Chapter 4: Alkanes and Cycloalkanes

[Sections: 4.1-4.14]

1. Nomenclature

hydrocarbons: comprised of just carbon and hydrogen

- **saturated** (no pi bonds)
  - alkanes

- **unsaturated** (one or more pi bonds)
  - alkenes
  - alkynes

 Benny benzene

naming alkanes

- CH₄
  - methane
- C₂H₆
  - ethane
- C₃H₈
  - propane

C₄H₁₀ butane
C₅H₁₂ pentane
C₆H₁₄ hexane
C₇H₁₆ heptane
C₈H₁₈ octane
C₉H₂₀ nonane
C₁₀H₂₂ deca

general molecular formula for alkanes: CₙH₂ₙ₊₂

1. Identifying Types of Isomers

- **Same Molecular Formula?**
  - NO
  - YES

- compounds are not isomers

- constitutional isomers verify by:
  - have different names (parent name is different or numbering [locants] of substituents)
  - nonsuperimposable

- possibly the same molecule
  - same name
  - superimposable

relationship?
Naming Organic Compounds According to IUPAC (International Union of Pure and Applied Chemistry) Rules

- identify the parent chain and all substituents
- parent chain: longest continuous carbon chain
- substituent: anything not part of the parent chain
- number the parent chain (i.e., assign locant values)
- locants should be minimized for the first substituents on the parent chain from either end
- if there is a tie, minimize the locant for the second substituent
- if the locants are the same in either direction, the first substituent alphabetically is assigned the lower locant (this is used ONLY if the locant values cannot prioritize the substituents!!)

alkyl groups

<table>
<thead>
<tr>
<th>P</th>
<th>C</th>
<th>H</th>
<th>CH₃</th>
<th>methyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td></td>
<td>-CH₃</td>
<td>methyl group</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P</th>
<th>C</th>
<th>C</th>
<th>H</th>
<th>-CH₂CH₃</th>
<th>ethyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>-CH₂CH₃</td>
<td>ethyl group</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P</th>
<th>C</th>
<th>C</th>
<th>C</th>
<th>H</th>
<th>&quot;propyl group&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>1-propyl group</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>P</th>
<th>C</th>
<th>C</th>
<th>C</th>
<th>H</th>
<th>&quot;propyl group&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>1-propyl group</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P</th>
<th>C</th>
<th>C</th>
<th>C</th>
<th>H</th>
<th>&quot;propyl group&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>n-propyl group</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>P</th>
<th>C</th>
<th>C</th>
<th>C</th>
<th>H</th>
<th>&quot;propyl group&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td></td>
<td>n-propyl group</td>
</tr>
</tbody>
</table>

P = parent chain

<table>
<thead>
<tr>
<th>P</th>
<th>C</th>
<th>C</th>
<th>C</th>
<th>H</th>
<th>2-propyl group</th>
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</thead>
<tbody>
<tr>
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<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>isopropyl group</td>
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</tbody>
</table>

<table>
<thead>
<tr>
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<th>C</th>
<th>C</th>
<th>C</th>
<th>H</th>
<th>tert-butyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>tert-butyl</td>
</tr>
</tbody>
</table>

halogens

- F: fluoro
- Cl: chloro
- Br: bromo
- I: iodo
- identify the parent chain and all substituents
- if there are two longest chains of the same length, select the one with more substituents
- properly assign locants to all substituents
- alphabetize substituents and place before name of parent chain along with locant values
- use di, tri, tetra, etc. for substituents if necessary (these are not used for alphabetizing)

P: 4.1-4.4, 4.5(a,b,e,g), 4.10 (a,c-e,g-o,q), 4.11 (a,b), 4.14, 4.15, 4.39, 4.41 (a), 4.42, 4.56
2. Cycloalkanes

Naming Cycloalkanes According to IUPAC rules

• identify the parent cycloalkane
• if there is one substituent, it is automatically at the "1" position
• for two substituents, minimize the locant values, prioritize based on alphabetizing
• if more than two substituents, minimize locants
• if there is more than one way to count around the ring while still minimizing locant values, prioritize based on alphabetizing (ONLY if the locant values cannot prioritize the substituents!!)
• use di, tri, tetra, etc. for substituents if necessary
• alphabetize substituents and place before name of parent cycloalkane along with locant values

Br

P: 4.1(g-i), 4.5(c-f), 4.10(b,f,p), 4.41(b), 4.45(a,b)
1. Identifying Types of Isomers

- **Same Molecular Formula?**
  - NO: compounds are not isomers
  - YES: Same Connectivity?

- **Same Connectivity?**
  - NO: constitutional isomers
  - YES: Different Orientation of Substituents in Space?

- **Different Orientation of Substituents in Space?**
  - NO: stereoisomers
  - YES: same molecule

- **constitutional isomers**
  - verify by:
    - have different names (parent name is different or numbering [locants] of substituents)
    - nonsuperimposable

- **stereoisomers**
  - verify by:
    - non-superimposable
    - names must be different (cis/trans)

- **same molecule**
  - verify by:
    - both must have the same name
    - two must be superimposable
Determine the relationship between the following pairs of molecules:

![Molecule 1](image1)

![Molecule 2](image2)

**Carbon and Proton Types**

Types of carbons
- $1^\circ$ carbon = a carbon attached to one other carbon
- $2^\circ$ carbon = a carbon attached to two other carbons
- $3^\circ$ carbon = a carbon attached to three other carbons
- $4^\circ$ carbon = a carbon attached to four other carbons

Types of hydrogens
- $1^\circ$ hydrogen = a hydrogen attached to a $1^\circ$ carbon
- $2^\circ$ hydrogen = a hydrogen attached to a $2^\circ$ carbon
- $3^\circ$ hydrogen = a hydrogen attached to a $3^\circ$ carbon
3. Alkane Source

- methane
- ethane
- propane
- butane
- pentane
- hexane
- heptane
- octane
- nonane
- decane
- C_{11-15}
- >C_{25}

4. Alkane (and Cycloalkane) Properties

Boiling Points

- Boiling points are dependent upon:
  - Molecular Weight: Generally as molecular weight increases, boiling point increases.
  - Intermolecular Forces (forces of attraction between molecules): Stronger intermolecular forces mean higher boiling points.
Determine the relationship between the following pairs of molecules:

![Image of molecules]

**Carbon and Proton Types**

Types of carbons
- 1° carbon = a carbon attached to one other carbon
- 2° carbon = a carbon attached to two other carbons
- 3° carbon = a carbon attached to three other carbons
- 4° carbon = a carbon attached to four other carbons

Types of hydrogens
- 1° hydrogen = a hydrogen attached to a 1° carbon
- 2° hydrogen = a hydrogen attached to a 2° carbon
- 3° hydrogen = a hydrogen attached to a 3° carbon
types of intermolecular forces: forces of attraction between individual molecules

1. ion-ion
   ionic molecules
   NaCl
   \(+\) \(-\)
   not typical for organic compounds!

2. dipole–dipole
   polar covalent molecules
   N–H and O–H bonds
   hydrogen bonding

   non-hydrogen bonding
   \[ \delta^+ \delta^- \]

3. instantaneous dipole
   non-polar molecules

Examples

| compound | NaCl | \(\begin{array}{c}
| mol. wt. | 58 \\
| b.p.    | 1400 °C |
\end{array}\) | \(\begin{array}{c}
| OH     | 60 \\
| Cl     | 64 \\
| 97 °C  | 12 °C \\
| 12 °C  | −0.5 °C |
\end{array}\) | \(\begin{array}{c}
| OH     | 82 °C \\
| 82 °C  | −12 °C |
\end{array}\) |

Effect of branching

- branching decreases boiling points due to decrease in surface area and therefore decrease in the extent of intermolecular forces
5. Solubility

- measure of how well one organic compound dissolves in another
- soluble: the two compounds mix well to form a homogeneous mixture
- insoluble: the two compounds do not mix well
- general rule of thumb: like dissolves like

CH₃OH / H₂O  hexane / H₂O  hexane / CH₃OH  hexane / 1-hexanol

6. Relative Thermodynamic Stability of Isomers

<table>
<thead>
<tr>
<th>Heat of Combustion</th>
<th>Heat of Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{C}<em>8\text{H}</em>{18} ] + [ \text{O}_2 ] → 8 ( \text{CO}_2 ) + 9 ( \text{H}_2\text{O} )</td>
<td>5471 kJ/mol</td>
</tr>
<tr>
<td>[ \text{C}<em>8\text{H}</em>{18} ] + [ \text{O}_2 ] → 8 ( \text{CO}_2 ) + 9 ( \text{H}_2\text{O} )</td>
<td>5466 kJ/mol</td>
</tr>
</tbody>
</table>

\[ 8 \text{ CO}_2 + 9 \text{ H}_2\text{O} \]

7. Newman Projections

- Wedge and dash
- Sawhorse
- Newman projection

Melvin Newman 1908-1993
8. Analyzing Conformations of Simple Alkanes

consider ethane

- there are two major conformations for ethane
- conformation: change in shape of a molecule due to bond rotation
- molecular strain: a force that results in a molecule being at a higher E state than its minimum
- torsional strain: molecular strain induced by electron-electron repulsion of overlapping bonds

consider propane

- steric strain: molecular strain induced by atoms or groups of atoms trying to occupy the same physical space
consider butane

9. Analyzing Conformations of Cycloalkanes

- simple planar cycloalkanes suffer from two major sources of strain E
- torsional strain results from C–H and C–C bond eclipsing, the more eclipsings, the worse the strain
- angle strain results from deviation bond angles from the ideal value, which for saturated cycloalkanes would be 109.5°
consider butane

\[
\begin{align*}
\text{Potential energy} & \\
16 \text{ kJ/mol} & \\
3.8 \text{ kJ/mol} & \\
19 \text{ kJ/mol} & \\
\end{align*}
\]

Dihedral angle

- Staggered conformation with 2 largest substituents across from one another

- 2 largest substituents next to one another

P: 4.19-4.21, 4.43, 4.46, 4.47, 4.50-4.52, 4.56, 4.58-4.60
• most stable cycloalkane:
• C8–C11 have approximately equivalent strain energies, then drops off from C12 on
• how can we account for the discrepancy between predicted strain E’s and the actual values?

Cycloalkanes are not planar!

- angle st.?
- torsional st.?

- conformation name?
- angle st.?
- torsional st.?

- strain energies lead to an increase in molecular potential energy
- some strain energies may be lowered at the expense of others, but the system strives for the lowest NET potential energy
- cyclohexane, having no strain energy, is at a minimum point of potential energies
9. Analyzing Conformations of Cyclolkanes

- Torsional strain results from C–H and C–C bond eclipsing, the more eclipsings, the worse the strain.
- Angle strain results from deviation bond angles from the ideal value, which for saturated cycloalkanes would be 109.5°.

Plot of Heat of Combustion per CH2 Group versus Cycloalkane Size
10. A Closer Look at Cyclohexanes

Drawing chair conformations

implications of the chair-chair flip
- Cis positions alternate axial/equatorial positions as you move from one atom to another going around the cyclohexane ring

- All of the substituents occupying the axial position in one chair form adopt the equatorial position in the other chair conformation (after the chair/chair flip) and vice versa

11. Energy Considerations

consider unsubstituted cyclohexane
In general, the larger the substituent, the worse the steric strain due to 1,3-diaxial interactions, and the greater preference for the substituent to occupy the equatorial position.

**Disubstituted Cycloalkanes**

Consider trans-1,2-dimethylcyclohexane

Compare to cis-1,2-dimethylcyclohexane

*chair-flip conformations of substituted cyclohexanes often have different energies*

*substituents prefer the equatorial orientation to prevent 1,3-diaxial interactions which lead to steric strain*
consider cis-1-ethyl-4-methylcyclohexane

\[ \text{Cis-1-ethyl-4-methylcyclohexane} \]

\[ 
\text{cis-1-ethyl-4-methylcyclohexane} 
\]

consider cis-1-chloro-3-ethylcyclohexane

\[ \text{cis-1-chloro-3-ethylcyclohexane} \]

\[ \text{cis-1-chloro-3-ethylcyclohexane} \]

• **NOTE:** both chair conformations are the same molecule in all cases. They are simply conformations!
• **DO NOT** transform cis– to trans– via a chair chair flip! This does NOT happen!

---

name:

\[ \text{name} \]

\[ \text{name} \]

consider the following molecule:

\[ \text{consider the following molecule:} \]

A. Draw the two chair conformations for this molecule

\[ \text{A. Draw the two chair conformations for this molecule} \]

B. Which chair form is most stable?

C. Draw the chair form (and the flat structure) corresponding to the most thermodynamically stable isomer of this compound:

\[ \text{B. Which chair form is most stable?} \]

\[ \text{C. Draw the chair form (and the flat structure) corresponding to the most thermodynamically stable isomer of this compound:} \]

\[ P: 4.31, 4.35, 4.49, 4.53-4.55, 4.57, 4.61, 4.66, 4.69, 4.70 \]