APATCC2019 @ Sydney
Ninth Conference of
the Asia-Pacific Association of Theoretical and Computational Chemists

2019/10/01 (IL17 – 10:50-11:10**)**

Quantum Chemical Exploration of Novel Chemistry on Potential Energy Surfaces

Koichi Ohno[1,2]

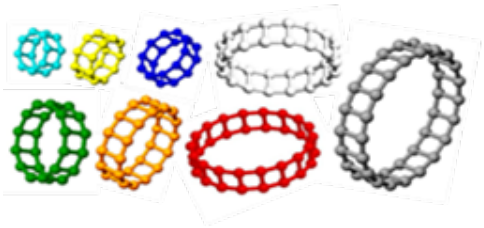
Tohoku University[1]
Institute for Quantum Chemical Exploration[2]

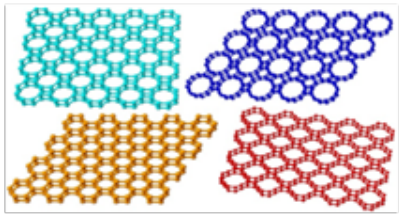
Exploration of New Chemical Structures is important but generally very difficult to perform by computations.

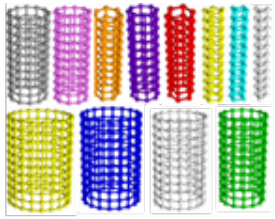
The space of the potential energy surface is too huge to search!

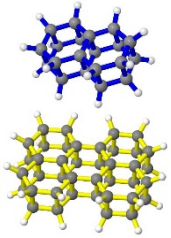
It is like to find a tiny piece of diamond lost in a big desert!

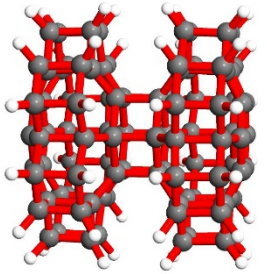
In this talk,
I will show you a ***computational challenge*** to find ***new carbon allotropes*** and ***new hydrocarbons***.







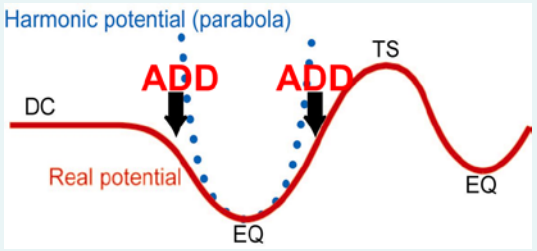


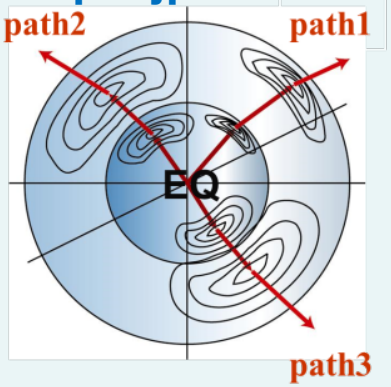


Computational Methods
for Quantum Chemical Explorations

- Electronic-state calculations for obtaining energies and gradients of the ground singlet state: **Gaussian09**.
- Levels: mostly DFT(B3LYP, B3LYP-D3)/ (6-31G*, cc-pVDZ, cc-pVTZ, aug-cc-pVTZ) except for **P**eriodic **B**oundary **C**ondition calculations by RHF/(STO-3G, 3-21G).
- Geometry optimizations, refinements, and reaction path searches: **GRRM14**. **https://iqce.jp/GRRM/**
- Lowest TS Search : **GRRM/ADDF**

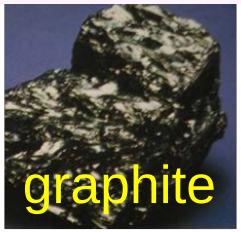
which can trace all reaction paths around an EQ structure.

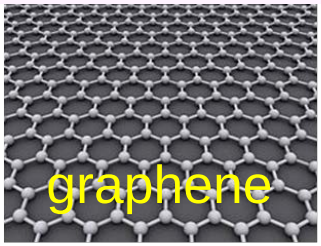


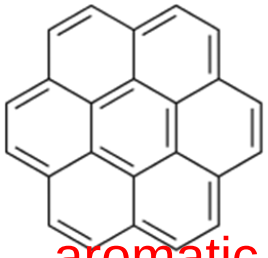


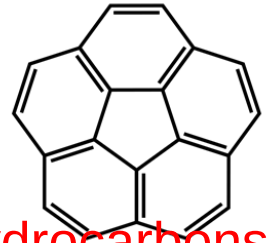
Selected Targets of Exploration : Carbons & Hydrocarbons

Mostly C-atoms constitute C-6 rings.

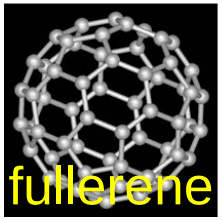

graphite

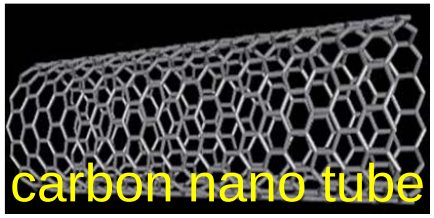

graphene





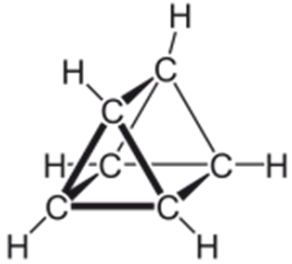
aromatic hydrocarbons


fullerene

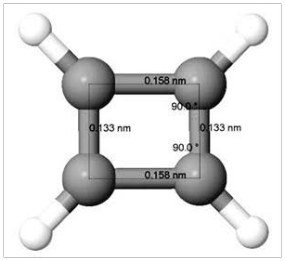

carbon nano tube

C-atoms also constitute C-4 rings.

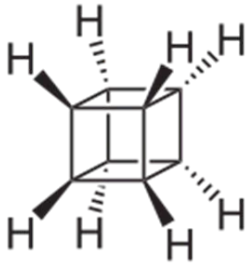
Prismane



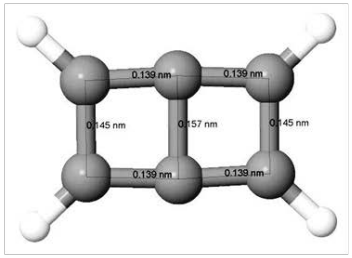
Cyclobutadiene



Cubane

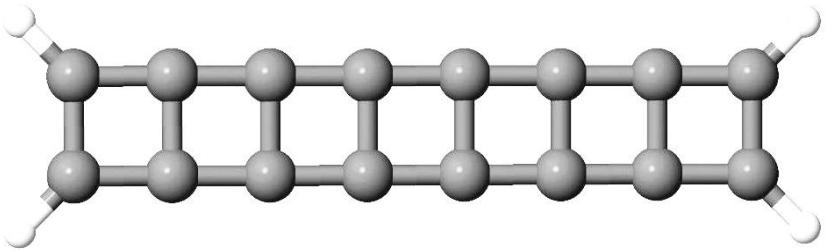


Butalene

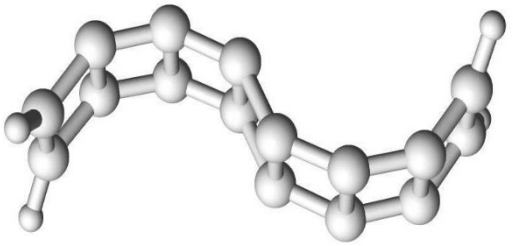


One may challenge to seek new chemical structures with C-4 rings.

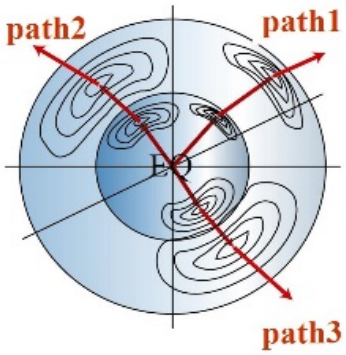
We challenged to produce straight planar ladder forms !

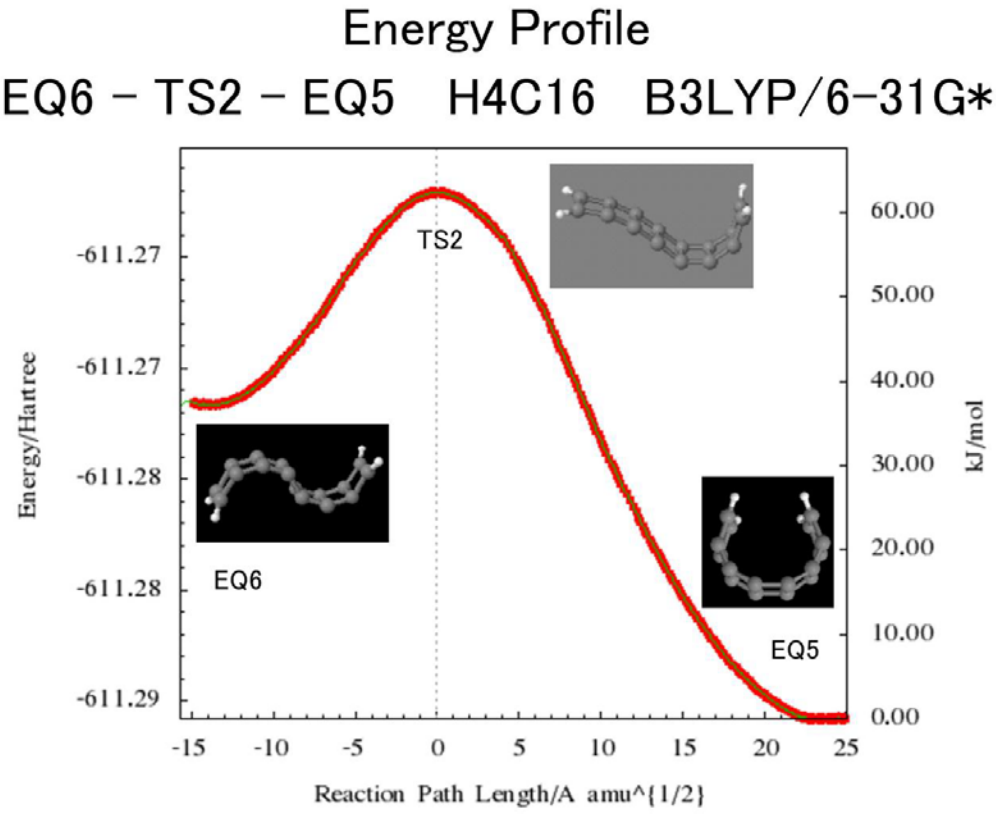


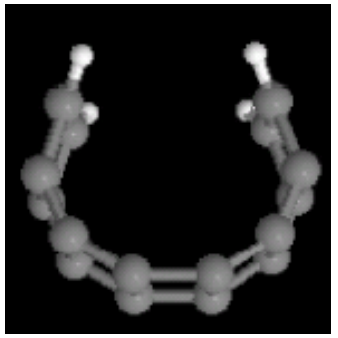
Geometry Optimization



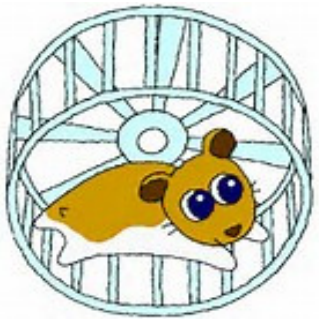
Lowest TS search by GRRM/ADDF







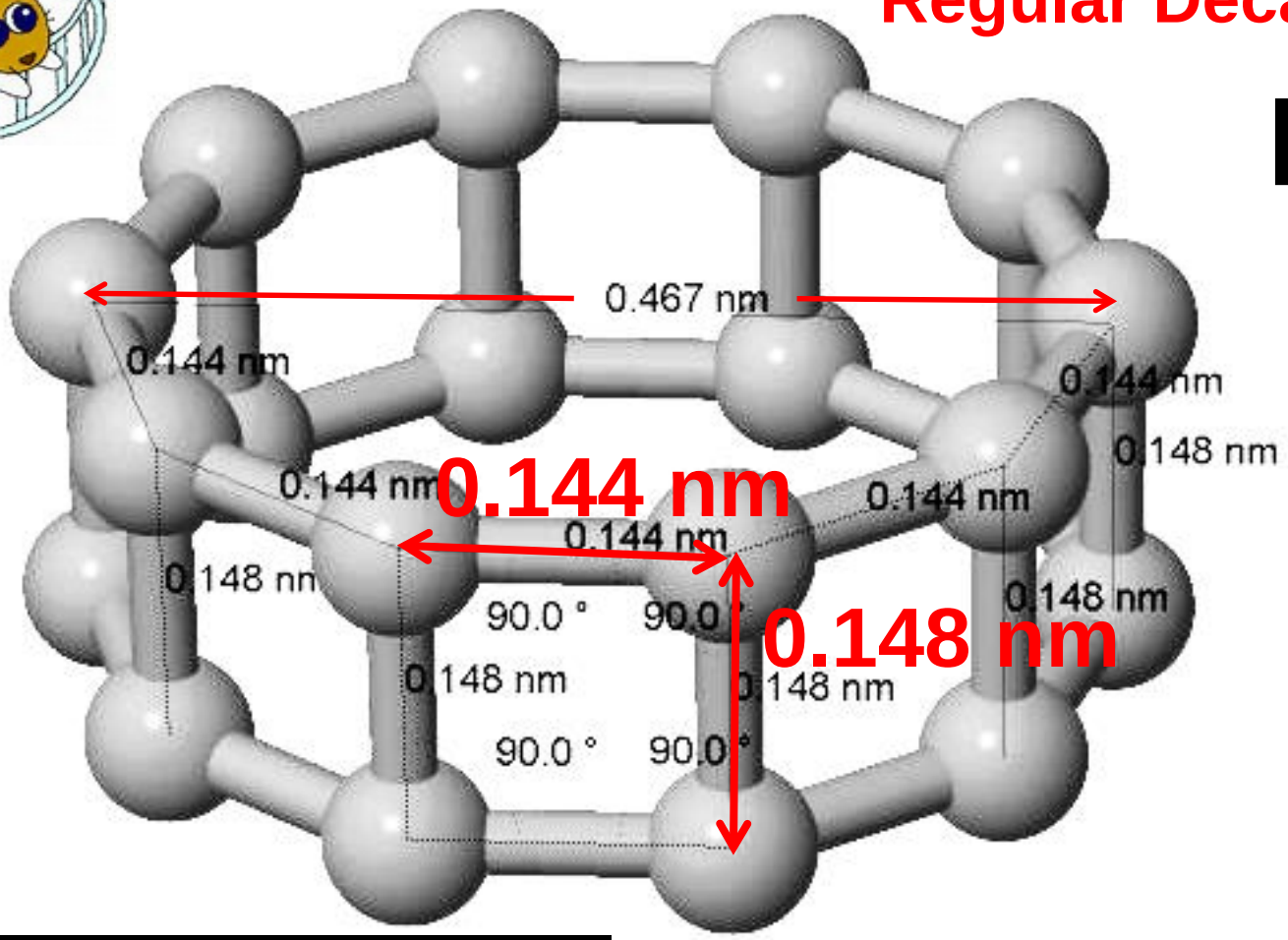
Circular ladder is much more stable !



Prism-C_{20}

Regular Decagon Prism

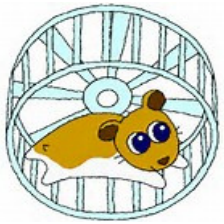
D_{10h}



CC bonds are unsaturated !

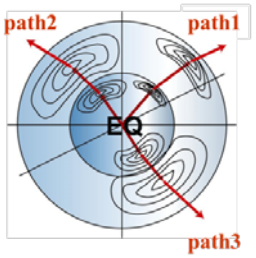
R(CC)=**0.144-0.148** nm < **0.154** nm (typical single bond)

Ohno, Satoh, Iwamoto, *Chem. Lett.* 44, 712 (2015)



Stability of Prism-C_{20}

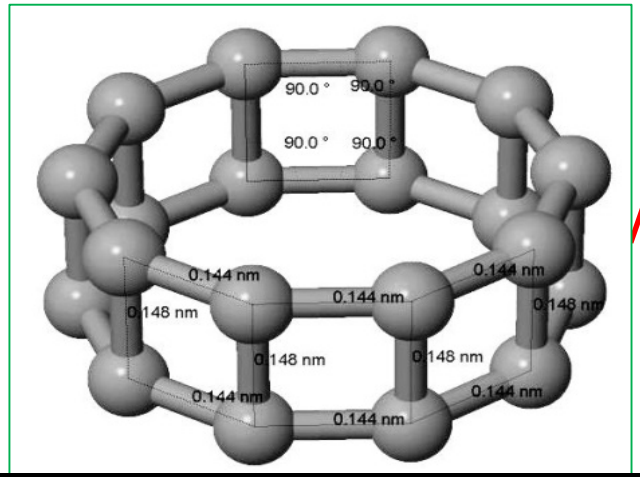
Lowest TS Search by GRRM/ADDF



Lowest Barrier = **158** kJ/mol (**ZPVE-corrected**)

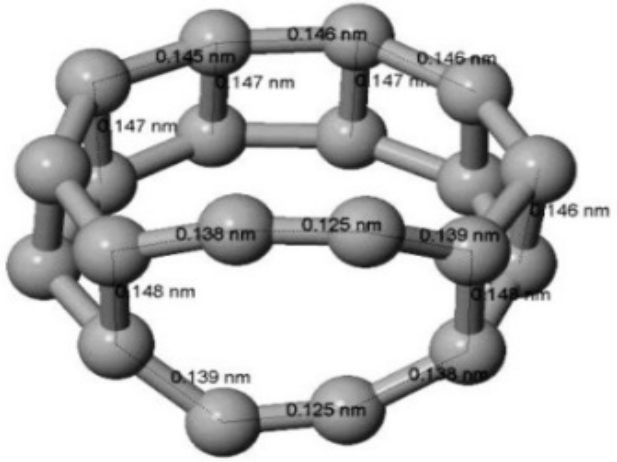
at B3LYP/6-31G(d)

Prism-C_{20}



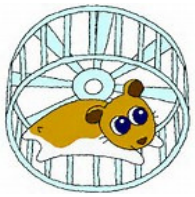
TS

Deformed form



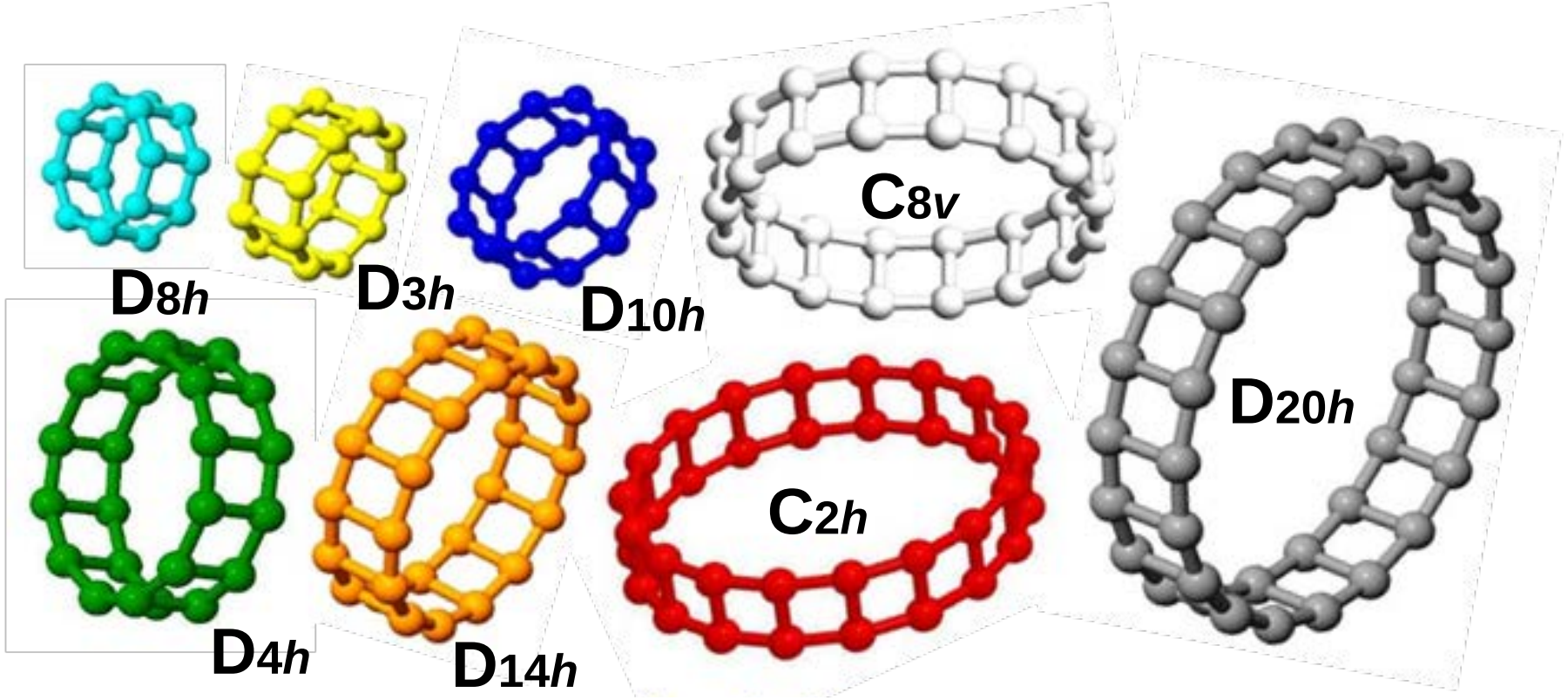
Stabilization Energy = 309 kJ/mol

Prism-C_{20} is kinetically stable enough with a high energy barrier !



Hamster Wheel Carbons

Prism-C_{2n} (*n*=8, 9, 10, 12, 14, 16, 18, 20)

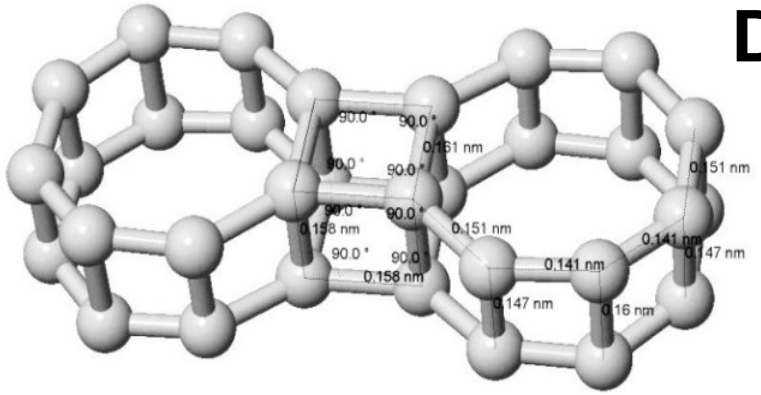


Ohno, Satoh, Iwamoto, *Chem. Lett.* 44, 712 (2015)

Noting unsaturated CC-bond characters, we obtained

Prism-C_{2n} Dimer (n=8)

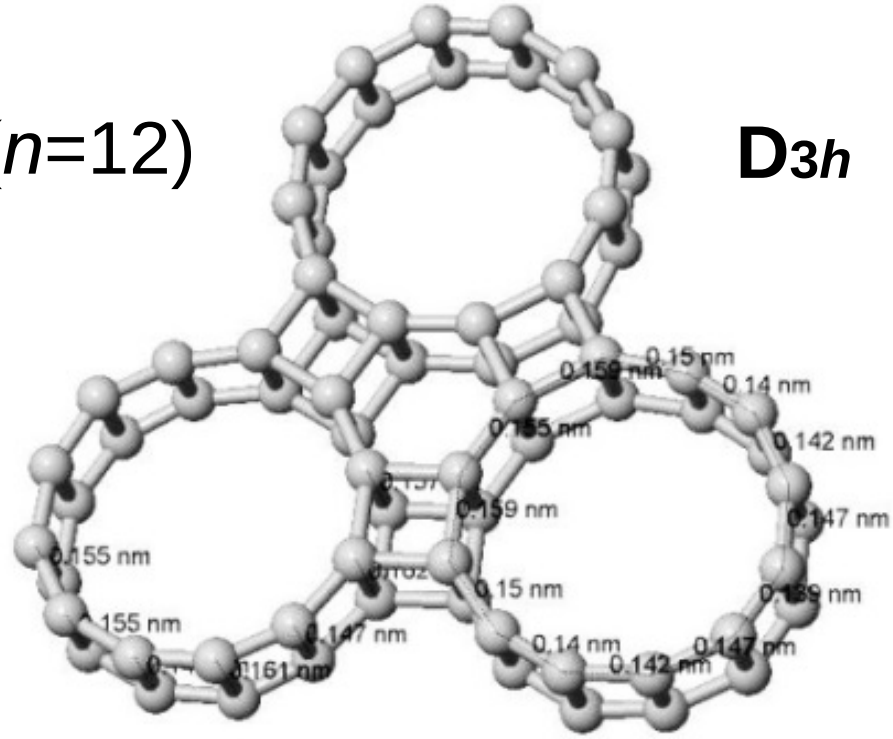
Exploration:
B3LYP/6-31G(d)
Confirmation:
B3LYP/6-311++G(2d,2p)
B3LYP/cc-pVDZ
B3LYP/cc-pVTZ



D_{2h}

Prism-C_{2n} Trimer (n=12)

Exploration:
B3LYP/6-31G(d)
Confirmation:
B3LYP/cc-pVDZ
RHF/STO-3G
RHF/3-21G



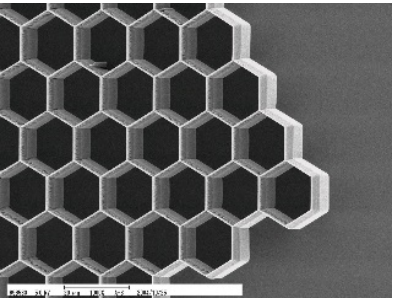
D_{3h}

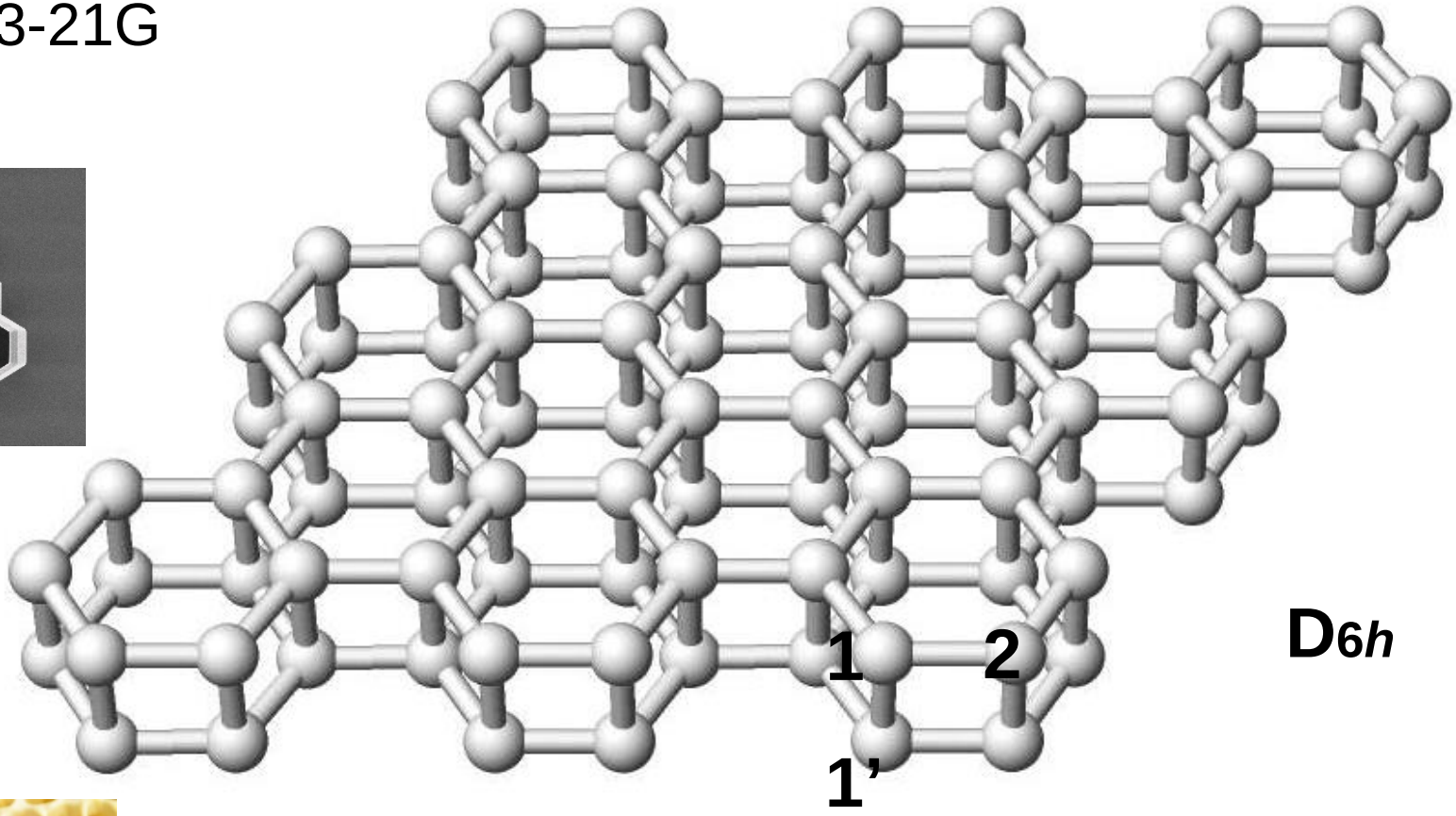
Prism Carbon Sheet

Periodic Boundary Condition Calculation (g09)

RHF/STO-3G
RHF/3-21G

Honeycomb carbon double layer





D_{6h}

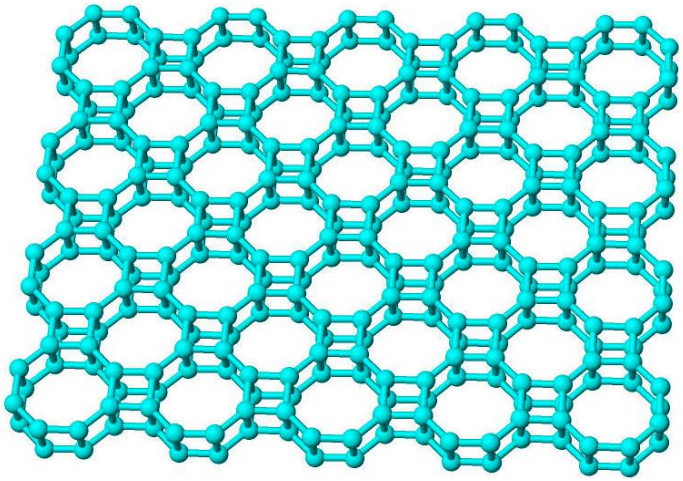
All Prisms are purely hexagonal.
All C-atoms are equivalent
and connected with 4-atoms.
All CC bonds are single bond.

1-2: 0.1566 nm
1-1': 0.1562 nm

Prism-C_{2n} Sheets

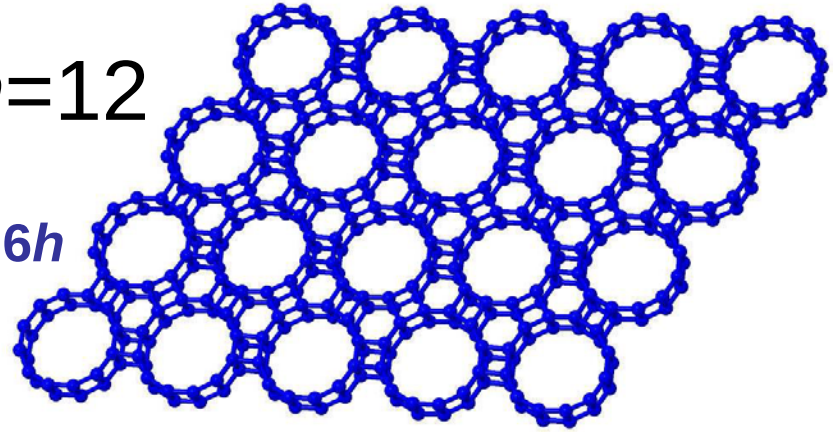
n=8

D_{4h}



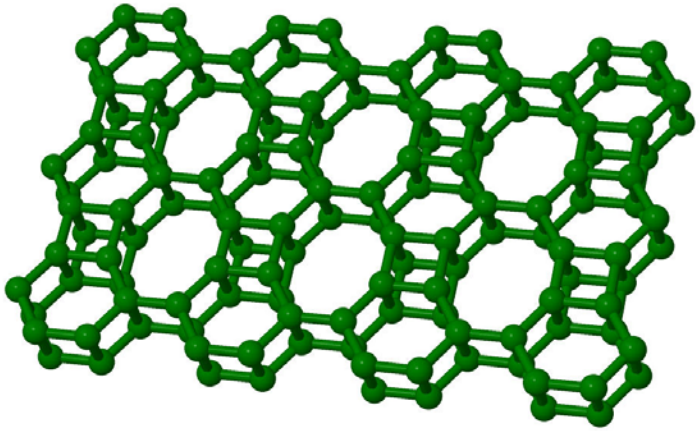
n=12

D_{6h}



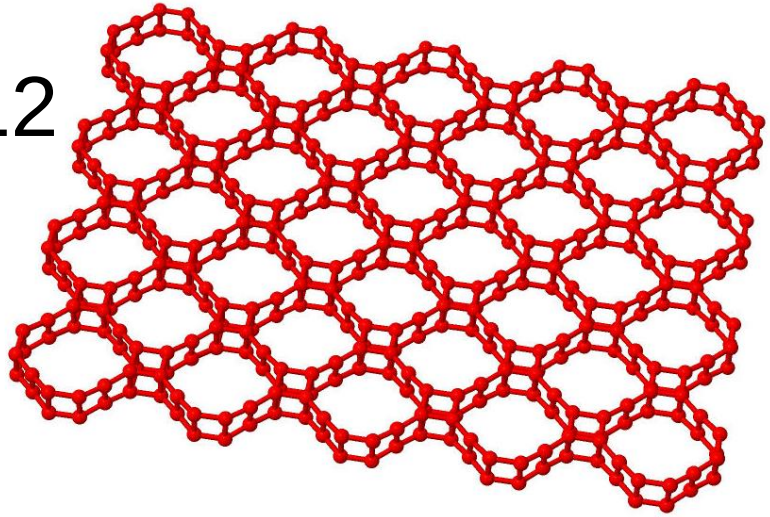
n=6

D_{2h}



n=12

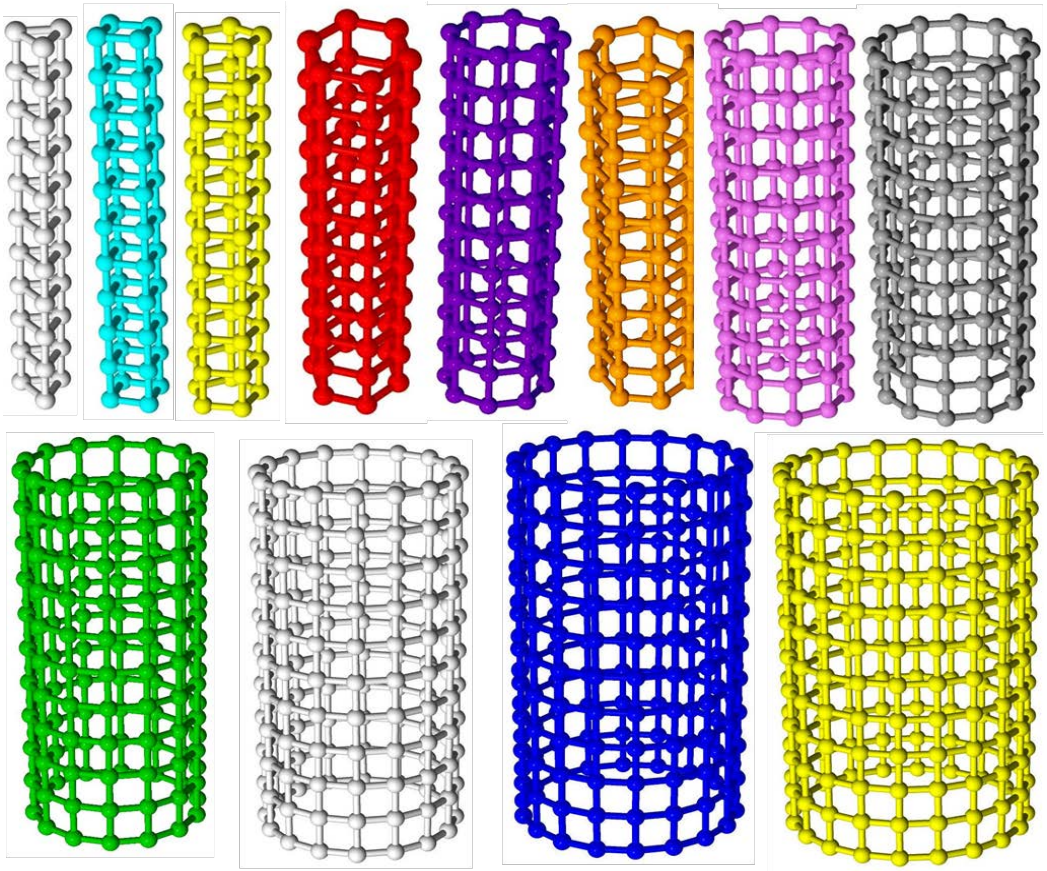
D_{4h}



Ohno, *Satoh, Iwamoto, Chem. Phys. Lett.* 633, 120 (2015)

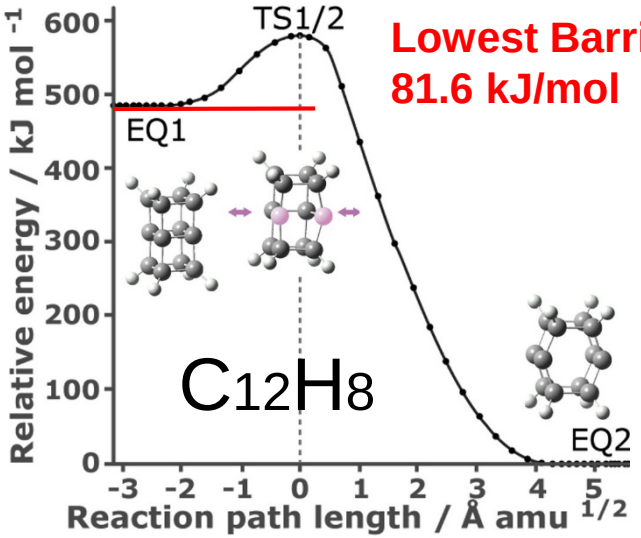
Polymerization of prisms can be made axially

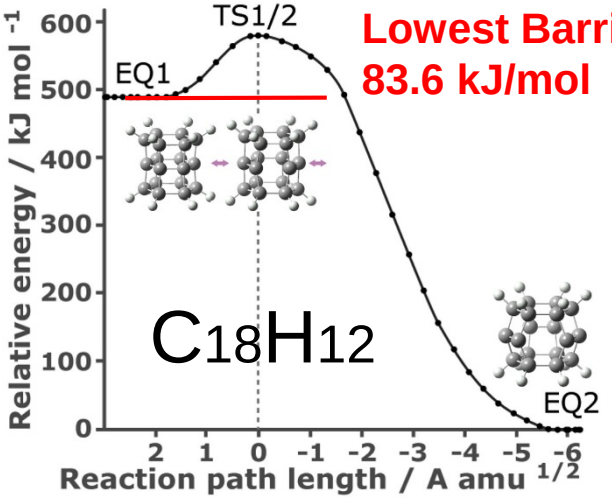
Prism-C*n* Tubes (*n*=3-8, 10, 12, 14, 16, 18, 20)



Polygon CC: 0.153 - 0.160 nm
Vertical CC: 0.160 - 0.161 nm

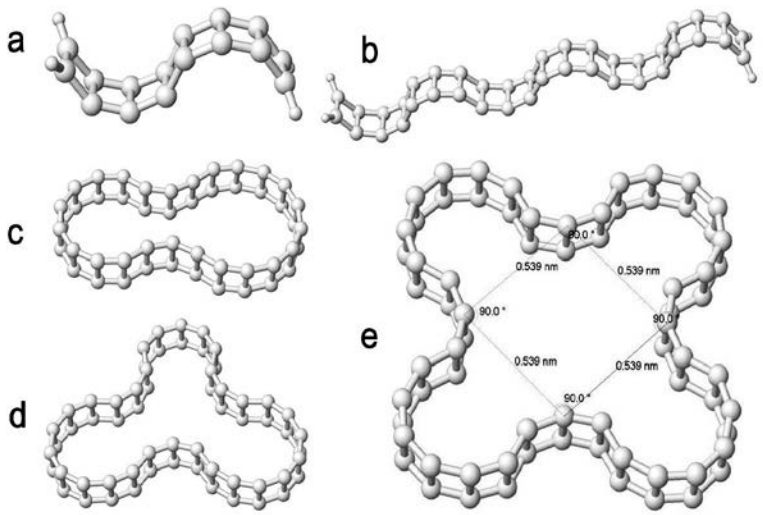
Stability Check by GRRM/ADDF

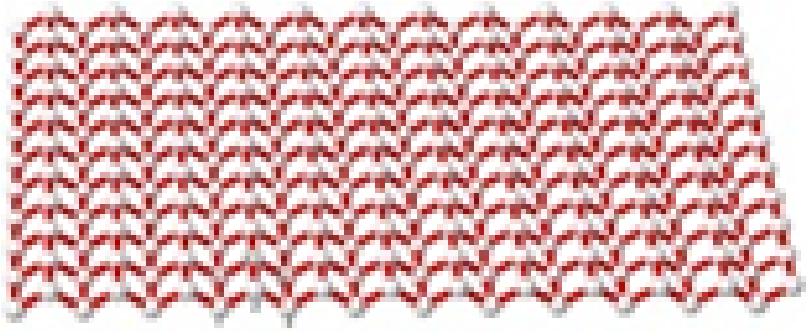


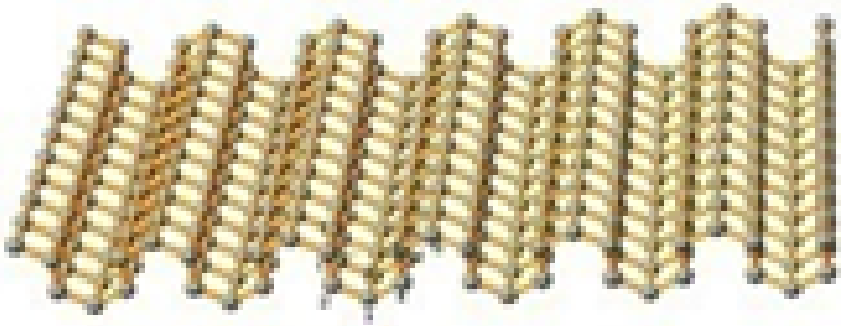


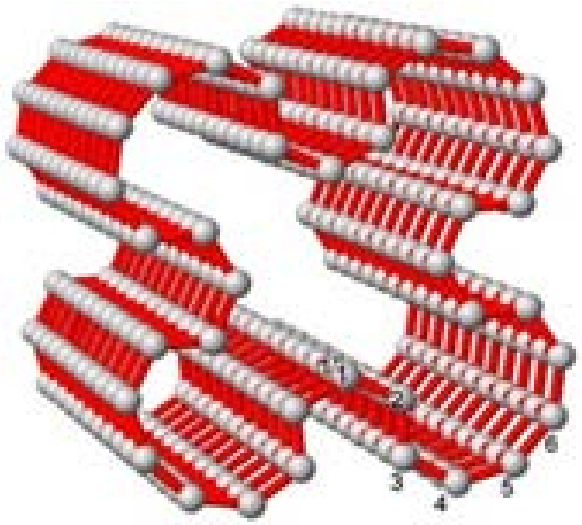
Ohno, *Tokoyama, Yamakado, Chem. Phys. Lett.* 635, 180 (2015)

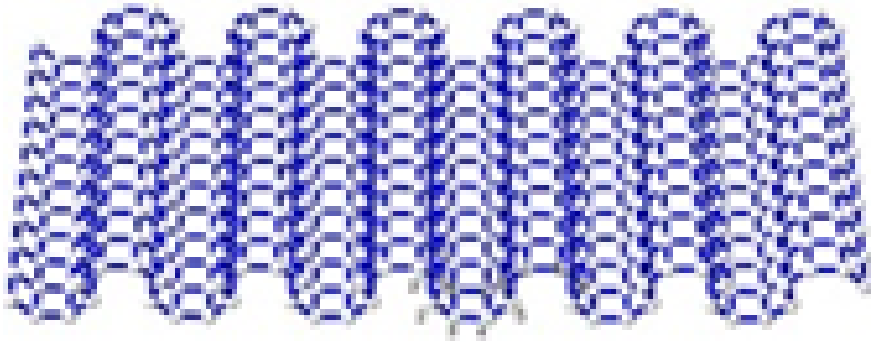
Wavy Carbon Tube & Sheet





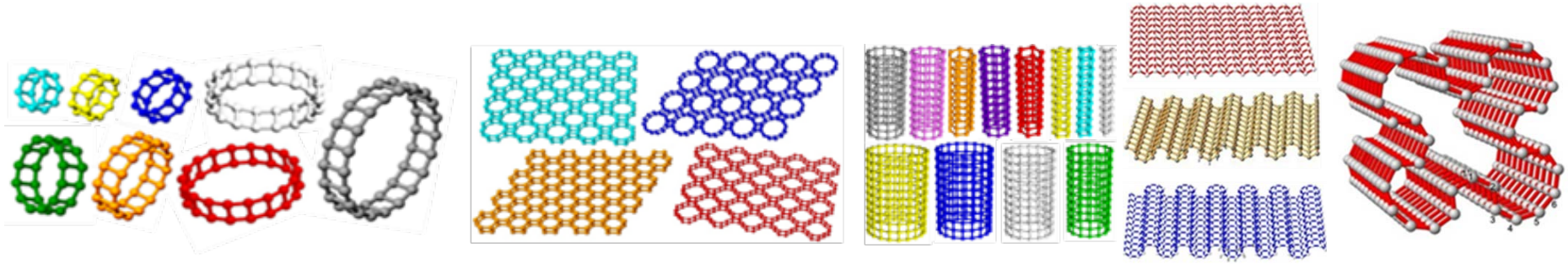






Ohno, *Satoh, Iwamoto, Tokoyama, Yamakado, Chem. Phys. Lett.* 639, 178-182 (2015)

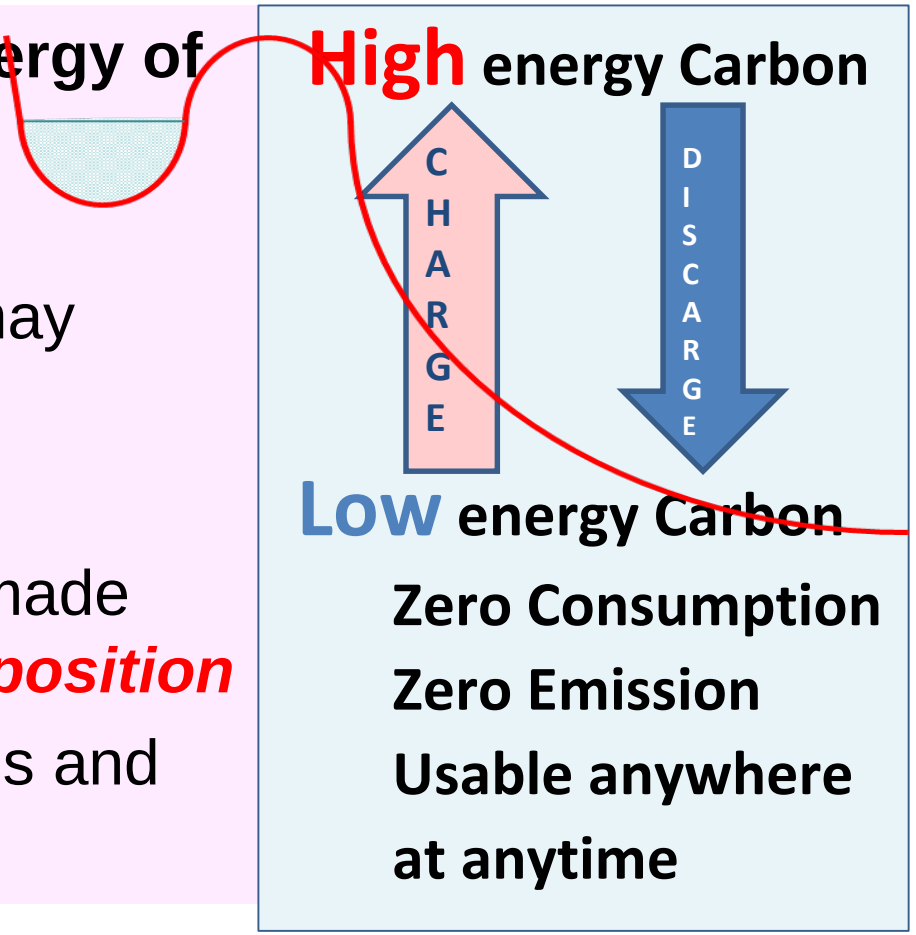
Important : High Energy Carbons



Containing Excess Chemical Energy of 130-350 kJ/mol per one C-Atom.

It is expected that these carbons may become *ideal* **Energy Reservoirs**.

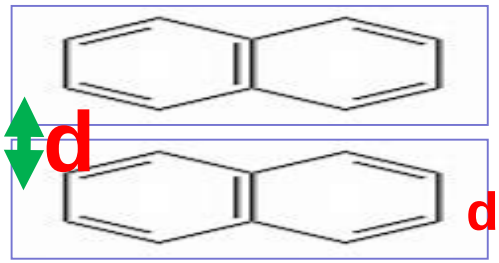
Energy-Charge/Discharge will be made with ***no change of chemical composition***
with ***no consumption*** of materials and
with ***no production*** of **wastes**.



Quests of New Hydrocarbons with C4-rings !

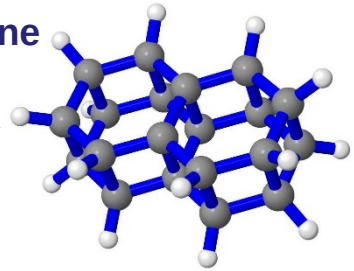
By placing two PAH molecules with their planes parallel,
PAH-Dimers were obtained !

Chem. Phys. Lett. 716, 147 (2019).
Chem. Phys. Lett. 725, 159 (2019).

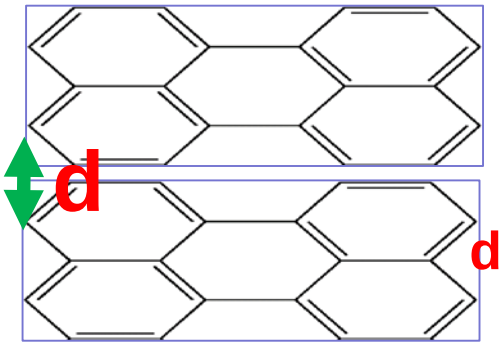


Di-naphthalene

d = 0.15 nm

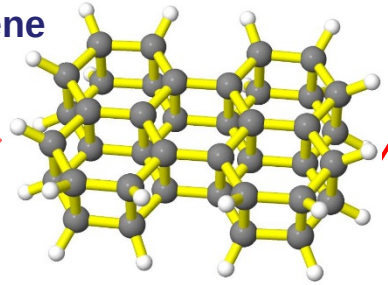


Fully bonded

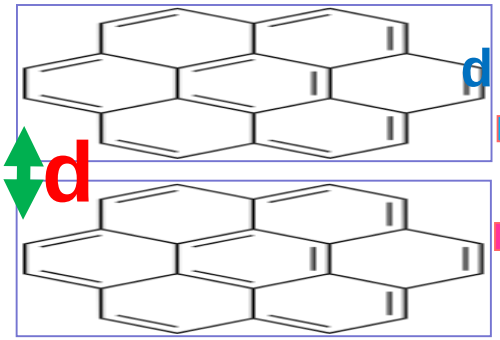


Di-perylene

d = 0.15 nm



Capsule Form
Bonded at
Edges only

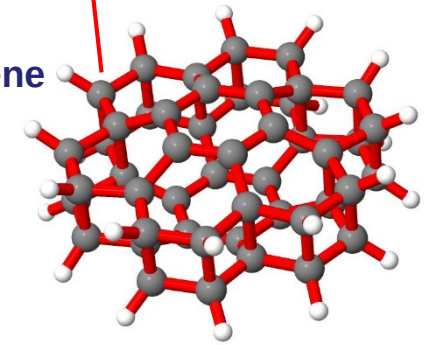


Di-coronene

d = 0.14 nm

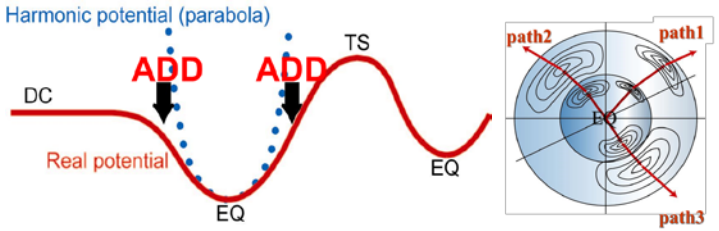
d = 0.15 nm

Di-coronene

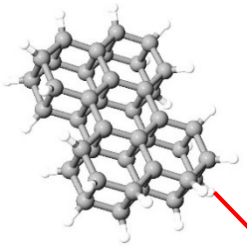


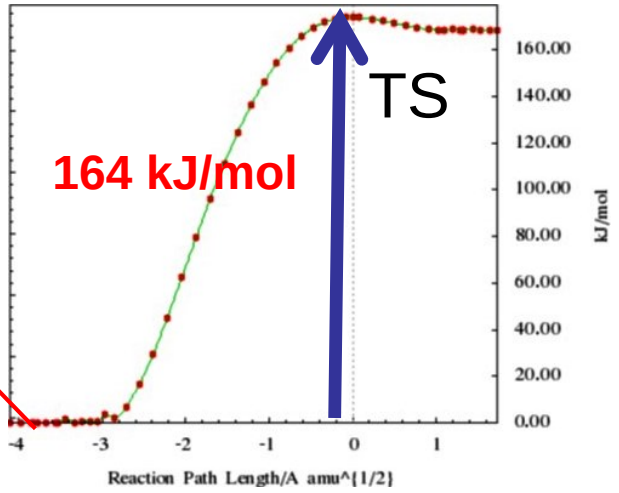
Stability check of Di-PAHs

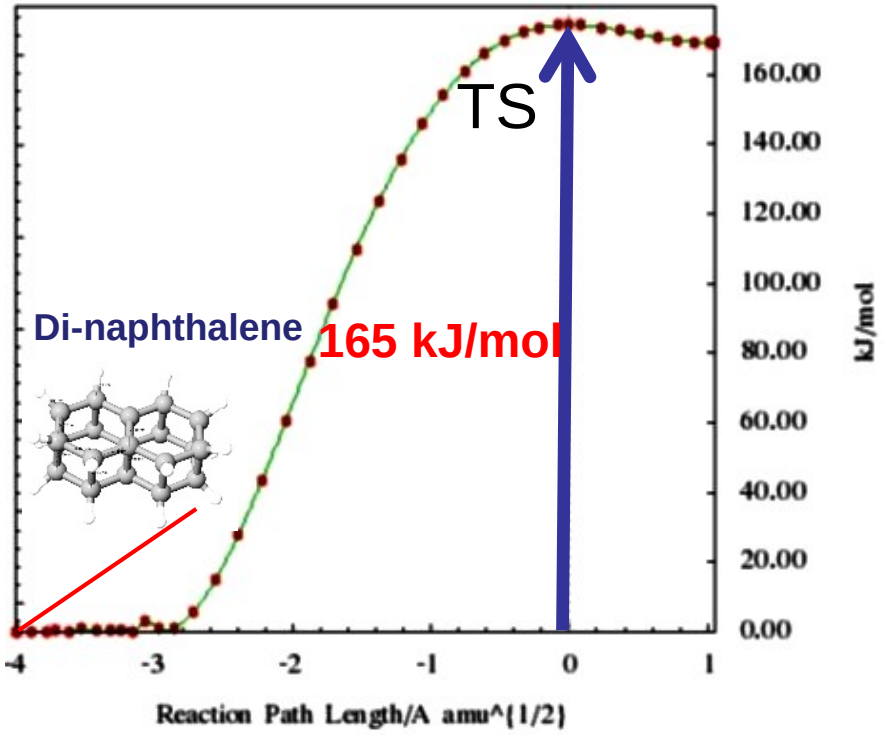
Lowest TS Search by GRRM/ADDF



Di-perylene

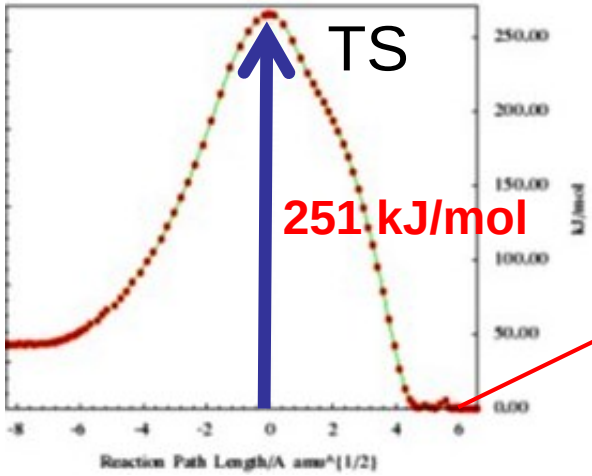




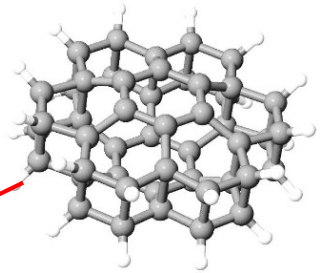


Di-naphthalene

165 kJ/mol

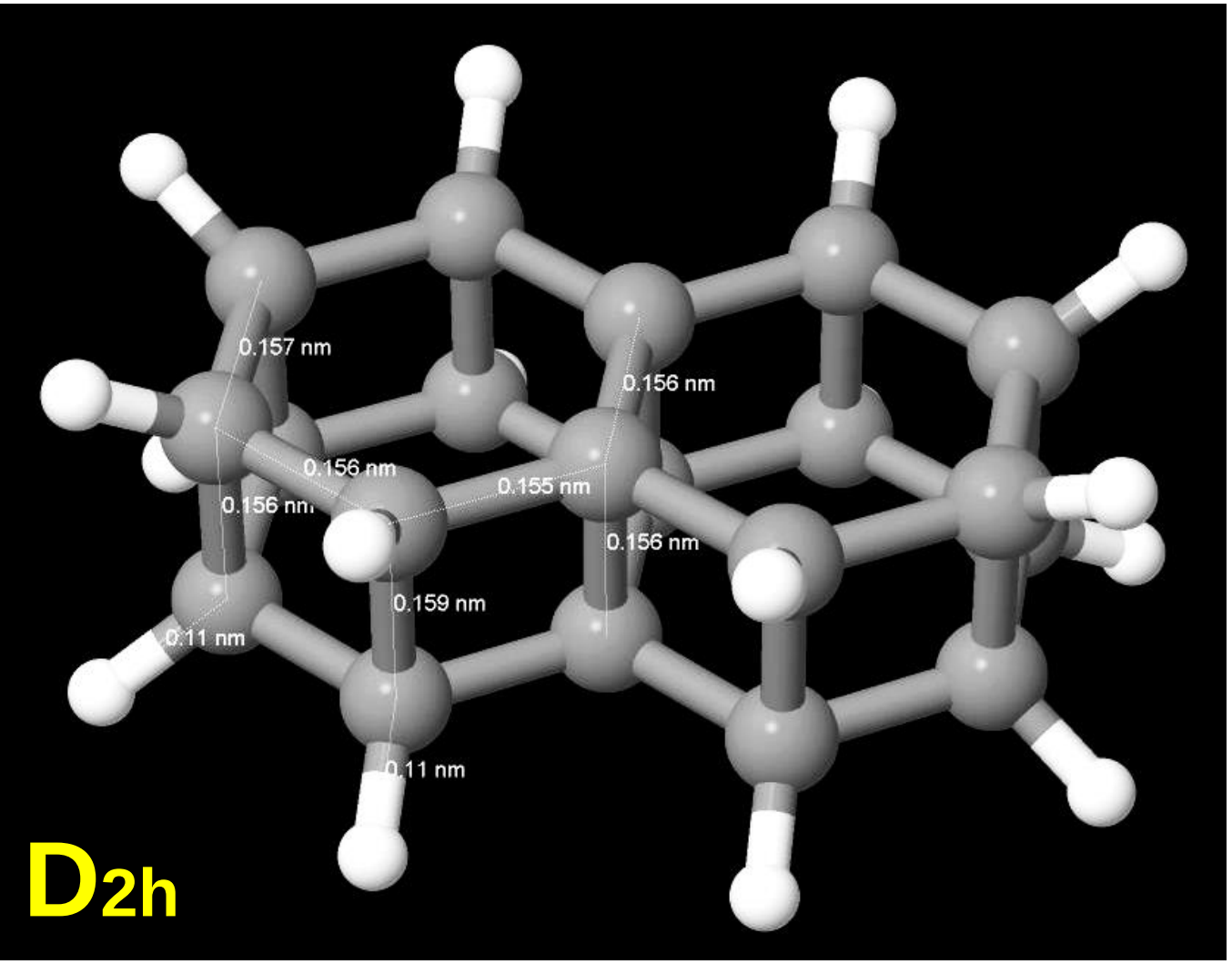


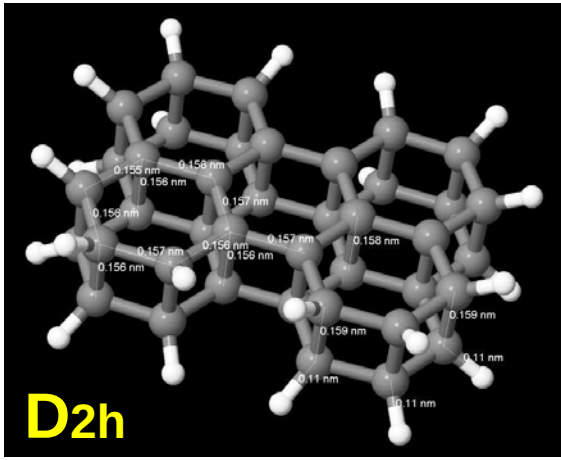
Di-coronene

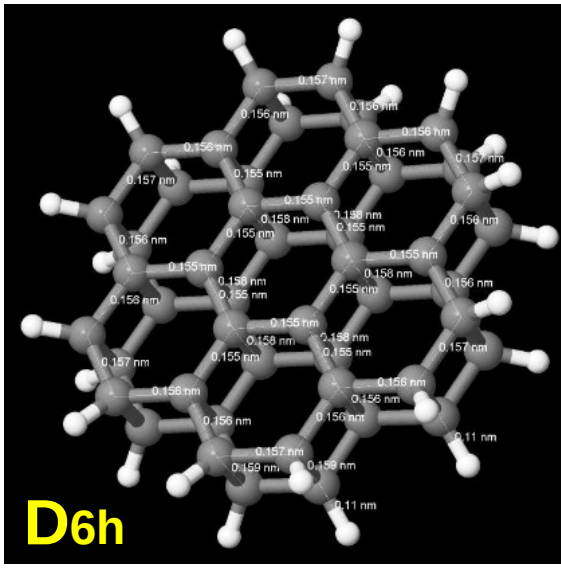


Di-PAHs are stable enough with high energy barriers !

Structures of Fully-bonded di-PAHs



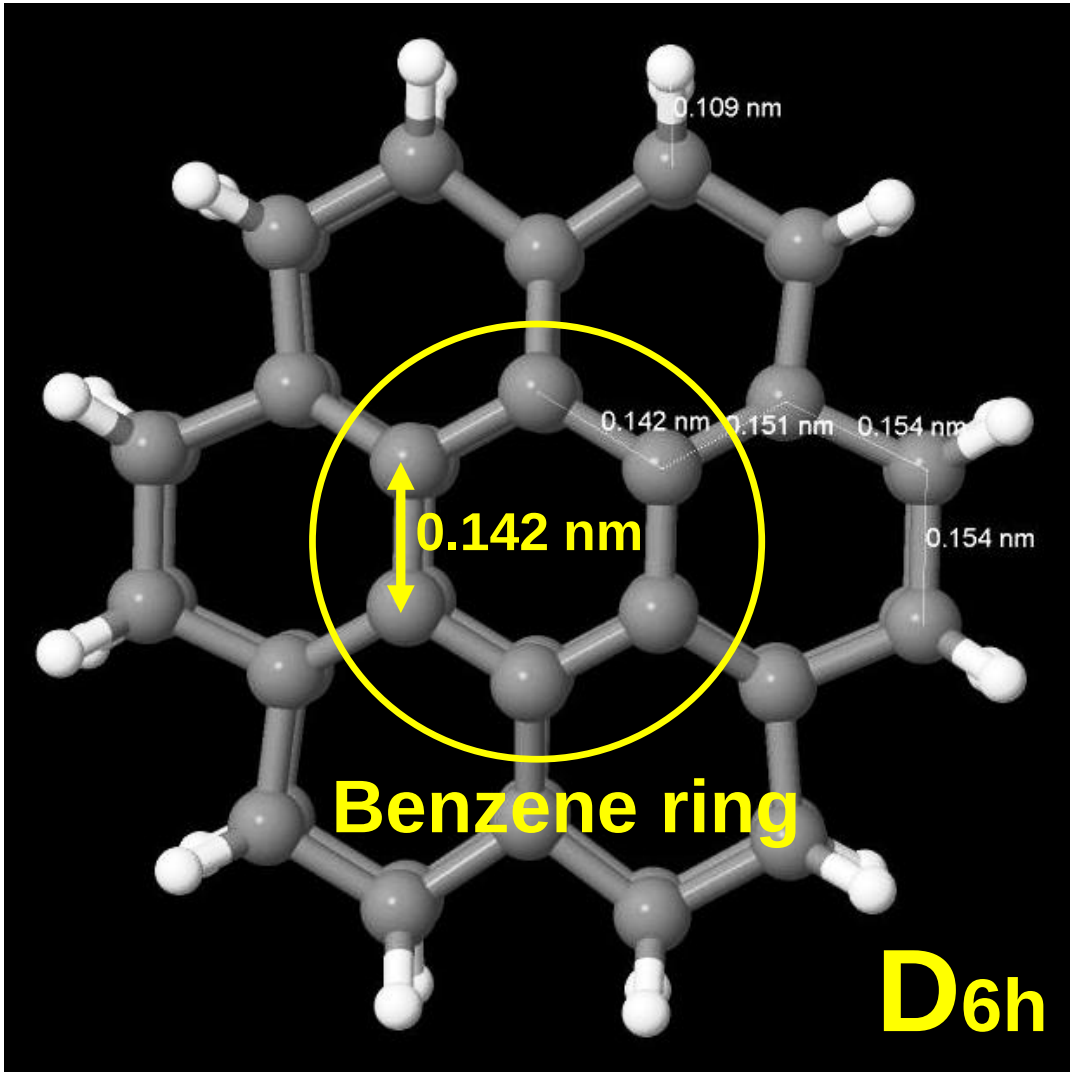




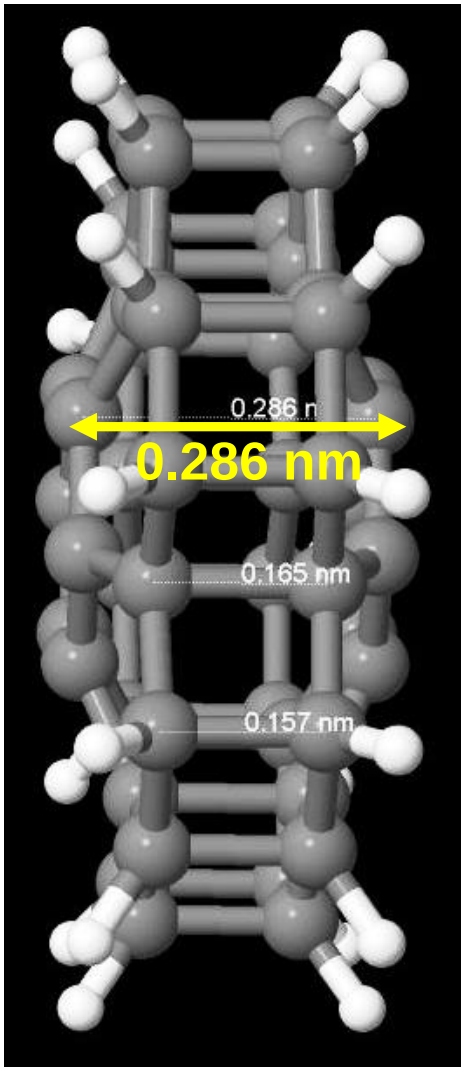
- All CC bonds : single bond (0.154 – 0.159 nm)
- All C atoms : tetra valent, bonded with 4 atoms

Structure of edge-bonded di-coronene

Top view



Side view



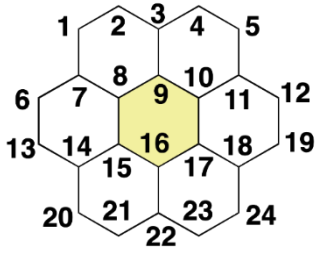
Central ring is like a benzene with aromatic CC bond of 0.142 nm

Polymerization of coronene

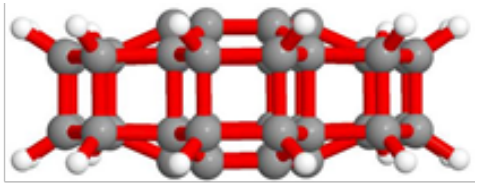
1 → 2 → 4: tetra-coronene D_{6h}

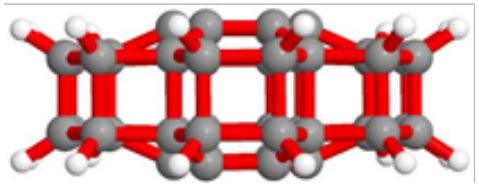
Monomer

$C_{24}H_{12}$



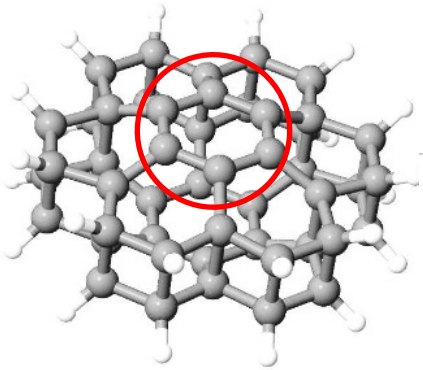
Dimer x 2



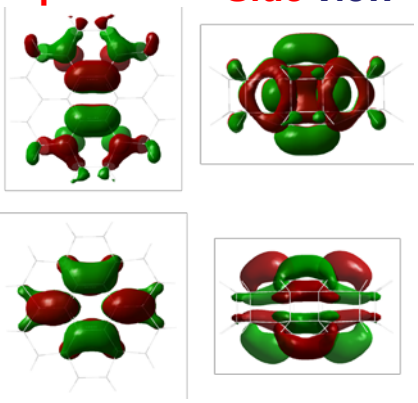


Dimer

$C_{48}H_{24}$

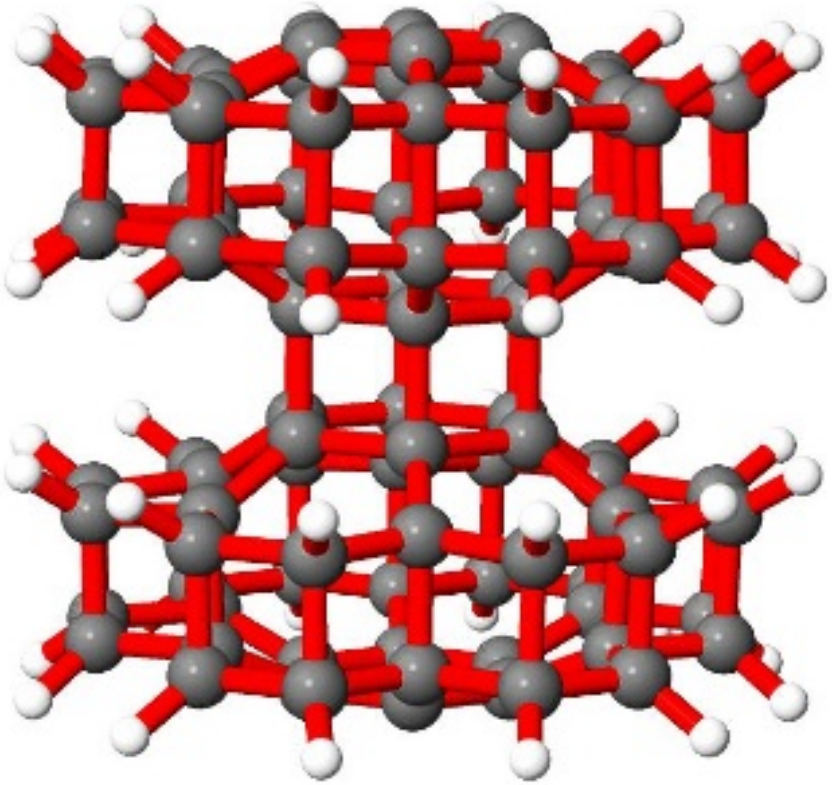


Top view **Side view**



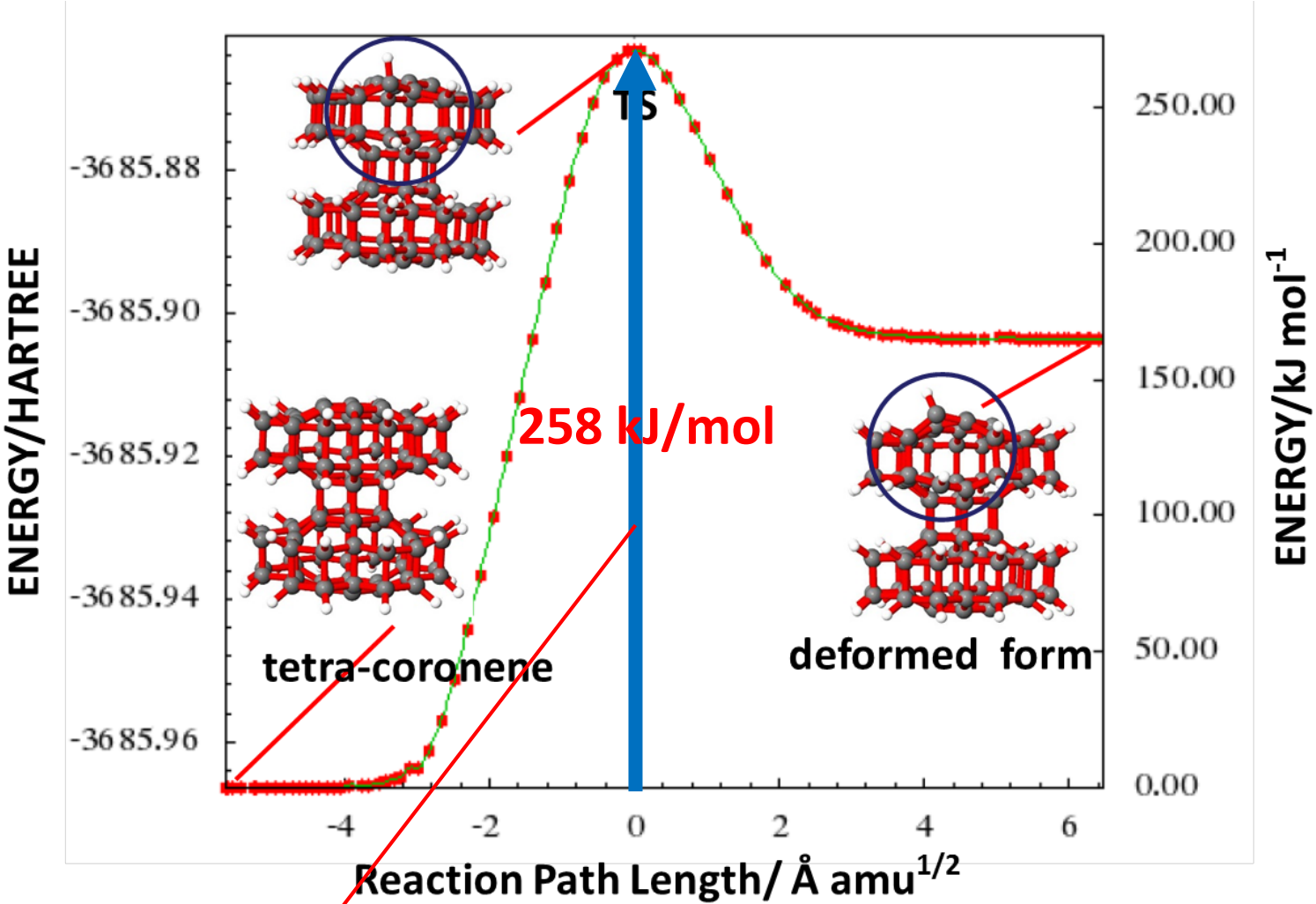
Tetramer

$C_{96}H_{48}$



Stability of tetra-coronene

Lowest TS search GRRM/ADDF B3LYP/6-31G*



Tetra-Coronene is stable enough with a high barrier !

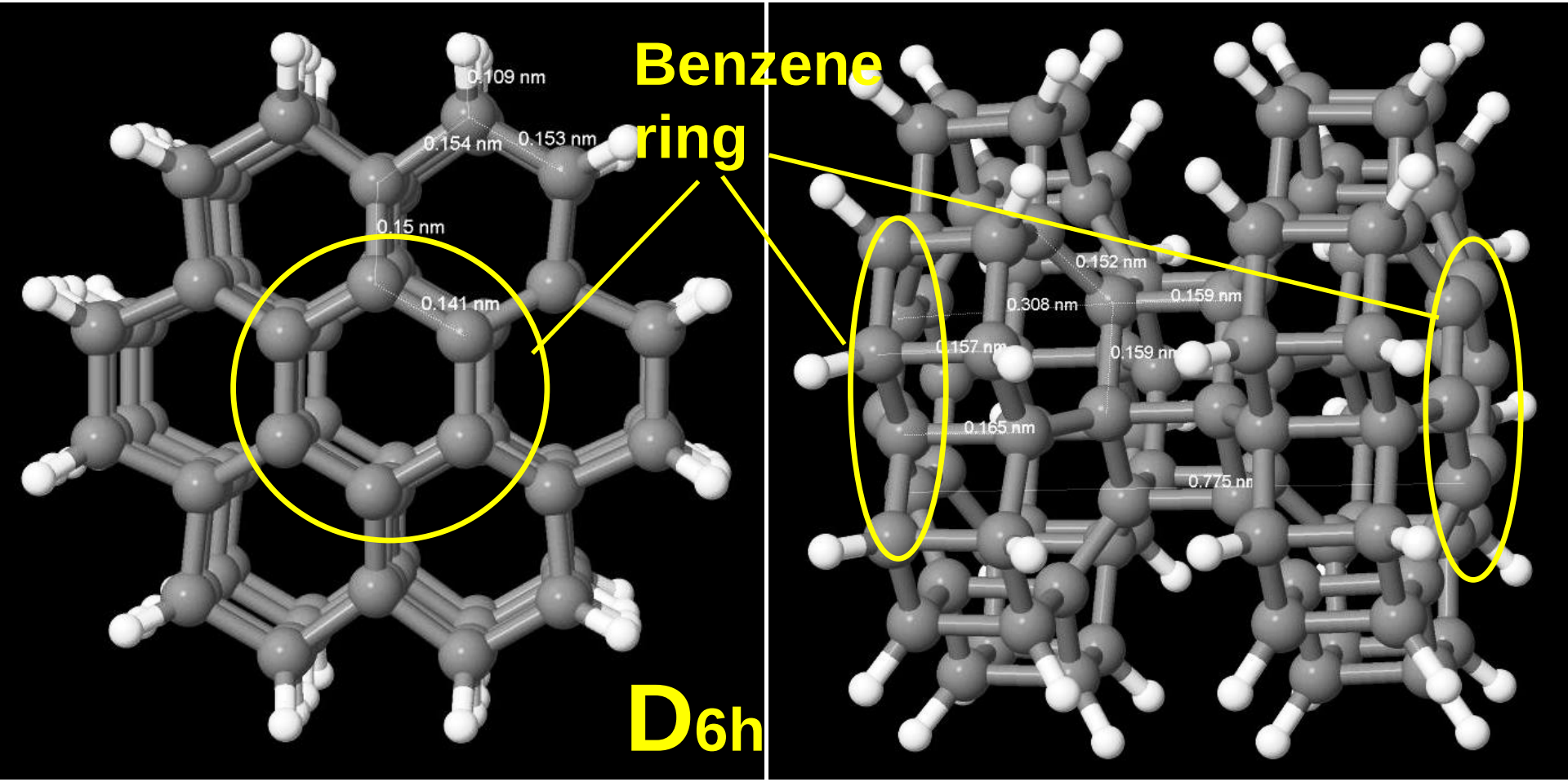
Structure of tetra-coronene D_{6h}

Tetramer

$C_{96}H_{48}$

Top view

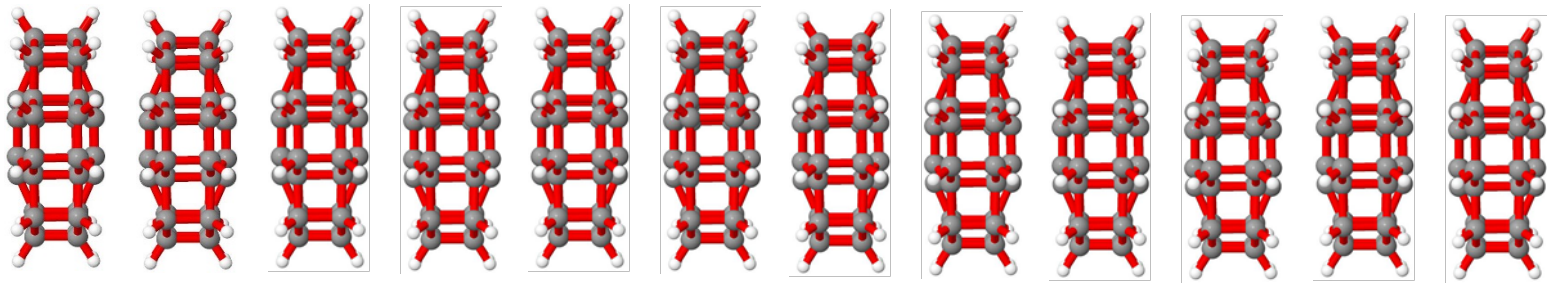
Side view



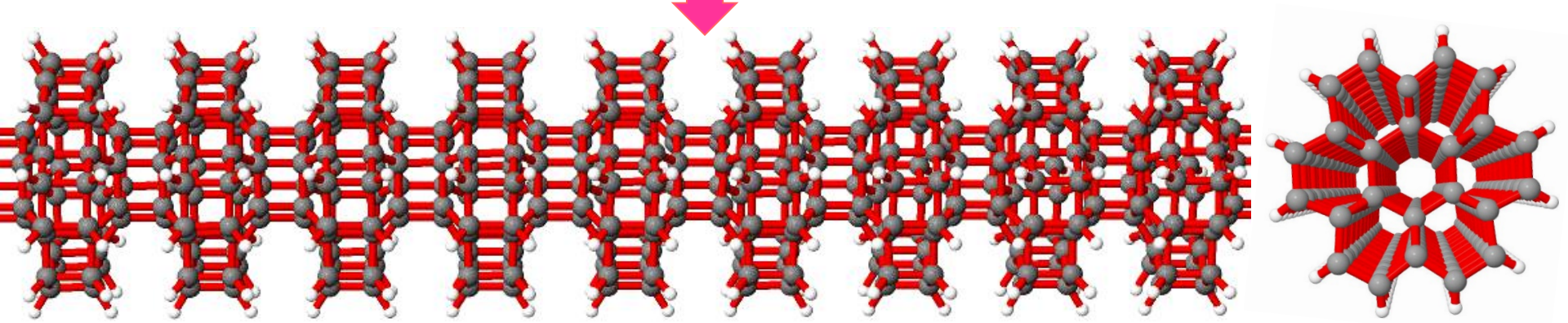
Tetra-coronene has benzene rings to polymerize !

Generation of Poly-coronene D_{6h}

Axial array of di-coronene leads to poly-coronene

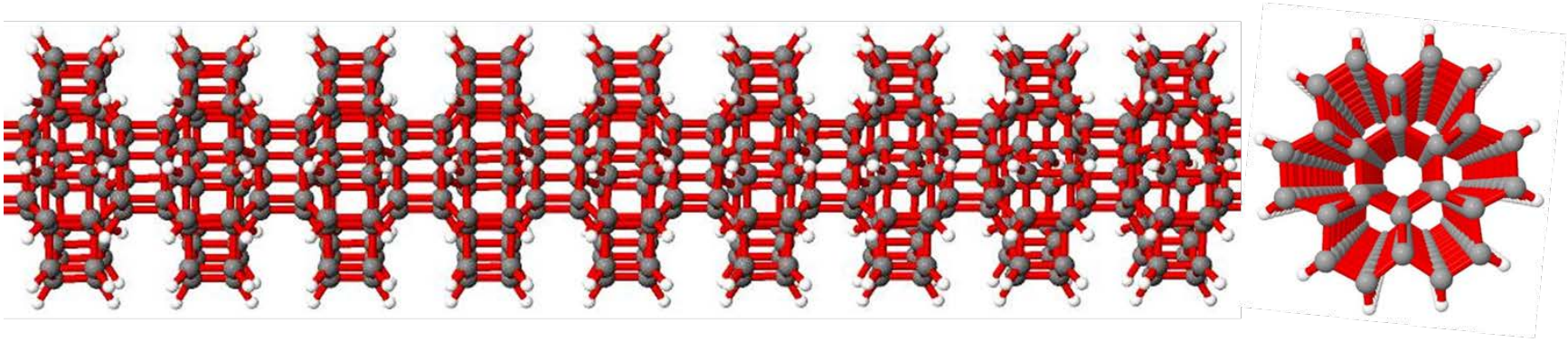


Periodic Boundary Condition (PBC) Calculation

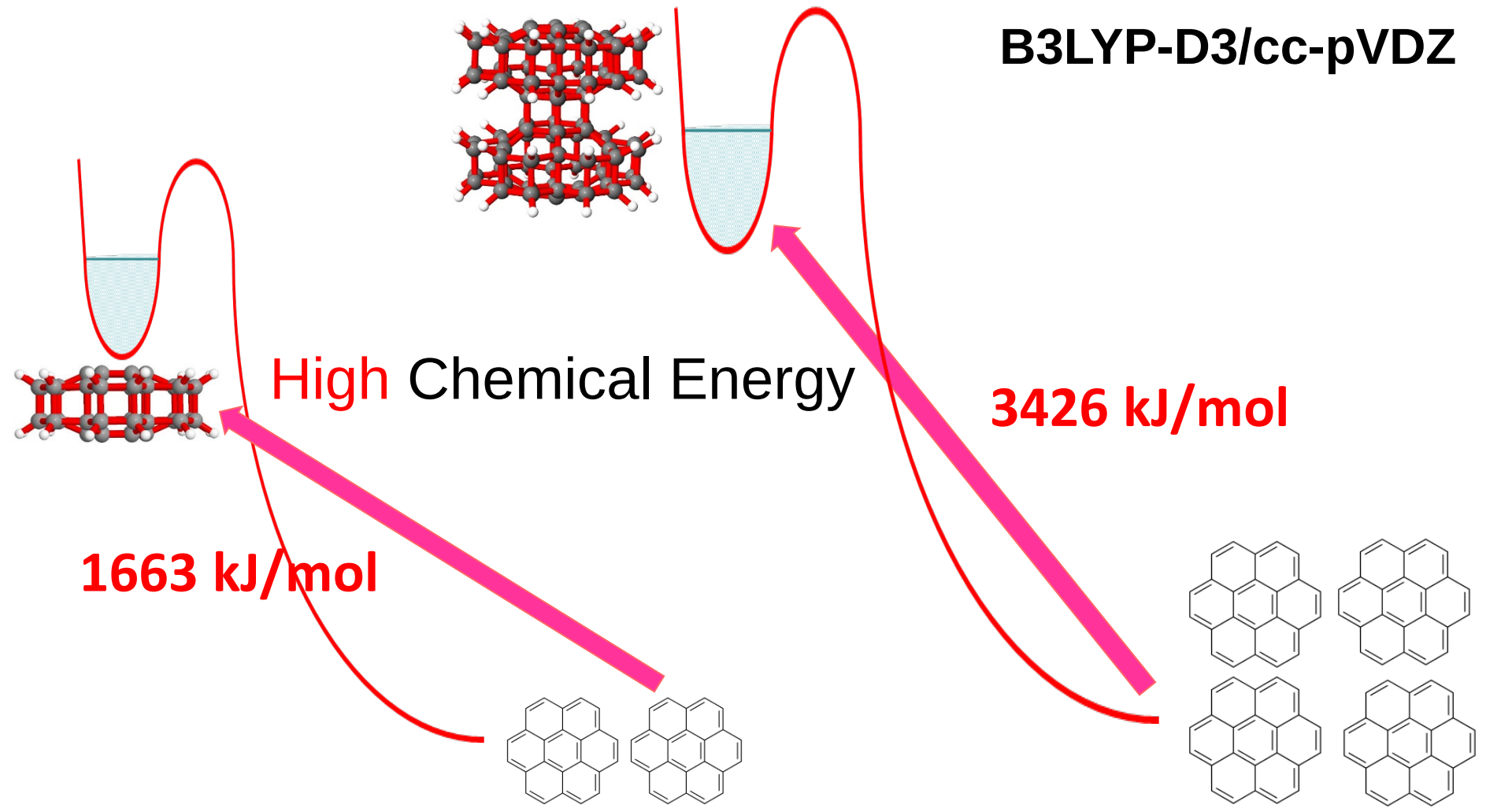


D_{6h} Gear Pipe Nano Structure

Structure of poly-coronene D_{6h}



Energies of $(Coronene)_n$, n=2,4



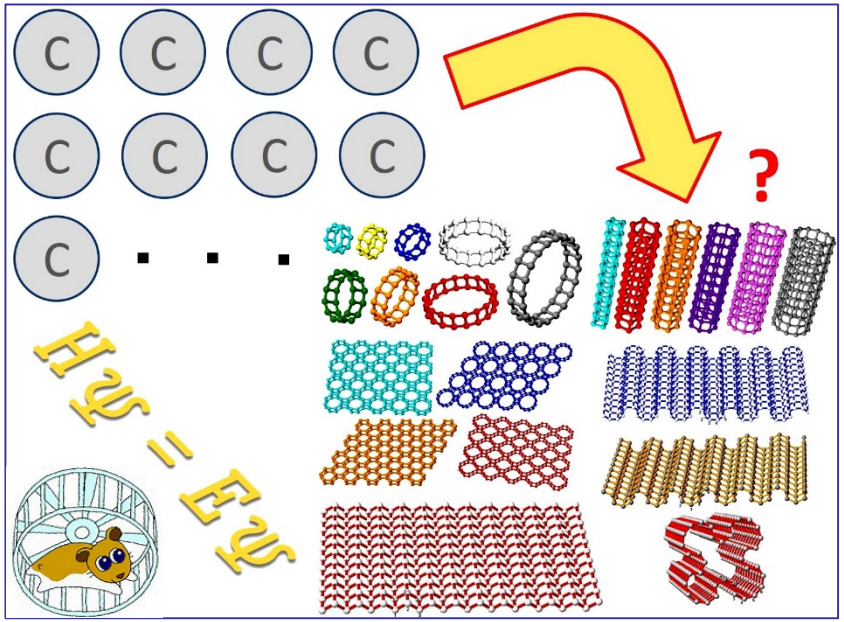
Polymerized-coronenes store chemical energies !

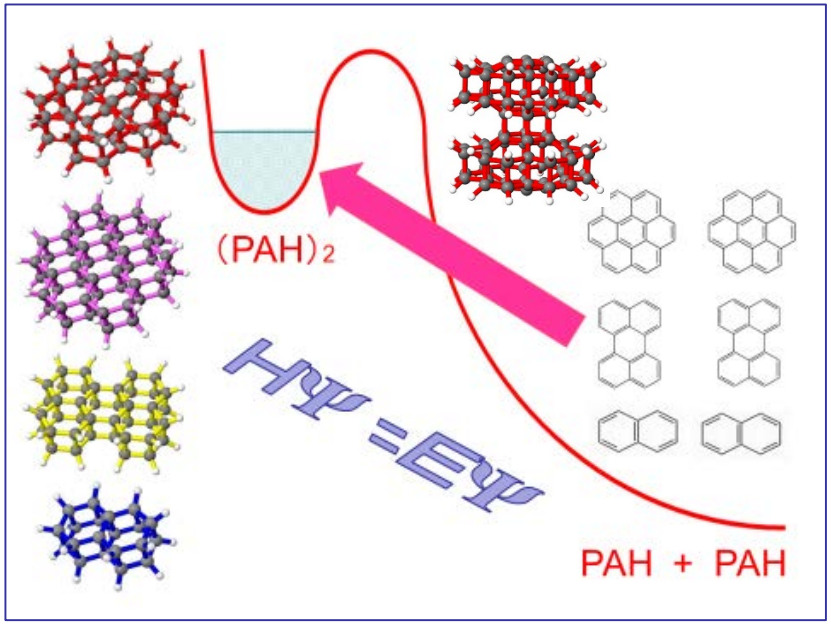
Summary

- Although only limited examples were shown in this talk, exploration of quantum chemical potential energy surfaces will open various new chemistries.
- For such explorations, GRRM program will help you;

GRRM programs (*GRRM*14, *GRRM*17)

are distributed, available at **https://iqce.jp/GRRM/**





Acknowledgement

Development of GRRM:

Satoshi **Maeda**

(***GRRM***1.2-11-14-17)

Y. Osada (*GRRM*11-14)

Keiji **Morokuma**

(***GRRM***11-14-17)

T. Taketsugu (*GRRM*14-17)

Y. Harabuchi (*GRRM*14-17)

Y. Sumiya (*GRRM*17)

M. Takagi (*GRRM*17)

K. Suzuki (*GRRM*17)

K. Sugiyama (*GRRM*17)

M. Hatanaka (*GRRM*17)

https://iqce.jp/GRRM/

Application of GRRM:

H. Satoh

T. Iwamoto

H. Yamakado

H. Tokoyama

X. Yang

B. Hajgato

Y. Luo

Y. Watanabe

M. Moteki

H. Isobe

S. Ohno

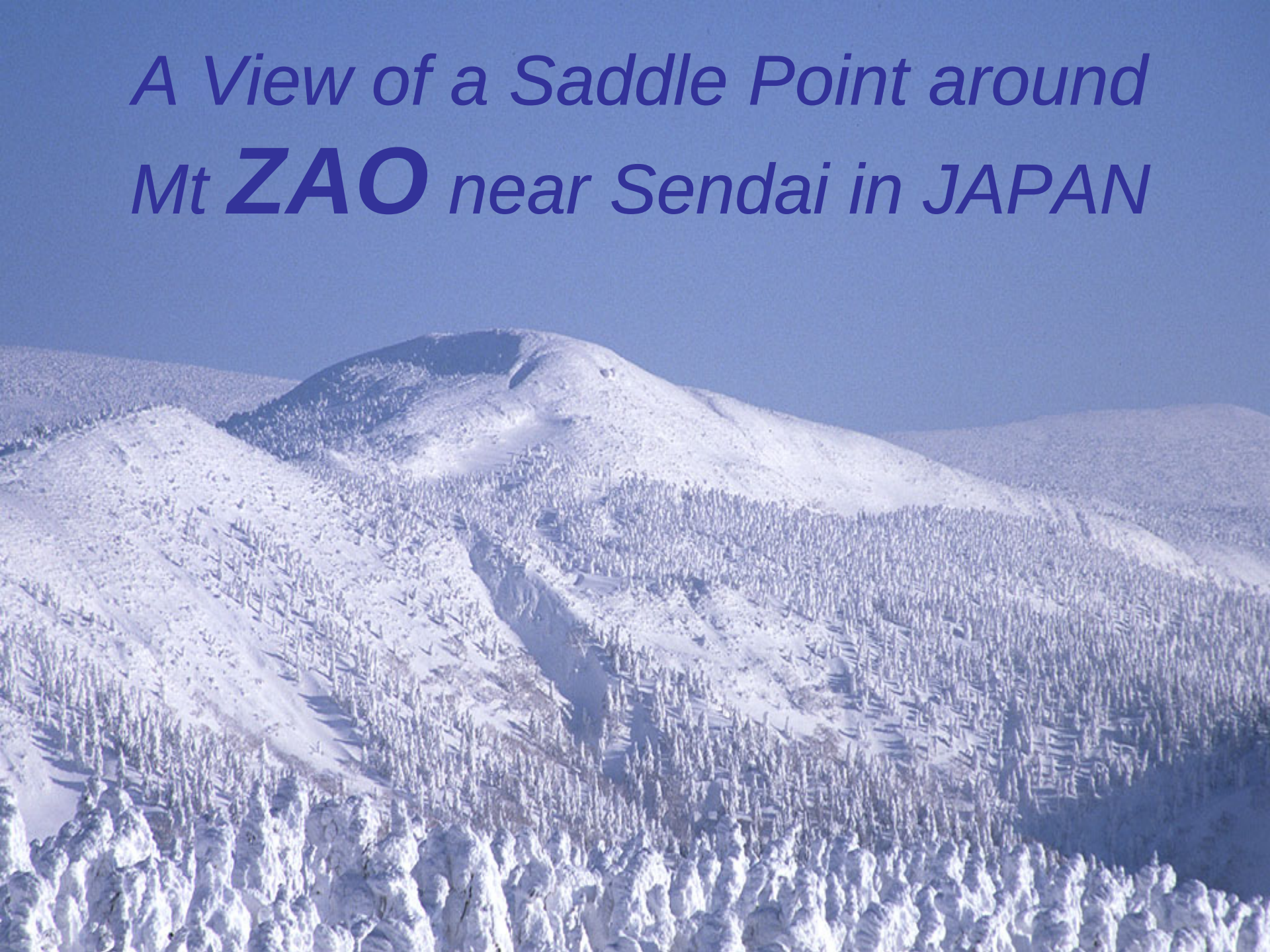
K. Shudo

Y. Matsuda

N. Kishimoto

Y. Kodaya

H. Watanabe


A View of a Saddle Point around
Mt ZAO near Sendai in JAPAN

A View from a Saddle Point