Alkanes and Cycloalkanes

Structure

- **Hydrocarbon**: A compound composed only of carbon and hydrogen.
- **Saturated hydrocarbon**: A hydrocarbon containing only single bonds.
- **Alkane**: A saturated hydrocarbon whose carbons are arranged in an open chain.
- **Aliphatic hydrocarbon**: Another name for an alkane.
Hydrocarbons

<table>
<thead>
<tr>
<th>Class</th>
<th>Example</th>
<th>Name</th>
<th>Carbon-carbon bonding</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>H-C-C-H</td>
<td>Ethane</td>
<td>Only carbon single bonds</td>
<td>Shape: tetrahedral about carbon, all bond angles are approximately 109.5°</td>
</tr>
<tr>
<td>Alkenes</td>
<td>H=C=C-H</td>
<td>Ethene (Ethylene)</td>
<td>One or more carbon-carbon double bonds</td>
<td></td>
</tr>
<tr>
<td>Alkynes</td>
<td>H-C≡C-H</td>
<td>Ethyne (Acetylene)</td>
<td>One or more carbon-carbon triple bonds</td>
<td></td>
</tr>
<tr>
<td>Arenes</td>
<td><a href="image">Benzene</a></td>
<td>One or more benzenelike rings</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Structure

- Shape
  - tetrahedral about carbon
  - all bond angles are approximately 109.5°
Drawing Alkanes

- Line-angle formulas:
  - an abbreviated way to draw structural formulas.
  - each vertex and line ending represents a carbon.

<table>
<thead>
<tr>
<th>Ball-and-stick model</th>
<th>Line-angle formula</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Ball-and-stick model" /></td>
<td><img src="image2" alt="Line-angle formula" /></td>
<td><img src="image3" alt="Structural formula" /></td>
</tr>
</tbody>
</table>

- $\text{CH}_3\text{CH}_2\text{CH}_3$ (Propane)
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (Butane)
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (Pentane)

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Constitutional isomers: Compounds with the same molecular formula but a different connectivity of their atoms.

- example: $C_4H_{10}$

$\text{(CH}_3\text{)}_2\text{CHCH}_2\text{CH}_3$

\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{Butane} \\
\text{bp} -0.5^\circ\text{C} \\
\text{CH}_3\text{CH}_2\text{CHCH}_3 & \quad \text{2-Methylpropane} \\
\text{bp} -11.6^\circ\text{C}
\end{align*}
Nomenclature IUPAC

• Suffix -ane specifies an alkane, e.g. ethane.
• Prefix tells the number of carbon atoms.

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Number of carbons</th>
<th>Prefix</th>
<th>Number of carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>meth-</td>
<td>1</td>
<td>undec-</td>
<td>11</td>
</tr>
<tr>
<td>eth-</td>
<td>2</td>
<td>dodec-</td>
<td>12</td>
</tr>
<tr>
<td>prop-</td>
<td>3</td>
<td>tridec-</td>
<td>13</td>
</tr>
<tr>
<td>but-</td>
<td>4</td>
<td>tetradec-</td>
<td>14</td>
</tr>
<tr>
<td>pent-</td>
<td>5</td>
<td>pentadec-</td>
<td>15</td>
</tr>
<tr>
<td>hex-</td>
<td>6</td>
<td>hexadec-</td>
<td>16</td>
</tr>
<tr>
<td>hept-</td>
<td>7</td>
<td>heptadec-</td>
<td>17</td>
</tr>
<tr>
<td>oct-</td>
<td>8</td>
<td>octadec-</td>
<td>18</td>
</tr>
<tr>
<td>non-</td>
<td>9</td>
<td>nonadec-</td>
<td>19</td>
</tr>
<tr>
<td>dec-</td>
<td>10</td>
<td>eicos-</td>
<td>20</td>
</tr>
</tbody>
</table>

Commit to Memory

Nomenclature IUPAC

• Parent name: The longest carbon chain.
• Substituent: A group bonded to the parent chain.
  – Alkyl group: A substituent derived by removal of a hydrogen from an alkane; given the symbol R-.

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Name</th>
<th>Alkyl group</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_4</td>
<td>Methane</td>
<td>CH_3-</td>
<td>Methyl group</td>
</tr>
<tr>
<td>CH_3CH_3</td>
<td>Ethane</td>
<td>CH_3CH_2-</td>
<td>Ethyl group</td>
</tr>
</tbody>
</table>
1. The name of a saturated hydrocarbon with an unbranched chain consists of a prefix and suffix.
2. The parent chain is the longest chain of carbon atoms.
3. Each substituent is given a name and a number. Use a hyphen to connect the number to the name.

```
CH3
CH3 CH2 CH3
1 2 3
2-Methylpropane
```

4. If there is one substituent, number the chain from the end that gives it the lower number.

```
CH3
CH3 CH2 CH2 CH CH3
5 4 3 2 1
2-Methylpentane (not 4-methylpentane)
```

5. If there are two or more identical substituents, number the chain from the end that gives the lower number to the substituent encountered first. Indicate the number of times the substituent appears by a prefix di-, tri-, tetra-, etc. Use commas to separate position numbers.

```
6 5 4 3 2 1
2,4-Dimethylhexane (not 3,5-dimethylhexane)
```
6. If there are two or more different substituents,
   – list them in alphabetical order.
   – number from the end of the chain that gives
     the substituent encountered first the lower
     number.

3-Ethyl-5-methylheptane  (not 3-methyl-5-ethylheptane)

7. The prefixes di-, tri-, tetra-, etc.
   are not included in alphabetization.
   Alphabetize the names of substituents
   first and then insert these prefixes.

4-Ethyl-2,2-dimethylhexane  (not 2,2-dimethyl-4-ethylhexane)
Nomenclature - IUPAC

• Alkyl groups

<table>
<thead>
<tr>
<th>Name</th>
<th>Condensed Structural Formula</th>
<th>Name</th>
<th>Condensed Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>-CH₃</td>
<td>butyl</td>
<td>-CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>ethyl</td>
<td>-CH₂CH₃</td>
<td>2-methylpropyl (isobutyl)</td>
<td>-CH₂CHCH₃CH₃</td>
</tr>
<tr>
<td>propyl</td>
<td>-CH₂CH₂CH₃</td>
<td>1-methylpropyl (sec-butyl)</td>
<td>-CHCH₂CH₃CH₃</td>
</tr>
<tr>
<td>1-methylethyl (isopropyl)</td>
<td>-CHCH₃CH₃</td>
<td>1,1-dimethylethyl (tert-butyl)</td>
<td>-CH₂CH₂CH₃CH₃</td>
</tr>
</tbody>
</table>

Nomenclature - Common

• The number of carbons in the alkane determines the name.
  – All alkanes with four carbons are butanes, those with five carbons are pentanes, etc.
  – iso- indicates the chain terminates in -CH(CH₃)₂; neo- that it terminates in -C(CH₃)₃.
Classification of C & H

Primary (1°) C: A carbon bonded to one other carbon.
   1° H: a hydrogen bonded to a 1° carbon
Secondary (2°) C: A carbon bonded to two other carbons.
   2° H: a hydrogen bonded to a 2° carbon
Tertiary (3°) C: A carbon bonded to three other carbons.
   3° H: a hydrogen bonded to a 3° carbon
Quaternary (4°) C: A carbon bonded to four other carbons.

IUPAC - General

- prefix-infix-suffix
  - Prefix: Tells the number of carbon atoms in the parent chain.
  - Infix: Tells the nature of the carbon-carbon bonds in the parent chain.
  - Suffix: Tells the class of the compound.

<table>
<thead>
<tr>
<th>Infix</th>
<th>Nature of Carbon-Carbon Bonds in the Parent Chain</th>
<th>Suffix</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>-an-</td>
<td>all single bonds</td>
<td>-e</td>
<td>hydrocarbon</td>
</tr>
<tr>
<td>-en-</td>
<td>one or more double bonds</td>
<td>-ol</td>
<td>alcohol</td>
</tr>
<tr>
<td>-yn-</td>
<td>one or more triple bonds</td>
<td>-al</td>
<td>aldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-amine</td>
<td>amine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-one</td>
<td>ketone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-oic acid</td>
<td>carboxylic acid</td>
</tr>
</tbody>
</table>
IUPAC - General

prop-en-e = propene \( \text{CH}_3\text{CH}=\text{CH}_2 \)
eth-an-o1 = ethanol \( \text{CH}_3\text{CH}_2\text{OH} \)
but-an-one = butanone \( \text{CH}_3\text{CCH}_2\text{CH}_3 \)
but-an-al = butanal \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} \)
pent-an-oic acid = pentanoic acid \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COH} \)
cyclohex-an-o1 = cyclohexanol
eth-yn-e = ethyne \( \text{HC}≡\text{CH} \)
eth-an-amine = ethanamine \( \text{CH}_3\text{CH}_2\text{NH}_2 \)

Cycloalkanes

• General formula \( \text{C}_n\text{H}_{2n} \)
  – Five- and six-membered rings are the most common.
• Structure and nomenclature
  – Add the prefix cyclo- to the name of the open-chain alkane containing the same number of carbons.
  – If only one substituent, no need to give it a number.
  – If two substituents, number from the substituent of lower alphabetical order.
  – If three or more substituents, number to give them the lowest set of numbers and then list substituents in alphabetical order.
Cycloalkanes

- Line-angle drawings
  - Each line represents a C-C bond.
  - Each vertices and line ending represents a C.

- Most common are 5 & 6 member rings

- Cyclopentane
- Cyclohexane
Conformation: Any three-dimensional arrangement of atoms in a molecule that results from rotation about a single bond.

- Staggered conformation: A conformation about a carbon-carbon single bond in which the atoms or groups on one carbon are as far apart as possible from the atoms or groups on an adjacent carbon.
- Newman projection: A way to view a molecule by looking along a carbon-carbon single bond.
Eclipsed conformation: A conformation about a carbon-carbon single bond in which the atoms or groups of atoms on one carbon are as close as possible to the atoms or groups of atoms on an adjacent carbon.

- **Torsional strain**
  - strain that arises when nonbonded atoms separated by three bonds are forced from a staggered conformation to an eclipsed conformation.
  - also called eclipsed interaction strain.
  - the torsional strain between eclipsed and staggered ethane is approximately 12.6 kJ (3.0 kcal)/mol.
• Dihedral angle \( \Theta \) (Greek theta): The angle created by two intersecting planes.

Conformations

• Figure 2.8 The energy of ethane as a function of dihedral angle.
Conformations

- Strain energy is the increase in energy resulting from distortion of bond angles and bond lengths from their optimal values.
- Steric strain (nonbonded interaction strain): The strain that arises when nonbonded atoms separated by four or more bonds are forced closer to each other than their atomic (contact) radii will allow.
- Angle strain: Strain that arises when a bond angle is either compressed or expanded compared to its optimal value.

Conformations

Anti conformation: A conformation about a single bond in which the groups on adjacent carbons lie at a dihedral angle of $180^\circ$. 

![Chemical structures showing anti conformation](image.png)
**Anti Butane**

Energy-minimized anti conformation (computed)
the C-C-C bond angle is 111.9° and all H-C-H bond angles are between 107.4° and 107.9°.
the calculated strain is 9.2 kJ (2.2 kcal)/mol.

**Eclipsed Butane**

The calculated energy difference between (a) the non-energy-minimized and (b) the energy-minimized eclipsed conformations is 5.6 kJ (0.86 kcal)/mol.
Gauche Butane

Gauche conformation: A conformation about a single bond of an alkane in which two groups on adjacent carbons lie at a dihedral angle of 60°.

Here is one of two energy-minimized gauche conformations of butane. The second one has equal energy.

Conformations

The energy of butane as a function of the dihedral angle about the bond between carbons 2 and 3.
**Cyclopentane**

- Puckering from planar cyclopentane reduces torsional strain, but increases angle strain.
- The conformation of minimum energy is a puckered “envelope” conformation.
- Strain energy is about 42 kJ (6.5 kcal)/mol.

**Cyclohexane**

- Chair conformation: The most stable puckered conformation of a cyclohexane ring.
  - All bond C-C-C bond angles are 110.9°.
  - All bonds on adjacent carbons are staggered.
• In a chair conformation, six H are equatorial and six are axial.

• For cyclohexane, there are two equivalent chair conformations.
  – all C-H bonds equatorial in one chair are axial in the alternative chair and vice versa.
**Cyclohexane**

- **Boat conformation**: A puckered conformation of a cyclohexane ring in which carbons 1 and 4 are bent toward each other.
  - There are four sets of eclipsed C-H interactions and one flagpole interaction (flagpole H green).
  - A boat conformation is less stable than a chair conformation by 27 kJ (6.5 kcal)/mol.

- **Twist-boat conformation**
  - Approximately 41.8 kJ (5.5 kcal)/mol less stable than a chair conformation.
  - Approximately 6.3 kJ (1.5 kcal)/mol more stable than a boat conformation.
Cyclohexane

- Energy diagram for the interconversion of chair, twist-boat and boat conformations of cyclohexane.

Cis, Trans Isomerism

Stereoisomers: Compounds that have
the same molecular formula.
the same connectivity.
a different orientation of their atoms in space.

Cis, trans isomers: Stereoisomers that are
the result of the presence of either a ring
(this chapter) or a carbon-carbon double bond (Chapter 5).
Isomers

Different compounds with the same molecular formula

Constitutional isomers
Different compounds with the same molecular formula but a different connectivity

Stereoisomers
Different compounds with the same molecular formula, the same connectivity, but a different orientation of their atoms in space

Cis, Trans Isomerism

• 1,2-Dimethylcyclopentane

\[ cis-1,2- \text{Dimethylcyclopentane} \]
\[ trans-1,2- \text{Dimethylcyclopentane} \]
**Stereocenter:** An atom, most commonly carbon, about which exchange of two groups produces a different stereoisomer.

example: 1,2-dimethylcyclobutane has two stereocenters.

**Configuration:** Refers to the arrangement of atoms about stereocenter.

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**Cis,Trans Isomerism**

- 1,4-Dimethylcyclohexane

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

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

The more stable chair conformation of each isomer
**Cis, Trans Isomerism**

- *trans*-1,4-Dimethylcyclohexane
  - the diequatorial-methyl chair conformation is more stable by approximately $2 \times (7.28) = 14.56 \text{ kJ/mol}$

- *cis*-1,4-Dimethylcyclohexane
  - conformations are of equal stability
Physical Properties of Alkanes

Intermolecular forces of attraction (example)
- ion-ion (Na⁺ and Cl⁻ in NaCl)
- ion-dipole (Na⁺⋯OH₂ and Cl⁻⋯H-O-H solvated in aqueous solution)
- dipole-dipole and hydrogen bonding
- dispersion forces (very weak electrostatic attraction between temporary dipoles)

Low-molecular-weight alkanes (methane to butane) are gases at room temperature.
Higher molecular-weight alkanes (pentane, decane, gasoline, and kerosene) are liquids at room temperature.
High-molecular-weight alkanes (paraffin wax) are semisolids or solids at room temperature.
Constitutional isomers have different physical properties.

<table>
<thead>
<tr>
<th>Name</th>
<th>mp (°C)</th>
<th>bp (°C)</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>-95</td>
<td>68.7</td>
<td>0.659</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>-154</td>
<td>60.3</td>
<td>0.653</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>-118</td>
<td>63.3</td>
<td>0.664</td>
</tr>
<tr>
<td>2,3-dimethylbutane</td>
<td>-129</td>
<td>58.0</td>
<td>0.661</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>-98</td>
<td>49.7</td>
<td>0.649</td>
</tr>
</tbody>
</table>

Oxidation of Alkanes

Oxidation is the basis for the use of alkanes as energy sources for heat and power.

heat of combustion: The heat released when one mole of a substance in its standard state is oxidized to carbon dioxide and water.

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} & \Delta H^0 &= -890.4 \text{ (kcal/mol)} \\
\text{CH}_3\text{CH}_2\text{CH}_3 + 5\text{O}_2 & \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} & \Delta H^0 &= -2220 \text{ (kcal/mol)}
\end{align*}
\]