4.8 Sigma Bonds and Bond Rotation
The different arrangements of atoms caused by rotation about a single bond are called conformations (构象) of the molecule, and a specific conformation is called a conformer (构象异构体, conformation isomer).

An analysis of the energy changes that a molecule undergoes as groups rotate about single bonds is called a conformational analysis (构象分析).

Unlike constitutional isomers, though, different conformers can’t usually be isolated because they interconvert too rapidly.
Conformations of Ethane

Representations of conformers

- Newman projections (Newman \( \square \square \square \))
- Sawhorse (\( \square \square \square \))
- Wedge-dash (\( \square \square \ -\square \square \square \), \( \square \square \))

[Diagrams of Newman projections, Sawhorse, and Wedge-dash representations of ethane conformations]
The Staggered Conformation and the Eclipsed Conformation (交叉式构象与重叠式构象)

The least stable conformation

The most stable conformation

Torsional barrier (转动能垒) 12.1 kJ·mol⁻¹
Conformational analysis of ethane

- Bond length: $\text{C—H } 1.07\ \text{Å, C—C } 1.54\ \text{Å}$
- Bond angle: $\angle \text{HCH } 109.5^\circ$
- The distance between two H atoms: $2.29\ \text{Å}$
- Atomic radius of H: $\gamma_H = 1.2\ \text{Å}$
Potential energy diagram for rotation about the C—C bond in ethane

12.1 kJ / mol
4.9 Conformational Analysis of Butane
The least stable conformation

The most stable conformation
Energy changes that arise from rotation about the C2—C3 bond of butane
### Compounds Anti conformations (%)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Anti conformations (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClCH₂CH₂Cl</td>
<td>~70</td>
</tr>
<tr>
<td>BrCH₂CH₂Br</td>
<td>84~91</td>
</tr>
<tr>
<td>PhCH₂CH₂Ph</td>
<td>&gt;90</td>
</tr>
</tbody>
</table>
Zig—Zag geometry of higher alkanes
4.10 The Relative Stabilities of Cycloalkanes: Ring Strain
4.10A Heats of Combustion (燃烧热)

The heat of combustion of a compound is the enthalpy change for the complete oxidation of the compound.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + 6\frac{1}{2} \text{O}_2 \rightarrow 4 \text{CO}_2 + 5 \text{H}_2\text{O} \quad \Delta H = -2877 \text{ kJ/mol}
\]

\[
\text{CH}_3\text{CCH}_3 + 6\frac{1}{2} \text{O}_2 \rightarrow 4 \text{CO}_2 + 5 \text{H}_2\text{O} \quad \Delta H = -2868 \text{ kJ/mol}
\]
### 4.10B Heats of Combustion of Cycloalkanes

The reaction for the combustion of cycloalkanes is given as:

\[
(CH_2)_n + \frac{3}{2}nO_2 \rightarrow n\ CO_2 + n\ H_2O + \text{heat}
\]

<table>
<thead>
<tr>
<th>Cycloalkanes</th>
<th>n</th>
<th>(\Delta H_{CH_2})</th>
<th>Ring Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropane</td>
<td>3</td>
<td>697.0</td>
<td>115</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>4</td>
<td>686.0</td>
<td>109</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>5</td>
<td>664.0</td>
<td>27</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6</td>
<td>658.7</td>
<td>0</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>7</td>
<td>662.4</td>
<td>27</td>
</tr>
</tbody>
</table>
4.11 The Origin of Ring Strain in Cyclopropane and Cyclobutane: Angle Strain and Torsional Strain
The “folded” or “bent” conformation
4.11A Cyclopentane

The “envelope” or “bent” form of cyclopentane
4.12 Conformations of Cyclohexane
Chair conformation (椅式构象)

2.51 Å
Boat conformation (船式构象)

1.83 Å

2.27 Å
Twist boat (扭船式构象)  Half-chair (半椅式构象)
4.13 Substituted Cyclohexanes: Axial and Equatorial Hydrogen Atoms
The cyclohexane ring rapidly flips back and forth between two equivalent chair conformations at room temperature.
(More stable by 7.5 kJ/mol) (Less stable)
4.14 Disubstituted Cycloalkanes: Cis-Trans Isomerism
4.14A Cis-Trans Isomerism and Conformational Structure

More stable conformation
优势构象
优势构象的判定

根据势能差计算

Hassel 规则：含相同基团的多取代环己烷如果没有其它因素的影响那么在两个构象转换体之间较多取代基取$\text{e-键向位}$的构象为优势构象

Barton 规则：含不同取代基的多取代环己烷如果没有其它因素的影响那么在两个构象转换体之间作用最强的或较强的基团处于$\text{e-键向位}$的构象为优势构象
4.15 Bicyclic and Polycyclic Alkanes
The Conformations of Decalin (十氢萘)

Naphthalene (萘)

Decalin (十氢萘)

Bicyclo[4.4.0]decane

[4.4.0]
cis-Decalin

trans-Decalin
Stability: trans > cis
4.16 Pheromones: Communication by Means of Chemicals
Pheromones (信息素)

Much of the communication between insects involves chemical messengers called pheromones.

- Aggregating pheromone
- Alarm pheromone
- Sex attractant
Aggregating pheromones

From cockroach

4-Methyl-3-heptanol

From European bark beetles
Alarm pheromone

$$(E)-2$$.Hexenal
from ant

2-Heptanone
from bees
Sex attractant

From codling moth

From honeybee

(Z)-9-Tricosene

From houseflies
4.17 Chemical Reactions of Alkanes

- C—C and C—H bonds are quite strong
- The C—H bonds of alkanes are only slightly polarized.
- They are generally unaffected by most bases and acids.
4.18 Synthesis of Alkanes and Cycloalkanes
4.18A Hydrogenation of Alkenes and Alkynes

\[
\text{Pd, Pt, or Ni} \quad \begin{array}{c}
\text{solvent, pressure} \\
+ \text{H}_2
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\]

\[
\text{C} \\
\text{H} \\
\text{C} \quad \begin{array}{c}
\text{Pt} \\
\text{solvent, pressure} \\
+ 2\text{H}_2
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array}
\]
4.18B Reduction of Alkyl Halides

\[ \text{R} - \text{X} + \text{Zn} + \text{HX} \rightarrow \text{R} - \text{H} + \text{ZnX}_2 \]

4.18C Alkylation of terminal Alkynes

\[ \text{R} - \text{C}≡\text{CH} \overset{\text{NaNH}_2}{\rightarrow} \text{R} - \text{C}≡\text{C}^- \overset{\text{R'}-\text{X}}{\rightarrow} \text{R} - \text{C}≡\text{C} - \text{R'} \]

\[ \text{Pt} \rightarrow \text{R} - \text{CH}_2 - \text{CH}_2 - \text{R'} \]
4.19 Some General Principles of Structure and Reactivity: A Look Toward Synthesis
4.20 An Introduction to Organic Synthesis
4.20A  Retrosynthetic Analysis — Planning an Organic Synthesis

Target molecule

1st precursors

2nd precursors

Starting compounds
4.20B Identifying Precursors

Target molecule

1st precursors A

1st precursors B

1st precursors C

2nd precursors a

2nd precursors b

2nd precursors c

2nd precursors d

2nd precursors e

2nd precursors f