V. Alkanes
   A. Properties
   B. Reactivity
   C. Uses
   D. Structure and Isomerism
   E. Nomenclature
      1. Straight chain alkanes
      2. Alkyl groups
      3. ‘R’
      4. Classifying sp³ atoms
      5. Branched alkanes
   F. Stereochemistry
      1. Representing Molecules in 3D
      2. Conformational Analysis
         a. Ethane
         b. Propane
         c. Butane

Suggesting reading for Friday and Wednesday: Chapters 3 & 4

A. Properties

Hydrocarbon - molecule with only C-C and C-H bonds

Alkane - hydrocarbon with only single bonds

\[ C_nH_{2n+2} \]
(sp³, 109.5° bond angles, \( \square \) bonds)

“saturated hydrocarbon” - maximum number of C-H bonds

\[
\begin{align*}
\text{saturated} & \quad \text{H}_2, \text{cat.} & \quad \text{no reaction} \\
\text{unsaturated} & \quad \text{H}_2, \text{cat.} & \quad \text{H} \\
\end{align*}
\]

“aliphatic” - fat (saturated fats vs. unsaturated fats)
B. Reactivity

- C-C, C-H bond very stable
- No functional groups
- Generally unreactive

Reactions that alkanes can undergo:

1. **Halogenation**
   \[ \text{CH}_4 + \text{Cl}_2 \xrightarrow{h\text{[i]}} \text{CH}_3\text{Cl} + \text{HCl} \]

2. **Combustion**
   \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{heat} \]

C. Uses

1. **Energy Source (natural gas & petroleum)**
   
   methane = 75% world’s natural gas (20% from animals!)

2. **Parts of Other Molecules**
   
   a. Waxes
   
   b. Lipids (fats - principle form of stored energy in body)

   "burn fat" - covert alkanes to CO\(_2\) (exhale) and H\(_2\)O (urine)

   9 kcal released per fat gram
D. Structure

<table>
<thead>
<tr>
<th># Carbon</th>
<th>$\text{C}<em>n\text{H}</em>{2n+2}$</th>
<th>Structure</th>
</tr>
</thead>
</table>
| 1        | CH$_4$          | \[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\] |
| 2        | C$_2$H$_6$      | \[
\text{H}_3\text{C} \quad \text{CH}_3
\] |
| 3        | C$_3$H$_8$      | \[
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3
\] |
| 4        | C$_4$H$_{10}$   | \[
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3
\] |
| 5        | C$_5$H$_{12}$   | \[
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3
\] |

Straight chain alkanes “normal (n)”  | Branched alkanes

Content removed due to copyright reasons.
D. Isomerism

Isomers - structures with the same molecular formula but different arrangement of atoms

Constitutional Isomers - isomers that differ in atom connectivity

The number of possible constitutional drastically increases with the number of carbon atoms!

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th># Constitutional Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₆</td>
<td>1</td>
</tr>
<tr>
<td>C₃H₁₂</td>
<td>3</td>
</tr>
<tr>
<td>C₁₀H₂₂</td>
<td>75</td>
</tr>
<tr>
<td>C₁₅H₃₂</td>
<td>4347</td>
</tr>
<tr>
<td>C₂₀H₄₂</td>
<td>366,319</td>
</tr>
</tbody>
</table>

E1. Nomenclature Straight Chain Alkanes

Prefix - Parent - Suffix

Alkane: suffix “-ane”

<table>
<thead>
<tr>
<th>CₙH₂ₙ₊₂</th>
<th>n-Alkane</th>
<th>CₙH₂ₙ₊₂</th>
<th>n-Alkane</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>methane</td>
<td>C₇H₁₆</td>
<td>heptane</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>ethane</td>
<td>C₈H₁₈</td>
<td>octane</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>propane</td>
<td>C₉H₂₀</td>
<td>nonane</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>butane</td>
<td>C₁₀H₂₂</td>
<td>decane</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>pentane</td>
<td>C₁₁H₂₄</td>
<td>undecane</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>hexane</td>
<td>C₁₂H₂₆</td>
<td>dodecane</td>
</tr>
</tbody>
</table>
Alkyl group - name for an alkane when it is a component of a larger molecule

a. Straight Chain Alkyl Groups

- “Pentyl”
  Pentane with 1 hydrogen atom removed
  To name: replace “-ane” with “yl”

b. Branched Alkyl Groups

- iso (i) 2 methyl groups on terminal carbon
- neo 3 methyl groups on terminal carbon
- sec attached carbon also connected to 2 other carbon atoms
- tert (t) attached carbon also connected to 3 other carbon atoms

### Nomenclature of Straight-Chain Alkanes

<table>
<thead>
<tr>
<th>$C_nH_{2n+2}$</th>
<th>n-Alkane</th>
<th>Alkyl Subst.</th>
<th>Alkyl Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>methane</td>
<td>-CH₃ (-Me)</td>
<td>methyl</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>ethane</td>
<td>-C₂H₅ (-Et)</td>
<td>ethyl</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>propane</td>
<td>-C₃H₇ (-n-Pr)</td>
<td>propyl</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>butane</td>
<td>-C₄H₉ (-n-Bu)</td>
<td>butyl</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>pentane</td>
<td>-C₅H₁₁</td>
<td>pentyl</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>hexane</td>
<td>-C₆H₁₃</td>
<td>hexyl</td>
</tr>
<tr>
<td>C₇H₁₆</td>
<td>heptane</td>
<td>-C₇H₁₅</td>
<td>heptyl</td>
</tr>
<tr>
<td>C₈H₁₈</td>
<td>octane</td>
<td>-C₈H₁₇</td>
<td>octyl</td>
</tr>
<tr>
<td>C₉H₂₀</td>
<td>nonane</td>
<td>-C₉H₁₉</td>
<td>nonyl</td>
</tr>
<tr>
<td>C₁₀H₂₂</td>
<td>decane</td>
<td>-C₁₀H₂₁</td>
<td>decyl</td>
</tr>
<tr>
<td>C₁₁H₂₄</td>
<td>undecane</td>
<td>-C₁₁H₂₃</td>
<td>undecyl</td>
</tr>
<tr>
<td>C₁₂H₂₆</td>
<td>dodecane</td>
<td>-C₁₂H₂₅</td>
<td>dodecyl</td>
</tr>
</tbody>
</table>
### Nomenclature for Branched Alkyl Groups

<table>
<thead>
<tr>
<th>Iso</th>
<th>Neo</th>
<th>Sec</th>
<th>Tert</th>
</tr>
</thead>
</table>
| iso-
\[
\begin{align*}
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{i}-\text{Pr} &
\end{align*}
\]
| neopentyl
\[
\begin{align*}
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{s}-\text{Bu} &
\end{align*}
\]
| sec-butyl
\[
\begin{align*}
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{t}-\text{Bu} &
\end{align*}
\]
| tert-butyl
\[
\begin{align*}
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{H}_2\text{C} - & \text{C} - \text{CH}_3 \\
\text{CH}_3 & \\
\text{t}-\text{Bu} &
\end{align*}
\]

**isopropyl**

**neopentyl**

**sec-butyl**

**tert-butyl**

**s-butyl**

**i-Pr**

**neohexyl**

**tert-pentyl**

**t-pentyl**

---

**E3. ‘R’**

‘R’ - generic group (rest of the molecule)

\[
\begin{align*}
\text{H}_3\text{C} & \text{OH} = \text{R-OH} \\
\text{H}_2\text{C} & \text{O} - \text{CH}_3 \\
\text{H}_2\text{C} & \text{O} - \text{CH}_3 \\
\text{CH}_2\text{CH}_3 & \text{OH} \\
\text{R} & \text{O} - \text{R} \\
\text{R}' & \text{O} - \text{R}^* \\
\text{R} & \text{O} - \text{R}^*
\end{align*}
\]

---

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E4. Classifying sp³ Atoms by Connectivity I

**sp³ C by C-C connectivity**

<table>
<thead>
<tr>
<th>R</th>
<th>R</th>
<th>R</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—C—H</td>
<td>R—C—H</td>
<td>R—C—R</td>
<td>R—C—R</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

primary carbon  
secondary carbon  
tertiary carbon  
quaternary carbon

**alcohols and halides by C-C connectivity**

<table>
<thead>
<tr>
<th>R</th>
<th>R</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—C—OH</td>
<td>R—C—OH</td>
<td>R—C—OH</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

primary alcohol  
secondary alcohol  
tertiary alcohol

<table>
<thead>
<tr>
<th>R</th>
<th>R</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—C—X</td>
<td>R—C—X</td>
<td>R—C—X</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

primary halide  
secondary halide  
tertiary halide

X = F, Cl, Br, I

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---

E4. Classifying sp³ atoms by Connectivity II

**H by C-C connectivity**

<table>
<thead>
<tr>
<th>R</th>
<th>R</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>H—C—H</td>
<td>R—C—H</td>
<td>R—C—R</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

primary hydrogens  
secondary hydrogens  
tertiary hydrogen

**sp³ C by C-H connectivity**

<table>
<thead>
<tr>
<th>R</th>
<th>R</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—C—H</td>
<td>R—C—H</td>
<td>R—C—R</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

methane  
methyl  
methylene  
methine

**sp³ N by C-N connectivity**

<table>
<thead>
<tr>
<th>R</th>
<th>R</th>
<th>R</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>R—N—H</td>
<td>R—N—R</td>
<td>R—N—R</td>
<td>R—N⁺</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

primary amine  
secondary amine  
tertiary amine  
ammonium ion

1°  
2°  
3°  
4°

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E4. Examples of Classifying Atoms

- 2° carbon, methylene
- 2° hydrogens
- 1° carbon, methylene
- 1° hydrogens
- 1° halide

E5. Naming Branched Alkanes

1. Circle the longest carbon chain (watch for turning corners!)
   If 2 different chains of equal length are present, choose the one with the greater number of branch points
2. Number the atoms in the main chain, beginning at the end nearest to a branch
   If the first branch point occurs at the same carbon number on both ends, begin at the end that has the second nearest branch point
3. Identify and number the substituents
4. Write the name as a single word
   a. Combine identical substituents, using the prefixes di-, tri-, tetra-, etc.
      Ex. 2-methyl & 5-methyl = 2,5-dimethyl
   b. Put the substituents in alphabetical order
      di-, tri-, tetra-, sec-, tert- ignored when alphabetizing
      iso, neo are included when alphabetizing
   c. Use a hyphen between words and numbers and to separate prefixes
   d. Use a comma between numbers
F2a. Conformational Energy of Ethane

The energy changes continuously as a function of the torsion angle. We represent this on a plot called the potential energy diagram.

The length of time that a molecule resides in one conformational minimum is determined by the barrier height ($\Delta G^\neq$).

Figure removed due to copyright reasons.

Barrier to rotation = $E_{\text{highest}} - E_{\text{lowest}} = 2.9$ kcal/mol

Why is Staggered Form Lower in Energy?

One explanation for the lower energy of staggered ethane is that the staggered conformer is stabilized by hyperconjugation (stabilizing overlap between $\sigma_{\text{CH}}$ and $\sigma^*_{\text{CH}}$ orbitals that does not occur in the eclipsed conformer).

Hyperconjugation (staggered)  \(\equiv\)  (good overlap)

A second explanation for the lower energy of the staggered ethane conformer is that electron-electron repulsion between the C-H bonds is occurring in the eclipsed conformer (same principles as VSEPR theory), which destabilizes it.

Please see the following articles for further information:

and others . . .
For ethane, each conformational minimum has an identical structure, and thus, the same energy (all the stable conformers are equally populated). The situation is different for butane.

The conformational maxima and minima of butane have different energies!

Conformational Analysis Summary

Torsional energy - higher energy associated with eclipsed conformation
Torsional strain - resistance to rotating to an eclipsed conformation
  (eclipsed ethane is *torsionally strained* by 3 kcal/mol)

Steric strain - repulsive interaction that occurs when atoms are forced closer together than their atomic radii allow

Gauche - spatial relationship with a 60° torsion (dihedral) angle

Anti - spatial relationship with a 180° torsion angle

**Interactions**

- H-H eclipsing (torsional strain) 1.0 kcal/mol
- H-Me eclipsing (mostly torsional strain) 1.4 kcal/mol
- Me-Me eclipsing (steric and torsional strain) 2.6 kcal/mol
- Me-Me gauche interaction (steric strain) 0.9 kcal/mol