台灣大學開放式課程

有機化學乙

蔡蘊明 教授

【本著作除另有註明，作者皆為蔡蘊明教授，所有內容皆採用 創用CC 姓名標示-非商業使用-相同方式分享 3.0 台灣 授權條款釋出】
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)
Petroleum fractional distillation (refining; 精製)

\[ \text{C}_1-\text{C}_4 (<20 \, ^\circ\text{C}) \text{ natural gas} \]

\[ \text{C}_5-\text{C}_6 (20-60 \, ^\circ\text{C}) \text{ pet. ether} \]

\[ \text{C}_6-\text{C}_7 (60-100 \, ^\circ\text{C}) \text{ ligroin (pet. ether)} \]

\[ \text{C}_5-\text{C}_{10} (40-200 \, ^\circ\text{C}) \text{ gasoline} \]

\[ \text{C}_{12}-\text{C}_{18} (175-325 \, ^\circ\text{C}) \text{ kerosene} \]

\[ \text{C}_{12--} (250-400 \, ^\circ\text{C}) \text{ diesel oil} \]

- lubricating oil...
- wax……

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

Methane (CH₄)

Ethane (C₂H₆)

Propane (C₃H₈)

A methylene unit
<table>
<thead>
<tr>
<th>C4H10</th>
<th>Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5H12</td>
<td>Pentane</td>
</tr>
<tr>
<td>C6H14</td>
<td>Hexane</td>
</tr>
<tr>
<td>C7H16</td>
<td>Heptane</td>
</tr>
<tr>
<td>C8H18</td>
<td>Octane</td>
</tr>
<tr>
<td>C9H20</td>
<td>Nonane</td>
</tr>
<tr>
<td>C10H22</td>
<td>Decane</td>
</tr>
<tr>
<td>C11H24</td>
<td>Undecane</td>
</tr>
<tr>
<td>C12H26</td>
<td>Dodecane</td>
</tr>
<tr>
<td>C20H42</td>
<td>Eicosane</td>
</tr>
</tbody>
</table>

Class name: Alkane

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

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}_n \quad = \quad C_nH_{2n+2}
\]
※ Structural isomers and common names (俗名)

- **isobutane**
  \[\text{CH}_3\text{CHCH}_3\]

- **isopentane**
  \[\text{CH}_3\text{CHCH}_2\text{CH}_3\]

- **isohexane**
  \[\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3\]

- **neopentane**
  \[\text{CH}_3\text{CCH}_3\]

- **neohexane**
  \[\text{CH}_3\text{CCH}_2\text{CH}_3\]
※ Substituent (取代基)

例：\[\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3\] \hspace{1cm} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3

pentane

命名

\[\text{H}_3\text{C}-\text{methyl (ane }\rightarrow\text{ yl)} = \text{Me- (H}_3\text{C}--\text{)}\]

\[\text{CH}_3\text{CH}_2-\text{ethyl}
\text{propyl}
\text{butyl}
\text{alkyl}\]

\[\text{Et-}
\text{Pr-}
\text{Bu-}
\text{R- (RH代表烷類)}\]

一律大寫
Problems:

\[ \text{CH}_3\text{CH}_2\text{CH}_3 \quad \Rightarrow \quad \text{CH}_3\text{CH}_2\text{CH}_2- \quad \text{propyl} \]

\[ \text{CH}_3\text{CHCH}_3 \quad \uparrow \quad \uparrow \quad \text{?} \quad \text{isopropyl} \]

\[ \text{CH}_3\text{CH}_2\text{CHCH}_3 \quad \uparrow \quad \uparrow \quad \text{?} \quad \text{Isobutyl} \]

(a homolog of isopropyl)
Classification of carbon

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
$CH_3CH_2CHCH_3$  \[ \text{secondary-butyl or sec-butyl or s-butyl} \]

$CH_3$ \[ \text{tertiary-butyl or tert-butyl or t-butyl} \]

$CH_3CH_2CH_2CH_2CH_2$  \[ \text{normal-butyl or n-butyl} \]
Structural classification of alkanes:

- Straight chain alkanes
- Branched chain alkanes
Nomenclature for branched chain alkanes

IUPAC rules:

- Name after the longest chain

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_3 \]

- hexane with a methyl substituent

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

- heptane with a methyl subst.
• Numbering from the end nearer the substituent

\[
\begin{array}{cccccc}
1 & 2 & 3 & 4 & 5 & 6 \\
6 & 5 & 4 & 3 & 2 & 1 \\
\end{array}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3 \\
\quad \text{CH}_3
\]

• 2-Methylhexane

↑

designate the location of subst.

• Arrange substituents in alphabetical order

\[
\begin{array}{cccccc}
1 & 2 & 3 & 4 & 5 & 6 \\
\end{array}
\]

\[
\text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{CH}_3 \\
\quad \text{CH}_3 \quad \text{CH}_2 \\
\quad \text{CH}_3
\]

(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

\[
\text{CH}_3\text{CH}_2\text{CHCHCHCHCH}_3 \\
\text{CH}_3 \text{CH}_2 \text{CHCHCHCH}_3 \text{CH}_3 \\
\text{CH}_3 \text{CH}_3 \\
\]

2,3,5-trimethyl-4-propylheptane

- Lowest number for the first point of difference

\[
\begin{array}{ccccccc}
1 & 2 & 3 & 4 & 5 & 6 \\
6 & 5 & 4 & 3 & 2 & 1 \\
\end{array}
\]

\[
\text{CH}_3\text{CH-CH}_2\text{-CH-CH-CH}_3 \\
\text{CH}_3 \text{CH}_3 \text{CH}_3\text{CH}_3 \\
\]

2,3,5-trimethylhexane
• When symmetrical:

CH₃CH₂CHCH₂CH₂CHCH₂CH₃

?)-ethyl-?-methylloctane

3,6- or 6,3-?

3-ethyl-6-methylloctane
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)

例:

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

2,2,4-trimethylpentane

common name: iso-octane

*octane rating = 100 for iso-octane
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

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH} - \text{Br} \\
\text{H}_3\text{C} & \\
\text{CH}_3 & \quad \text{C} - \text{CH}_2\text{Cl} \\
\text{CH}_3 & \quad \text{C} - \text{CH}_2\text{Cl} \\
\text{CH}_3 &
\end{align*}
\]

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

\[ CH_3CHCH_2CH_2CH_2OH \]  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

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} & \quad \text{butyl alcohol} \\
\text{H}_3\text{C} & \\
\text{H}_3\text{C} - \text{C} - \text{OH} & \\
\text{H}_3\text{C} & \quad t\text{-butyl alcohol}
\end{align*}
\]

◎ Containing two hydroxyl groups

common names: glycols

IUPAC: diols (ane + diol; e 要保留)

<table>
<thead>
<tr>
<th>common names</th>
<th>IUPAC names</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene glycol</td>
<td>1,2-ethanediol</td>
</tr>
<tr>
<td>propylene glycol</td>
<td>1,2-propanediol</td>
</tr>
<tr>
<td>trimethylene glycol</td>
<td>1,3-propanediol</td>
</tr>
</tbody>
</table>
※ Cycloalkanes (環烷類)

◎ Monocyclic compounds

- **cyclopropane**
- **cyclopentane**
- **isopropylcyclohexane**
- **1-ethyl-3-methylcyclohexane**
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

立体结构

表示法：

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

also a bicycloheptane!

Nomenclature

- bridgehead
- two carbon bridge
- one carbon bridge

IUPAC name: bicyclo[2.2.1]heptane

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

\[
\begin{align*}
\text{MW} & \uparrow \\
\text{bp} & \uparrow \\
\text{mp} & \uparrow
\end{align*}
\]

(depends on surface area, crystal packing)

Low density

Water insoluble
Structure and bonding, conformations (構形)

◎ Methane (CH₄)

C: uses four sp³ orbitals

→ Tetrahedral structure (四面體)

![Tetrahedral structure diagram](image-url)
Ethane

Different structures available:

Different structures due to: C-C single bond (σ bond) rotation (represented in sawhorse formula)

Conformational isomers (構形異構物): Isomerism due to single bond rotation
© Newman projection formula

- **Eclipsed conformation**
- **Staggered conformation**

- **交會構形**
- **相錯構形**
**Energy profile**

- very close (electronic repulsion)
- least stable
- energy maxima

- torsional strain

- torsional barrier (very small)
- 12 kJ/mol (2.8 kcal/mol)

- most stable energy minimum

- most predominant

- \( \phi = \text{dihedral angle or torsional angle} \)

- \( \Delta G = \frac{-RT \ln K}{(\text{at rt: } \Delta G \text{ of } 5.5 \text{ kJ/mol } \rightarrow \sim 9:1 \text{ ratio})} \)
Conformational analysis of butane

least stable

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

least stable

most stable (largest group anti to each other)

repulsive interaction

All eclipsed conformations are bad
Long chain hydrocarbons:

Zig-zag form is preferred locally
※ Stability of cycloalkanes

◎ Heats of combustions

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \frac{61}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} \quad \Delta H^\circ = -2877 \text{ kJ/mol}
\]

\[
\text{CH}_3\text{CHCH}_3 + \frac{61}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} \quad \Delta H^\circ = -2868 \text{ kJ/mol}
\]

Isobutane is more stable by 9 kJ/mol
**Cycloalkanes**

\[(CH_2)_n + \frac{3}{2}nO_2 \rightarrow nCO_2 + nH_2O + \text{heat of combustion (kJ/mol)}\]

<table>
<thead>
<tr>
<th>n</th>
<th>Heat of combustion (per CH(_2))</th>
<th>Relative energy</th>
<th>Total (ring strain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopropane 3</td>
<td>2091</td>
<td>697.0</td>
<td>38.3</td>
</tr>
<tr>
<td>cyclobutane 4</td>
<td>2744</td>
<td>686.0</td>
<td>27.3</td>
</tr>
<tr>
<td>cyclopentane 5</td>
<td>3320</td>
<td>664.0</td>
<td>5.3</td>
</tr>
<tr>
<td>cyclohexane 6</td>
<td>3952</td>
<td>658.7</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>4637</td>
<td>662.4</td>
<td>3.7</td>
</tr>
<tr>
<td>8</td>
<td>5310</td>
<td>663.8</td>
<td>5.1</td>
</tr>
<tr>
<td>9</td>
<td>5981</td>
<td>664.6</td>
<td>5.9</td>
</tr>
<tr>
<td>10</td>
<td>6636</td>
<td>663.6</td>
<td>4.9</td>
</tr>
<tr>
<td>15</td>
<td>9885</td>
<td>659.0</td>
<td>0.3</td>
</tr>
<tr>
<td>unbranched alkane</td>
<td></td>
<td>658.6</td>
<td></td>
</tr>
</tbody>
</table>
* 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 = 109.5°

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$^2$)

Chain of C:

- $\text{H}_3\text{C}$
- Bond length 1.10 Å
- Bond length 1.54 Å

Chain of O:

- Bond length 1.089 Å
- Bond length 1.510 Å
- Angle 115°
If planar:

Cyclobutane

Severe torsional strain

90°: severe angle strain

Solution of the molecule:

Adopts a twist conformation

Torsional strain relieved

But angle → 88°

Angle strain is sacrificed
Cyclopentane

If planar:  
- 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

109.5°

perfectly staggered

half-chair

increased torsional and angle strain
flagpole interaction

boat form

no angle strain
but severe torsional strain
plus flagpole interaction

twist boat

torsional strain
flagpole interaction

relieved partially
45.2 kJ/mol

half-chair

boat

twist

ring flipping

(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 and bad chair forms]

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

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

What’s bad about axial position?

1,3-diaxial interaction

relative relationship
basically a butane gauche

A total of two gauches:
3.8 \times 2 = 7.6 \text{ kJ/mol}

cf.

3.8 \text{ kJ/mol}
higher than anti

cf.

anti
H3C CH₃

 worse

CH₃

more stable by about 21 kJ/mol

the only one present
Disubstituted cycloalkanes

\[
\text{cis-1,2-dimethylcyclopentane (順式)}
\]

\[
\text{trans-1,2-dimethylcyclopentane (反式)}
\]

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

*Interconversion not possible unless $\sigma$ bond is broken
Conformations of disubstituted cyclohexane

\[ \text{cis-1,4-dimethylcyclohexane} \]

\[ \text{trans-1,4-dimethylcyclohexane} \]

Conformations of \textit{trans}-1,4-dimethylcyclohexane:

- 1,4-diaxial
- 1,4-diequatorial

1,4-diequatorial is more stable.
Exercises:  *cis* or *trans*?

cis

trans
**cis-1,4-dimethylcyclohexane**

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\text{CH}_3 & \quad \text{H} \\
\text{H} & \quad \text{CH}_3
\end{align*}
\]

**equatorial-axial** ↔ **axial-equatorial**

same structure → same energy

**cis-1,3-dimethylcyclohexane**

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H} & \quad \text{CH}_3 \\
\text{H} & \quad \text{H}
\end{align*}
\]

diequatorial

more stable

diaxial
Bicyclic and polycyclic

A bicyclic alkane: cis, trans isomers possible

decalin

cis-decalin

trans-decalin
Conformation of cis-decalin

\[ \text{cis-decalin} \]

\[ \text{trans-decalin} \]
Some interesting polycyclic structures

Admantane
金鋼烷

How many different hydrogen?

extending in three dimension

Prismane

Graphene

extending in three dimension
diamond

Graphite

weak $\pi-\pi$ interaction between sheets
Reactions of alkanes

In general: quite inert \[\rightarrow\] also called paraffins

\[\text{good solvent}\]

Combustion (oxidation)

\[\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}\]

Halogenation (a substitution reaction)

\[\text{CH}_4 + \text{Cl}_2 \xrightarrow{\Delta} \xrightarrow{\text{or}} \text{CH}_3\text{Cl}\]

\[\text{or}\]

\[h\nu\]