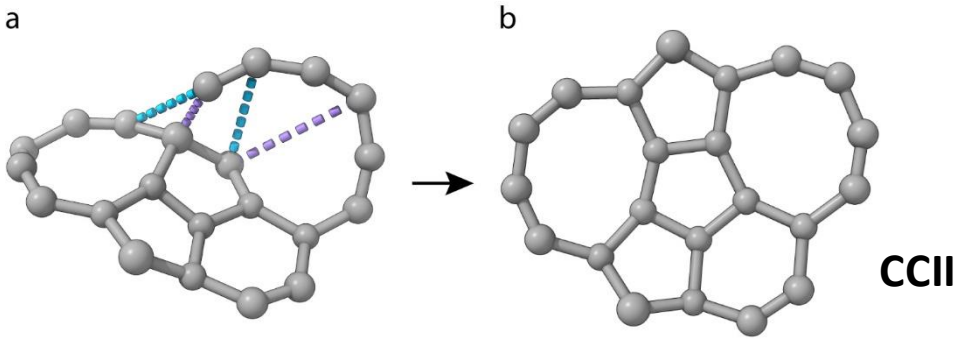
C72SC

C72[4,5,6,7,8,10]fullerene



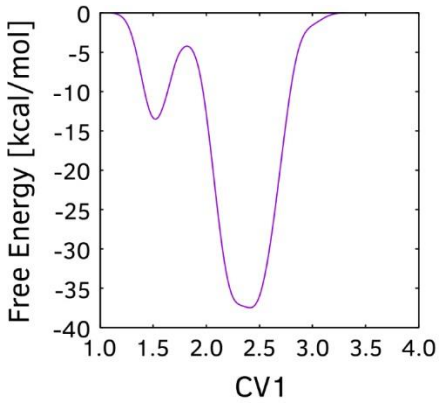
Насочена реформация: CCIITMP -> CCII

CV разстояния
Реактивни разстояния

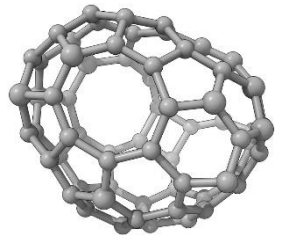


CCII

Изцяло sp^2
Градивен блок за затворена клетка

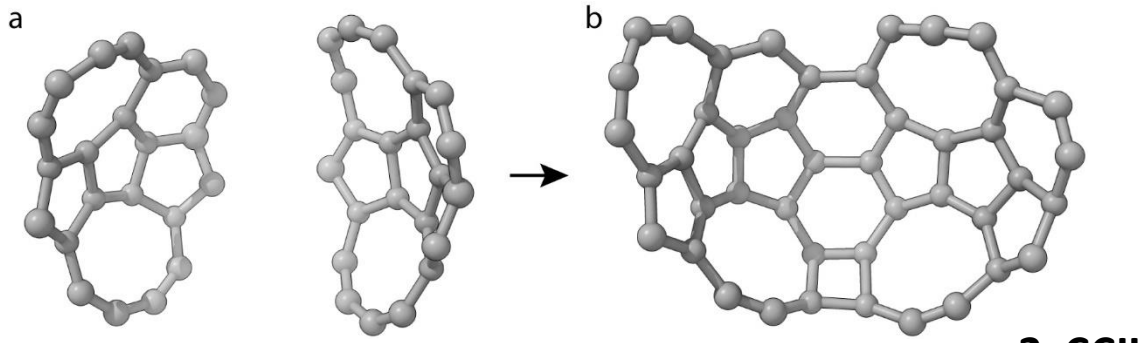


Профил на свободната енергия
Значително екзотермична



Насочени симулации на асемблиране

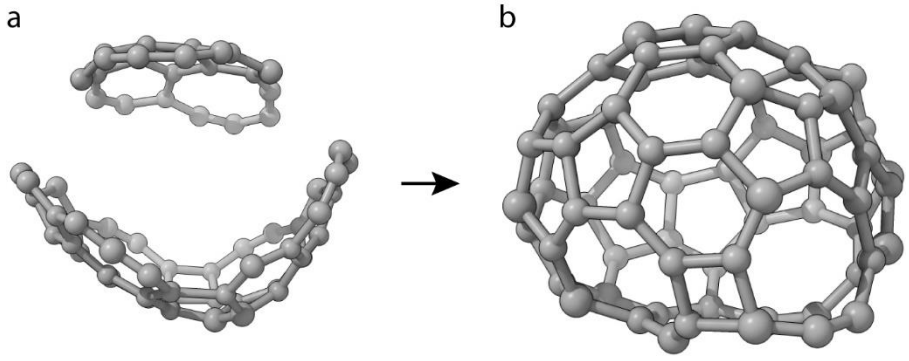
2 x CCII



2xCCII

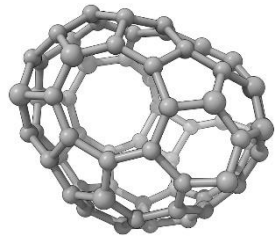
2/3 сферична

2 x 2xCCII

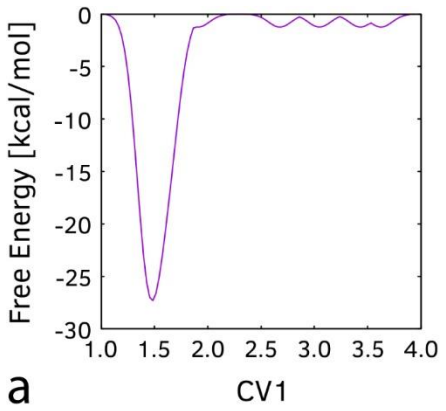


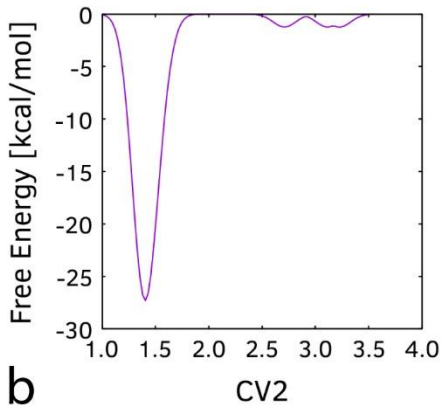
3xCCII

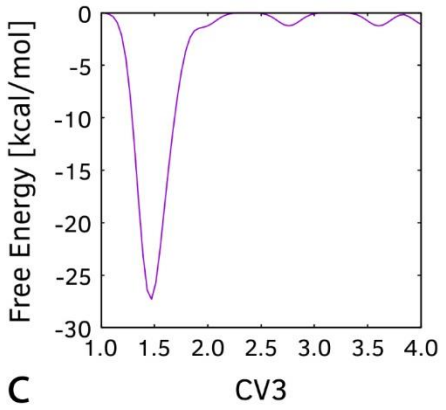
Сфероидна /
Затворена клетка

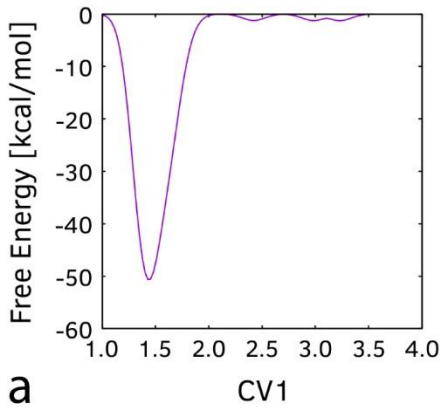


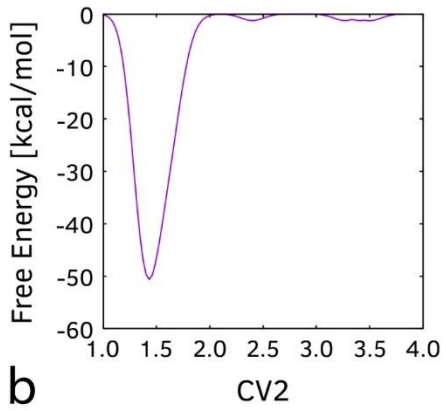
Енергетични профили на асемблиране

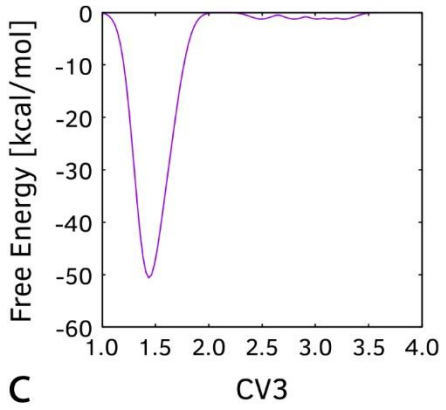


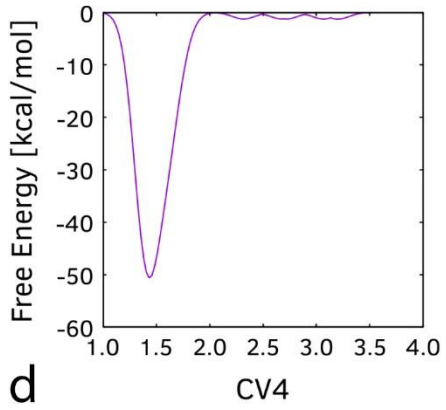






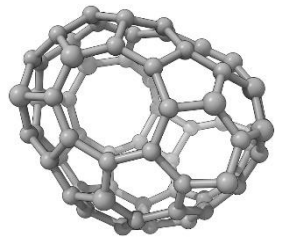




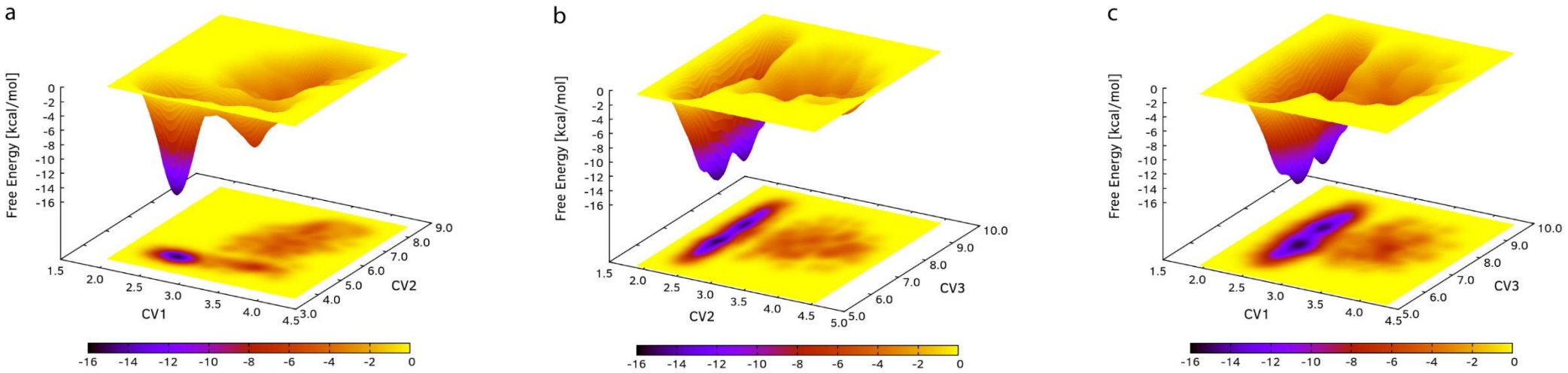


CCII + CCII -> 2xCCII

CCII + 2xCCII -> 3xCCII

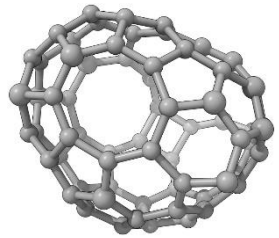


FES на закърпване

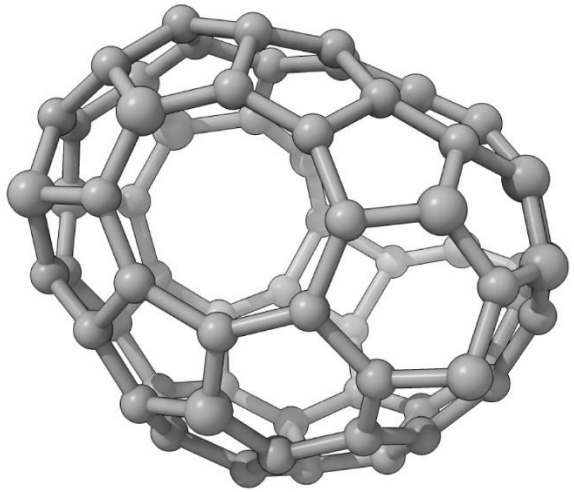


2 x 2 CV FES на насочени реакции на „закърпване“

- Бариери на закърпване: единствена над 10 kcal/mol
- *Хипотетично спонтанно реформиране до C60 и C70 - „острови на стабилност“ [4]*

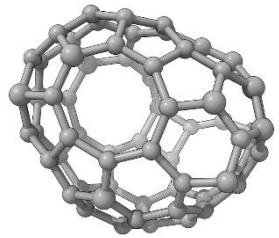


Насочена симулация на закърпване

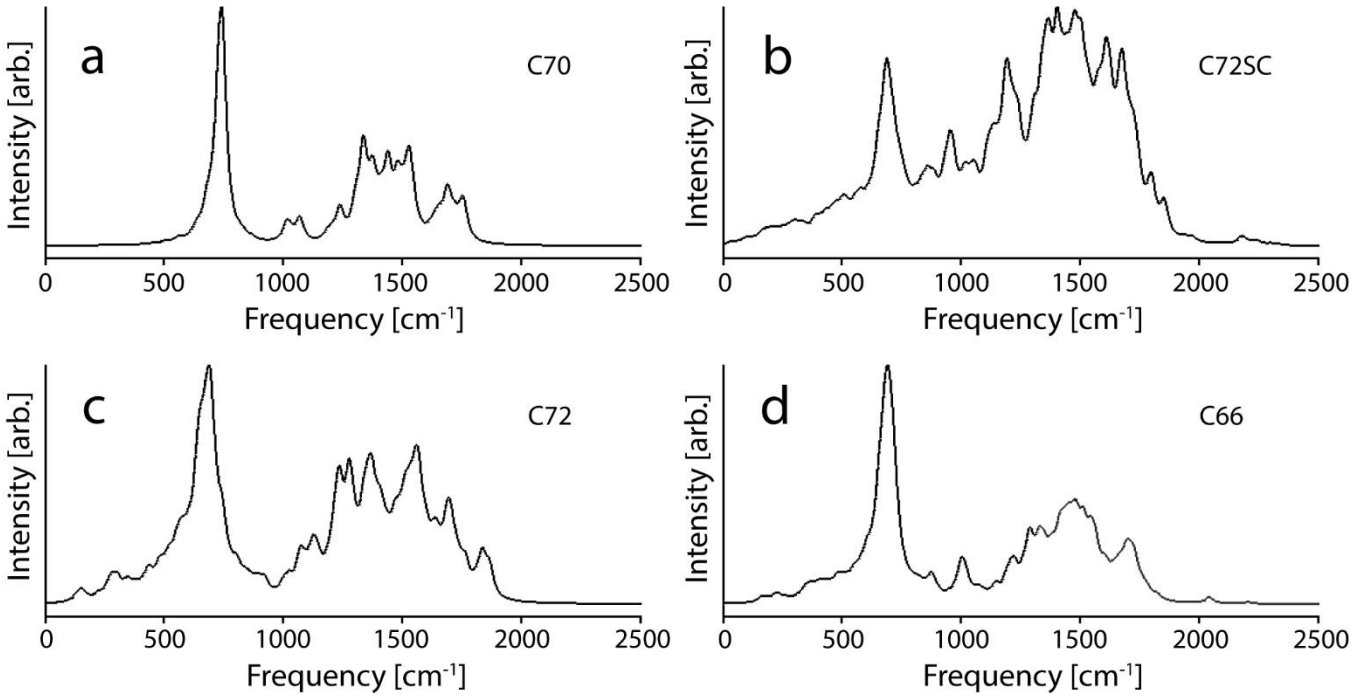


C66

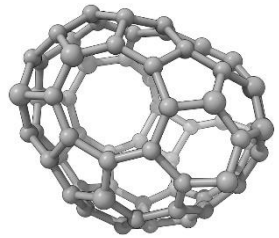
C66[4,5,6,7,8,13]fullerene



ИЧ спектри



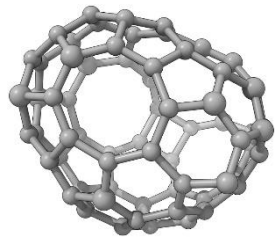
C72 и C66 могат да бъдат сбъркани с C70

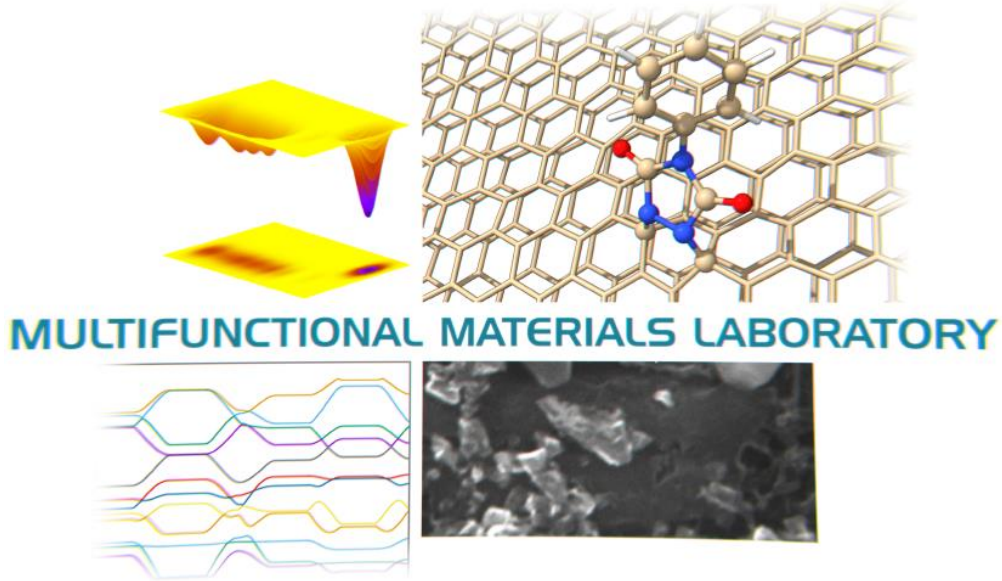


Заключения и причини

- Не се минава през малко вероятният графен
- Процеса не спира с оплетени полициклични
- Първият цял теоретичен модел за образуване на въглеродни НЧ със затворена клетка

- Какви са най-първите въглеродни съединения във Вселената
- Какви интересни структури могат да се получат от тях





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