台灣大學開放式課程

有機化學乙

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Chapter 4
Alkanes and Cycloalkanes

烷類與環烷類化合物

亦通稱為碳氫化合物(hydrocarbons)

Alkanes: saturated (飽合的), containing only C-C single bonds
Cycloalkanes: cyclic (環狀的)

※ Source (來源)

Petroleum —fractional distillation (分餾)→ C_1-C_4 (<20 °C) natural gas

(refining;精製)

C_5-C_6 (20-60 °C) pet. ether 石油醚

C_6-C_7 (60-100 °C) ligroin (pet. ether)

catalytic cracking
thermal cracking

→ C_5-C_{10} (40-200 °C) gasoline

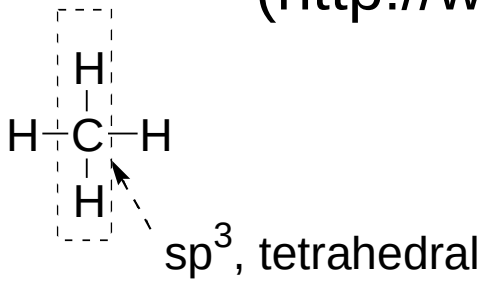
C_{12}-C_{18} (175-325 °C) kerosene

C_{12}-- (250-400 °C) diesel oil

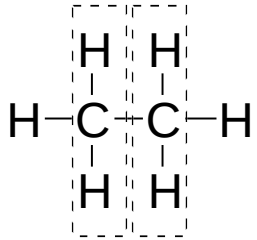
- lubricating oil..
- wax……

※ IUPAC systematic nomenclature
命名

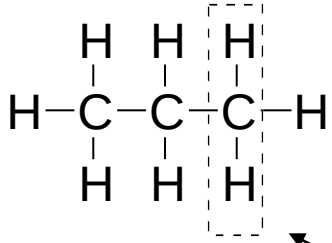
IUPAC: International Union of Pure and Applied Chemistry
(http://www.acdlabs.com/iupac/nomenclature/)



Methane (CH_4)



Ethane (C_2H_6)

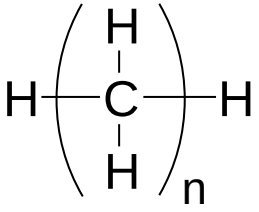


Propane (C_3H_8)

A methylene unit

C_4H_{10} Butane
C_5H_{12} Pentane
C_6H_{14} Hexane
C_7H_{16} Heptane
C_8H_{18} Octane
C_9H_{20} Nonane
$C_{10}H_{22}$ Decane
$C_{11}H_{24}$ Undecane
$C_{12}H_{26}$ Dodecane

$C_{20}H_{42}$ Eicosane

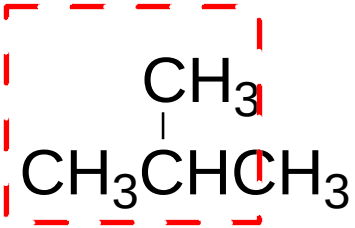


$\equiv$ C_nH_{2n+2}

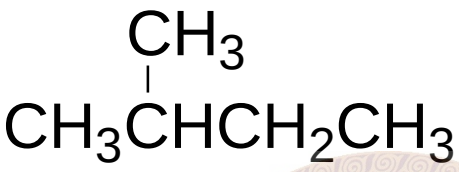
Class name: Alkane

A homologous series:
each differs by a const. unit,
i.e., the methylene unit

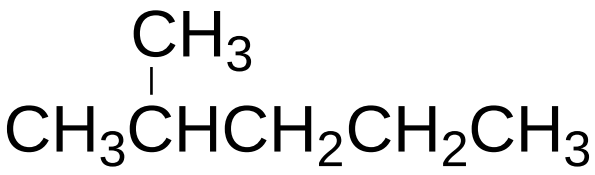
※ Structural isomers and common names (俗名)



isobutane

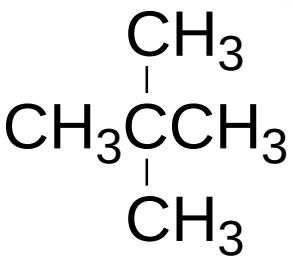


isopentane

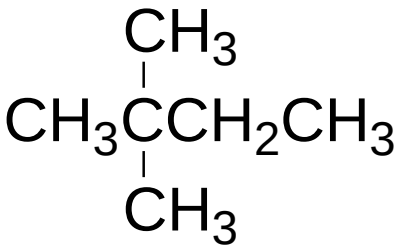


isohexane

homologs



neopentane



neohexane

※ Substituent (取代基)

例: $CH_3CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_2CH_3$ pentane

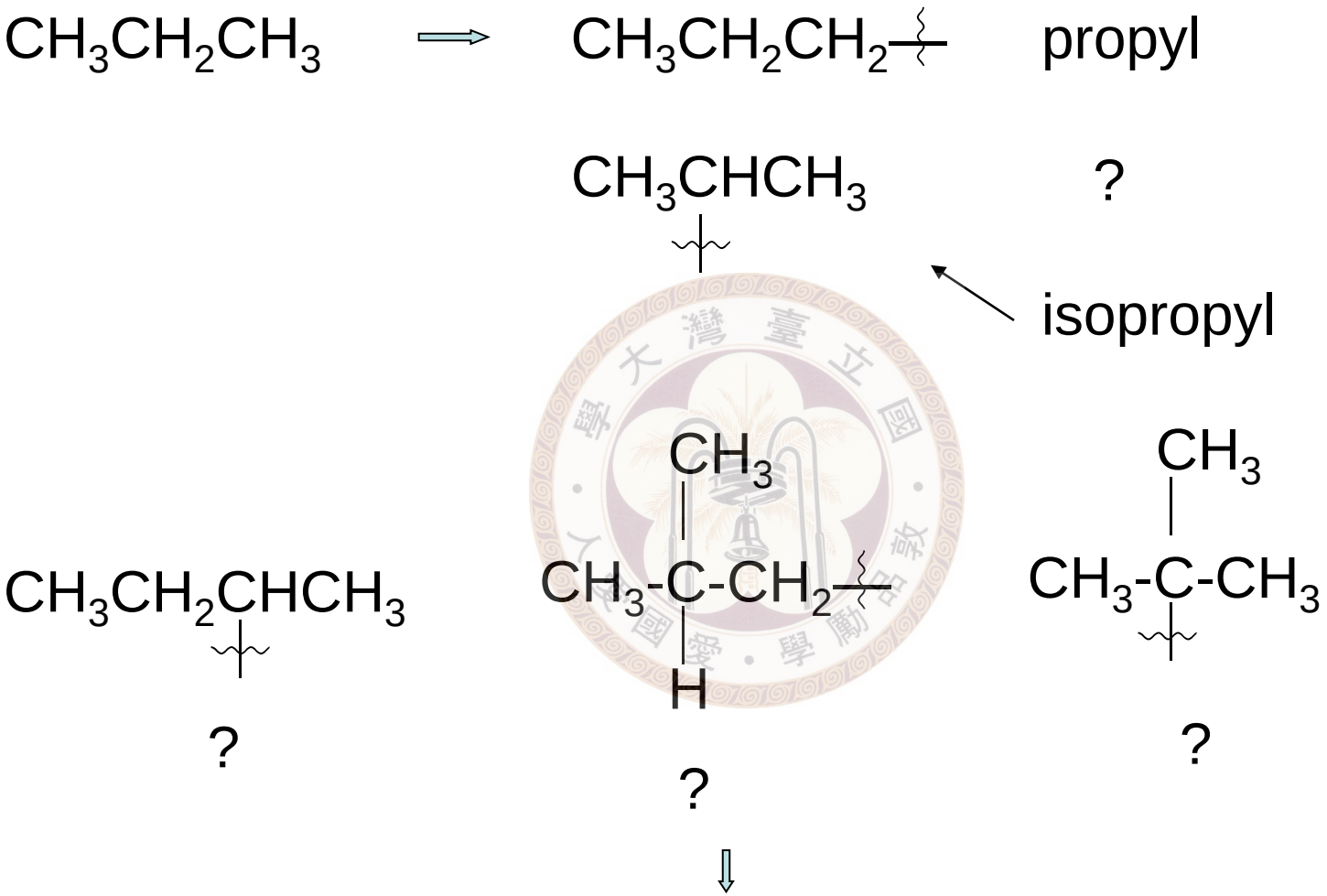
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$ ← a substituent

命名

H_3C-	methyl (ane → yl)	= Me-	(H_3C—)
CH_3CH_2-	ethyl	Et-	
	propyl	Pr-	
	butyl	Bu-	
	⋮	⋮	
	alkyl	R-	(RH代表烷類)

R- ← 一律大寫

Problems:

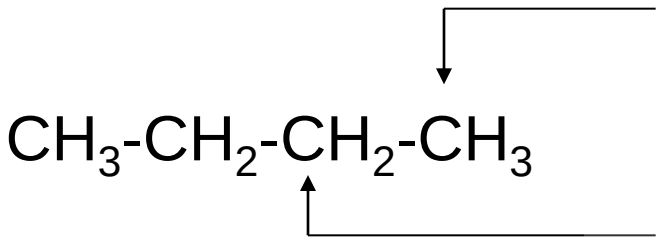


Isobutyl

(a homolog of isopropyl)

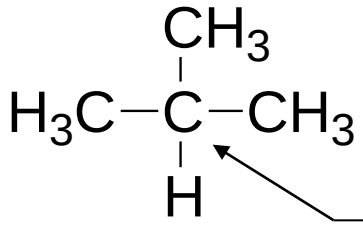
※ Classification of carbon

碳的分級

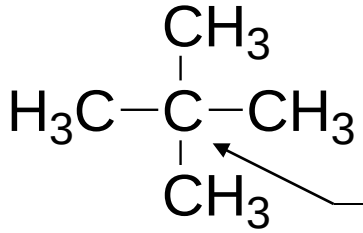


A primary (1°) carbon:
with one C-C bond attached

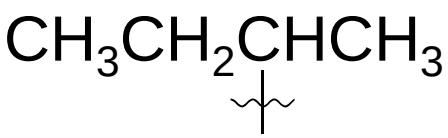
A secondary (2°) carbon:
with two C-C bonds attached



A tertiary (3°) carbon:
with three C-C bonds attached

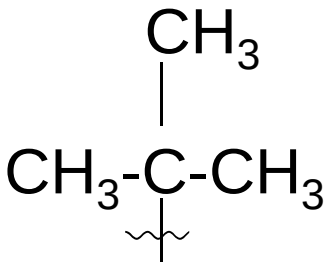


A quaternary (4°) carbon:
with four C-C bonds attached

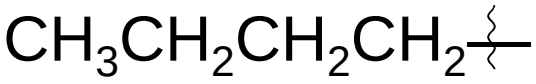


secondary-butyl or *sec*-butyl or *s*-butyl

斜體字



tertiary-butyl or *tert*-butyl or *t*-butyl



normal-butyl or *n*-butyl

可省略

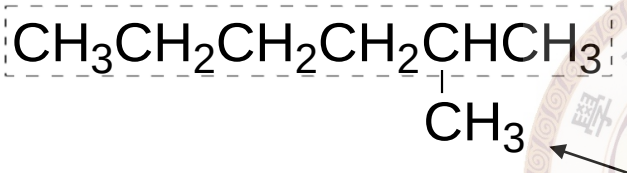
Structural classification of alkanes:

- Straight chain alkanes
- Branched chain alkanes

※ Nomenclature for branched chain alaknes

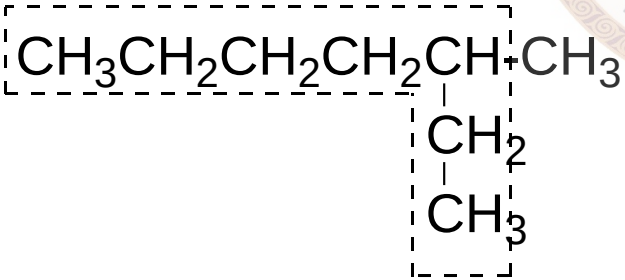
IUPAC rules:

- Name after the longest chain



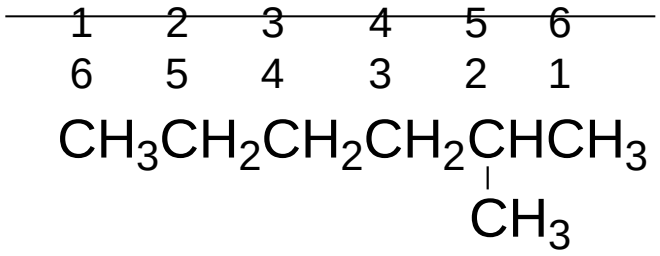
parent name

hexane with a methyl substituent



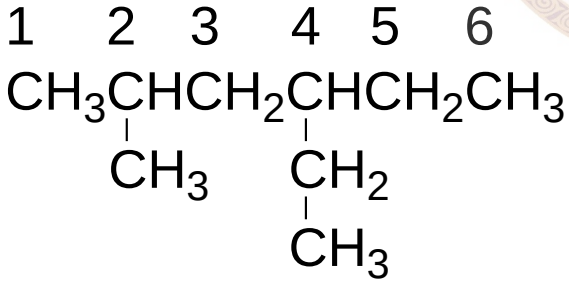
heptane with a methyl subst.

- Numbering from the end nearer the substituent



- 2-Methylhexane
  ↑
  designate the location of subst.

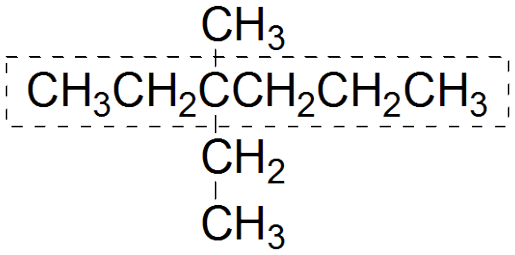
- Arrange substituents in alphabetical order



(lowest number for the first point of difference)

4-ethyl-2-methylhexane
↑ ↑

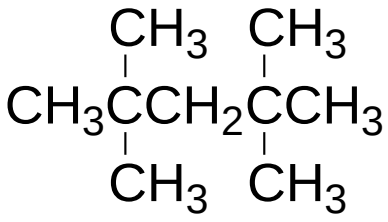
- Substituents at the same carbon



3-ethyl-3-methylhexane

- Use of di-, tri-, tetra-, penta-, hexa-, …….

(2) (3) (4) (5) (6)

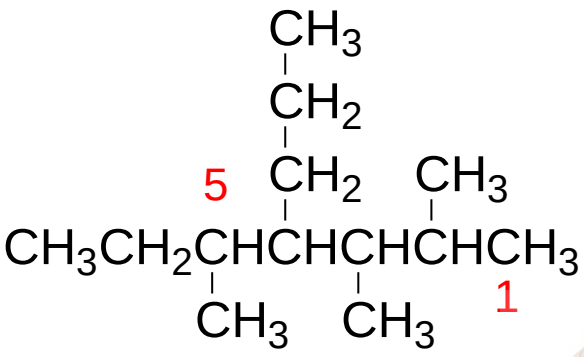


2,2,4,4-tetramethylpentane

排序時用m

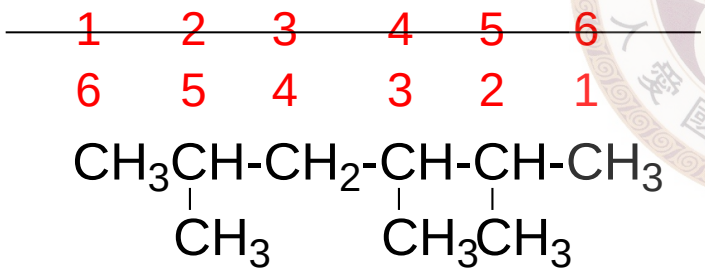
註: 結構複雜的取代基則用字頭比較 (IUPAC rule 2.3: the name of a complex radical is considered to begin with the first letter of its complete name)
例如: dimethylpentyl (as complete single substituent) is alphabetized under "d"

- Equal length: choose the one with more substituents



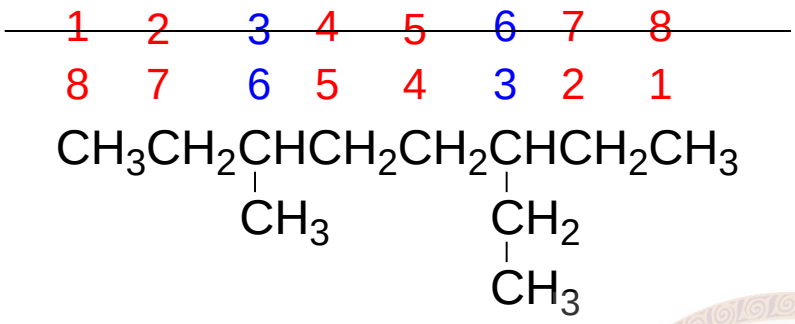
2,3,5-trimethyl-4-propylheptane

- Lowest number for the first point of difference



2,3,5-trimethylhexane

- When symmetrical:



3,6- or 6,3- ?

?-ethyl-?-methyloctane

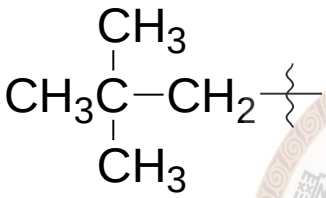
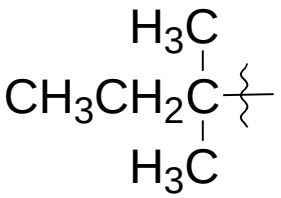
在前面的給小編號

⇩

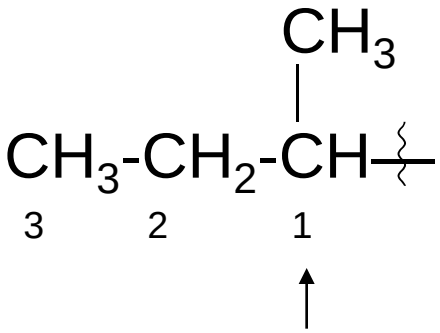
3-ethyl-6-methyloctane

※ Systematic nomenclature for branched alkyl groups

Some common names accepted by IUPAC:
isopropyl , isobutyl, *sec*-butyl, *tert*-butyl, isopentyl,

neopentyl  , *tert*-pentyl  , isohexyl

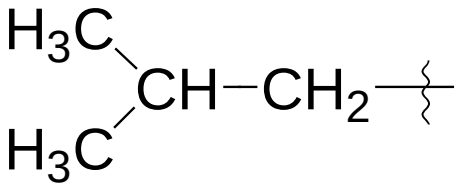
IUPAC rules:



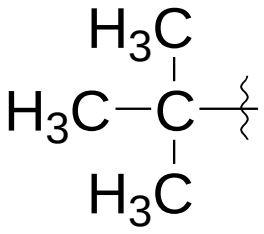
1-methylpropyl = *sec*-butyl

this carbon always number 1

(parent: longest straight chain containing the attach point)



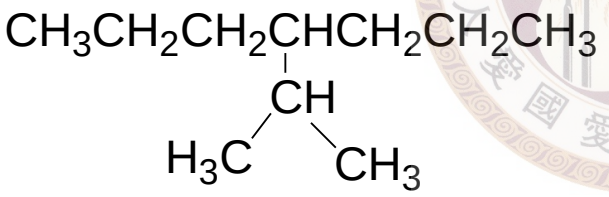
2-methylpropyl (= isobutyl)



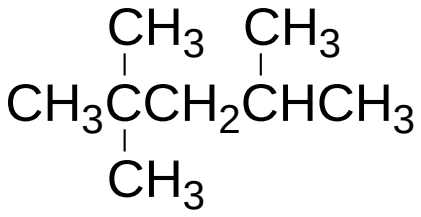
1,1-dimethylethyl (= *t*-butyl)

(錯誤命名: 2-methyl-2-propyl)

例:



4-(1-methylethyl)heptane
or 4-isopropylheptane



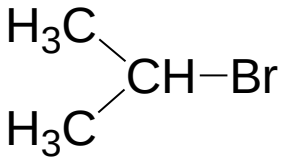
2,2,4-trimethylpentane

common name: isooctane

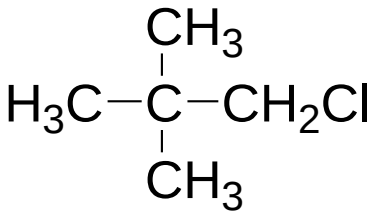
*octane rating = 100 for isooctane
0 for heptane

※ Alkyl halides
(R-X, X = F, Cl, Br, I)

Common names (or trivial names): alkyl halides
alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides

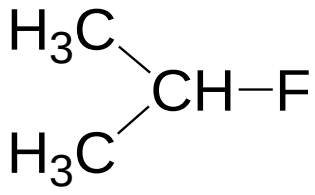


isopropyl bromide

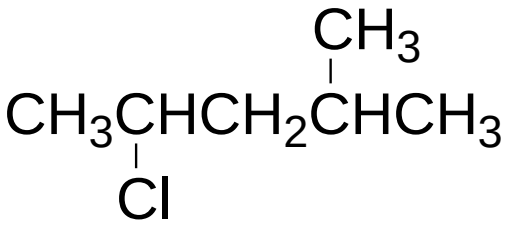


neopentyl chloride

IUPAC names: haloalkanes
fluoroalkanes
chloroalkanes
bromoalkanes
iodoalkanes



2-fluoropropane



2-chloro-4-methylpentane

※ Alcohols (醇類)

R-OH

hydroxyl group

IUPAC rules:

<1> Find the longest chain containing -OH

$CH_3CHCH_2CH_2CH_2OH$ (with CH_3 substituent)

pentanol (e → ol)
with methyl substituent

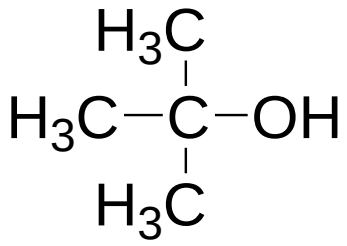
<2> Lowest number for –OH attached carbon

4-methyl-1-pentanol

例: $ClCH_2CH_2CH_2OH$ 3-chloro-1-propanol

◎ Common names: alkyl alcohols

$CH_3CH_2CH_2CH_2OH$ butyl alcohol

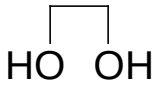
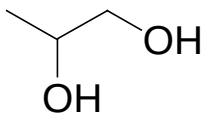
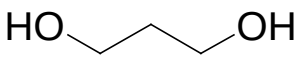


t-butyl alcohol

◎ Containing two hydroxyl groups

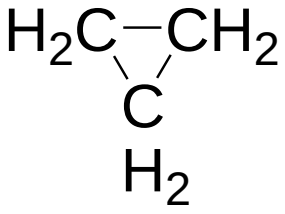
common names: glycols

IUPAC: diols (-ane + diol; e要保留)

	common names	IUPAC names
	ethylene glycol	1,2-ethanediol
	propylene glycol	1,2-propanediol
	trimethylene glycol	1,3-propanediol

※ Cycloalkanes (環烷類)

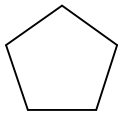
◎ Monocyclic compounds



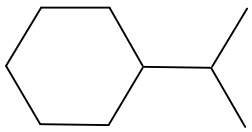
cyclopropane

↑

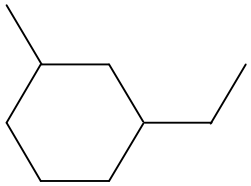
prefix



cyclopentane



isopropylcyclohexane

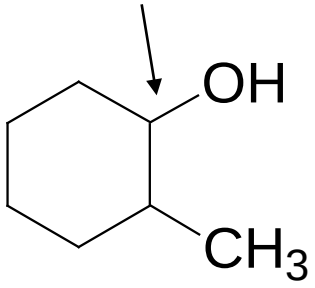


1-ethyl-3-methylcyclohexane

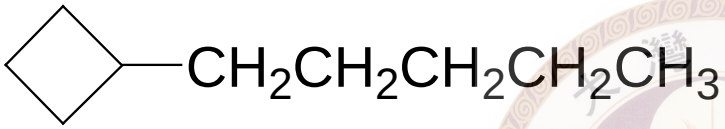
↖ ↗

lowest combination

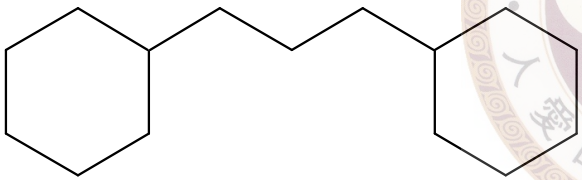
must be number one



2-methylcyclohexanol



1-cyclobutylpentane

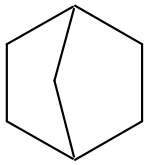


1,3-dicyclohexylpropane

IUPAC Rule A-61.2 …. (*a*) the maximum number of substitutions into a single unit of structure; (*b*) treatment of a smaller of structure as a substituent into a larger. ….

◎ Bicyclic compounds

bicycloalkanes



平面畫法

≡

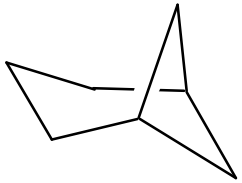
立體結構

bicycloheptane

表示法:

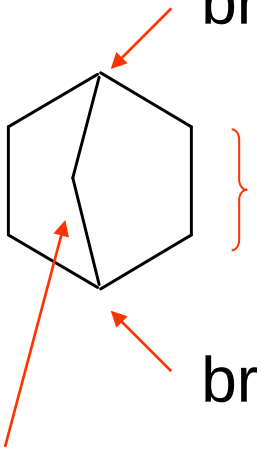
“the number of cyclic = the number of scissions to open”

Problem:



also a bicycloheptane!

Nomenclature

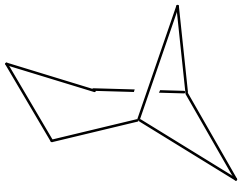


IUPAC name:
bicyclo[2.2.1]heptane

句點 沒句點

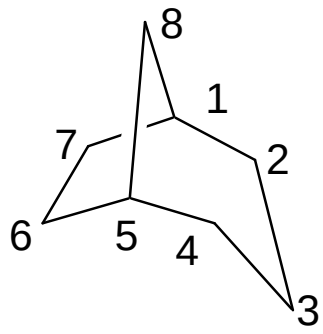
數字由大至小

Common name:
norbornane



bicyclo[3.1.1]heptane

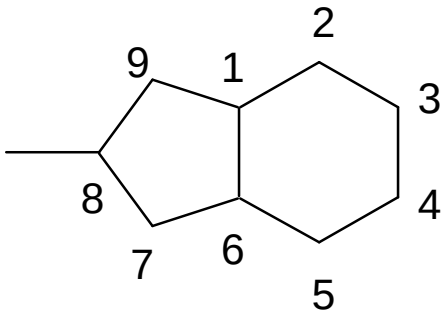
Numbering:



8-methylbicyclo[3.2.1]octane

Bridged type

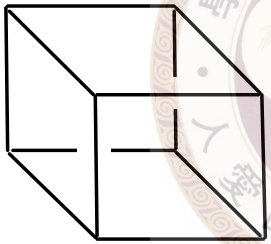
Fused type (共享一鍵)



8-methylbicyclo[4.3.0]nonane

A note:
CA (chemical abstract) uses a slightly different system

A challenge:



The IUPAC name of cubane?

※ Physical properties

Nonpolar: intermolecular van der Waals interactions

MW ↑ → bp ↑, mp ↑ (depends on surface area, crystal packing)

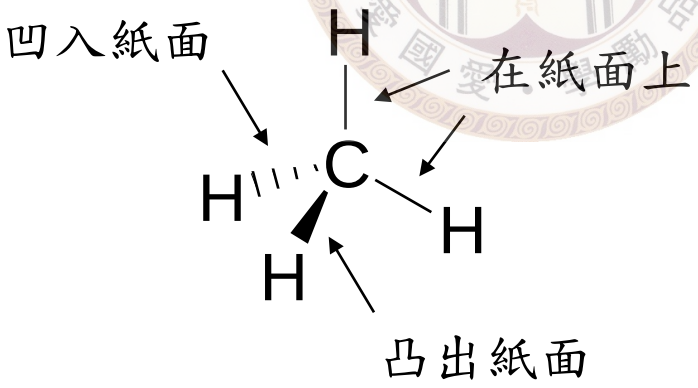
Low density
Water insoluble

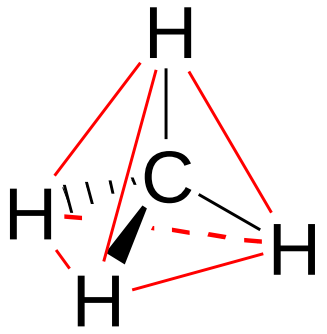
※ Structure and bonding, conformations (構形)

◎ Methane (CH_4)

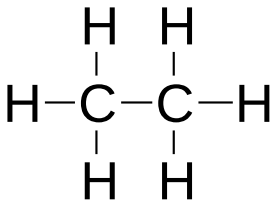
C: uses four sp^3 orbitals

⟹ Tetrahedral structure (四面體)





◎ Ethane



different structures available:

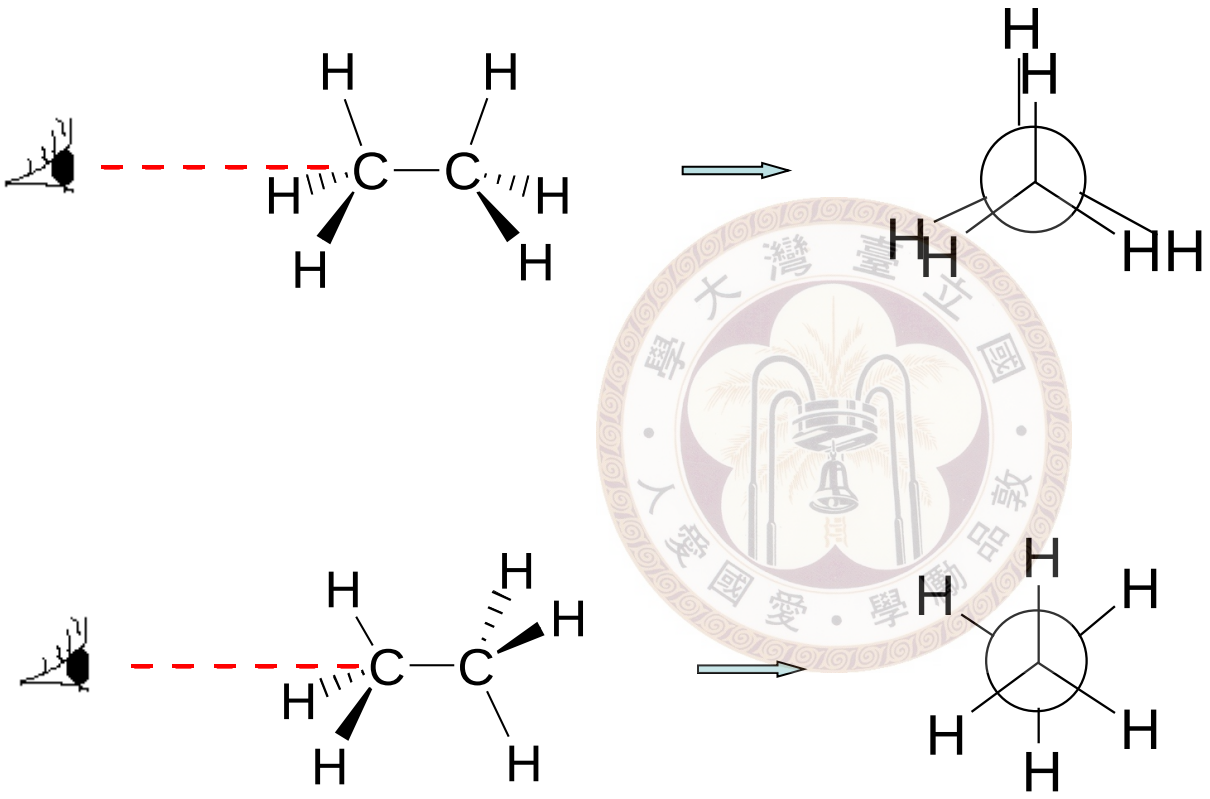
Different structures due to:
C-C single bond (σ bond) rotation

(represented in sawhorse formula)

鋸馬

Conformational isomers (構形異構物):
Isomerism due to single bond rotation

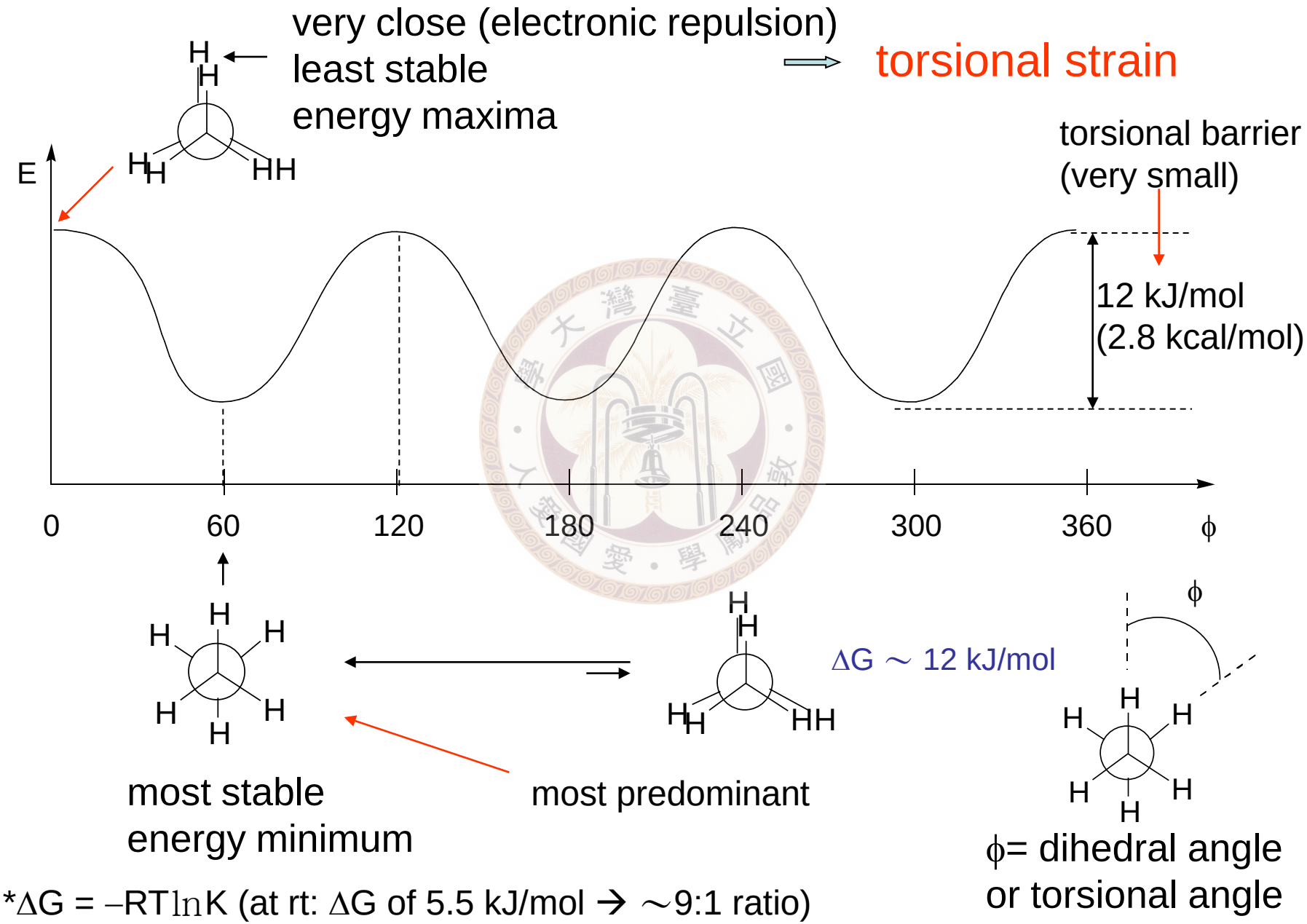
◎ Newman projection formula



eclipsed
conformation
交會構形

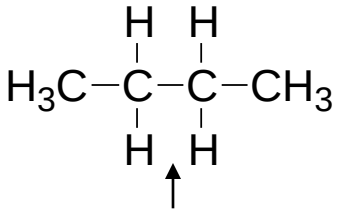
staggered
conformation
相錯構形

◎ Energy profile



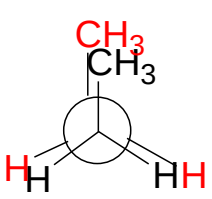
*$\Delta G = -RT\ln K$ (at rt: ΔG of 5.5 kJ/mol → ~9:1 ratio)

◎ Conformational analysis of butane

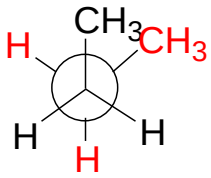


only consider the C(2)-C(3) bond

least stable

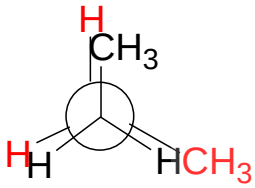


syn

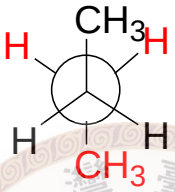


gauche

間扭式

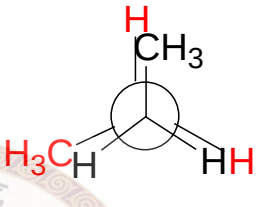


eclipsed

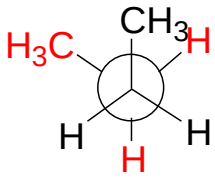


anti

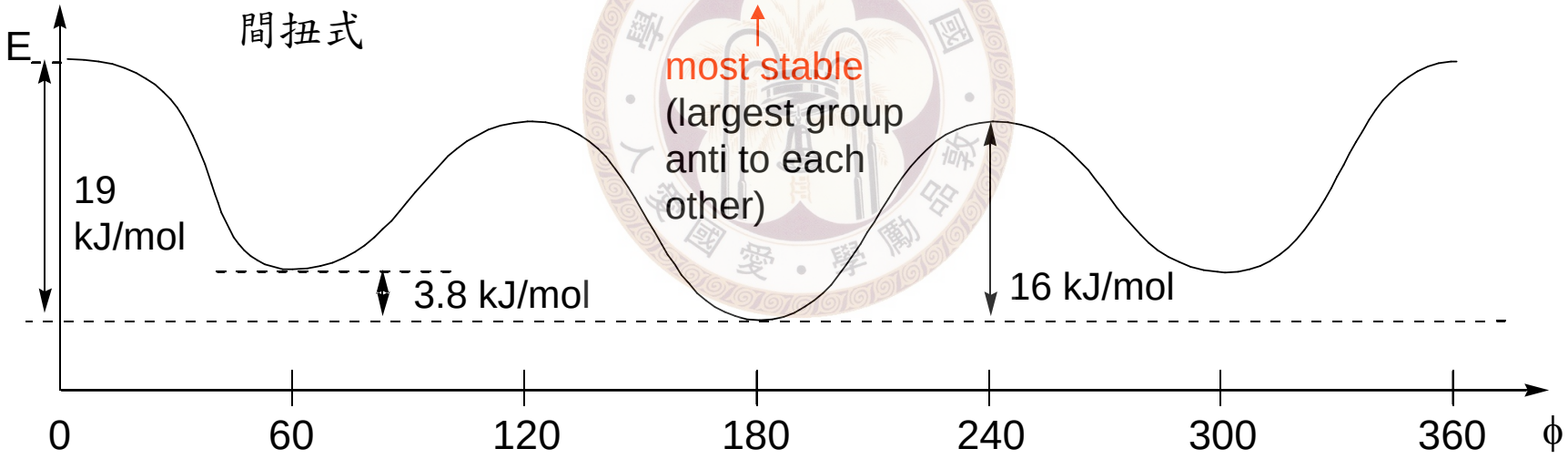
most stable
(largest group
anti to each
other)

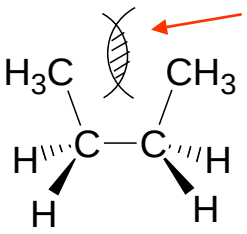


eclipsed

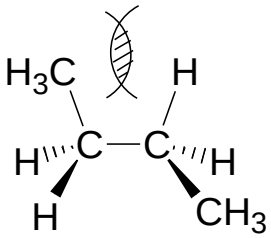


gauche



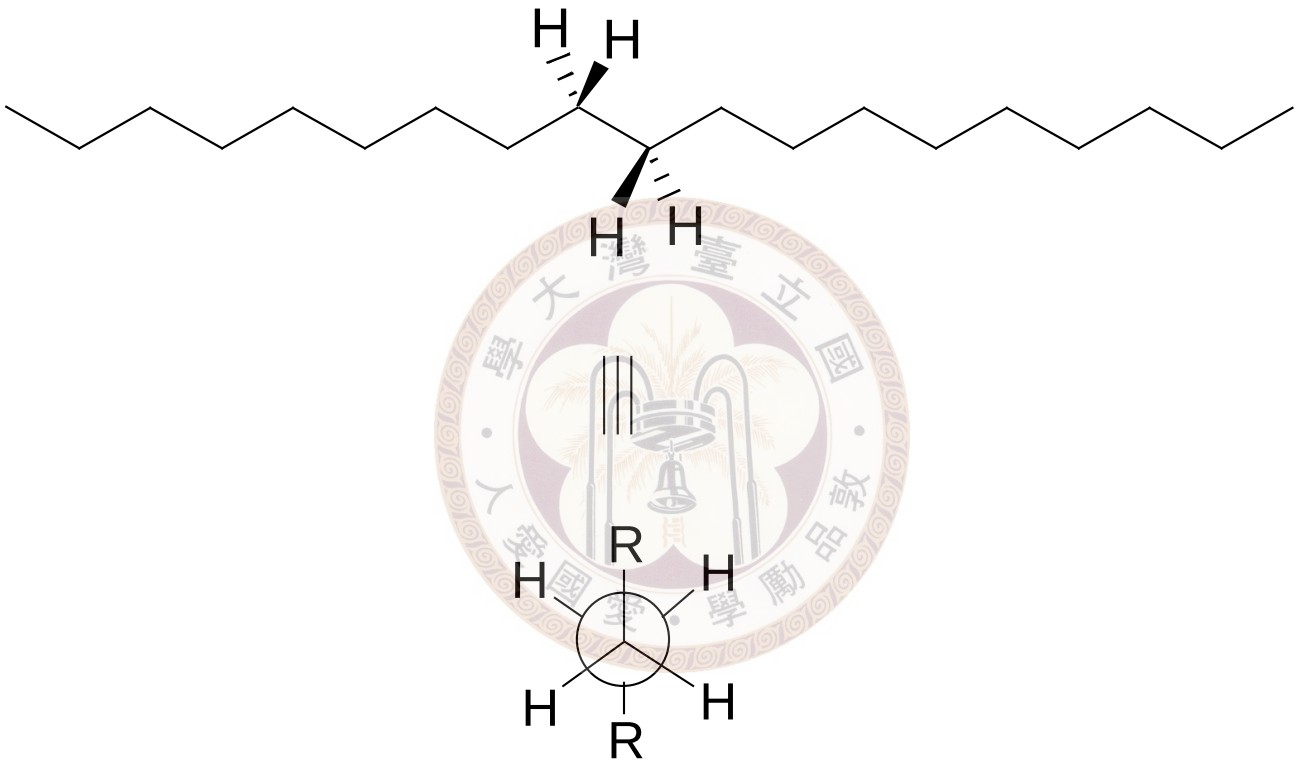


repulsive
interaction



All eclipsed conformations are bad

Long chain hydrocarbons:



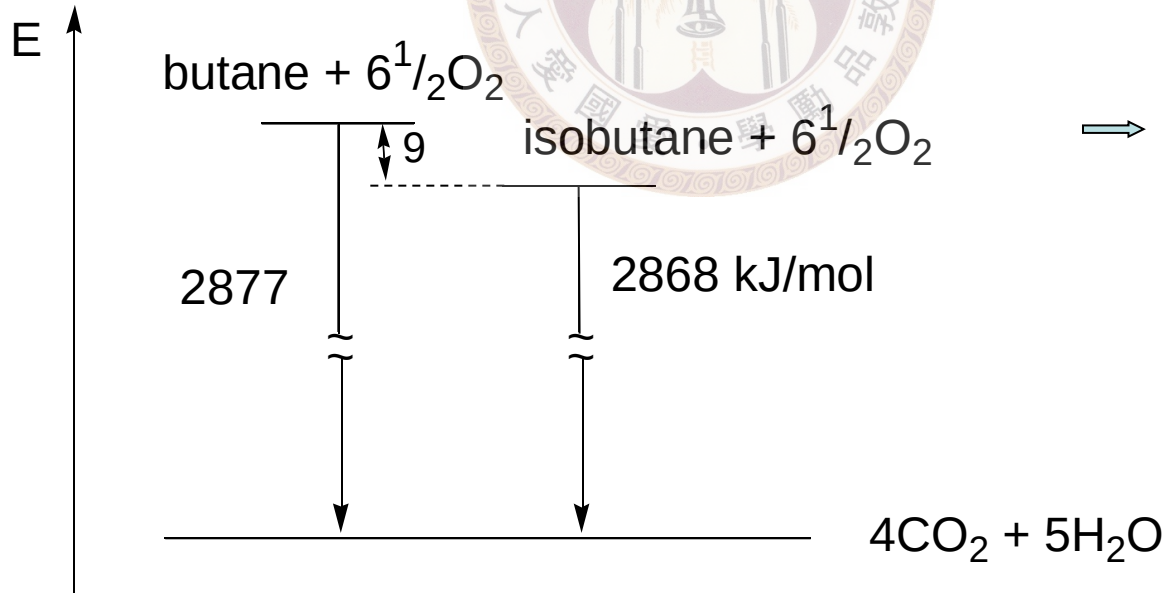
Zig-zag form is preferred locally

※ Stability of cycloalkanes

◎ Heats of combustions

$CH_3CH_2CH_2CH_3 + 6^1/_2O_2 \rightarrow 4CO_2 + 5H_2O \quad \Delta H^o = -2877$ kJ/mol

CH_3CHCH_3 (with CH_3 branch) $+ 6^1/_2O_2 \rightarrow 4CO_2 + 5H_2O \quad \Delta H^o = -2868$ kJ/mol



⟹ Isobutane is more stable by 9 kJ/mol

◎ Cycloalkanes

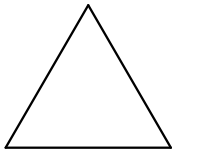
$(CH_2)_n + {}^3/_2nO_2 \rightarrow nCO_2 + nH_2O +$ heat of combustion (kJ/mol)

	n	heat of combustion	per CH_2	relative energy	total (ring strain)
cyclopropane	3	2091	697.0	38.3	115
cyclobutane	4	2744	686.0	27.3	109
cyclopentane	5	3320	664.0	5.3	27
cyclohexane	6	3952	658.7	0	0
	7	4637	662.4	3.7	26
	8	5310	663.8	5.1	41
	9	5981	664.6	5.9	53
	10	6636	663.6	4.9	49
	15	9885	659.0	0.3	4.5
unbranched alkane			658.6		

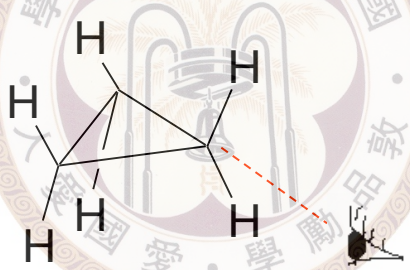
- Cyclohexane has no ring strain
- Cyclopropane has the highest ring strain
- Cyclobutane: second highest
- Ring strain goes up from 8 to 9 and then goes down till 15

◎ Cyclopropane

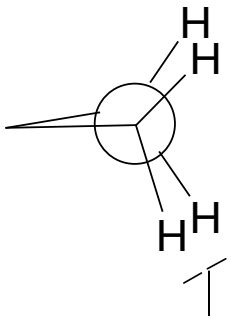
must be planar



≡



≡



sp^3 ideal angle = 109.5º

eclipsed

⇩

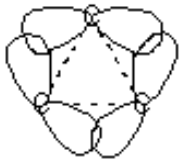
⇒ far from ideal

⇒ severe angle strain

torsional strain

origin of strain

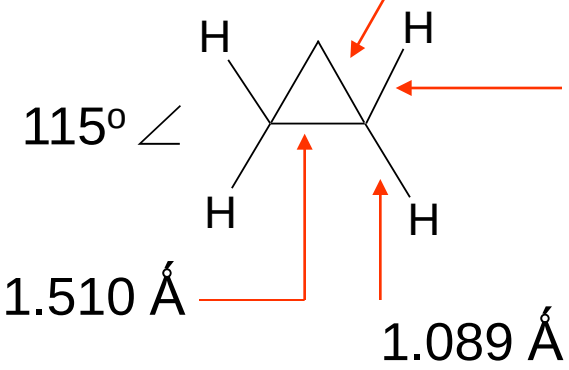
Solution of the molecule:



a bent bond
(banana bond)

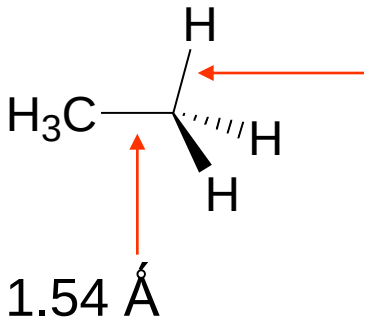
decreased s character (more like sp^5)
to decrease electronic repulsion

Increased s character (more like sp^2)



shorter

cf.

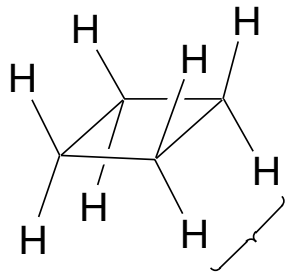


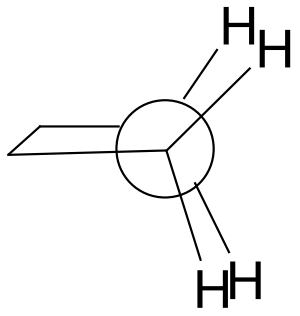
註

$\frac{1}{6}$ s	$\frac{5}{6}$ p
$\frac{1}{6}$ s	$\frac{5}{6}$ p
$\frac{1}{3}$ s	$\frac{2}{3}$ p
$\frac{1}{3}$ s	$\frac{2}{3}$ p
$\frac{6}{6}$ s	$\frac{18}{6}$ p

◎ Cyclobutane

If planar:



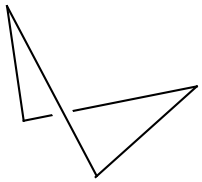


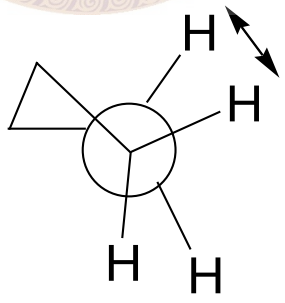
severe torsional strain

90º ∠: severe angle strain

Solution of the molecule:

adopts a twist conformation





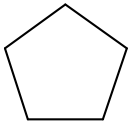
torsional strain relieved

but angle → 88º

⇩

angle strain is sacrificed

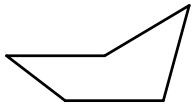
◎ Cyclopentane

If planar: 

108° ∠

very little angle strain
but severe torsional strain

In fact:



envelope
conformation

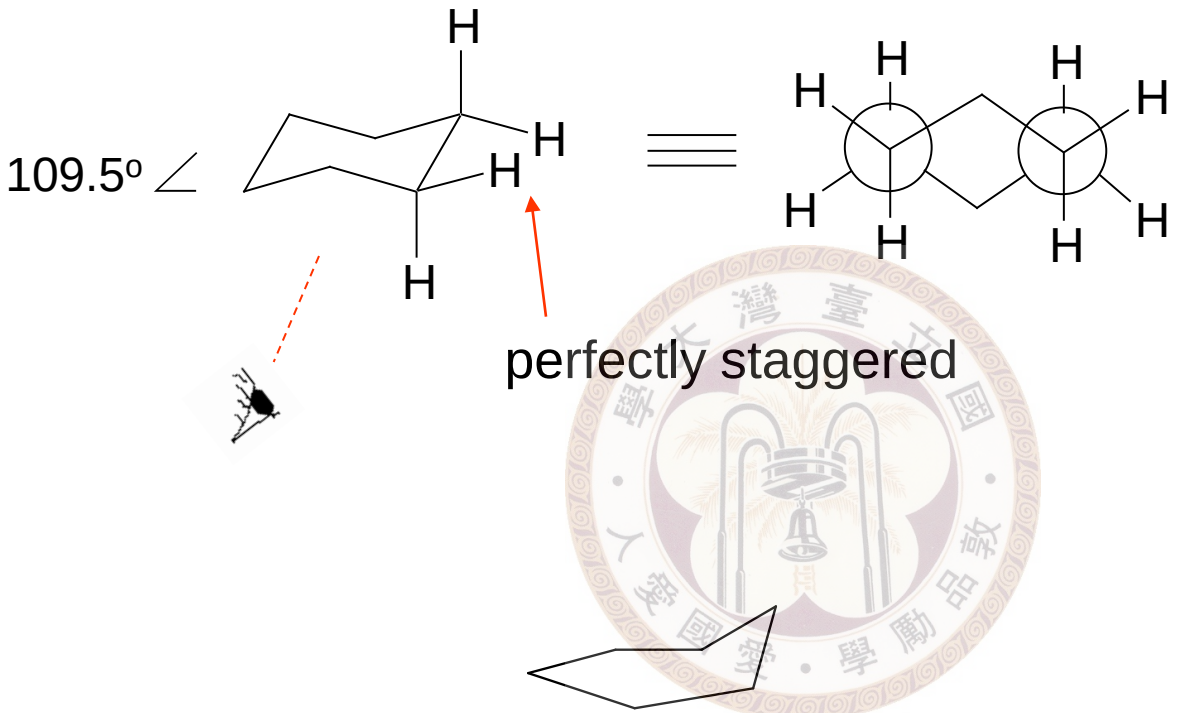
half-chair
conformation

Energy barriers between conformers are small

Pseudo rotation occurs

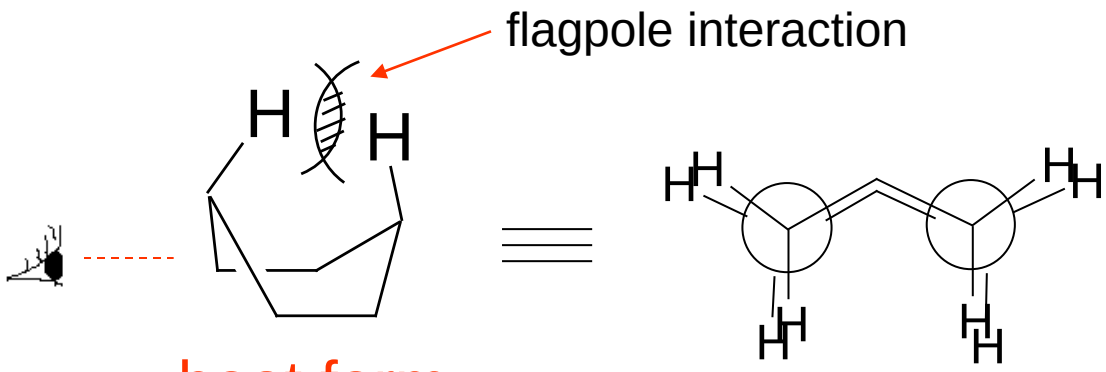
◎ Cyclohexane

Most stable conformation: chair form



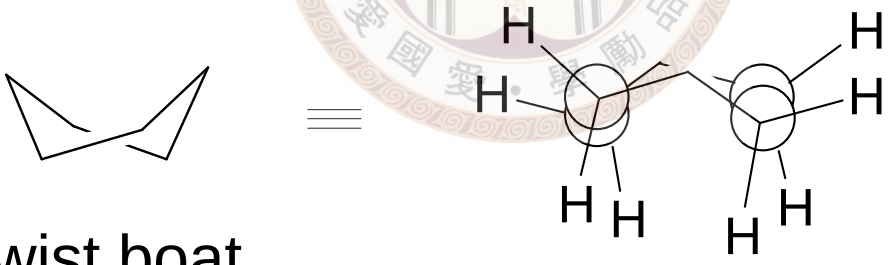
half-chair

increased torsional and angle strain



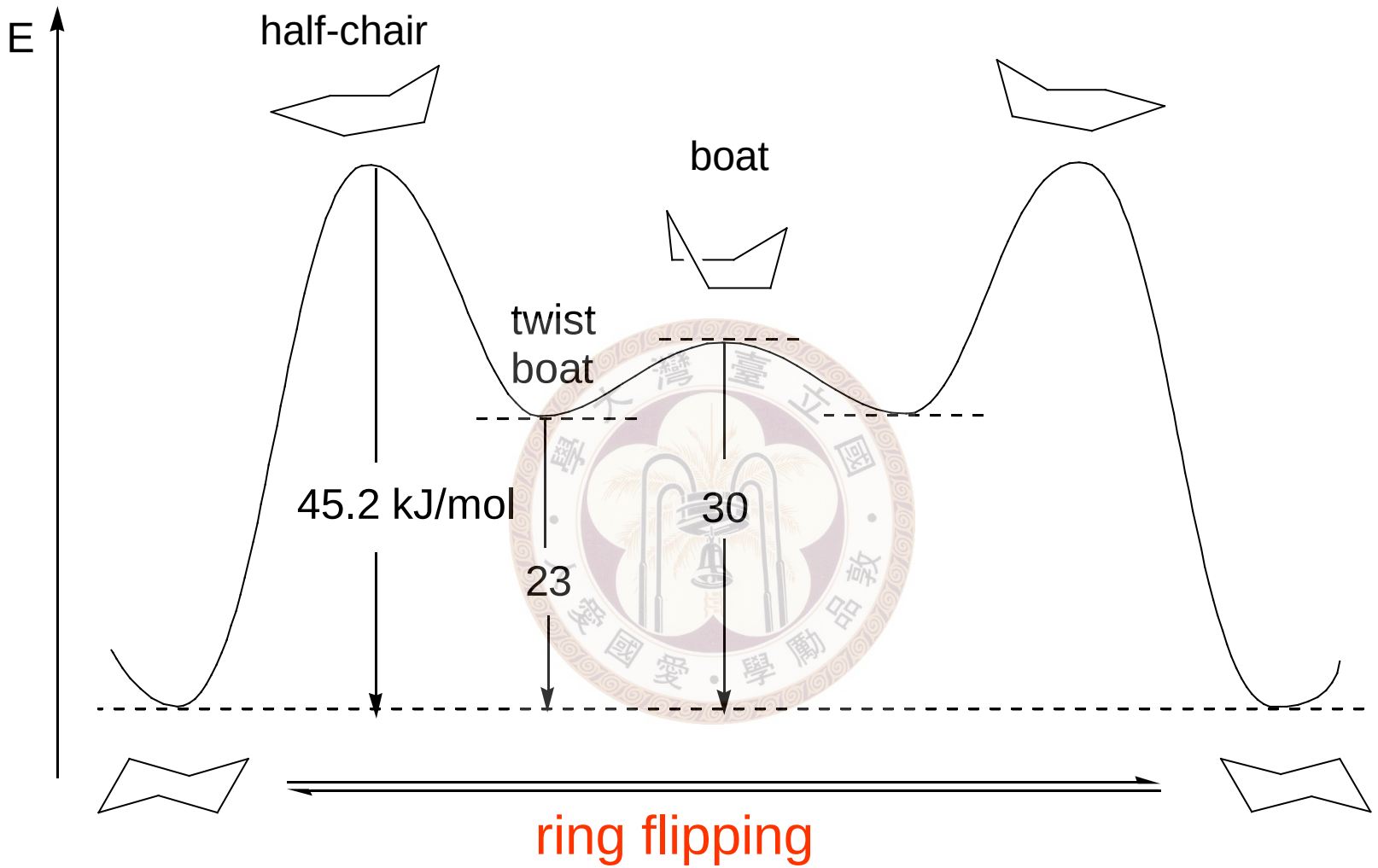
boat form

no angle strain
but severe torsional strain
plus flagpole interaction



twist boat

torsional strain
flagpole interaction
} relieved partially

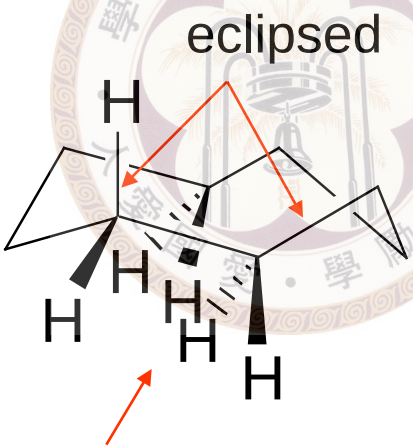


(注意：不同於翻面)

◎ Higher cycloalkanes

＊ Usually free of angle strain
but with torsional strain
+ transannular interactions

例: The chair-chair conformation of cyclooctane:



＊ 環大到15才與cyclohexane一樣

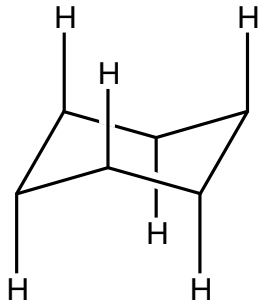
☆ How to draw a good chair

∗ Same bond length

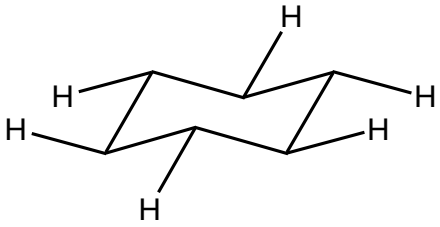
good bad

∗ axial (軸) and equatorial (赤道) hydrogens

anti relationship → must be parallel

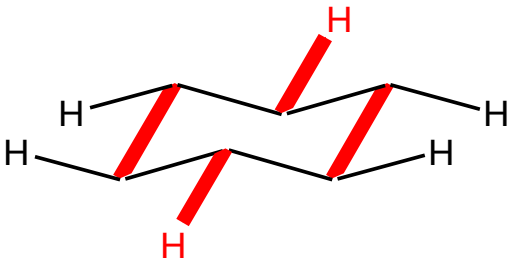


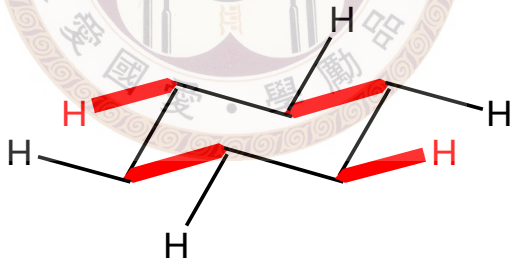
axial hydrogens:
vertical and parallel to each other

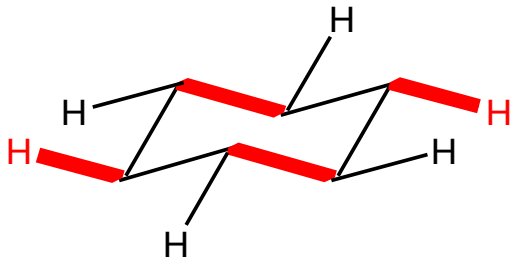


equatorial hydrogens:
roughly horizontal

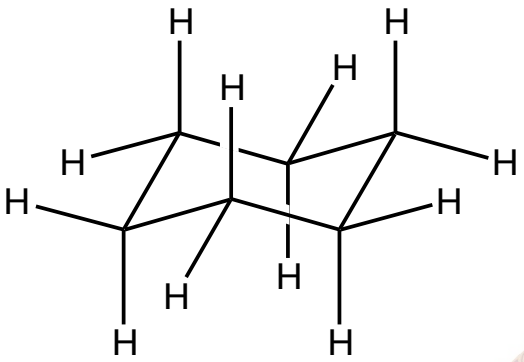
Three parallel pairs

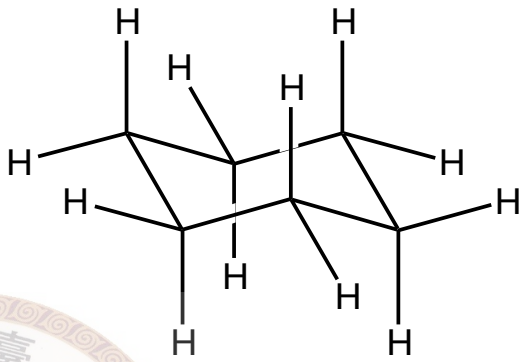


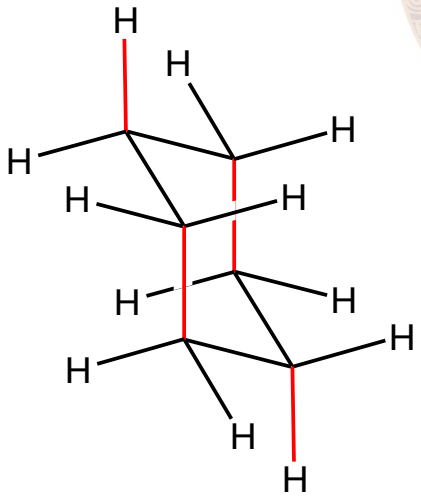


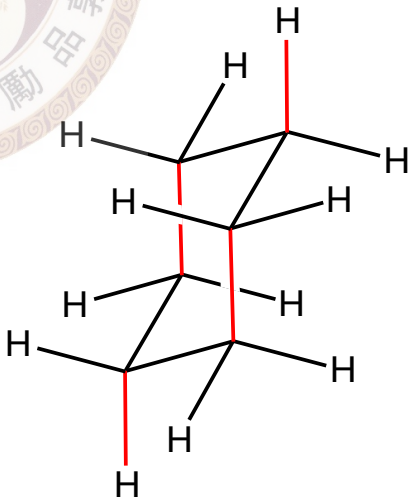


Practice the following drawings on a piece of paper:



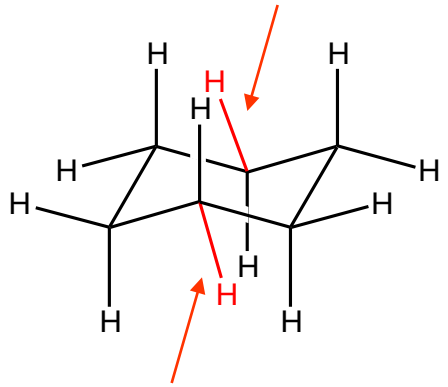




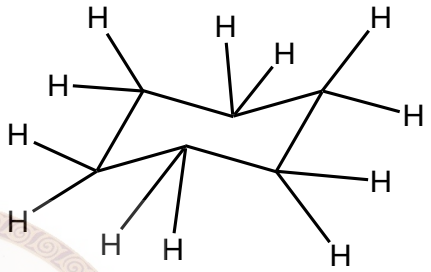


錯誤示範:

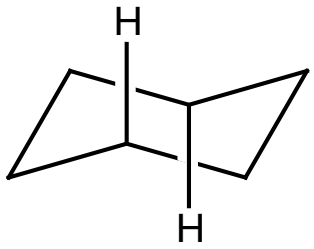
方位不對



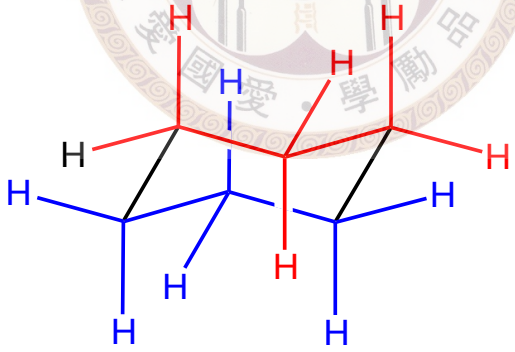
方位不對

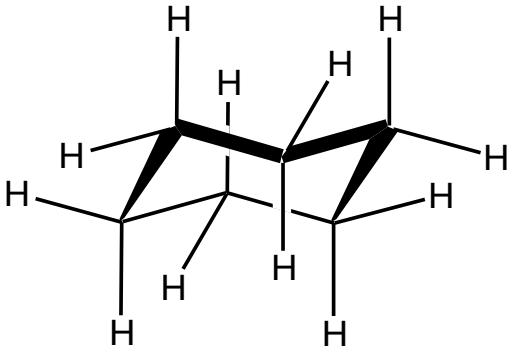


無法辨認軸位與赤道位



前後錯亂



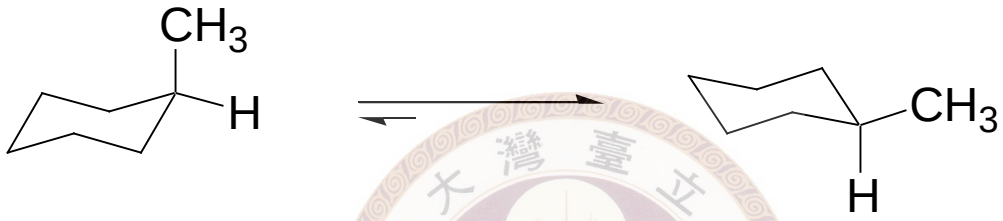


OK but not popular

☆ Flipping causes axial-equatorial exchange

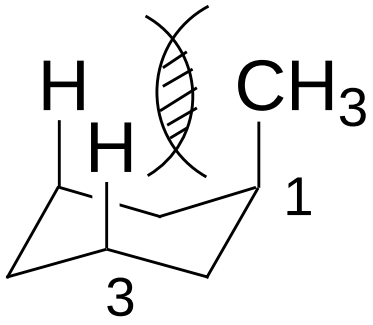
◎ Substituted cycloalkanes

methylcyclohexane



more stable by 7.6 kJ/mol

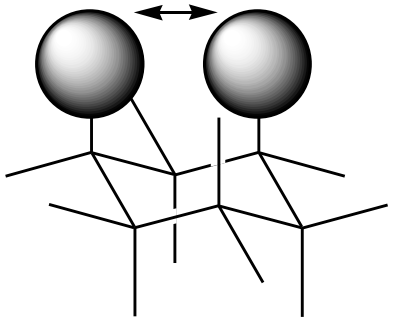
What's bad about axial position?



1,3-diaxial interaction

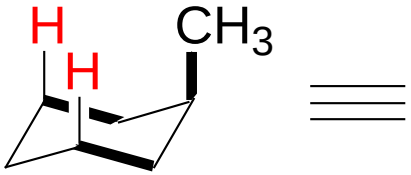
relative relationship

軸位排斥

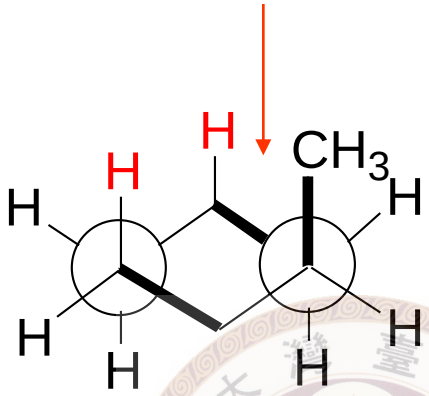


大的取代基在赤道位為佳

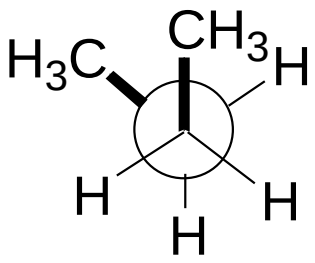
basically a butane gauche



≡

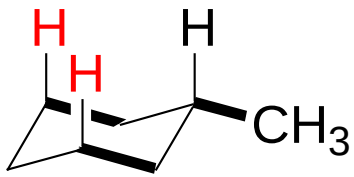


cf.

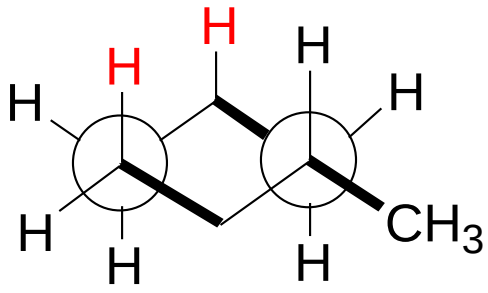


3.8 kJ/mol
higher than anti

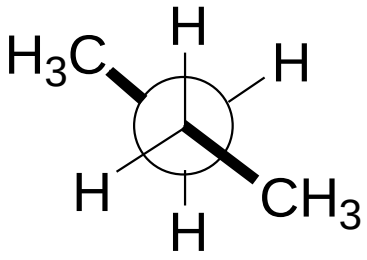
A total of two gauches:
3.8 × 2 = 7.6 kJ/mol



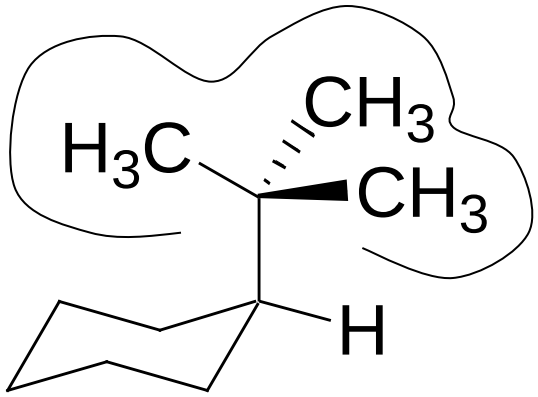
≡

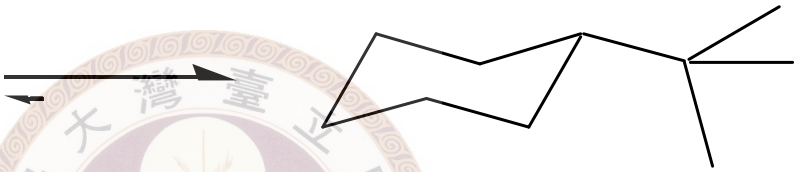


cf.



anti



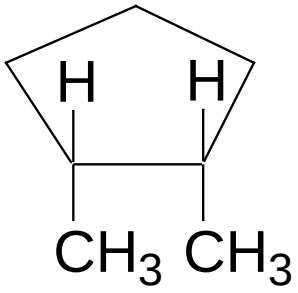


worse

more stable by about 21 kJ/mol

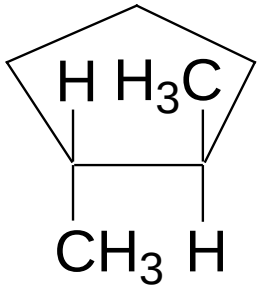
⇒ the only one present

※ Disubstituted cycloalkanes



cis-1,2-dimethylcyclopentane
(順式)

斜體

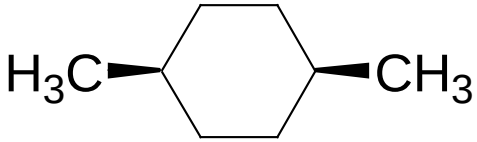


trans-1,2-dimethylcyclopentane
(反式)

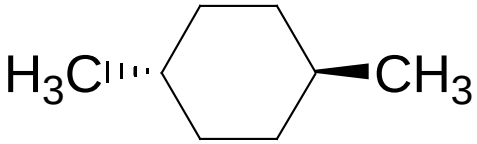
stereoisomers (立體異構物):
same structures but
different arrangement in space

*Interconversion not possible unless σ bond is broken

※ Conformations of disubstituted cyclohexane

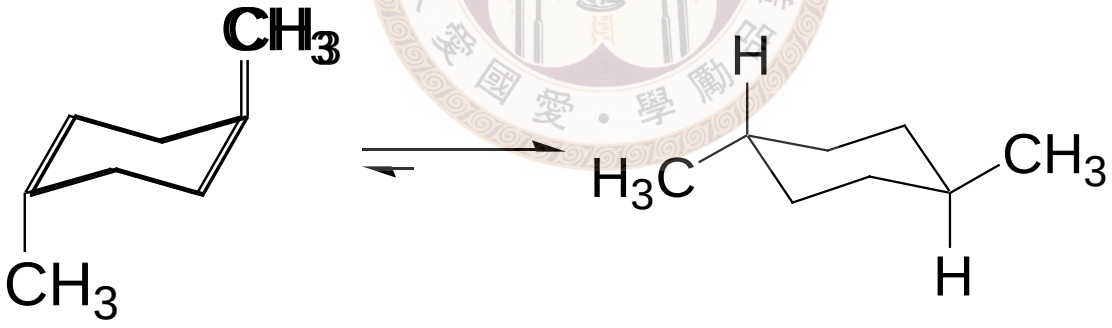


cis-1,4-dimethylcyclohexane



trans-1,4-dimethylcyclohexane

Conformations of *trans*-1,4-dimethylcyclohexane:

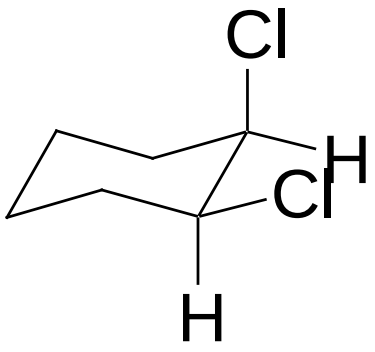


1,4-diaxial

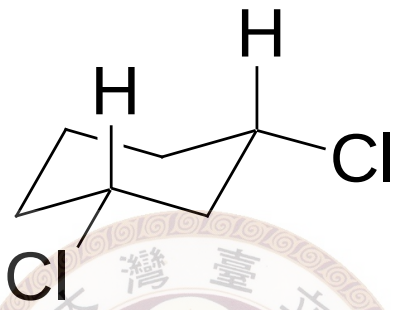
1,4-diequatorial

more stable

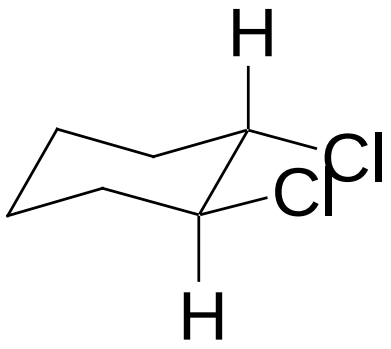
Exercises: *cis* or *trans*?



cis

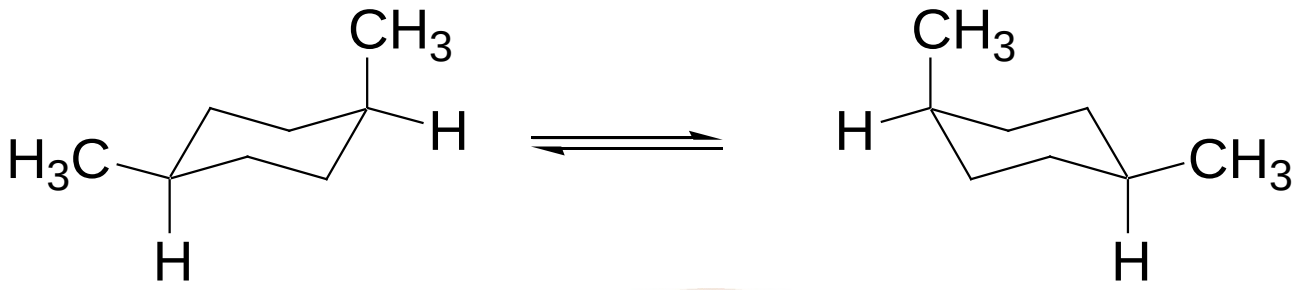


cis



trans

cis-1,4-dimethylcyclohexane

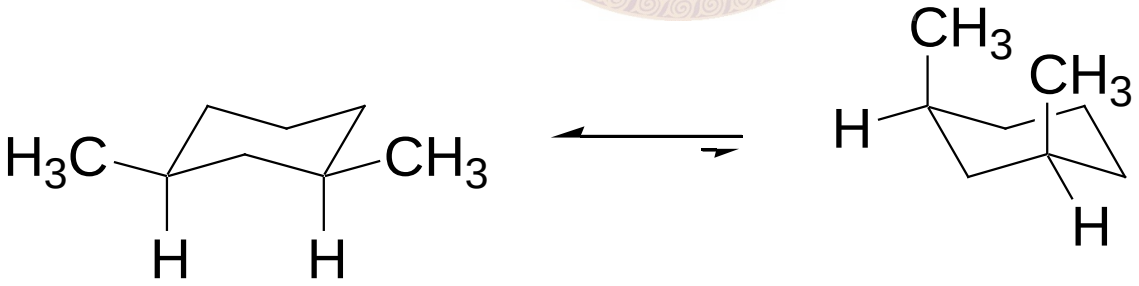


equatorial-axial

axial-equatorial

same structure → same energy

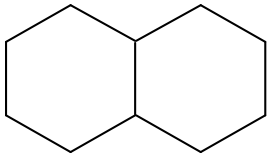
cis-1,3-dimethylcyclohexane



diequatorial
more stable

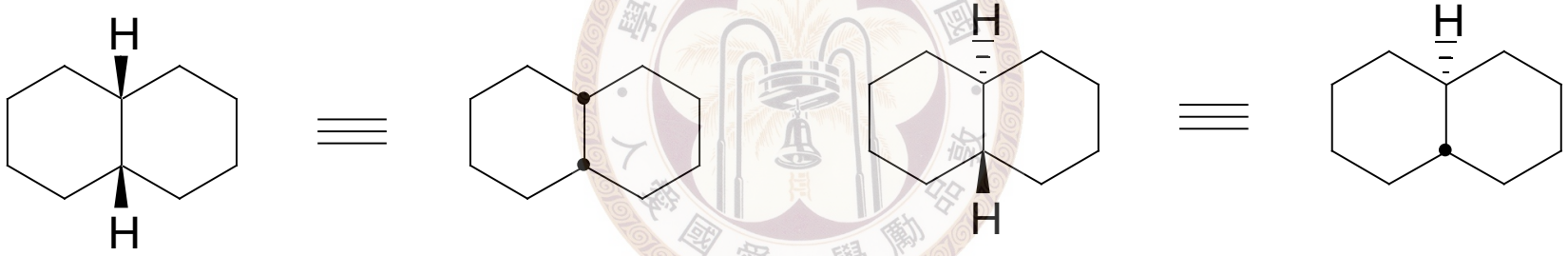
diaxial

※ Bicyclic and polycyclic



decalin

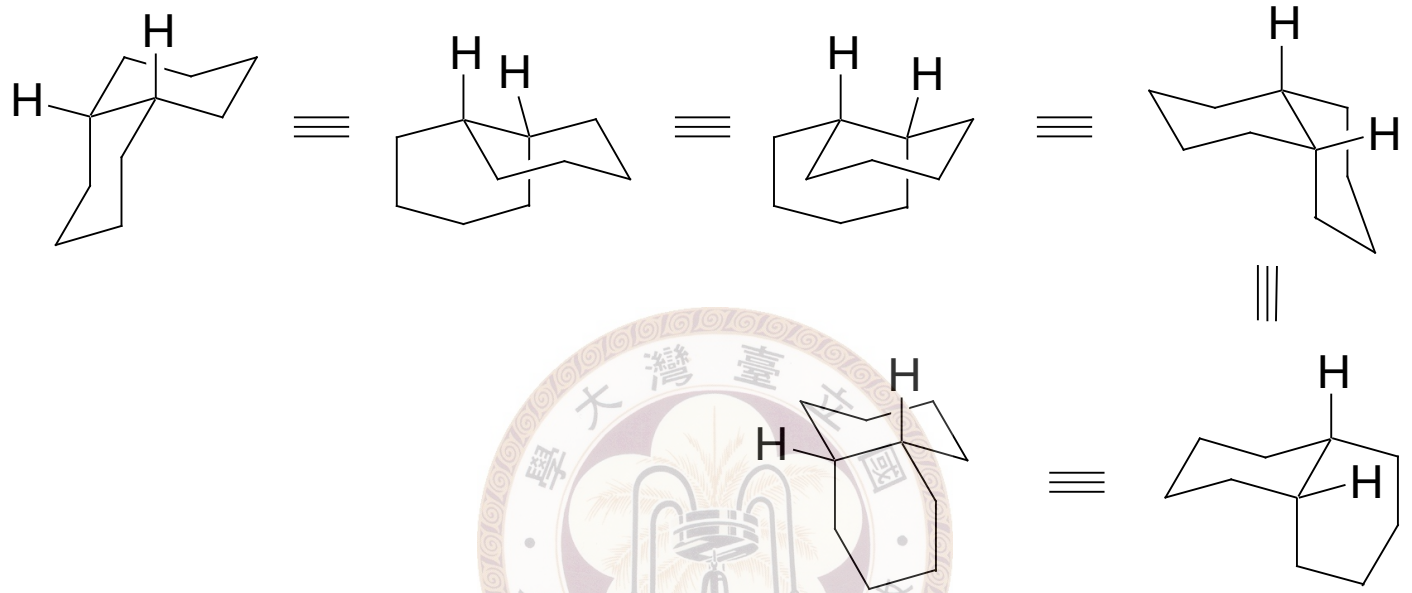
A bicyclic alkane: cis, trans isomers possible



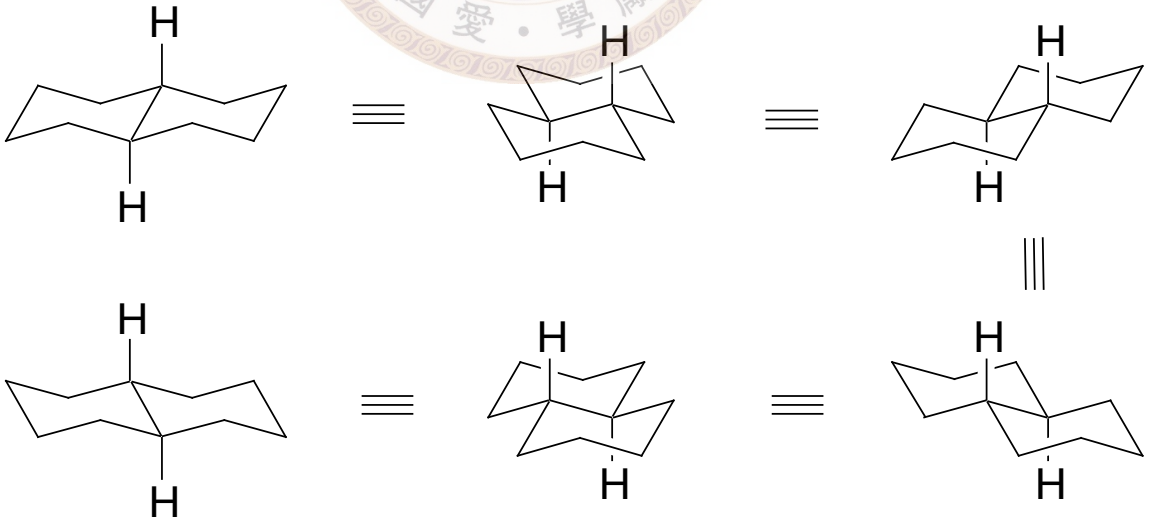
cis-decalin

trans-decalin

Conformation of *cis*-decalin



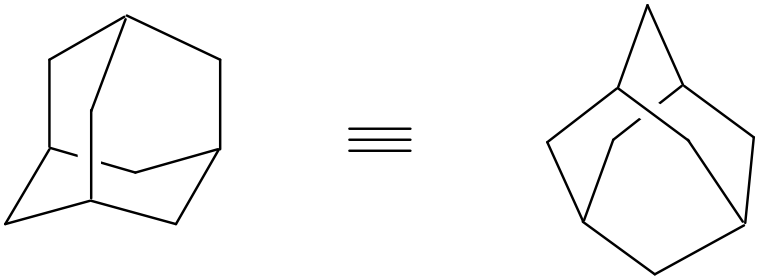
trans-decalin



Some interesting polycyclic structures

Admantane

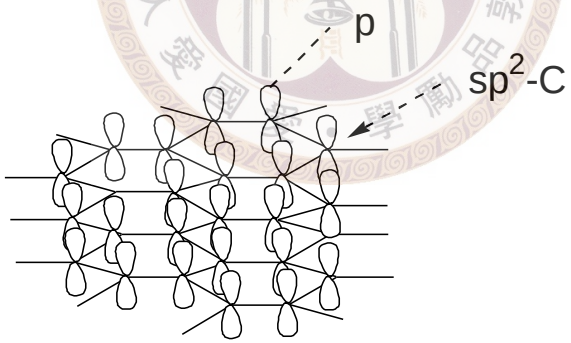
金鋼烷



How many different hydrogen?

→ extending in three dimension → diamond

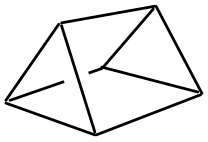
Graphene



→ graphite

weak π-π interaction
between sheets

Prismane



※ Reactions of alkanes

In general: quite inert ⟹ also called paraffins

⇩

good solvent

Combustion (oxidation)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Halogenation (a substitution reaction)

取代反應

$$CH_4 + Cl_2 \xrightarrow[\text{or } h\nu]{\Delta} CH_3Cl$$