Alkyl Groups

The IUPAC system uses a short list of the alkyl groups normally found in organic molecules:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3 - \\
\text{Methane} & \rightarrow \text{Methyl} \\
\text{CH}_3 - \text{CH}_2 & \rightarrow \text{CH}_3 - \text{CH}_2 - \\
\text{Ethane} & \rightarrow \text{Ethyl} \\
\text{CH}_3 - \text{CH}_2 - \text{CH}_3 & \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_3 - \\
\text{Propene} & \rightarrow \text{Propyl} \\
\text{CH}_3 - \text{CH} - \text{CH}_3 & \rightarrow \text{Isopropyl} \\
\end{align*}
\]
In organic chemistry, molecules are often written in the generalized form: R-X, where R represents an alkyl group and X represents an attached substituent: -H, -OH, -Cl, etc.
NAMING ALKANES

IUPAC Nomenclature System

1. The name of the longest continuous chain becomes the base, or parent name of the compound. The suffix (ending) of the family name is added to the end of this base name. Note that, even if the subsequent rules are correctly applied, a failure to correctly identify the longest continuous chain will result in an incorrect name for the compound.

2. The base name accounts only for the carbons in the longest continuous chain. The carbons that are not part of the longest continuous chain—those attached as branches to the longest continuous chain and called substituents or groups—also must be included in the name. Substituents are included as follows:
   a. The name(s) of any alkyl group(s) in the compound is placed in front of the base name.
   b. Use the prefixes di-, tri-, tetra-, penta-, and hexa- before the name of the alkyl group when there are two, three, four, five, or six, respectively, of the same group.
   c. Alphabetize the names of alkyl groups when there are two or more different types of groups. Ignore all prefixes (both the branching prefixes e- and t- and the multiplying prefixes such as di-, tri-, and tetra-) in alphabetizing, with one exception: iso- is not ignored in alphabetizing.

3. Number the carbons in the longest continuous chain, starting from whichever end will result in the lowest number (or set of lowest numbers) for the alkyl group(s). An alternate rule is useful for most compounds: Number from the end nearest a branch.

4. In front of the name of each alkyl group, place the number of the carbon to which the group is attached.

5. Use hyphens to separate numbers from words; use commas to separate numbers.

Two different-looking structural formulas of the same compound will yield the same name if the nomenclature rules are correctly applied.
NAMING ALKANES

Example 11.6  Using the IUPAC nomenclature system to name alkanes: I

Give the IUPAC name for the following compound:

\[
\begin{align*}
\text{CH}_3 \\
| \\
\text{CH} \longrightarrow \text{CH}_3 \\
| \\
\text{CH}_3 \text{CH}_2 \text{CH}_3 \text{CH} \longrightarrow \text{CH} \longrightarrow \text{CH}_3 \\
| \\
\text{CH}_2 \\
| \\
\text{CH}_3
\end{align*}
\]

Solution

\[
\begin{align*}
\text{CH}_3 \\
| \\
\text{CH} \longrightarrow \text{CH}_3 \\
\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \longrightarrow \text{CH} \longrightarrow \text{CH}_3 \\
\text{CH}_2 \\
\text{CH}_3
\end{align*}
\]

NAMING ALKANES

Solution

\[
\begin{align*}
\text{CH}_3 \\
| \\
\text{CH} \longrightarrow \text{CH}_3 \\
\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH} \longrightarrow \text{CH} \longrightarrow \text{CH}_3 \\
\text{CH}_2 \\
\text{CH}_3
\end{align*}
\]

- Numbers for location of alkyl groups
- Family
- Base name
- Alkyl groups on longest chain
- Longest chain
Alkanes are acyclic or open-chain molecules.

Cycloalkanes differ only in that they possess a cyclic chain of 3 or more carbon atoms. Cycloalkanes and alkanes constitute the saturated hydrocarbons.
Cycloalkanes are often represented by a condensed structural formula in the form of a geometrical shape:

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular formula</th>
<th>Expanded*</th>
<th>Condensed</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopropane</td>
<td>C₃H₆</td>
<td>H₂</td>
<td>H₂</td>
<td>35</td>
</tr>
<tr>
<td>cyclobutane</td>
<td>C₄H₈</td>
<td>H₂</td>
<td>H₂</td>
<td>12</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>C₅H₁₀</td>
<td>H₂</td>
<td>H₂</td>
<td>49</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>C₆H₁₂</td>
<td>H₂</td>
<td>H₂</td>
<td>81</td>
</tr>
<tr>
<td>cycloheptane</td>
<td>C₇H₁₄</td>
<td>H₂</td>
<td>H₂</td>
<td>119</td>
</tr>
</tbody>
</table>

* Chains are not expanded.

The general molecular formula for a cycloalkane is CₙH₂ₙ. This formula contains two fewer hydrogen atoms than an ordinary alkane, CₙH₂ₙ₊₂.
Cycloalkanes

1. The base name of the ring structure consists of the prefix cyclo- followed, without hyphen or space, by the name of the straight-chain alkane that has the same number of carbons.

2. The names of substituents are placed in front of the base name. Numbers indicate the placement of substituents on the ring. The numbering of the ring carbons starts with a carbon holding a substituent and moves around the ring from there. When different sets of numbers can be obtained by starting at different carbons or counting in different directions, the correct name is the one with the set of lowest numbers.

Example 11.8 Using the IUPAC nomenclature system to name cycloalkanes

Give the IUPAC name for the following compound:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \\
\text{CH}_3\text{CH}_2\text{CH}_2
\end{align*}
\]
Naming Alkyl Halides

The prefixes fluoro-, chloro-, bromo- and iodo- are added to an alkane to name the corresponding halo-alkane.

In the common nomenclature system, the prefix is added to the name of the alkyl group, followed by the suffix –ide.

Example 11.16 Naming alkyl halides

Give the IUPAC and common names for the following alkyl halides:

(a) \( \text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—Cl} \)

(b) \( \text{CH}_3\text{—CH—CH—CH}_2\text{—CH}_3 \)
The C-C bonds in cycloalkanes are not free to rotate relative to each other. They are said to have restricted rotation.

Because of restricted rotation, cycloalkanes possess another type of isomerism, geometrical or cis-trans, stereoisomerism.

Cycloalkanes possess constitutional isomers of the same formula.

For \( \text{C}_5\text{H}_{10} \):

Note that the number 1 is not required in methylcyclobutane and ethylcyclopropane. Use the number 1 only when there are two or more substituents attached to the ring.
When examining the conformational isomers of $\text{C}_5\text{H}_{10}$, there are actually six distinct structures rather than five:

- Cyclopanene
- Methylcyclohexane
- 1,2-Dimethylcyclopropane
- $\text{CH}_3\text{CH}$
- $\text{CH}_3\text{CH}_2\text{H}$

These two structures are geometric, or cis-trans isomers of each other.

Stereoisomerism results from differences in configuration, not connectivity.

Cis-trans stereoisomers have two similar substituents on the same side of the ring. Trans stereoisomers have two similar substituents on opposite sides of the ring.

Cis-trans isomers are often called diastereomers to distinguish them from another type of stereoisomers called enantiomers.

Cis and trans isomers are different compounds with different chemical and physical properties.

Cis and trans isomers are not easily interconvertible because the C-C bonds within the ring are not free to rotate.
Conformations of Alkanes

- Ethane
  - Staggered conformation
  - Newman projection:

\[ \theta = 60^\circ \]

CIS-TRANS STEREOISOMERISM IN CYCLOALKANES

Geometrical isomers are possible only when two of the ring atoms are stereocenters—that is, two ring atoms each bear two different substituents.
Conformations of Alkanes

• Ethane
  – Eclipsed conformation
  – Newman projection:

  ~3 kcal/mole higher in energy than staggered conformation

Conformations of Alkanes

• Butane

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$E_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$180^\circ$</td>
<td>0 kcal/mol</td>
</tr>
<tr>
<td>$120^\circ$</td>
<td>3.4 kcal/mol</td>
</tr>
<tr>
<td>$60^\circ$</td>
<td>0.9 kcal/mol</td>
</tr>
<tr>
<td>$0^\circ$</td>
<td>6.1 kcal/mol</td>
</tr>
</tbody>
</table>
Conformations of Alkanes

• Cyclohexane
  – “Chair” conformation

Conformations of Alkanes

• Cyclohexane
  – “Chair” conformation

Equatorial hydrogens

Equatorial hydrogens
Conformations of Alkanes

• Cyclohexane
  – “Chair” conformation

Conformations of Alkanes

• Cyclohexane
  – “Boat” conformation
Conformations of Alkanes

• Cyclohexane
  – “Boat” conformation

Eclipsing

Steric interactions
Conformations of Alkanes

- Cyclohexane
  - “Twist-boat” conformation
  - “Half-chair” conformation

Conformations of Cyclohexane

\[ E \]
Conformations of Substituted Cyclohexanes

• Monosubstituted Cyclohexanes
  – Methylcyclohexane

Conformations of Substituted Cyclohexanes

• Monosubstituted Cyclohexanes
  – Methylcyclohexane

Equatorial methyl group

Axial methyl group
Conformations of Substituted Cyclohexanes

• Monosubstituted Cyclohexanes
  – Methylcyclohexane

Steric interactions

more stable

Copyright © 2010 Pearson Education, Inc.