

Menton
2018.6.19
9:45-10:15

Global Reaction Route Mapping and Exploration of Novel Chemistry on Potential Energy Surfaces

Koichi Ohno^{1,2}

Tohoku University¹
Institute for Quantum Chemical Exploration²

Global Mapping of the World

We are here!



Ptolemaios's map



Discovery of New Routes

- 1492 Christopher Columbus
- 1498 Vasco da Gama
- 1497 Sebastien Gabbot
- 1499 Amerigo Vespucci
- 1519 Ferdinand Magellan

Exploration of New Worlds!



*How to Explore
the Chemical World?*

*Global Map?
Tool for Exploration?*

Basic Problems in Chemistry

for a given Chemical Formula, such as $C_NH_MO_L$.

- (1) What kinds of chemical species (isomers) exist?
- (2) How are they converted each other?
- (3) How do they dissociate into smaller species?
or How are they produced from smaller species?

To solve These Problems *Theoretically, Global Mapping of Potential Energy Surfaces (PES)* is needed.

- **Minima:**

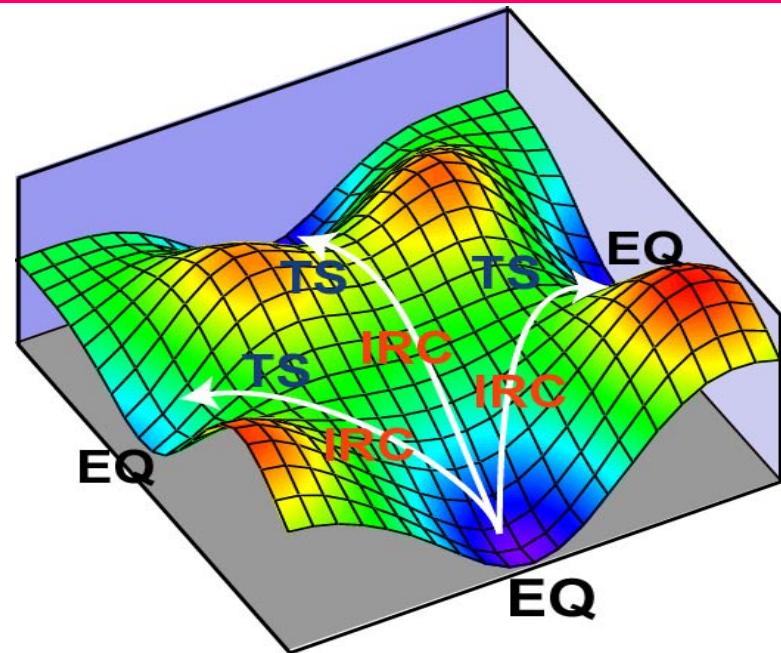
Equilibrium Structures (**EQ**)

- **Saddles:**

Transition Structures (**TS**)

- **Minimum Energy Paths:**

Intrinsic Reaction Coordinates (**IRC**)



Reaction path search methods

1. Geometry optimization methods

- Eigen Vector Following: Cerjan and Miller (1981)
- Berny optimization: Shregel (1982)
- Geometry DIIS: Császár and Pulay (1983)
- Rational Function Optimization: Banerjee et al. (1985)

2. Double-ended methods

- Synchronous Transit: Halgren and

Targeted Methods

- Reaction Path Sampling: Jorgensen and Tirrell (1987)
- Nudged Elastic Band (NEB): Henkelman et al. (2000)
- String: Ren and Vanden-Eijnden (2002)
- Growing String: Peters et al. (2004)

3. Coordinate driving methods

- Single Coordinate driving
- Metadynamics: Laio and Parrinello (2002)
- First Marching: Burger and Ayers (2010)

4.

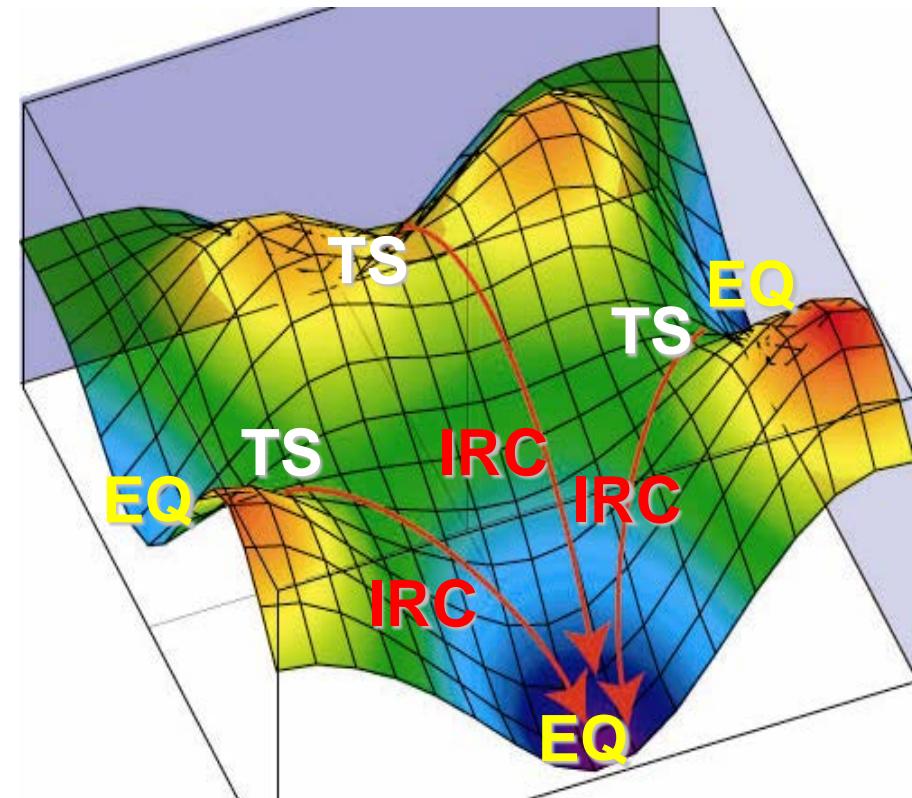
-
-
-
-
-

Unbiased Untargeted Methods

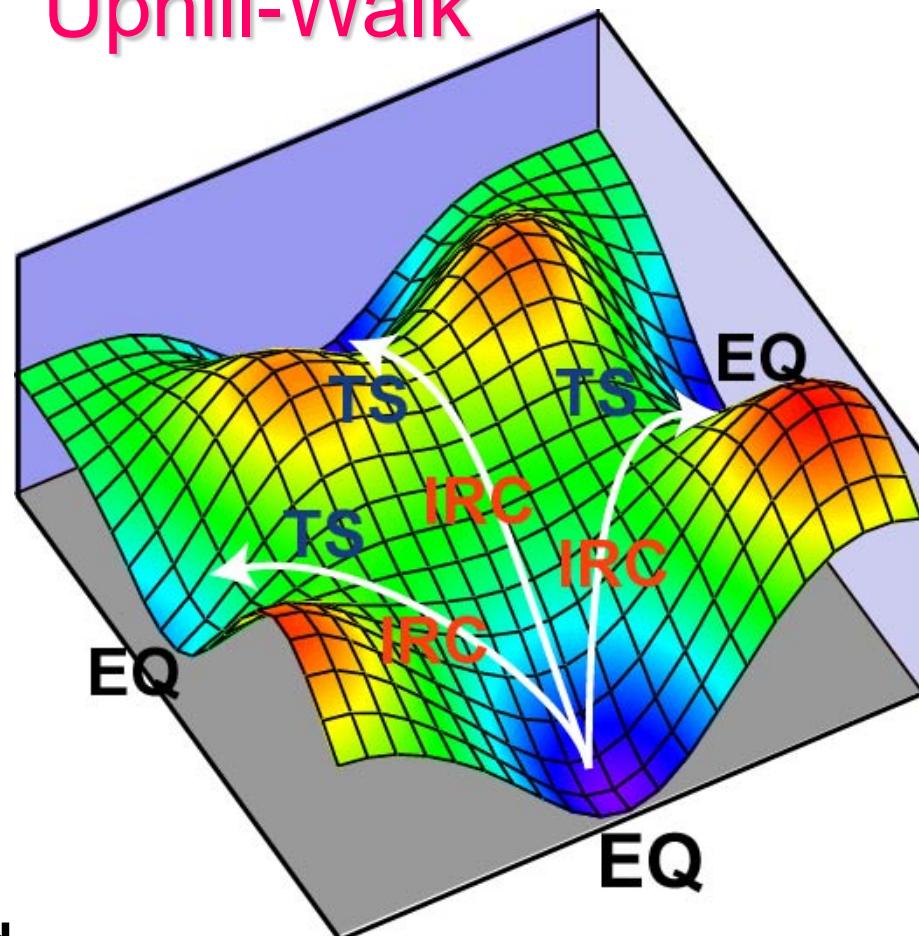
- **Global Reaction Route Mapping (Anharmonic Downward Distortion Following): Ohno and Maeda (2004)**
- **Artificial Force Induced Reaction: Maeda and Morokuma (2010)**

Traces along reaction pathways

Downhill-Walk



Uphill-Walk

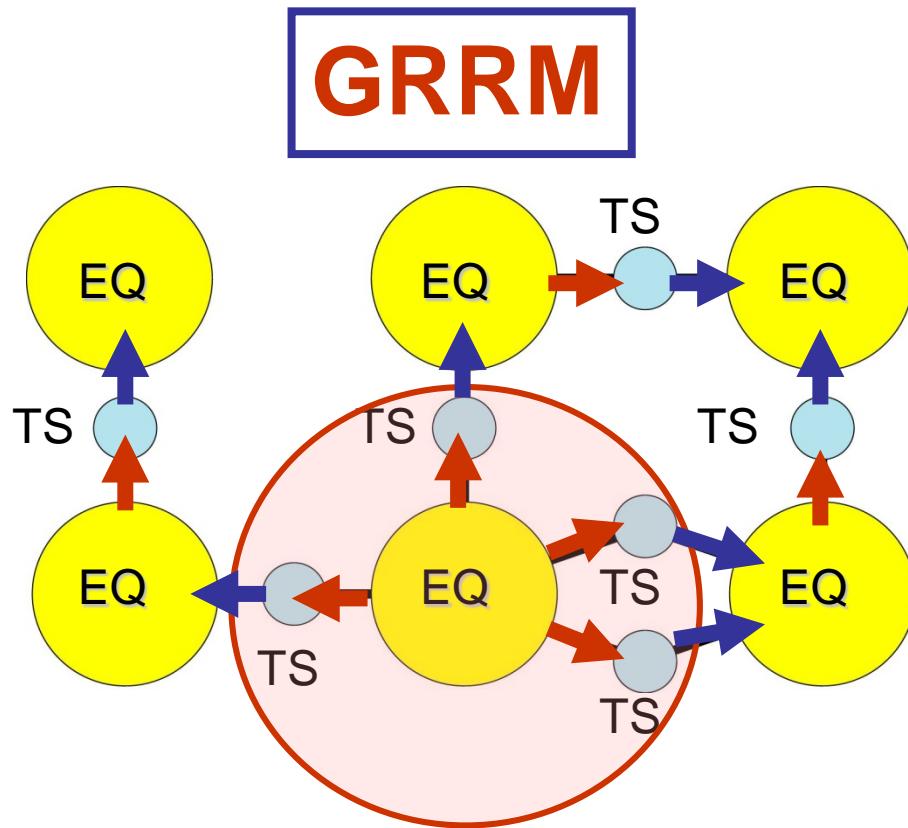


Steepest Descent Method can be used from anywhere to find an EQ.
If a TS is known, IRC can be followed.

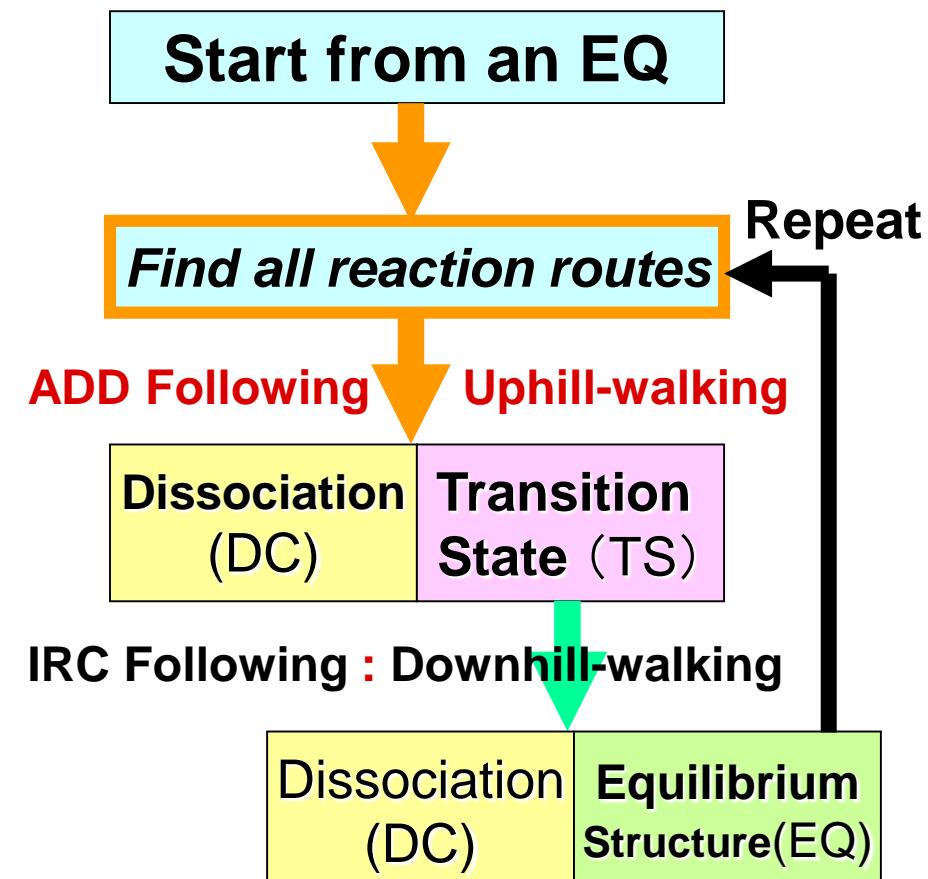
Anharmonic Downward Distortion (ADD) Following:
K.Ohno & S.Maeda,
Chem. Phys. Lett. 384,277(2004).

Uphill walks on PES enable us to perform Global Reaction Route Mapping (GRRM) !

Repeated One-After-Another-Search
EQ-TS-EQ

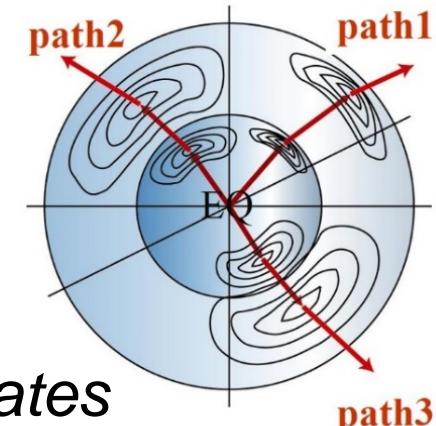
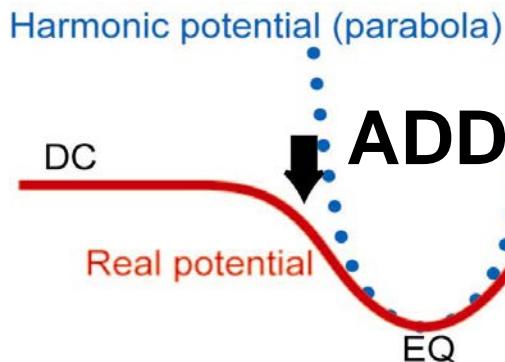


Automated Search



Anharmonic Downward Distortion Following (ADDF) method

Ohno, Maeda, *Chem. Phys. Lett.* 384, 277 (2004)



- Anharmonic Downward Distortion (ADD) indicates the direction of reaction! The problem becomes to find minima on the hypersphere, using frequency-scaled normal coordinates.

$$V = (1/2) \sum \lambda_i Q_i^2 = (1/2) \sum q_i^2 \quad : \quad q_i = \lambda_i^{1/2} Q_i$$

- Can find all the EQ and TS automatically
- Full-ADDF of GRRM is in general **expensive**, like a **full-CI**. Limited-ADDF reduces computational costs drastically.

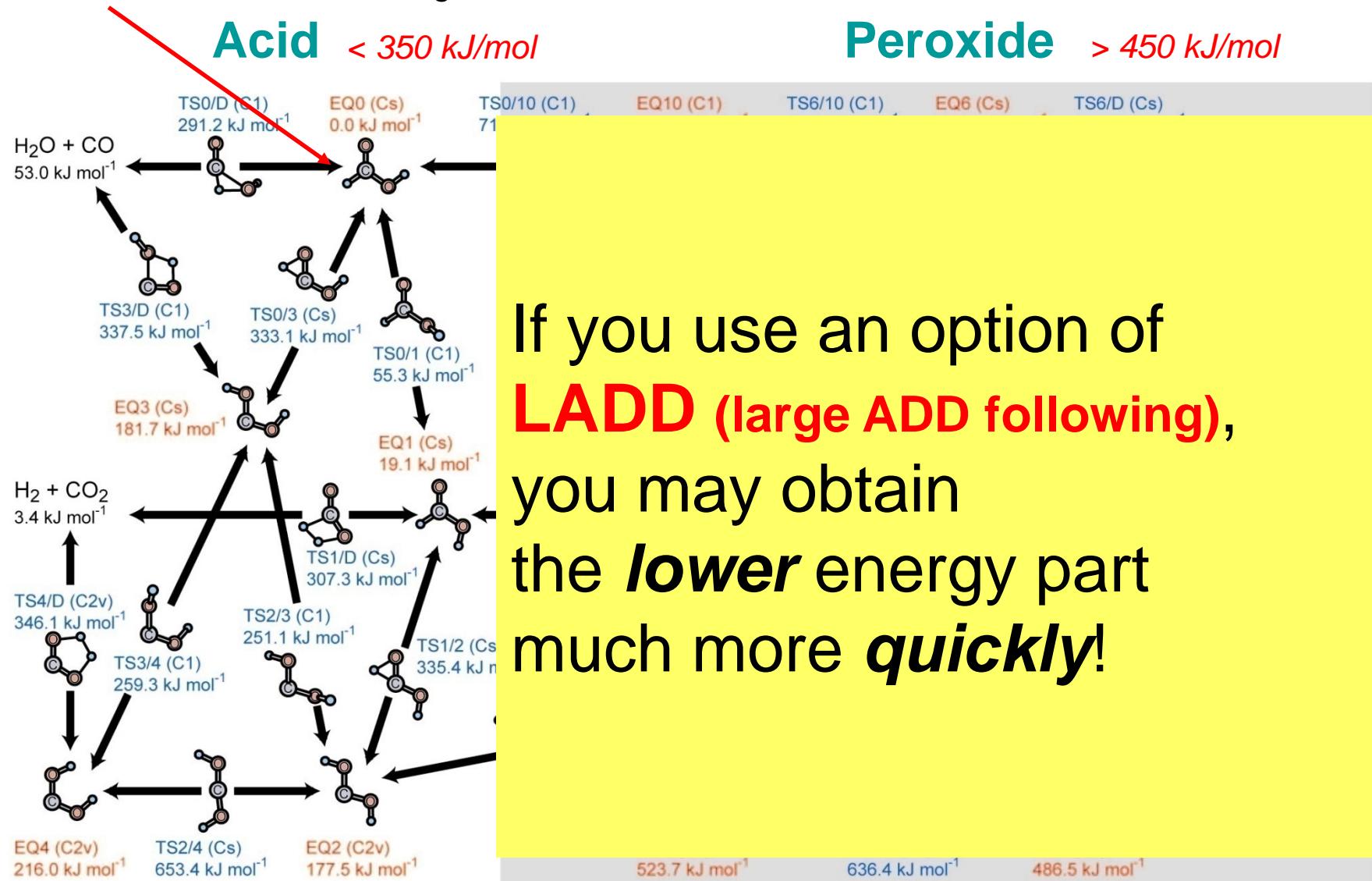
Options for GRRM/ADDF: Large ADDF method (**LADD**)

Double-ended Method (**2P-SHS, d-ADDF**)

Micro-iteration Method (**μ -ADDF**)

An example of Global Reaction Route Map by full-ADDF for 5-atom system H₂CO₂ 13 EQ 30 TS

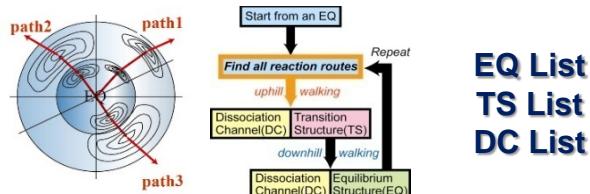
Formic Acid HCOOH is the global minimum



Parallel GRRM saves computation time considerably

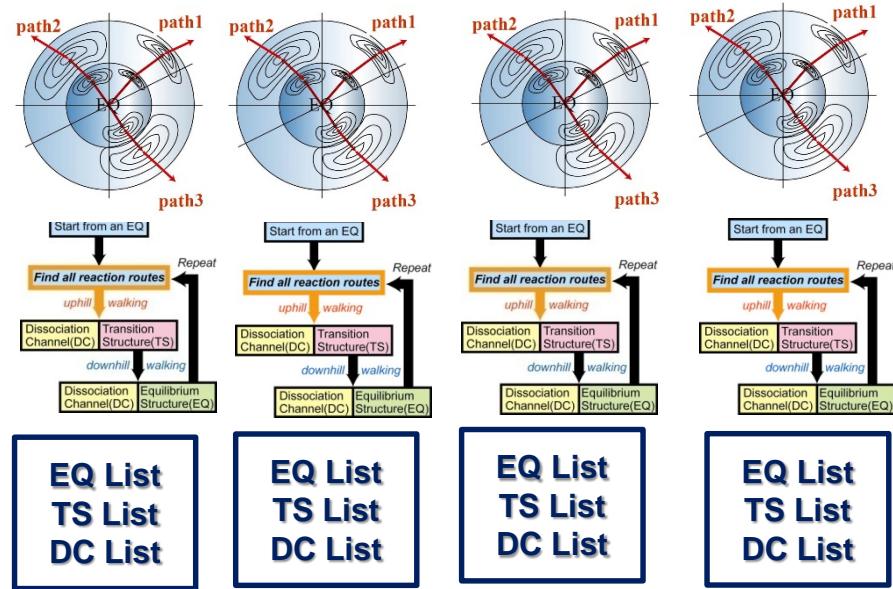
in Single GRRM

ADDF is applied to one EQ at one time



With using many cpu/multicores ADDF can be applied to Many EQs at the same time

in Parallel GRRM



Done List

TOTAL EQ List
TOTAL TS List
TOTAL DC List

List of Global Search by GRRM/*full*-ADDF

for the ground singlet-state at the B3LYP/6-31G* level with a 16-core computer

Atom	Formula	EQ	TS	cpu time/hour	6	H4CO	2	14	16.9	7	H2C2O3	179	1077	647
3	H2O	1	1	0.3	6	H4NCI	5	24	18.6	7	H3C3N	70	452	792
3	HCN	2	1	0.7	6	H3C2Cl	8	36	26.2	7	H3N3O	93	384	937.9
4	H3N	1	1	2.8	6	C2O4	18	79	26.6	7	H2C3O2	207	1158	1499.8
4	H2O2	2	2	3.1	6	H3N3	9	49	42.7	8	H6BN	2	8	29.3
4	H2CO	4	12	5.1	6	H2C2Cl2	18	69	44.8	8	H6C2	2	8	47.6
4	H2N2	3	7	5.5	6	H3C2N	19	73	57	8	H6B2	2	5	69.2
4	H2C2	2	2	5.9	6	HC2Cl3	11	54	63.2	8	H5CNO	16	126	122.4
4	H2OS	3	7	7.7	6	H2C3O	36	161	81.3	8	H6Si2	7	25	129.4
4	P4	4	4	13.8	6	H3CNO	30	159	92	8	H5C2Cl	22	133	173.2
4	HCNO	9	22	22	6	H4CO	2	10	98	8	H4C2Cl2	20	133	216.8
4	CN2O	13	35	30	6	H2C4	13	44	117.3	8	H4C2O2	118	782	468.9
4	BCNO	15	32	51.8	6	H2CO3	29	149	148.2	8	H4C4	32	171	688
5	H4C	1	1	6.7	6	H2C2F2	16	61	150	8	H4C3O	84	586	971.5
5	H2CO2	14	44	16.4	6	H2C2O2	50	223	233	8	S8	60	415	1157.2
5	H3CN	3	17	17	6	H2C2N2	63	343	375.1	8	H5C2NO	219	957	1935.4
5	H3NO	5	15	17	6	H3CClCu	27	72	559	8	H2C2O4	581	3932	5873.2
5	HCCI3	5	17	18.1	6	HC2NO2	217	1054	588.3	8	H3CNO3	676	5181	8664
5	H2CCI2	3	7	19.6	6	H2CN2O	87	233	647	9	H6C3	8	45	104.2
5	HC3N	11	38	25.1	6	Si3O3	63	255	727.2	9	H6C2O	7	59	139.5
5	H3CCI	8	23	32	6	H3C2NO	201	1218	1044.5	10	H6C2O2	95	697	732.9
5	CCl4	6	23	32.9	7	H5CN	2	10	16	10	H6C3O	113	843	2290.5
5	HCO2Cl	26	103	40.1	7	H4C3	7	31	56.1	10	H5C2NO2	3210	23278	1603.2
5	C2O3	11	37	56	7	H4CN2	19	143	89.9	11	H8C3	1	12	51
5	HCN3	19	81	56.7	7	H4CO2	11	50	100.6	11	H7C2NO	151	1413	4526.8
5	H2N2O	20	77	63.9	7	H5B2	7	39	134.6	11	H6C3O2	1243	10100	12455.7
5	HC2NO	49	191	88.4	7	H4C2O	14	100	137.5	14	H10C4	3	35	176
5	CN2O2	34	148	154.8	7	H3CNO2	157	1027	461.5	17	H12C5	8	70	972.1

- Explored number of EQs ranges from only 1 to over 3000!*
- Explored number of TS increases with the increase of EQ.*
- cpu time expands from less than 1 hour to longer than 1 year!*

Number of EQs

Number of EQ ranges from only one to over three thousands!

Only **one** EQ: H_2O , NH_3 , CH_4 , C_3H_8 (propane)

Many EQs (Many isomers / Many conformers)

3210 EQ: $\text{H}_5\text{C}_2\text{NO}_2$ (glycine)

1369 EQ: $\text{H}_6\text{C}_3\text{O}_2$ (methyl acetate)

676 EQ: H_3CNO_3 (aminoxy formate)

Number of EQ does not simply depend on the number of atoms!

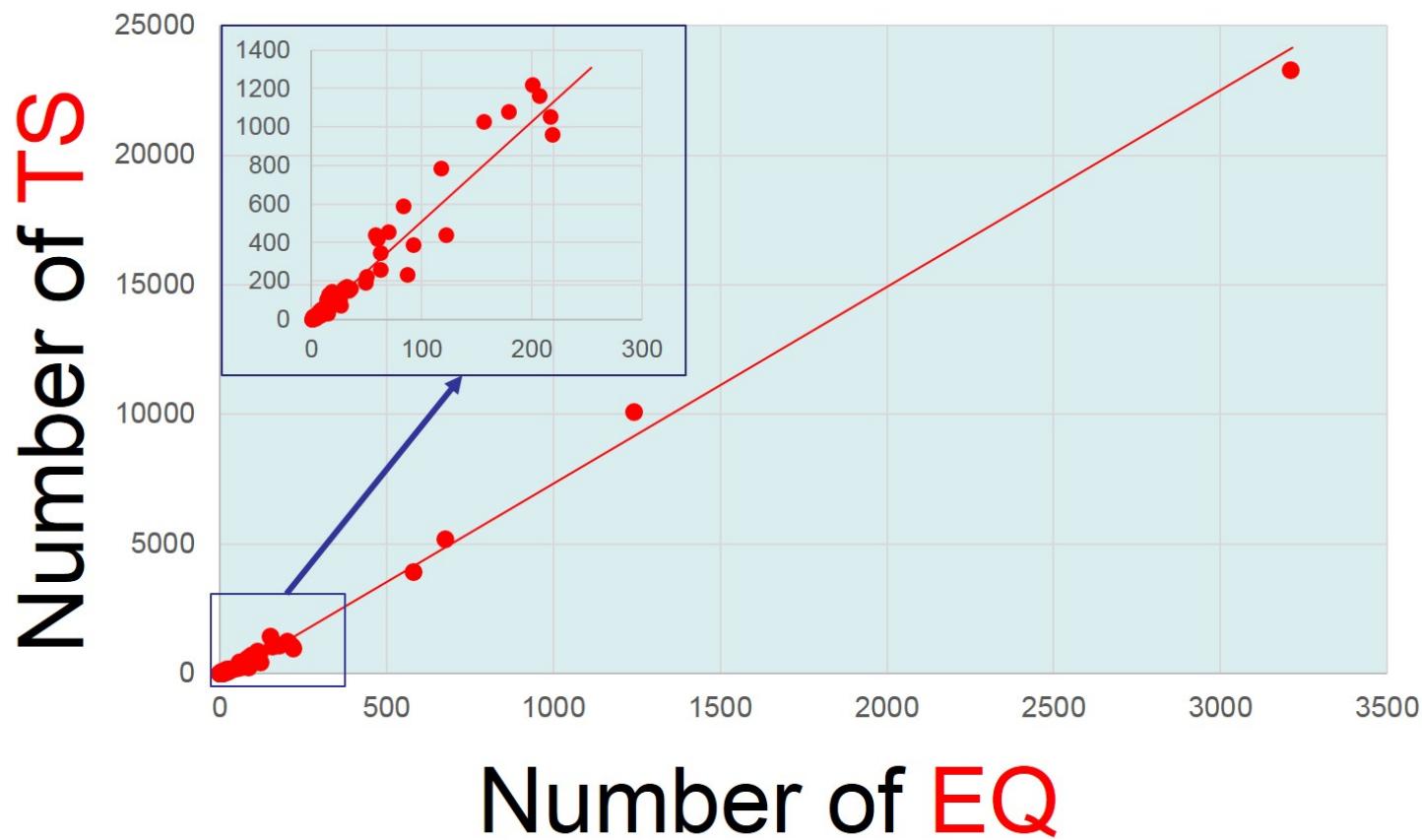
Even if N-atoms are the same, N-EQs can be very much different!

	N-Atoms	N-EQs
C_3H_8 (propane)	11	1
$\text{H}_6\text{C}_3\text{O}_2$ (methyl acetate)	11	1369

Number of TSs

Number of TS increases simply with the increase of EQ.

$$N(\text{TS})/N(\text{EQ}) \doteq 6 \sim 8$$

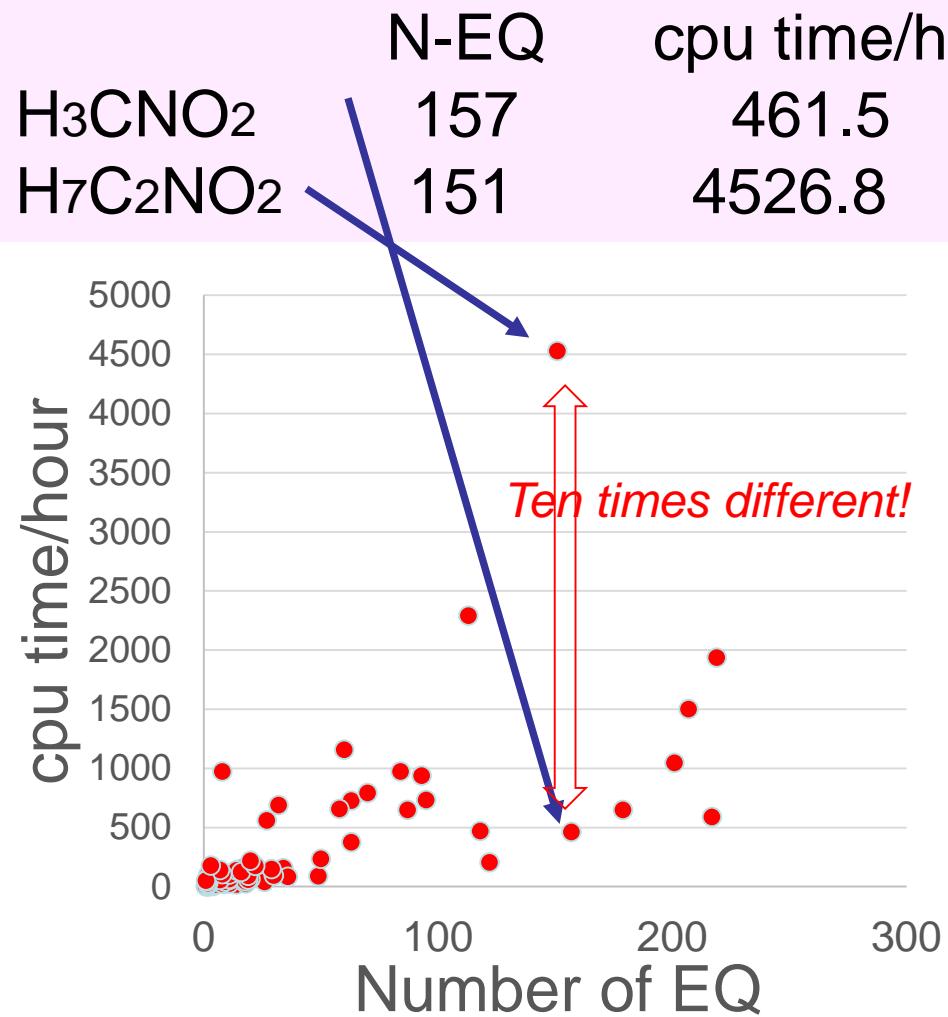


CPU time for GRRM/*full*-ADDF with a 16-core computer

cpu time expands from less than 1 hour to longer than 1 year!

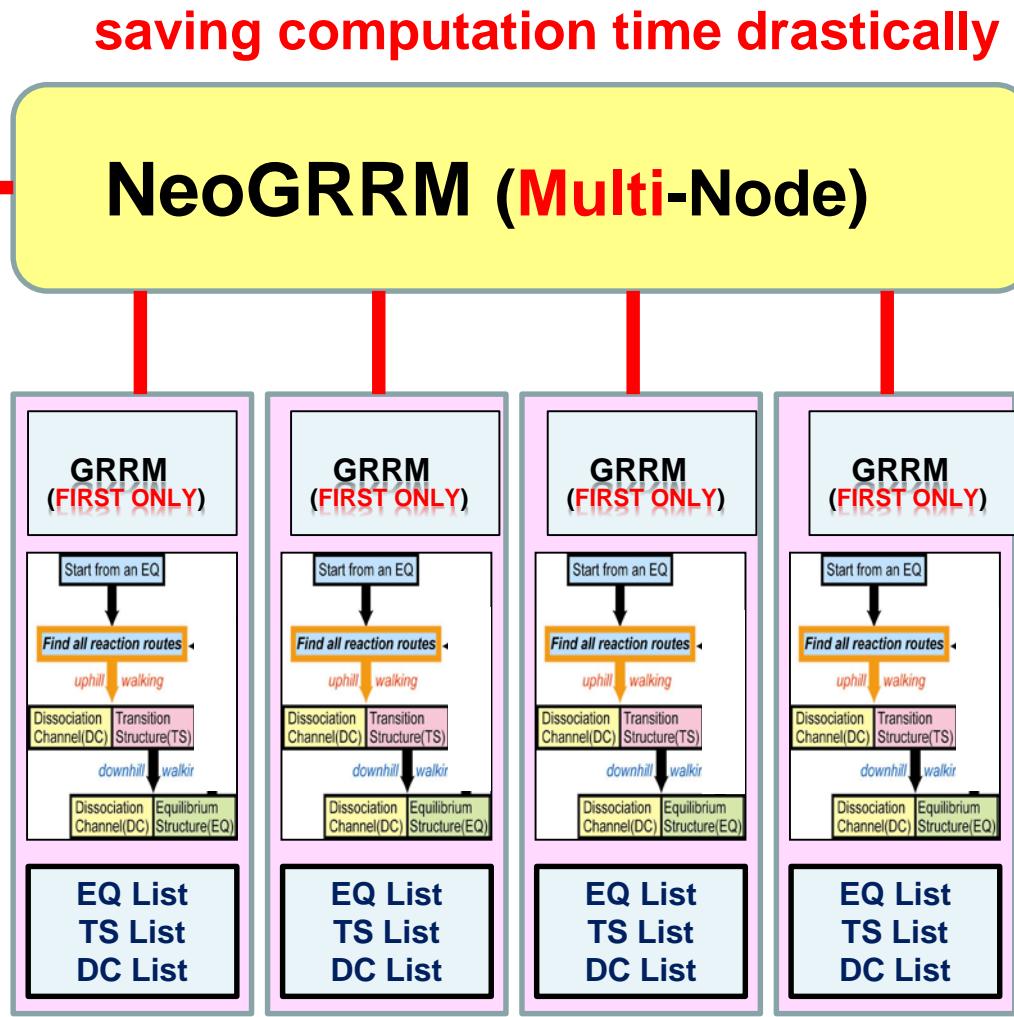
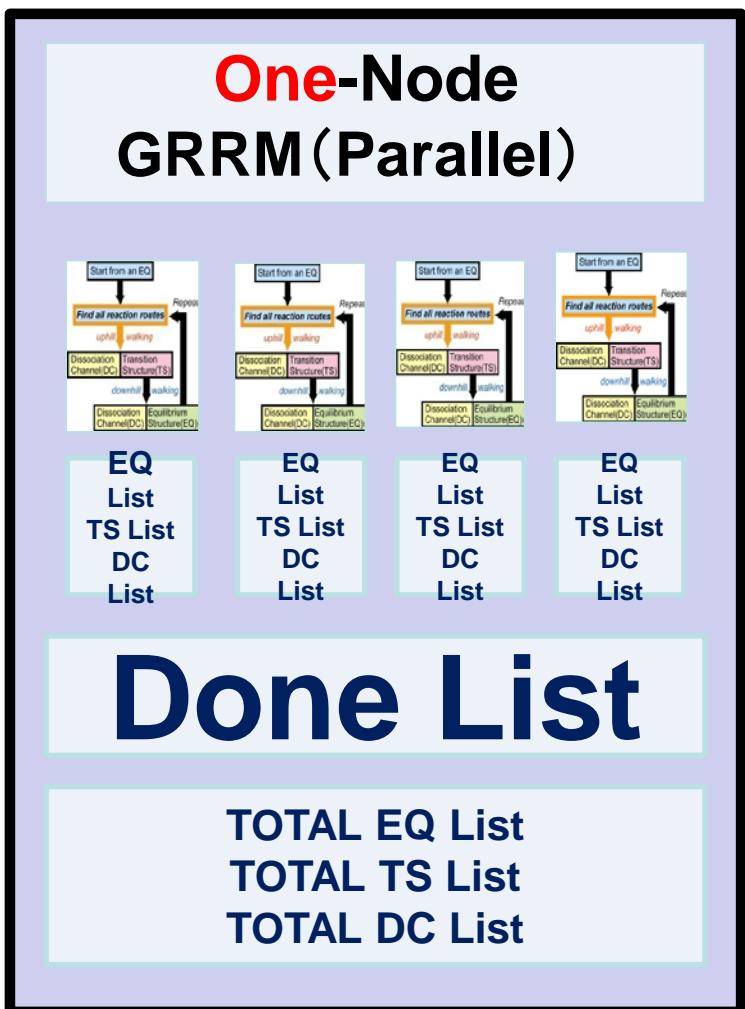
cpu time is not a simple function of the EQ number (N-EQ) !

Formula	cpu time/h
H ₂ O	0.3
HCN	0.7
H ₂ CO	5.1
H ₂ CO ₂	16.4
.....
H ₂ C ₂ O ₄	5873.2 (0.7 year)
H ₃ CNO ₃	8664.0 (1.0 year)
H ₆ C ₃ O ₂	12455.7 (1.4 year)



To overcome explosion of cpu-time, we have developed

Multi-Node GRRM/ADDF : NeoGRRM



Extensive GRRM

for the system of 8-atom

H₃CNO₃

676 EQ

5181 TS

3161 DC (Dissociation Channel)

at B3LYP/6-31G(d) level

via huge numbers of

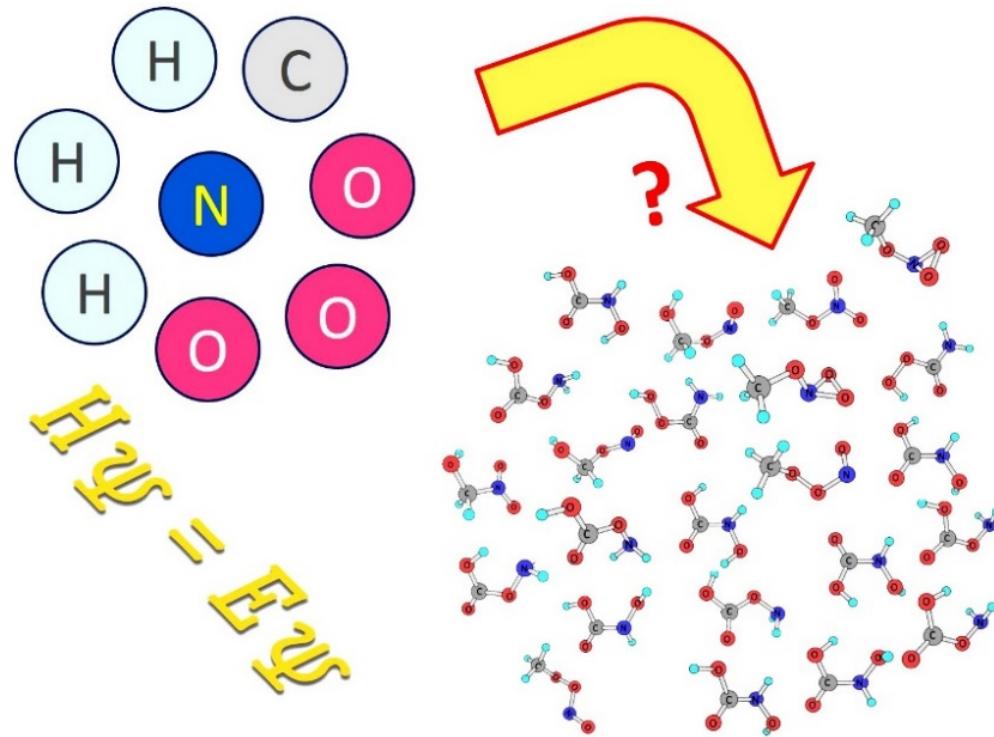
Force Calculations 18719781

Hessian Calculations 534726

CPU time for this Job took

8661 h (just **1 year**)

by **One-node GRRM**
with 16 cores



Ohno, Kishimoto, Iwamoto, Satoh,
J. Compt. Chem. 38, 669 (2017).

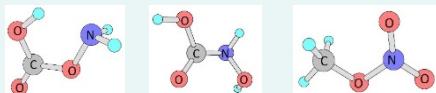
but it was **shortened** to
240 h (only **10 days**)
by **Multi-node GRRM**
with 256 cores

GRRM of H₃CNO₃

676 EQs

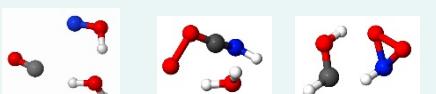
EQs are
classified into

465 isomers



...

211 clusters



...

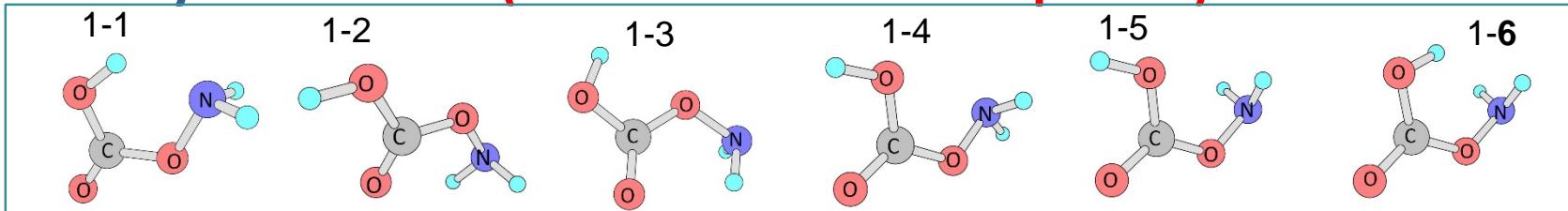
Further, *isomers*
are classified into
many chemical
compounds

Structural Formula of 47 H₃CNO₃

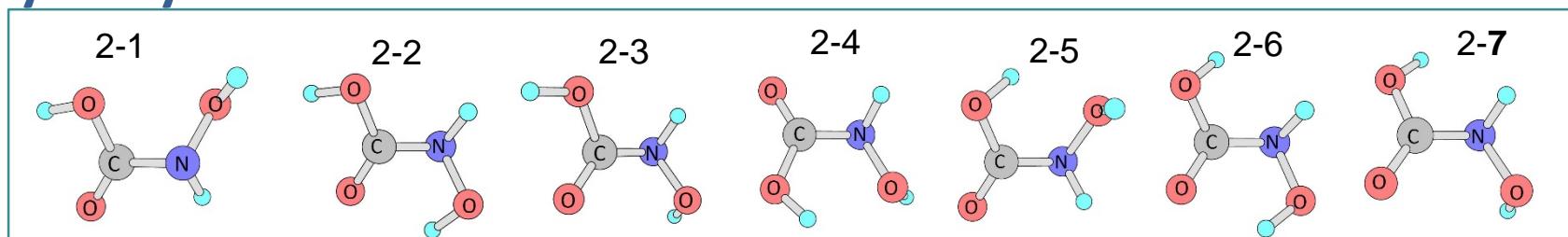
<chem>O=C(O)N</chem> 1 : 0.0 (6)	<chem>O=C(O)N(O)O</chem> 2 : 9.1 (7)	<chem>O=C(O)N(O)O</chem> 3 : 60.3 (6)	<chem>O=C(O)N(O)O</chem> 4 : 79.2 (2)	<chem>O=C(O)[NH3+]</chem> 5 : 127.3 (1)	<chem>O=C(O)[NH3+]</chem> 6 : 129.4 (5)
<chem>O=C(O)N(O)O</chem> 7 : 157.8 (7)	<chem>O=C(O)N(O)O</chem> 8 : 165.0 (8)	<chem>O=C(O)N(O)O^-</chem> 9 : 167.5 (3)	<chem>O=C(O)N(O)O^-</chem> 10 : 165.5 (5)	<chem>O=C(O)N(O)O^-</chem> 11 : 165.6 (9)	<chem>O=C(O)N(O)O^-</chem> 12 : 170.7 (1)
<chem>O=C(O)N(O)O^-</chem> 13 : 182.4 (2)	<chem>O=C(O)N(O)O^-</chem> 14 : 188.9 (1)	<chem>O=C(O)N(O)O^-</chem> 15 : 198.6 (4)	<chem>O=C(O)N(O)O^-</chem> 16 : 216.2 (3)	<chem>O=C(O)N(O)O^-</chem> 17 : 227.6 (1)	<chem>O=C(O)N(O)O^-</chem> 18 : 226.8 (1)
<chem>O=C(O)N(O)O^-</chem> 19 : 228.5 (6)	<chem>O=C(O)N(O)O^-</chem> 20 : 230.7 (12)	<chem>O=C(O)N(O)O^-</chem> 21 : 250.7 (1)	<chem>O=C(O)N(O)O^-</chem> 22 : 268.5 (4)	<chem>O=C(O)N(O)O^-</chem> 23 : 266.9 (4)	<chem>O=C(O)N(O)O^-</chem> 24 : 270.9 (5)
<chem>O=C(O)N(O)O^-</chem> 25 : 280.5 (1)	<chem>O=C(O)N(O)O^-</chem> 26 : 281.3 (2)	<chem>O=C(O)N(O)O^-</chem> 27 : 302.4 (8)	<chem>O=C(O)N(O)O^-</chem> 28 : 343.1 (11)	<chem>O=C(O)N(O)O^-</chem> 29 : 369.1 (4)	<chem>O=C(O)N(O)O^-</chem> 30 : 375.6 (3)
<chem>O=C(O)N(O)O^-</chem> 31 : 368.0 (2)	<chem>O=C(O)N(O)O^-</chem> 32 : 378.5 (5)	<chem>O=C(O)N(O)O^-</chem> 33 : 383.8 (2)	<chem>O=C(O)N(O)O^-</chem> 34 : 390.7 (5)	<chem>O=C(O)N(O)O^-</chem> 35 : 395.0 (8)	<chem>O=C(O)N(O)O^-</chem> 36 : 393.0 (12)
<chem>O=C(O)N(O)O^-</chem> 37 : 421.9 (2)	<chem>O=C(O)N(O)O^-</chem> 38 : 444.2 (1)	<chem>O=C(O)N(O)O^-</chem> 39 : 487.0 (3)	<chem>O=C(O)N(O)O^-</chem> 40 : 500.4 (1)	<chem>O=C(O)N(O)O^-</chem> 41 : 493.8 (3)	<chem>O=C(O)N(O)O^-</chem> 42 : 506.1 (3)
<chem>O=C(O)N(O)O^-</chem> 43 : 518.3 (1)	<chem>O=C(O)N(O)O^-</chem> 44 : 539.1 (1)	<chem>O=C(O)N(O)O^-</chem> 45 : 563.4 (2)	<chem>O=C(O)N(O)O^-</chem> 46 : 598.7 (4)	<chem>O=C(O)N(O)O^-</chem> 47 : 721.6 (2)	

Conformers for some compounds of H₃CNO₃

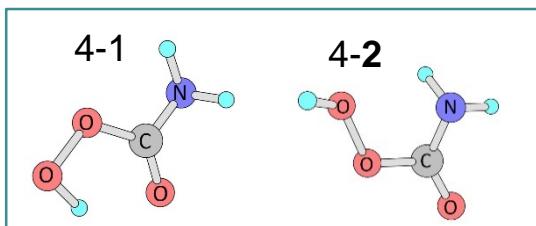
1: Aminoxy formic acid (The most stable compound)



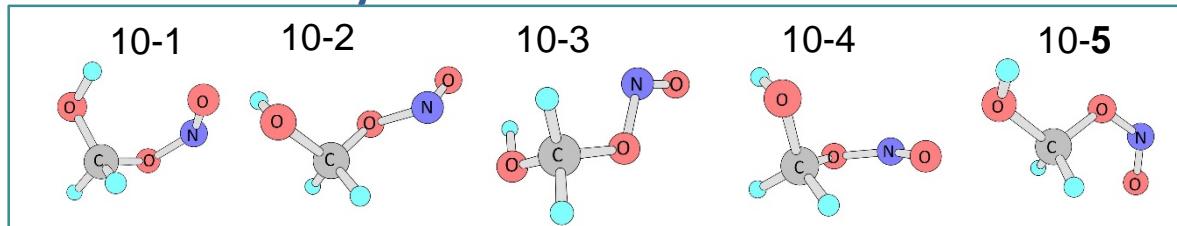
2: Hydroxy carbamic acid



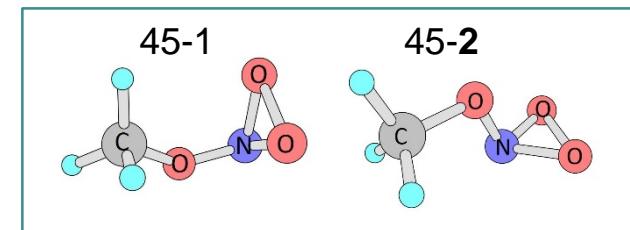
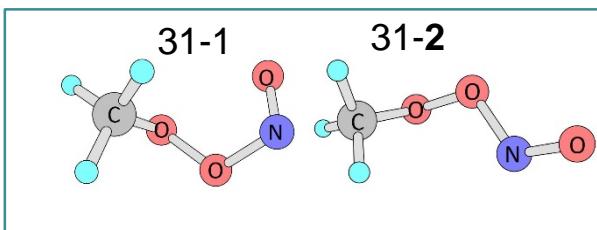
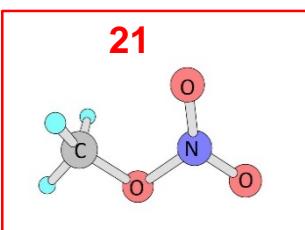
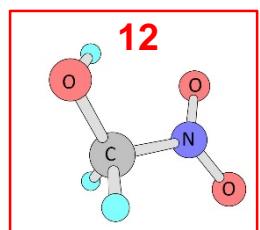
4: Aminoperformic acid



10: Nitroso oxymethanol



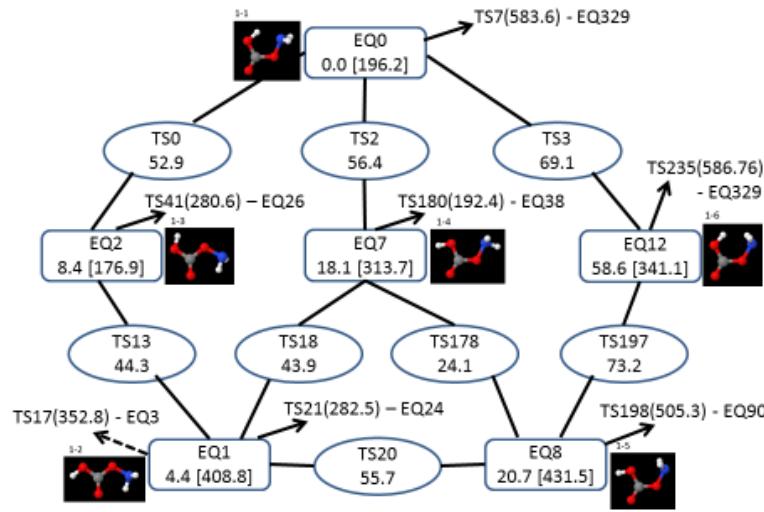
12: Nitromethanol 21: Methyl nitrate 31: Nitrous acid methoxy ester 45: Methoxy dioxaziridine



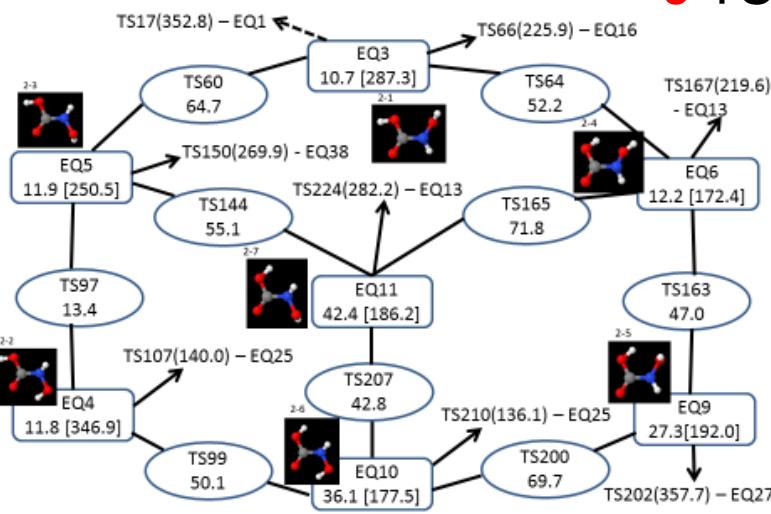
Reaction pathways via **5181** TS were explored by GRRM/full-ADDF.

Local Reaction Route Maps for H₃CNO₃

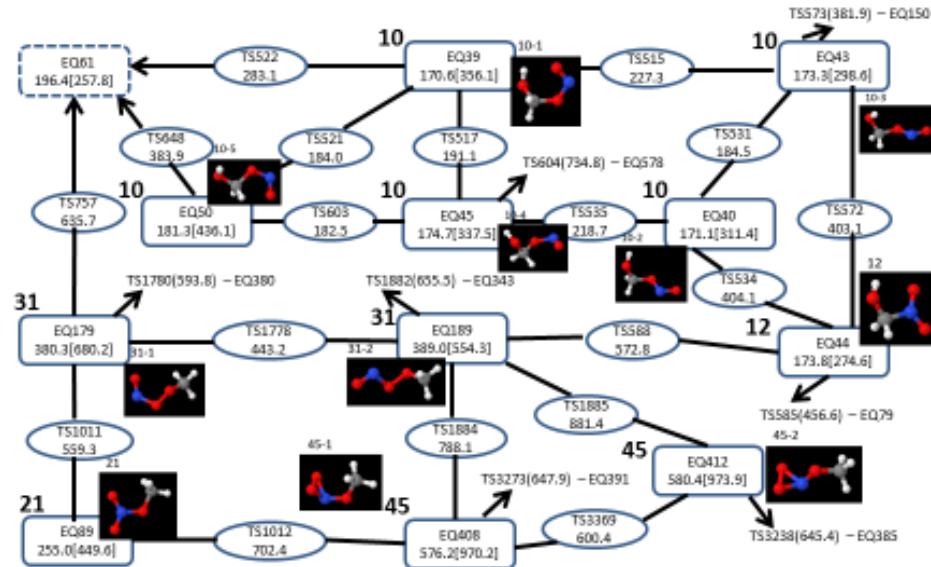
Local map of compound 1 **8** TS



Local map of compound 2 **9** TS



Local map around 10, 12, 21, 31, and 45 **18** TS



Connected! or **Not connected!**

Energy Barrier Heights Δ

Between the **same** compounds

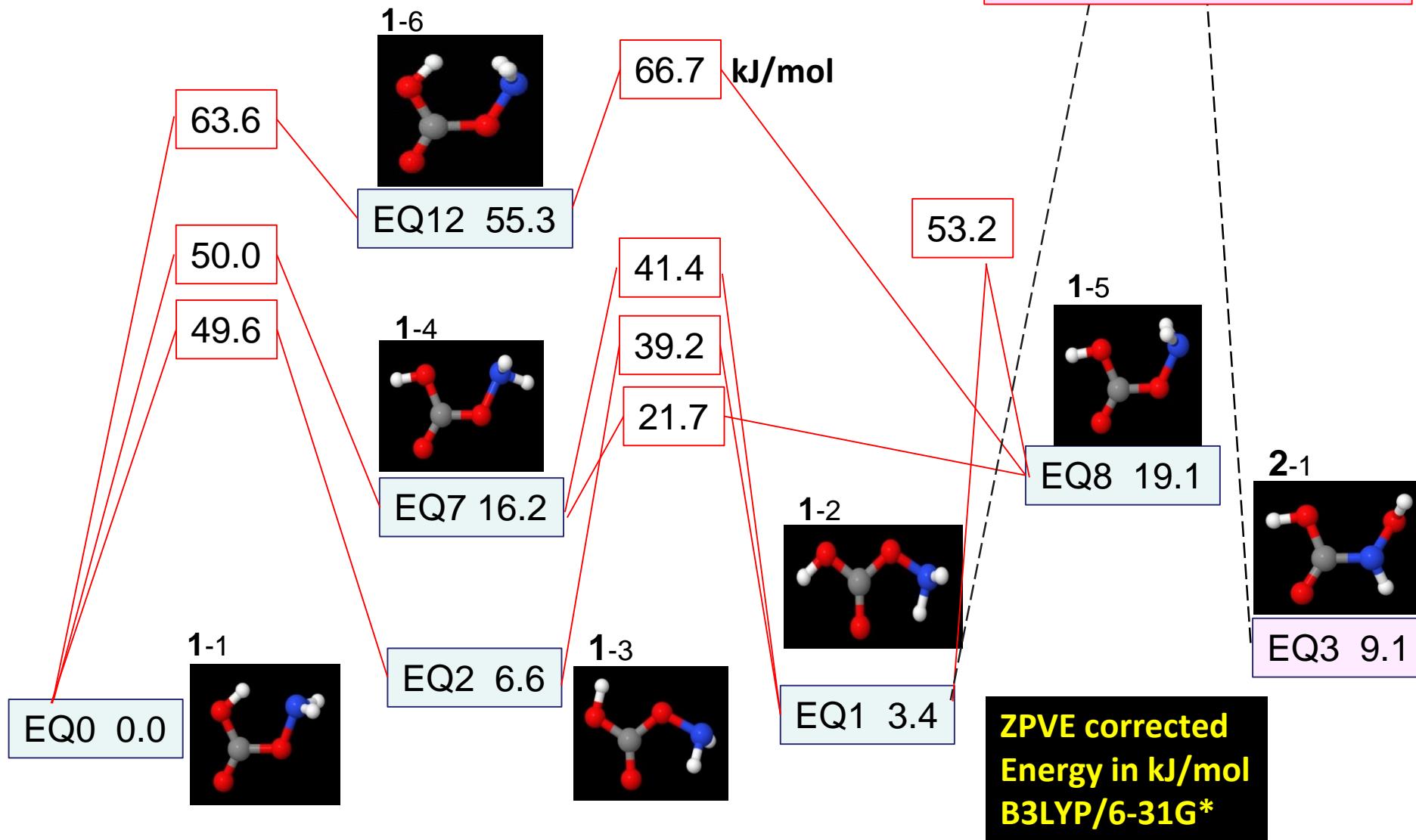
$$\Delta < 70 \text{ kJ/mol}$$

Between the **different** compounds

$$\Delta > 120 \text{ kJ/mol}$$

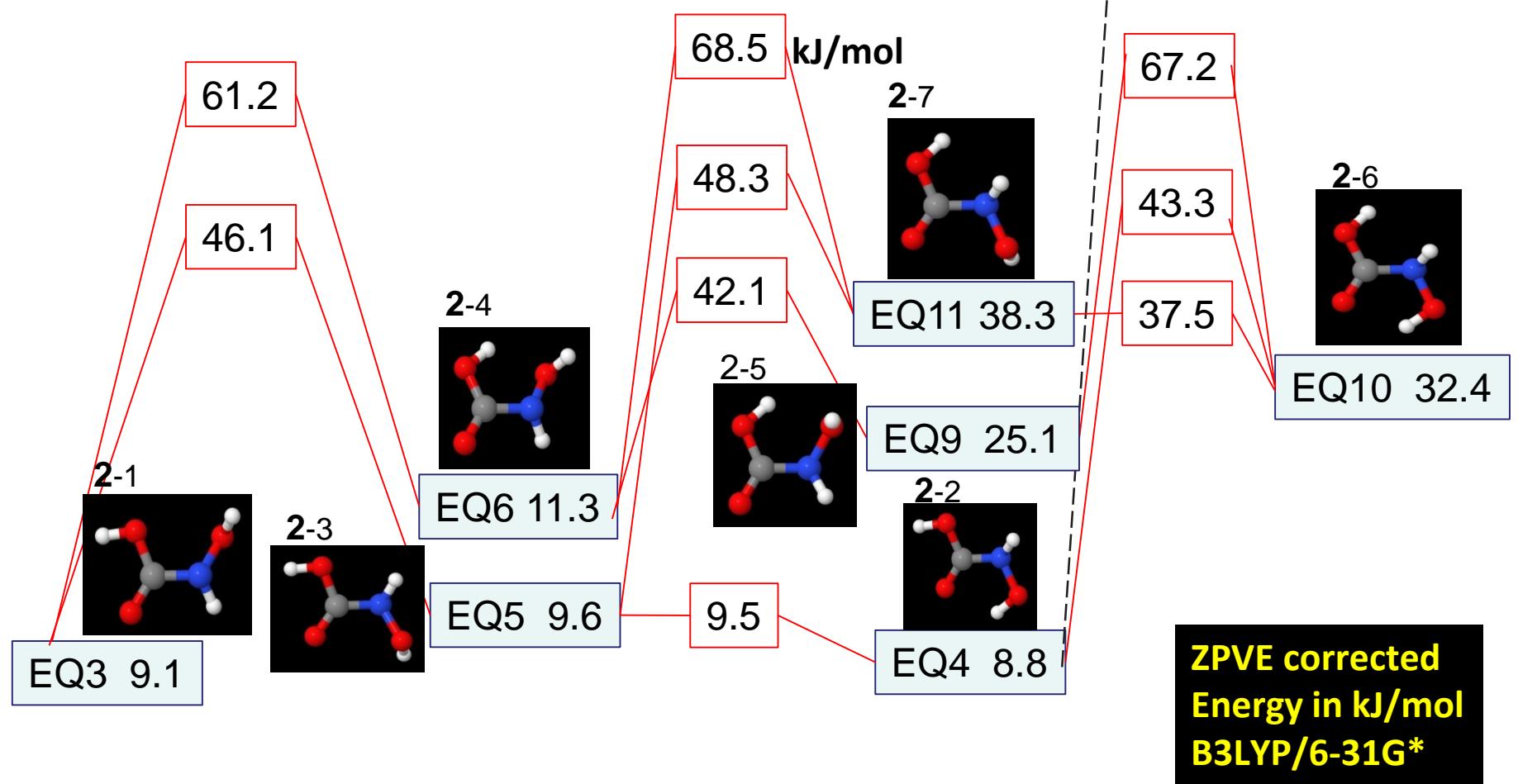
Energy Diagram around compound 1 of H₃CNO₃

Coformation changes of Aminoxy formic acid (1-n)



Energy Diagram around compound 2 of H₃CNO₃

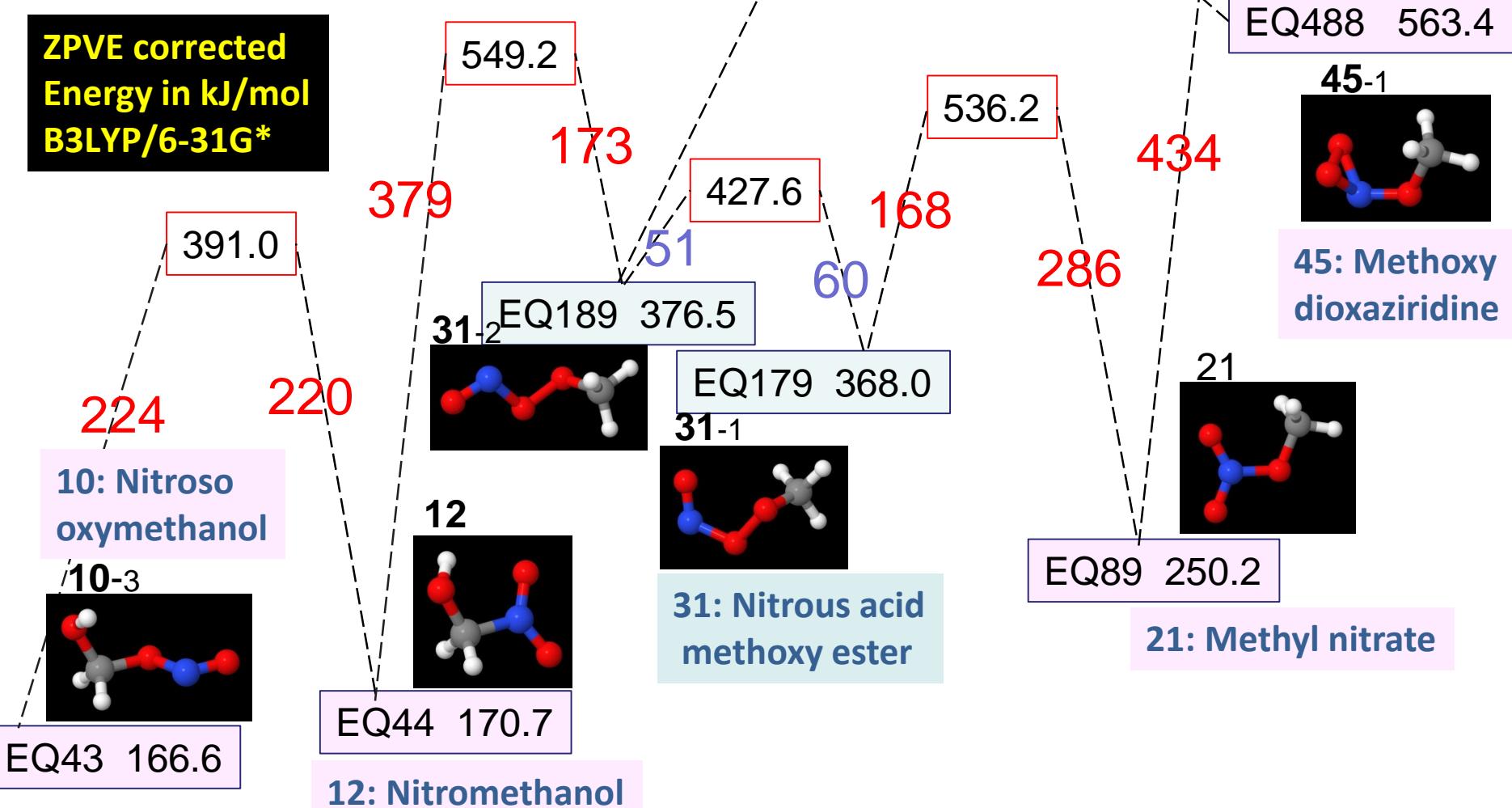
Conformation changes for Hydroxy carbamic acid (2-n)



Energy Diagram between 10, 12, 21, 31, & 45 of H₃CNO₃

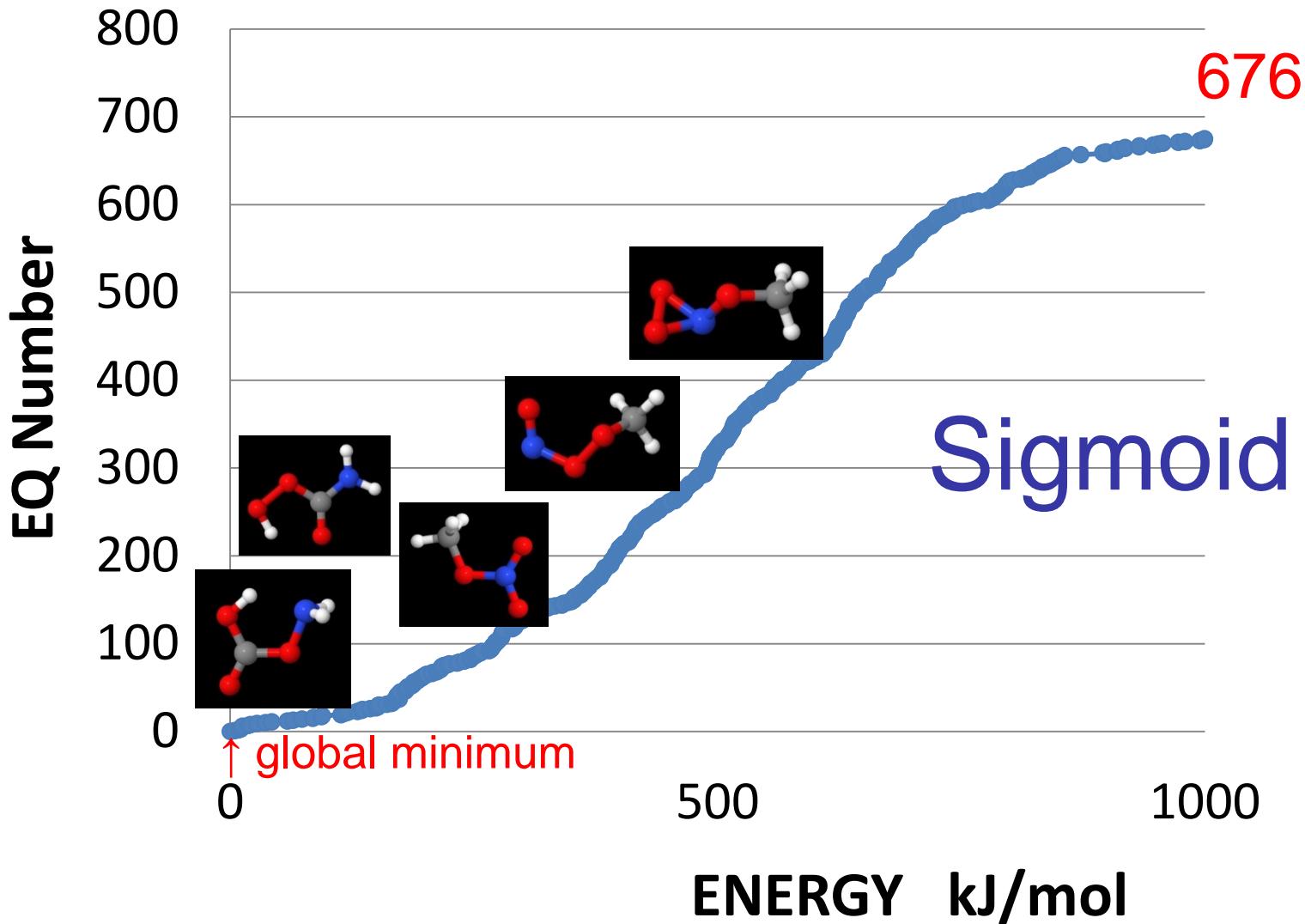
Different compounds are well separated from others via high barriers

ZPVE corrected
Energy in kJ/mol
B3LYP/6-31G*



Energy Distribution of EQs

H_3CNO_3 (B3LYP/6-31G*)



GRRM elucidated
stereo reaction mechanisms,
which have been eluded
experimental observation!

Stereo Reaction Mechanisms (1)

Stereo Reaction Mechanisms (2)

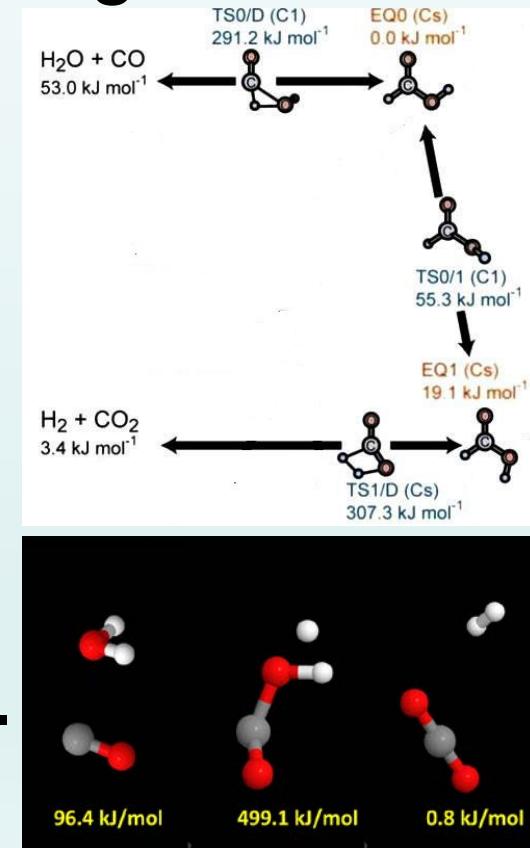
Water-Gas-Shift Reaction



is a well-known process producing H₂ from H₂O.

This reaction has long been understood as ***three-step*** processes via HCOOH,

but **GRRM/ADDF** has shown that it can be a ***single*** process.

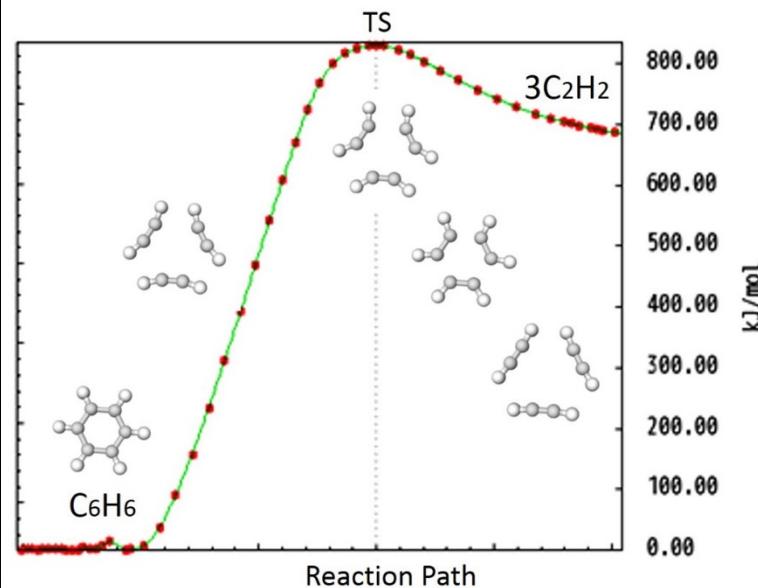
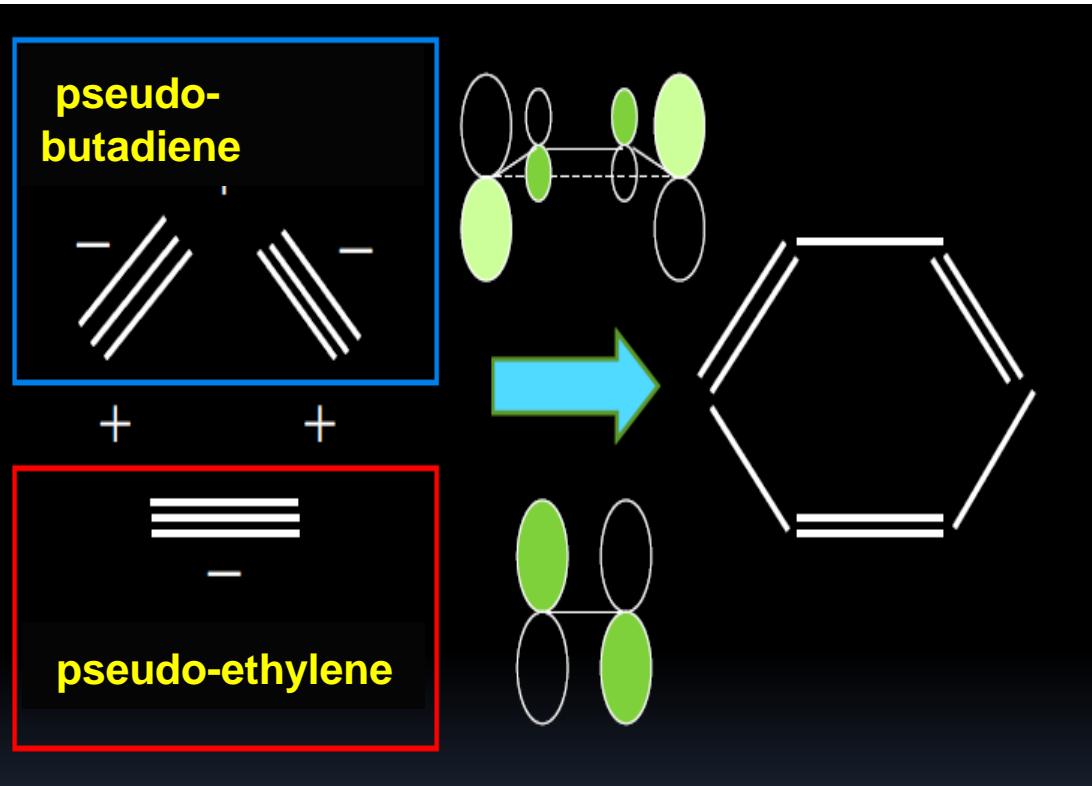


Reppe Reaction producing Benzene from acetylene

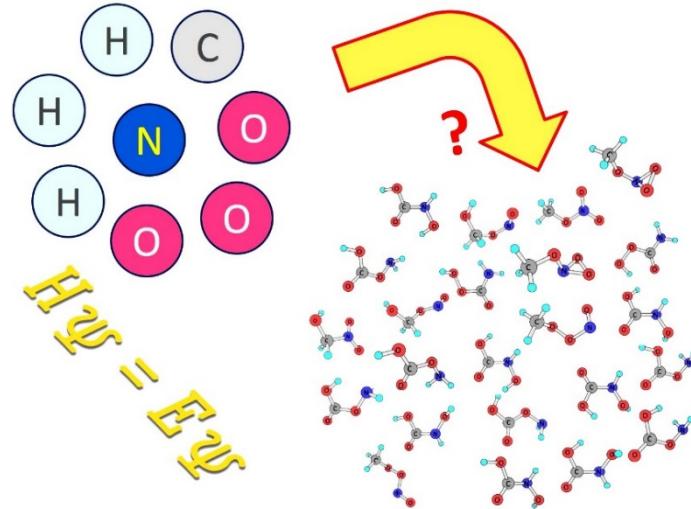


GRRM/ADDF has shown that it can proceed as **one-step** reaction ***without catalyst***!

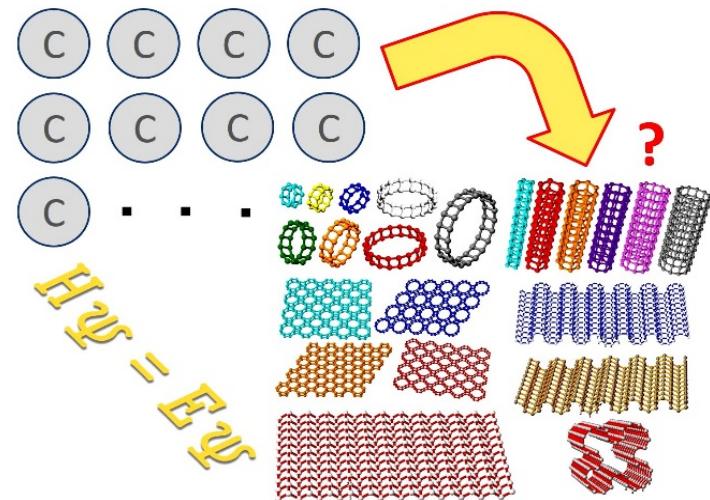
The mechanism is similar to the Diels-Alder reaction



1) Guided by ADDF,
GRRM opened
a new world of chemistry.



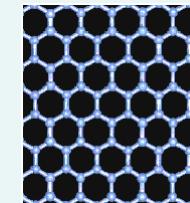
2) Aided by GRRM/ADDF,
exploration of new chemistry
may be made further on PES.



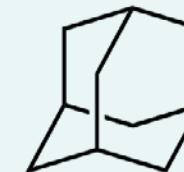
Next, we made exploration
of **new carbon allotropes**

Typical Carbons are composed of C6 or C5 rings

- Graphite & Graphene



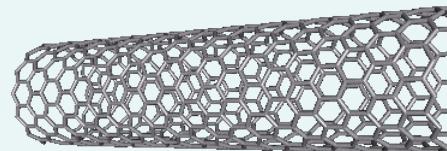
- Diamond



- Fullerene

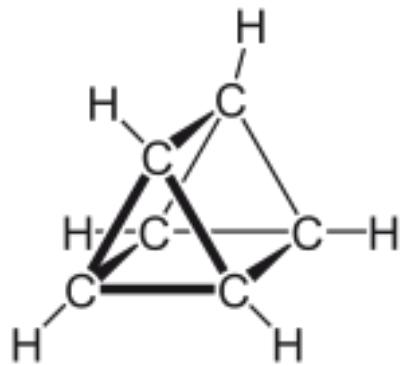


- Carbon Nano Tube

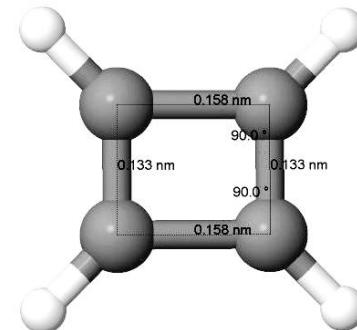


Some Hydrocarbons have C₄ rings

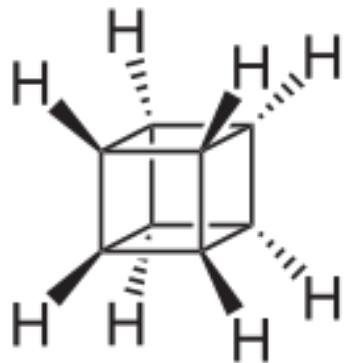
Prismane



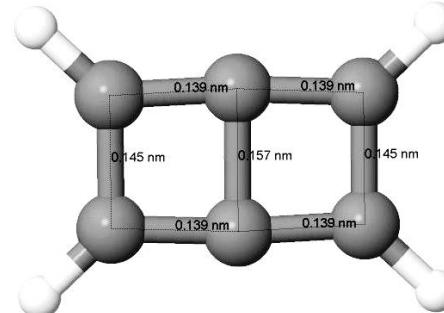
Cyclobutadiene



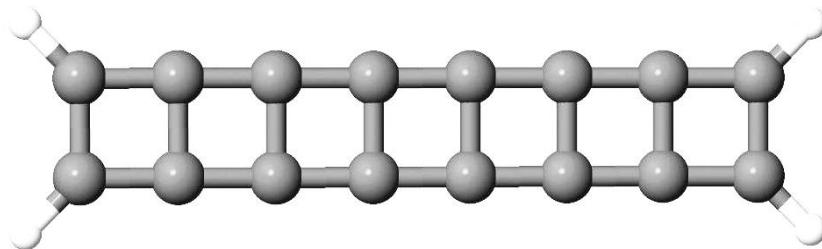
Cubane



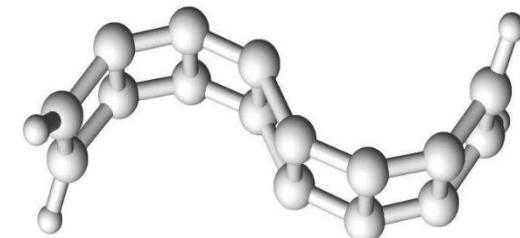
Butalene



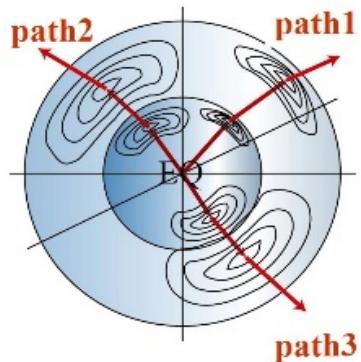
We challenged to produce straight planar ladder forms !



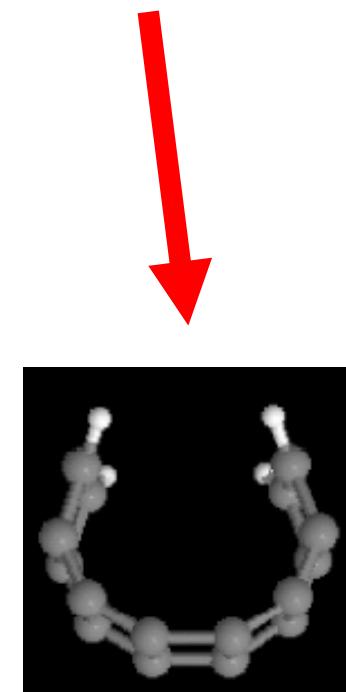
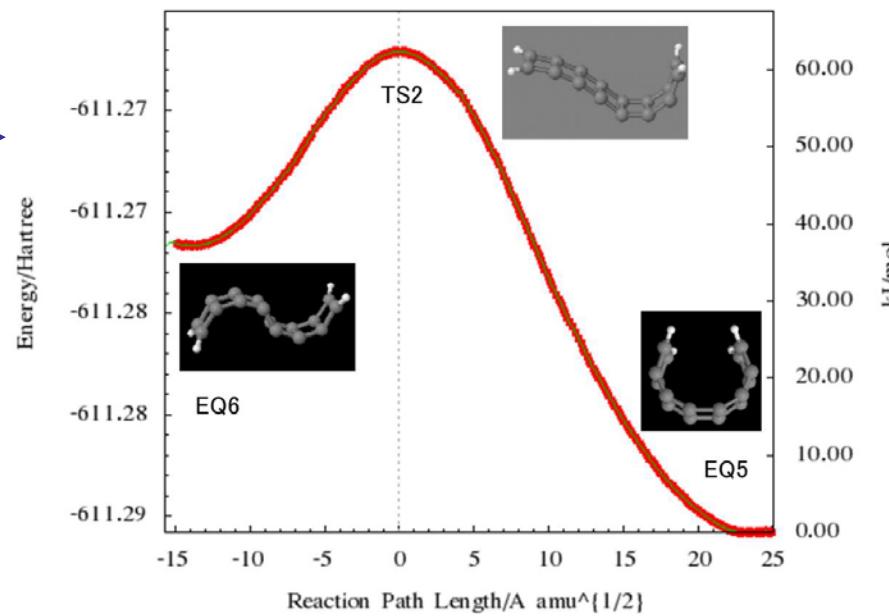
Geometry
Optimization

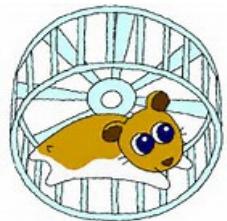


GRRM/ADDF
search



Energy Profile
EQ6 – TS2 – EQ5 H4C16 B3LYP/6-31G*

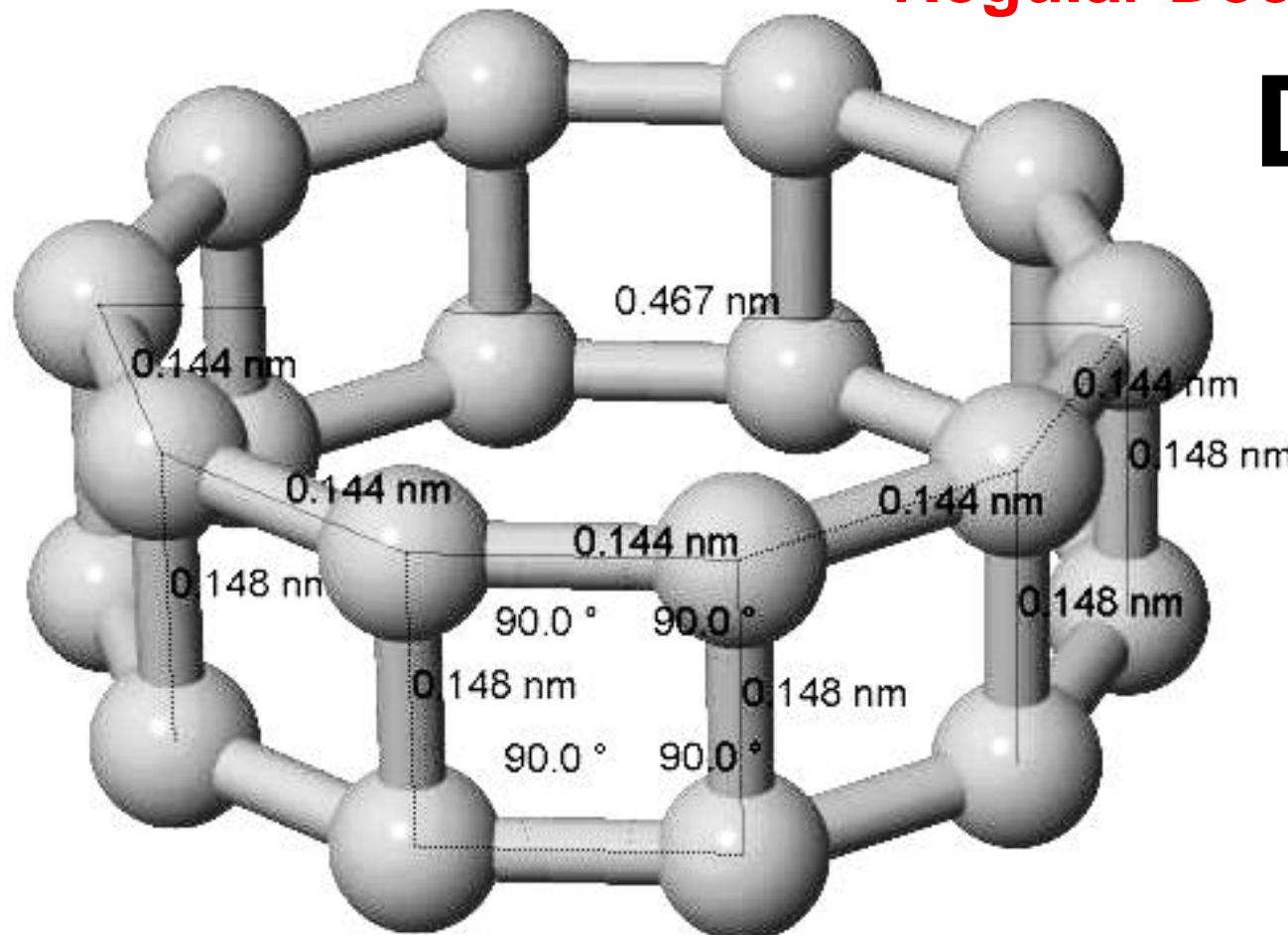




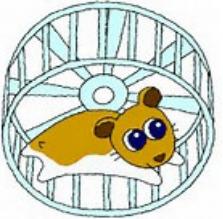
Prism-C₂₀

Regular Decagon Prism

D_{10h}



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



Prism-C₂₀

QTAIM electron density analysis

a) Critical points

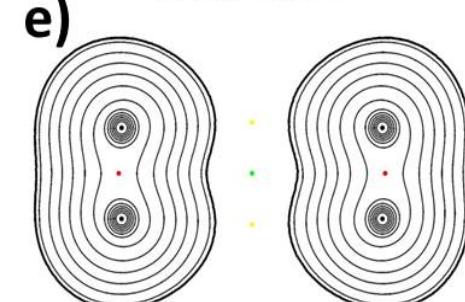
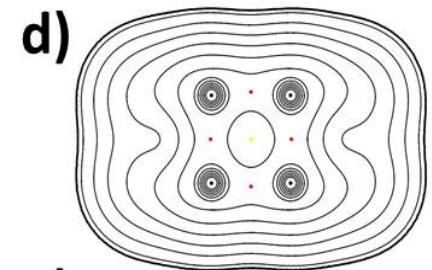
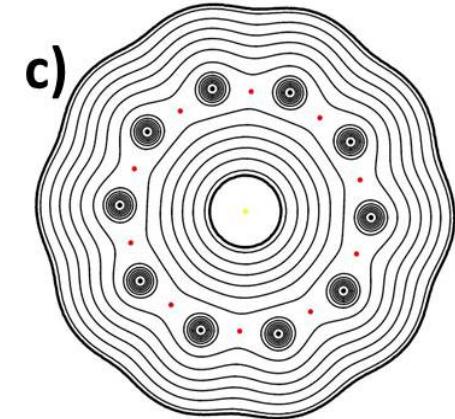
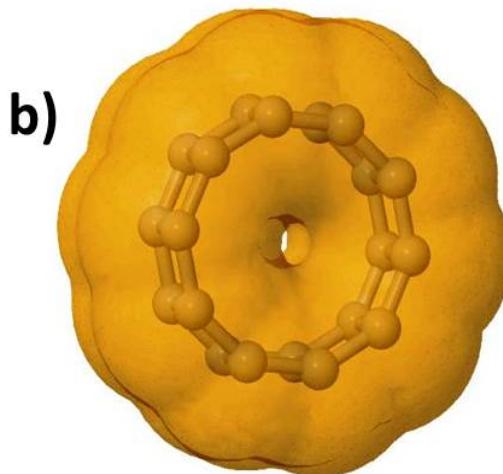
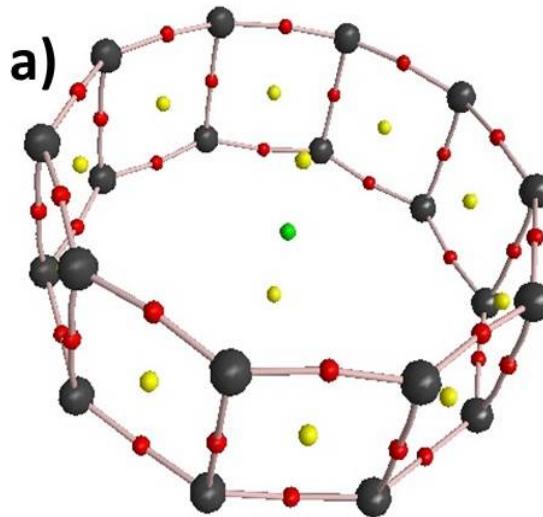
- **Bond Critical Point**
- Ring Critical Point
- Cage Critical Point

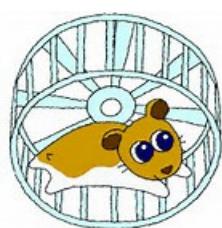
b) Van der Waals Surface

c) Density on the decagon face

d) Density on the square face

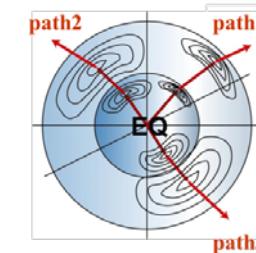
e) Density on the vertical cut





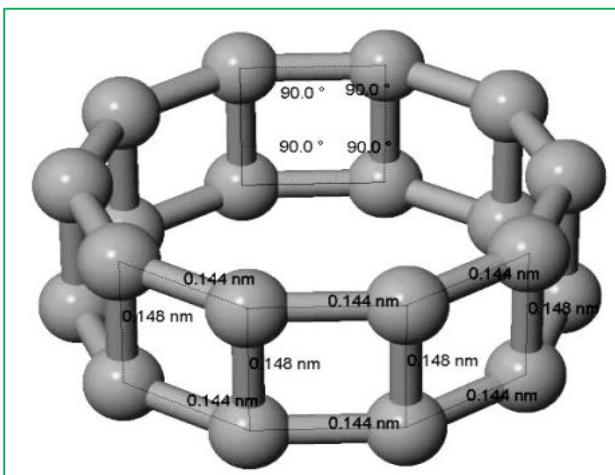
Stability of Prism-C₂₀

GRRM / FirstOnly Search

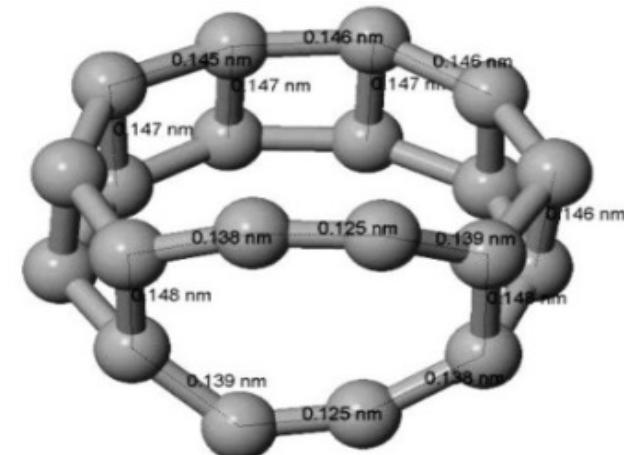


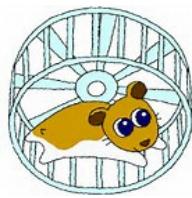
Lowest Barrier = **158.0 kJ/mol (ZPVE-corrected)**

at B3LYP/6-31G(d)



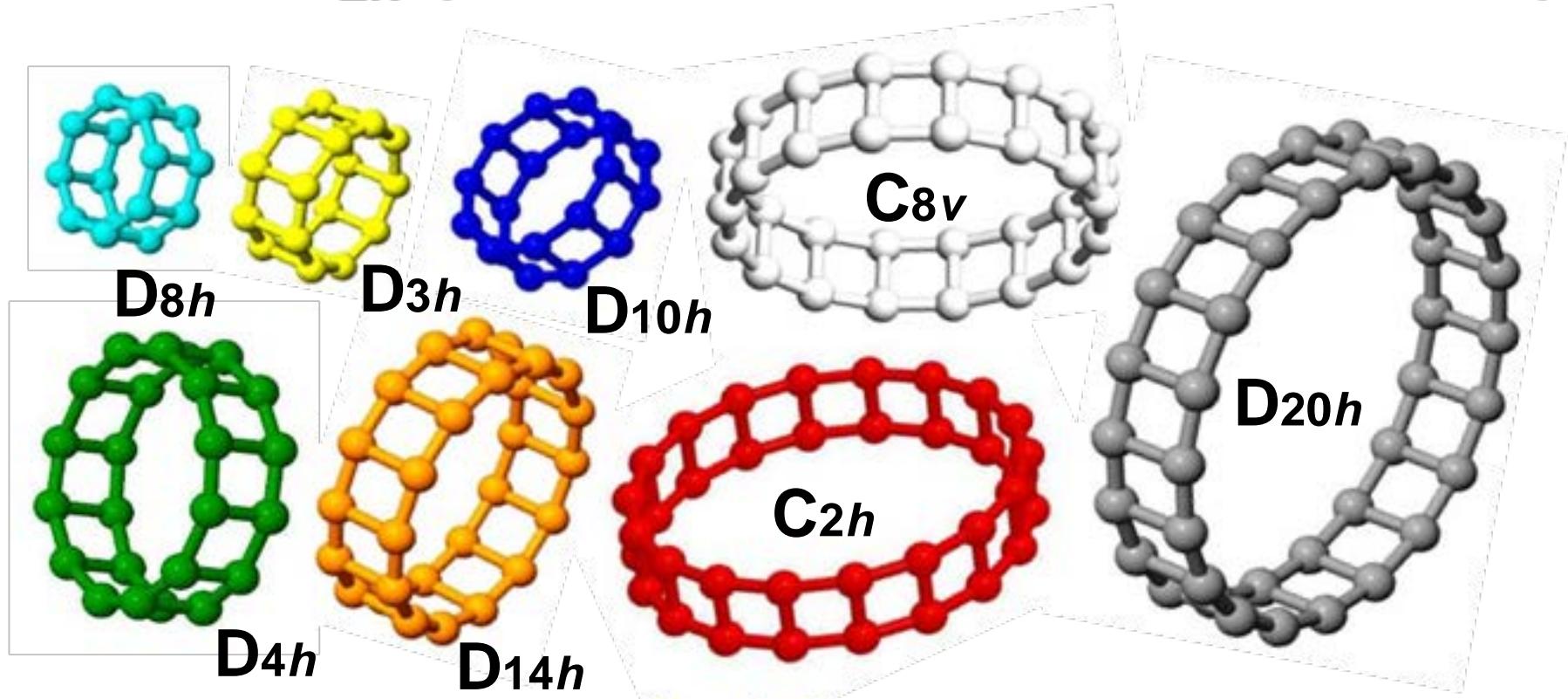
Stabilization Energy = 309.2 kJ/mol





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:

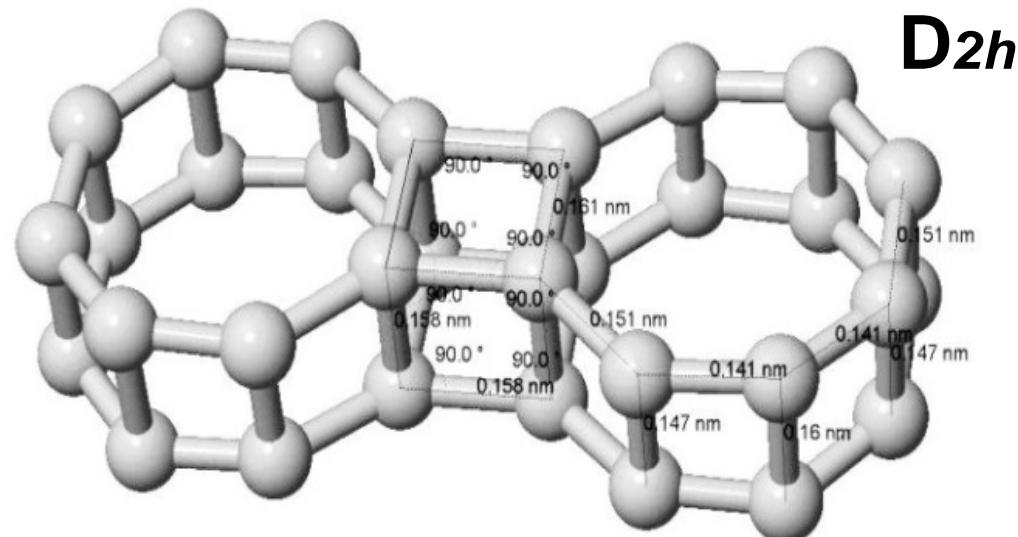
B3LYP/6-31G(d)

Confirmation:

B3LYP/6-311++G(2d,2p)

B3LYP/cc-pVDZ

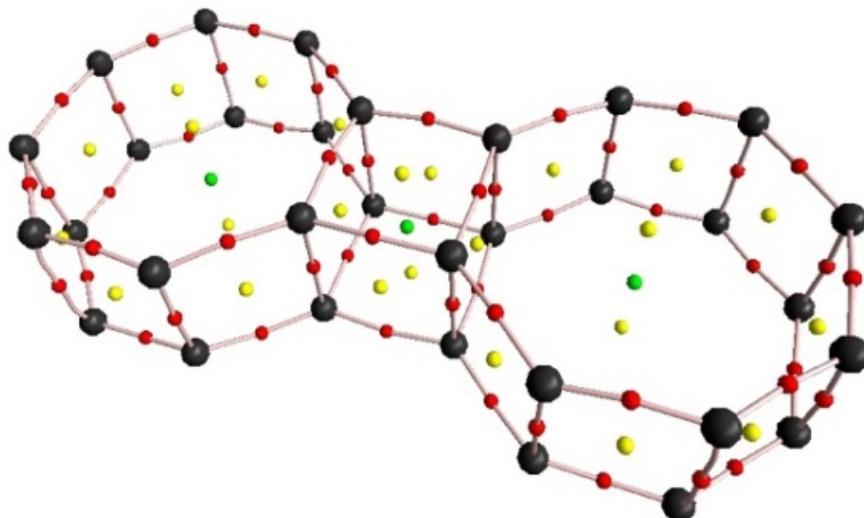
B3LYP/cc-pVTZ



QTAIM

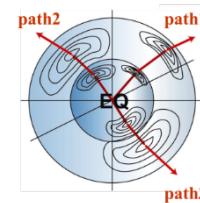
Electron Density Analysis

- Bond Critical Point
- Ring Critical Point
- Cage Critical Point



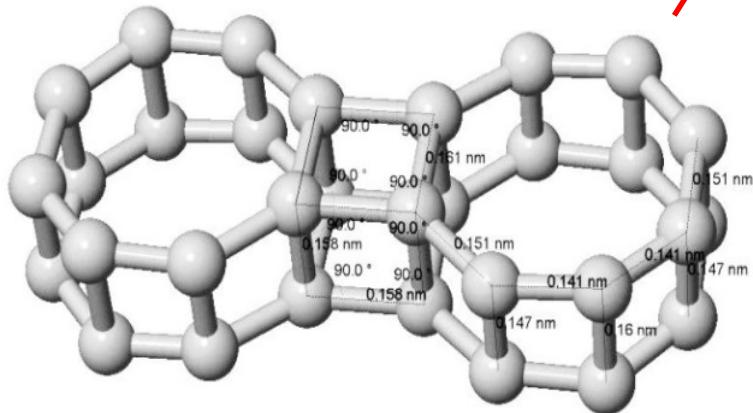
Stability Analysis

GRRM/ADDF FirstOnly Search



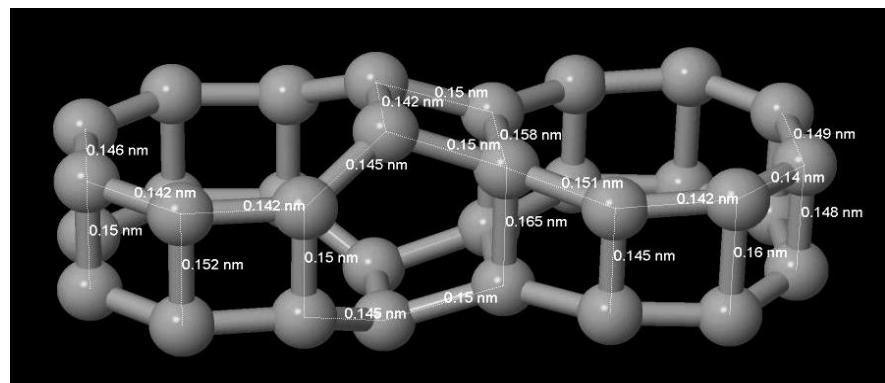
Lowest Barrier = 34.3 kJ/mol (B3LYP/6-31G(d))

33.4 kJ/mol (B3LYP/cc-pVDZ)
ZPVE-corrected



Stabilization Energy

= 632.5 kJ/mol (B3LYP/6-31G(d))
625.8 kJ/mol (B3LYP/cc-pVDZ)



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

Exploration:

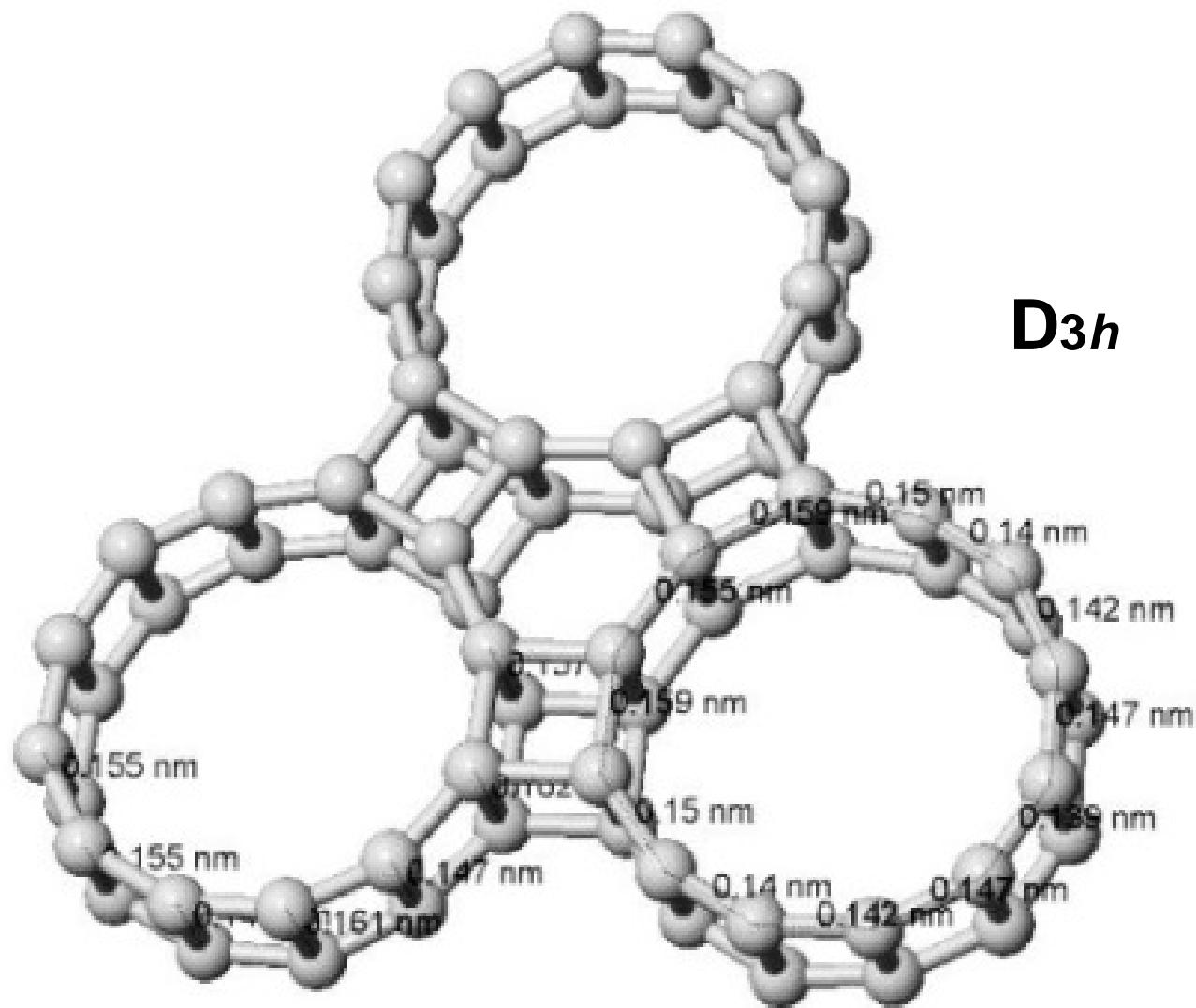
B3LYP/6-31G(d)

Confirmation:

B3LYP/cc-pVDZ

RHF/STO-3G

RHF/3-21G

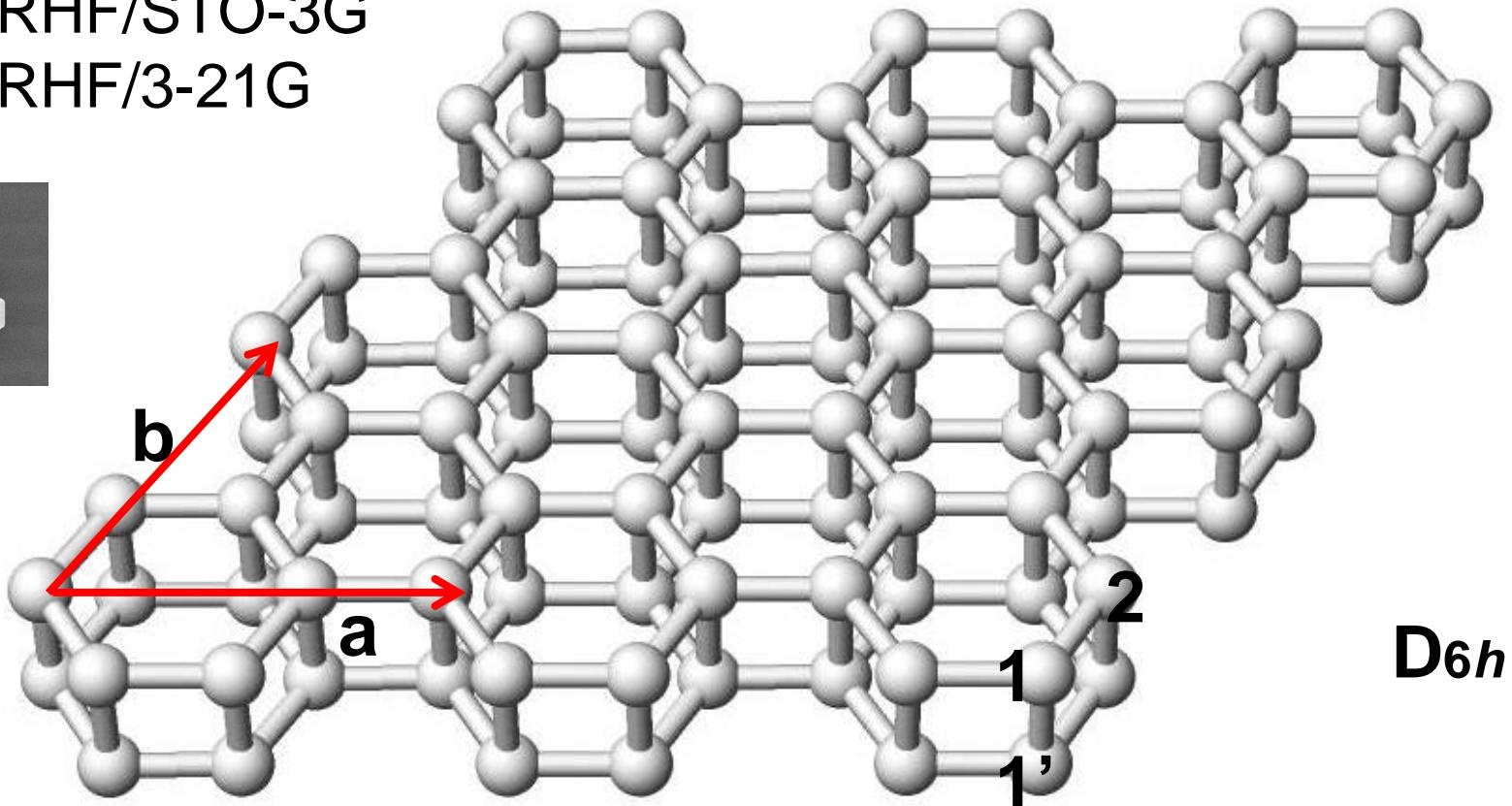
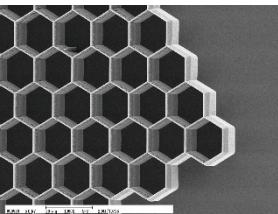


Prism Carbon Sheet

Periodic Boundary Condition Calculation (g09)

RHF/STO-3G

RHF/3-21G



All Prisms are purely hexagonal.

*All C-atoms are equivalent
and connected with 4-atoms*



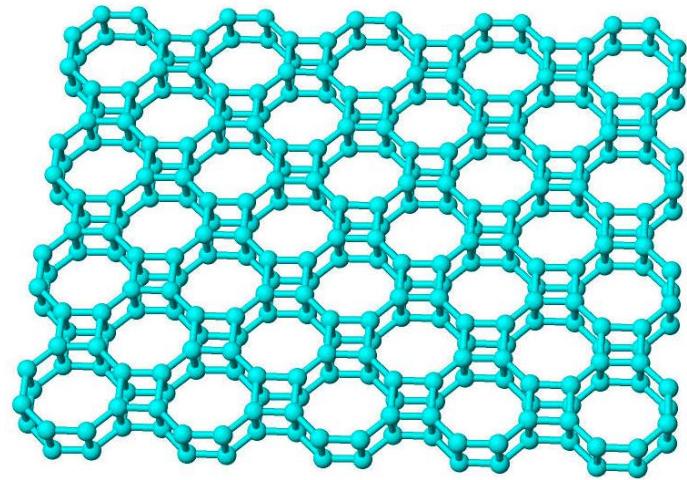
1-2: 0.1566 nm

1-1': 0.1562 nm

Prism- C_{2n} Sheets

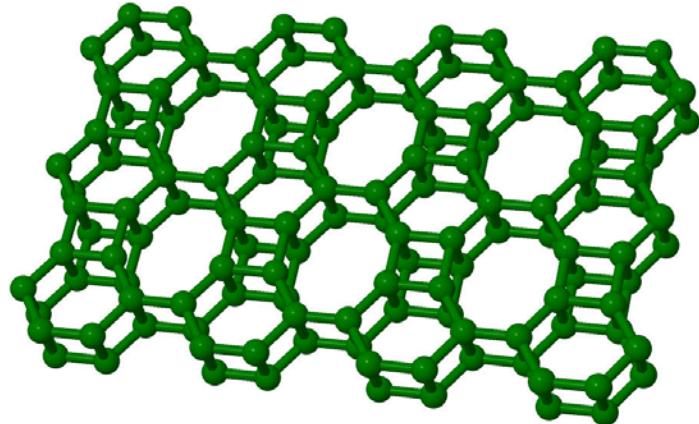
$n=8$

D_{4h}



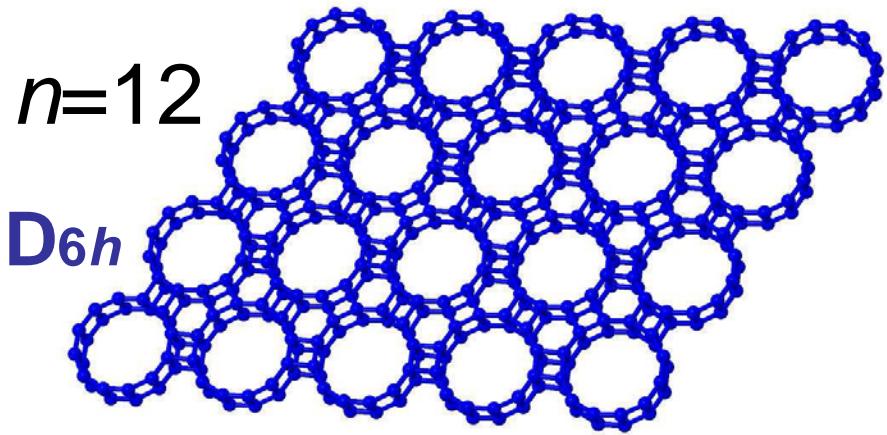
$n=6$

D_{2h}



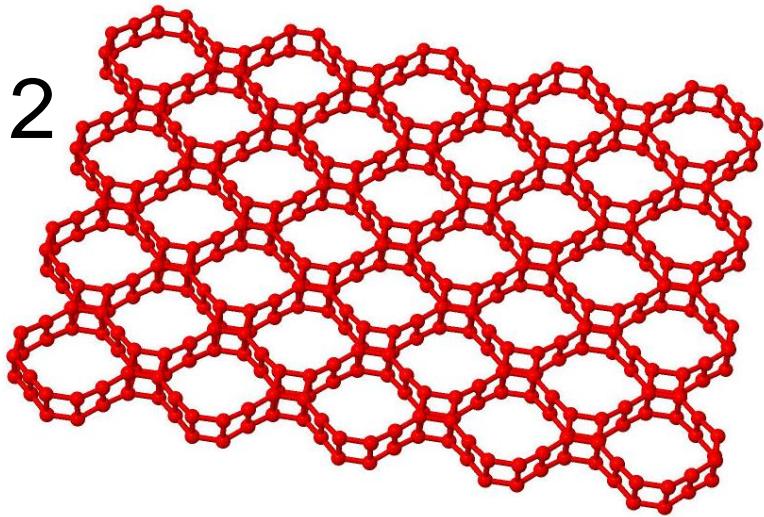
$n=12$

D_{6h}



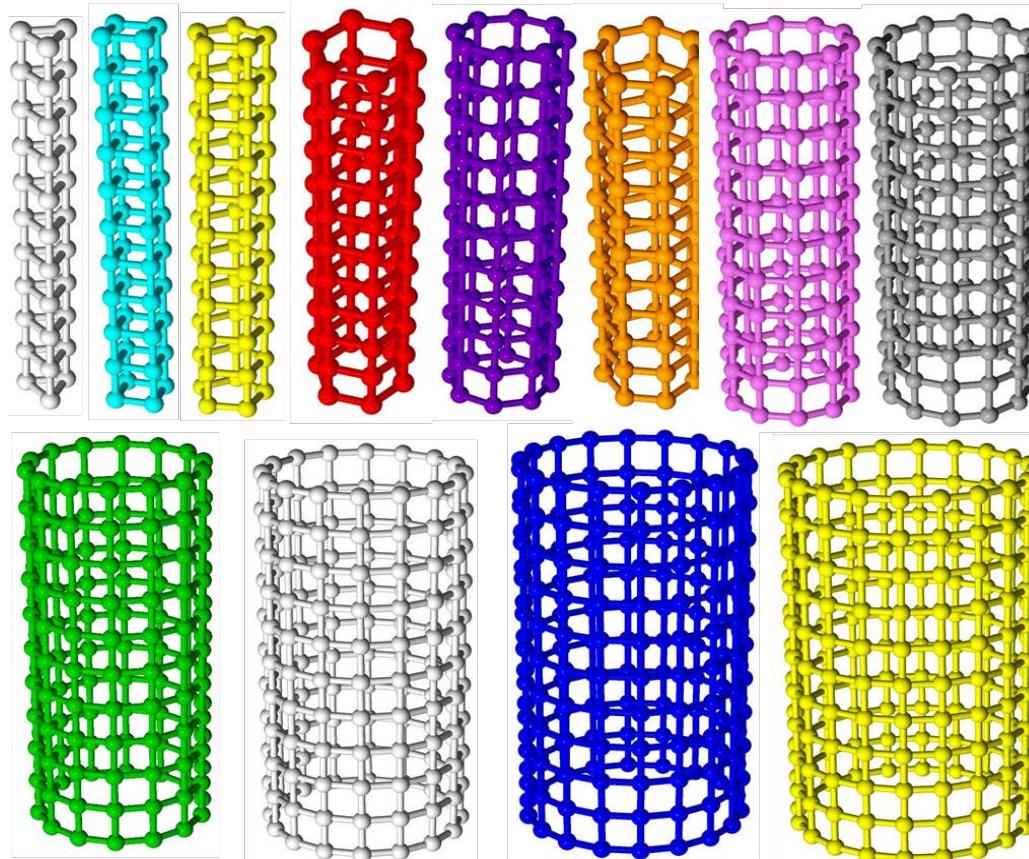
$n=12$

D_{4h}



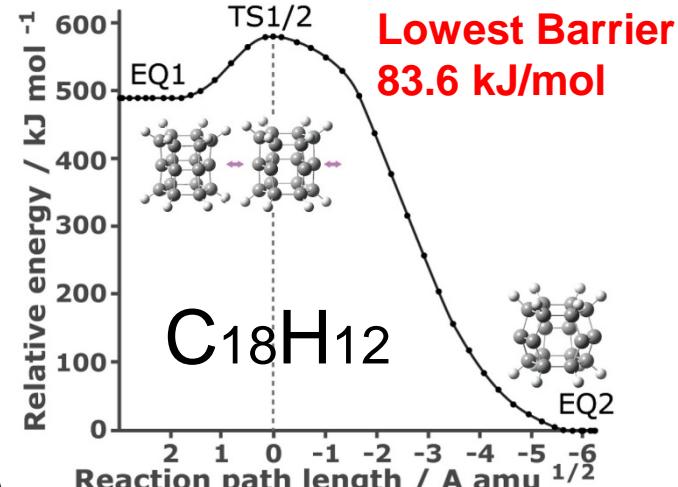
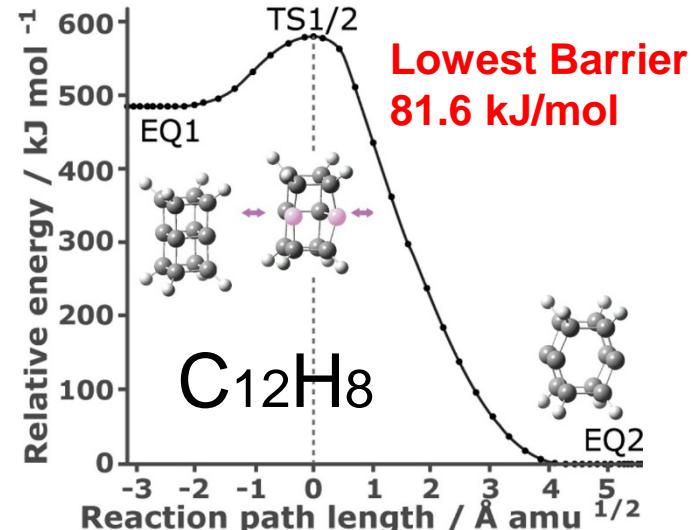
Vertical polymerization of the prism-unit axially

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

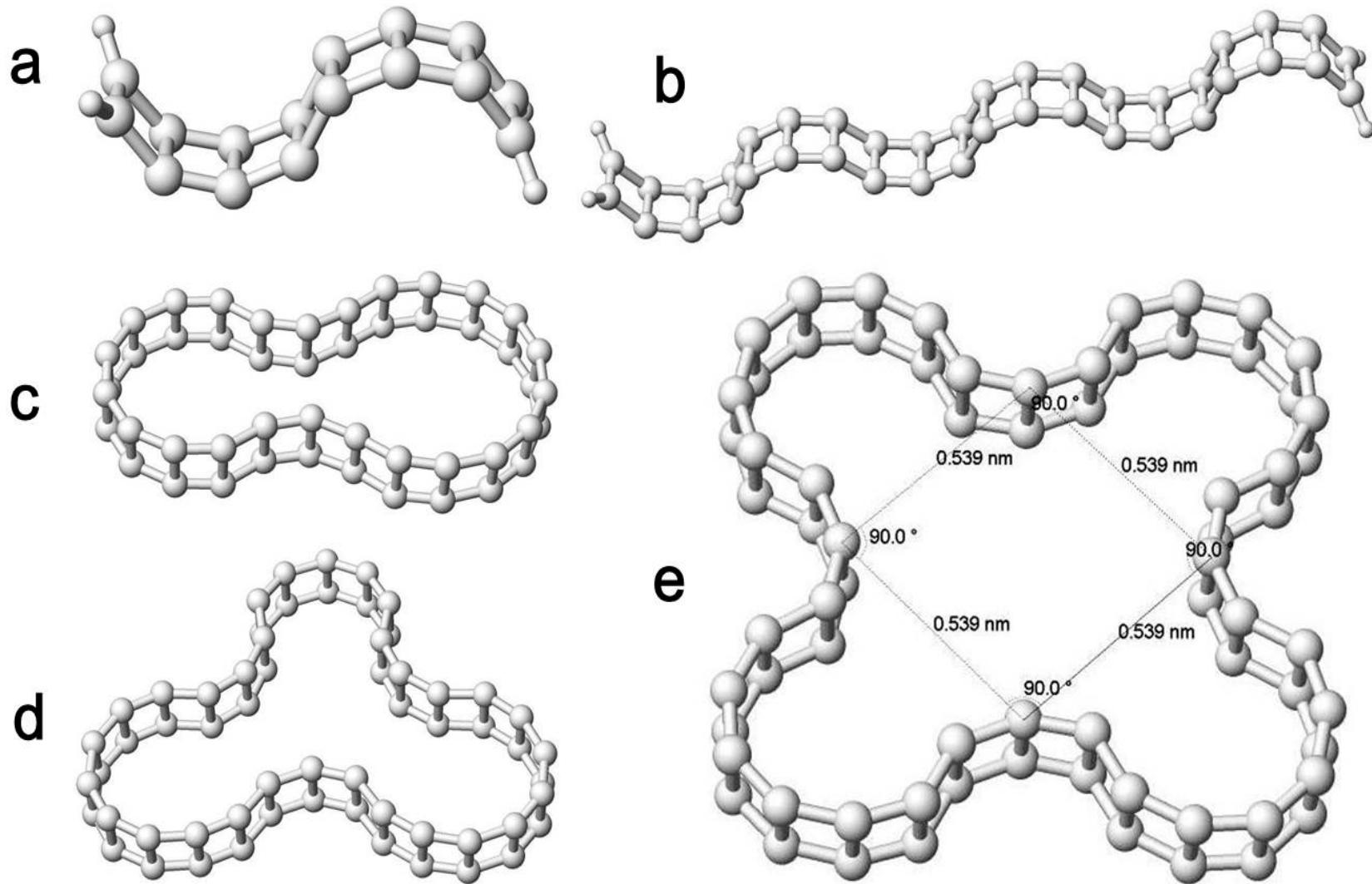


Polygon CC: 0.153 - 0.160 nm
Vertical CC: 0.160 - 0.161 nm

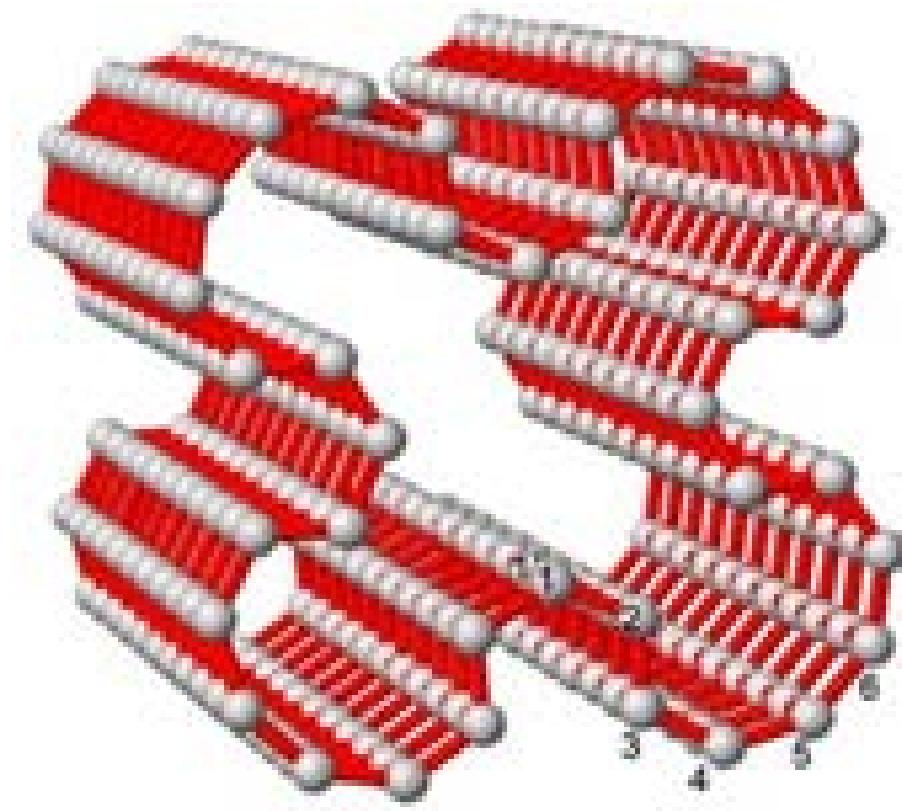
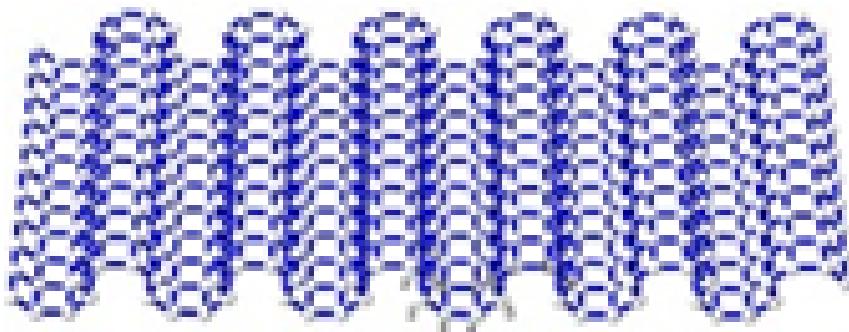
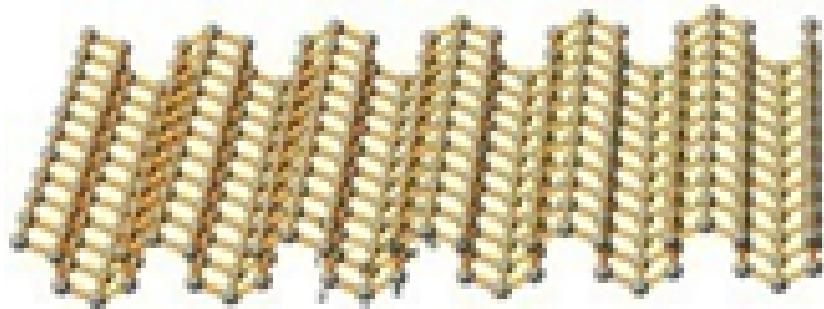
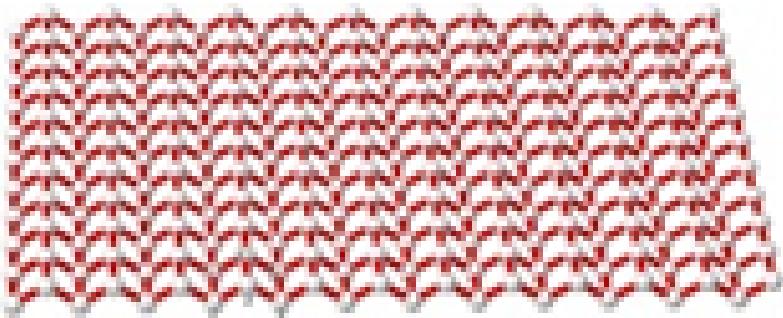
Stability Check by GRRM/ADDF



Exploration of Wavy Carbons

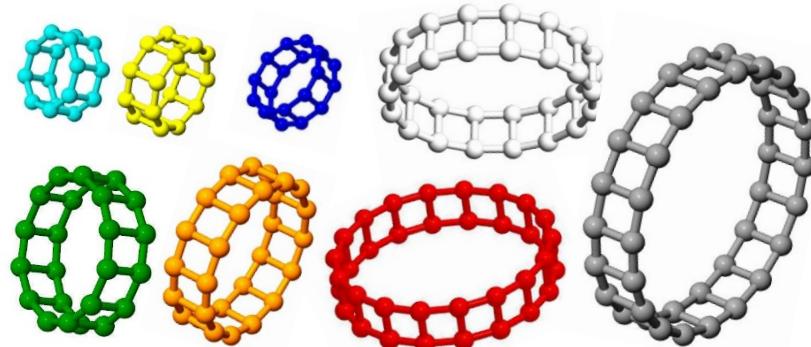


Wavy Carbon Sheet & Tube



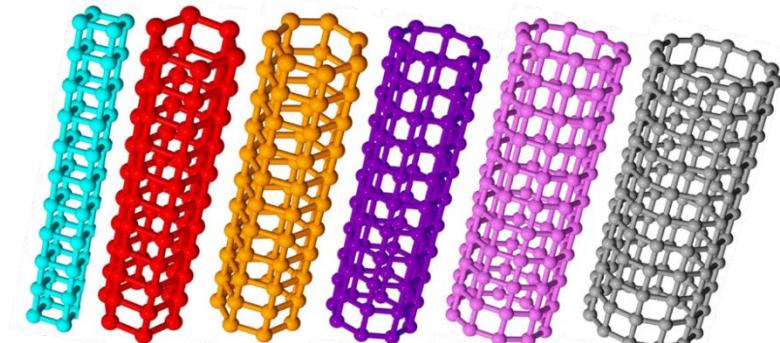
New Carbon Allotropes explored on Quantum Chemical PES

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



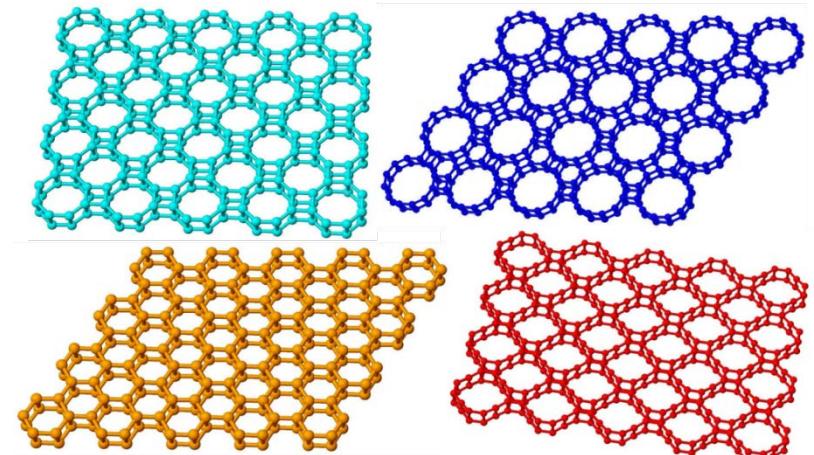
Chem. Lett. 44, 712 (2015).

Prism-Carbon Tube



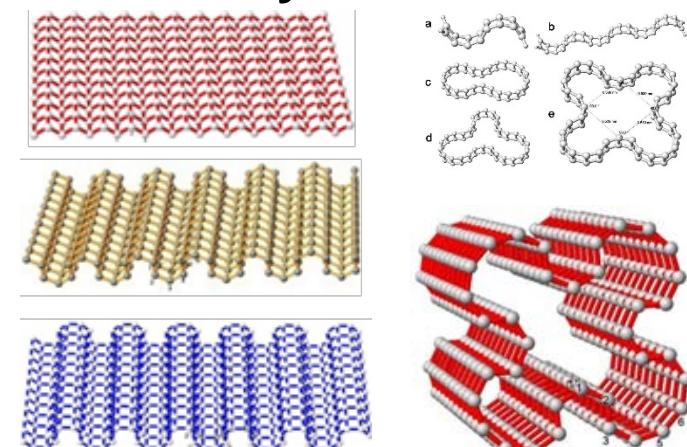
Chem. Phys. Lett. 635, 180 (2015).

Prism-Carbon Sheet



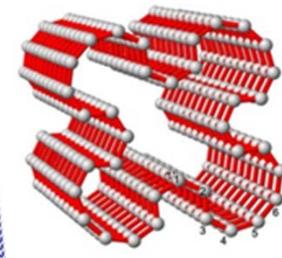
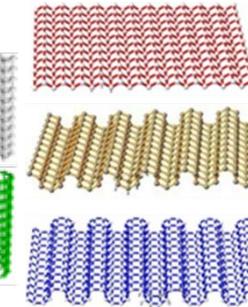
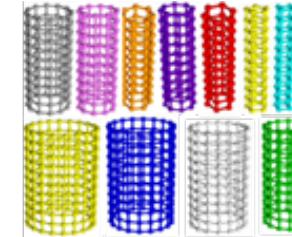
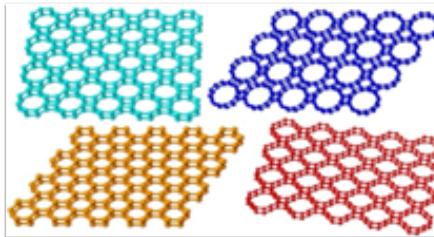
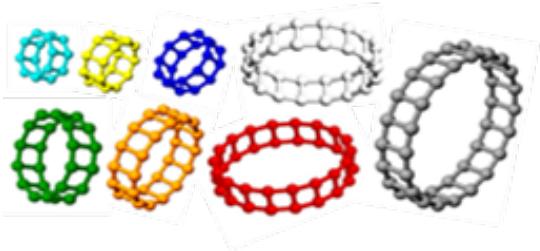
Chem. Phys. Lett. 633, 120 (2015).

Wavy Carbons



Chem. Phys. Lett. 639, 178 (2015).

Important : High Energy Carbons

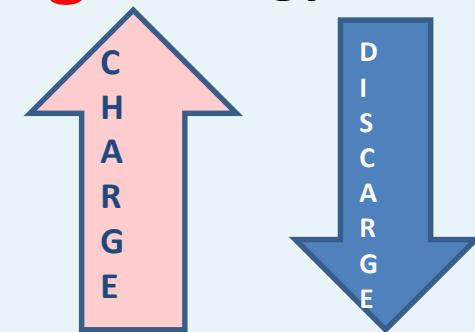


Containing Excess Chemical Energy
of **130-350 kJ/mol** per one C-Atom.

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

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

High energy Carbon



Low energy Carbon

Zero Consumption
Zero Emission
Usable anywhere
at anytime

Summary

- Although only limited results 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 (*GRRM14*, *GRRM17*) are distributed, available at
http://iqce.jp/GRRM/index_e.shtml

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)



Application of GRRM:

X. Yang

B. Hajgato

Y. Luo

Y. Watanabe

M. Moteki

T. Iwamoto

H. Satoh

H. Isobe

S. Ohno

K. Shudo

Y. Matsuda

N. Kishimoto

H. Yamakado

H. Tokoyama

Y. Kodaya

H. Watanabe

A View from a Saddle Point



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

