

5.12

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 sp^3 atoms
 - 5. Branched alkanes
- F. Stereochemistry
 - 1. Representing Molecules in 3D
 - 2. Conformational Analysis
 - a. Ethane
 - b. Propane
 - c. Butane

Pset #1 Due Tomorrow at 4:00!

Recitations finalized by Friday

Build a model of cyclohexane and bring it to class on Friday!

Undecane



Cockroach pheromone that causes the critters to aggregate

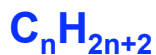
Suggesting reading for Friday and Wednesday: Chapters 3 & 4

Suggested problems: 3.29, 3.30, 3.32, 3.36, 3.37, 3.39, 3.43, 3.44, 3.45, 3.47, 3.48, 3.49, 3.50, 3.52-3.54, 3.57, 3.58, 4.24-4.29, 4.31-4.49, 4.52, 4.53, 4.55, 4.56

A. Properties

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

Alkane - hydrocarbon with only single bonds



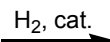
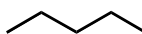
(sp^3 , 109.5° bond angles, \square bonds)

$C_{11}H_{24}$



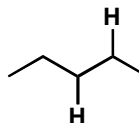
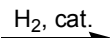
"saturated hydrocarbon" - maximum number of C-H bonds

saturated



no reaction

unsaturated



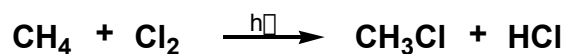
"aliphatic" - fat (saturated fats vs. unsaturated fats)

B. Reactivity

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

Reactions that alkanes can undergo:

1. Halogenation

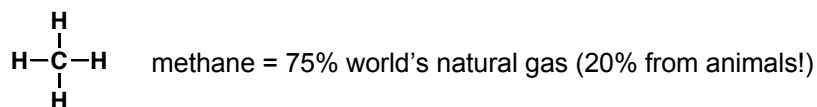


2. Combustion



C. Uses

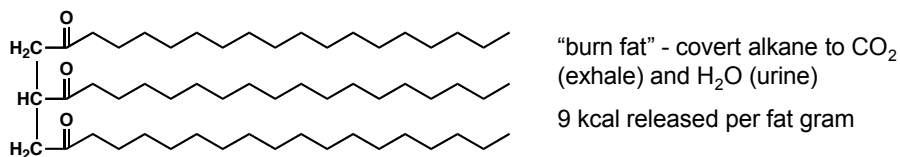
1. Energy Source (natural gas & petroleum)



2. Parts of Other Molecules

a. Waxes

b. Lipids (fats - principle form of stored energy in body)



Re-Moo-able Energy

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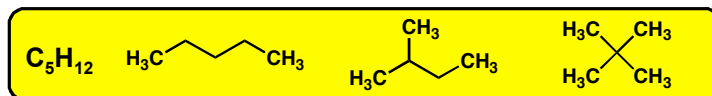
D. Structure

| # Carbon | C_nH_{2n+2} | Structure |
|----------|---------------|--|
| 1 | CH_4 | $\begin{array}{c} H \\ \\ H-C-H \\ \\ H \end{array}$ |
| 2 | C_2H_6 | H_3C-CH_3 |
| 3 | C_3H_8 | $H_3C-CH_2-CH_3$ |
| 4 | C_4H_{10} | $H_3C-CH_2-CH_2-CH_3$ $\begin{array}{c} H_3C \\ \\ CH_2-CH_3 \\ \\ H_3C \end{array}$ |
| 5 | C_5H_{12} | $H_3C-CH_2-CH_2-CH_2-CH_3$ $\begin{array}{c} CH_3 \\ \\ H_3C-CH-CH_2-CH_3 \\ \\ H_3C \end{array}$ $\begin{array}{c} H_3C \quad CH_3 \\ \diagdown \quad / \\ C \\ / \quad \diagdown \\ H_3C \quad CH_3 \end{array}$ |

Straight chain alkanes **Branched alkanes**
"normal (n)"

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 isomers increases drastically with the number of carbon atoms!

| Molecular Formula | # Constitutional Isomers |
|-------------------|--------------------------|
| C_2H_6 | 1 |
| C_5H_{12} | 3 |
| $C_{10}H_{22}$ | 75 |
| $C_{15}H_{32}$ | 4347 |
| $C_{20}H_{42}$ | 366,319 |

E1. Nomenclature Straight Chain Alkanes

Prefix - Parent - Suffix

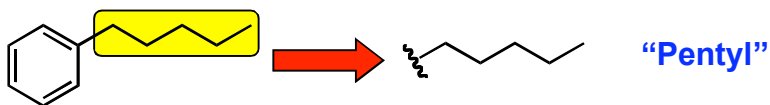
Alkane: suffix “-ane”

| | | | |
|---------------|------------------|----------------|------------------|
| C_nH_{2n+2} | <i>n</i> -Alkane | C_nH_{2n+2} | <i>n</i> -Alkane |
| CH_4 | methane | C_7H_{16} | heptane |
| C_2H_6 | ethane | C_8H_{18} | octane |
| C_3H_8 | propane | C_9H_{20} | nonane |
| C_4H_{10} | butane | $C_{10}H_{22}$ | decane |
| C_5H_{12} | pentane | $C_{11}H_{24}$ | undecane |
| C_6H_{14} | hexane | $C_{12}H_{26}$ | dodecane |

E2. Alkyl Groups

Alkyl group - name for an alkane when it is a component of a larger molecule

a. Straight Chain Alkyl Groups



Pentane with 1 hydrogen atom removed

To name: replace “-ane” with “yl”

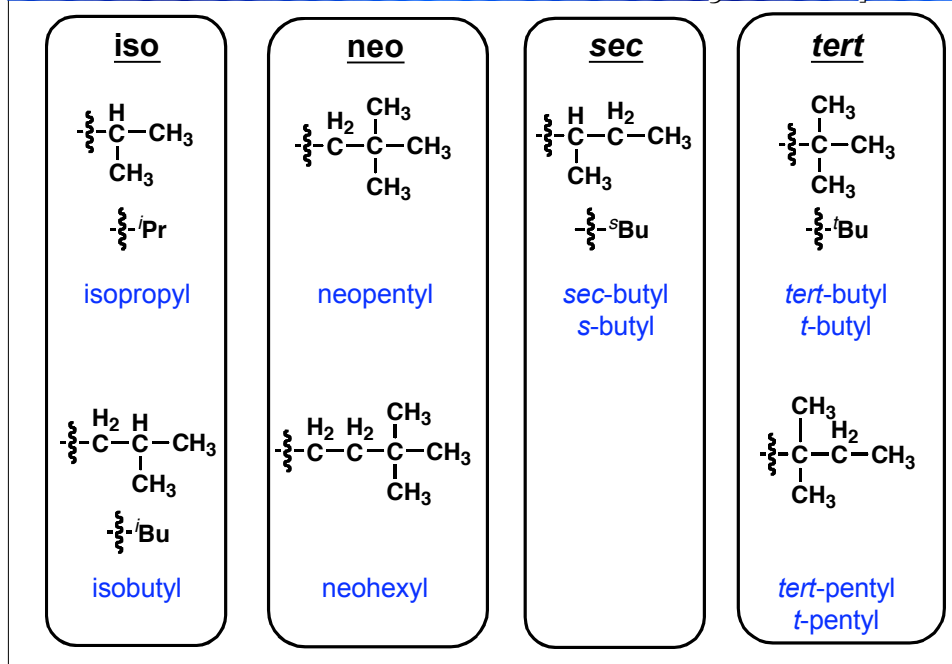
b. Branched Alkyl Groups

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

Nomenclature of Straight-Chain Alkanes

| C_nH_{2n+2} | <i>n</i> -Alkane | Alkyl Subst. | Alkyl Name |
|---------------------------------|------------------|--|------------|
| CH ₄ | methane | -CH ₃ (-Me) | methyl |
| C ₂ H ₆ | ethane | -C ₂ H ₅ (-Et) | ethyl |
| C ₃ H ₈ | propane | -C ₃ H ₇ (<i>n</i> -Pr) | propyl |
| C ₄ H ₁₀ | butane | -C ₄ H ₉ (<i>n</i> -Bu) | butyl |
| C ₅ H ₁₂ | pentane | -C ₅ H ₁₁ | pentyl |
| C ₆ H ₁₄ | hexane | -C ₆ H ₁₃ | hexyl |
| C ₇ H ₁₆ | heptane | -C ₇ H ₁₅ | heptyl |
| C ₈ H ₁₈ | octane | -C ₈ H ₁₇ | octyl |
| C ₉ H ₂₀ | nonane | -C ₉ H ₁₉ | nonyl |
| C ₁₀ H ₂₂ | decane | -C ₁₀ H ₂₁ | decyl |
| C ₁₁ H ₂₄ | undecane | -C ₁₁ H ₂₃ | undecyl |
| C ₁₂ H ₂₆ | dodecane | -C ₁₂ H ₂₅ | dodecyl |

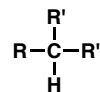
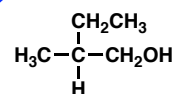
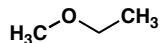
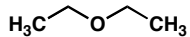
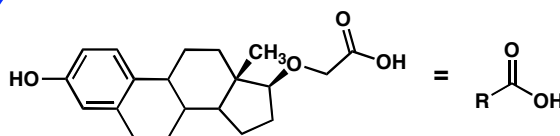
Nomenclature for Branched Alkyl Groups



Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign. Used with permission. Adapted by Kimberly Berkowski.

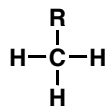
E3. 'R'

'R' - generic group (rest of the molecule)

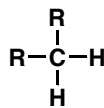


E4. Classifying sp^3 Atoms by Connectivity I

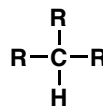
sp^3 C by C-C connectivity



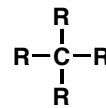
primary carbon
 1°



secondary carbon
 2°

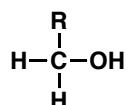


tertiary carbon
 3°

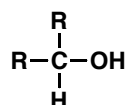


quaternary carbon
 4°

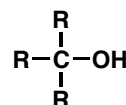
alcohols and halides by C-C connectivity



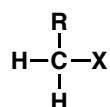
primary alcohol
 1°



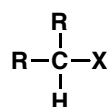
secondary alcohol
 2°



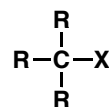
tertiary alcohol
 3°



primary halide
 1°



secondary halide
 2°



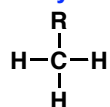
tertiary halide
 3°

X = F, Cl, Br, I

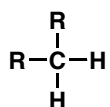
Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign. Used with permission. Adapted by Kimberly Berkowski.

E4. Classifying sp^3 atoms by Connectivity II

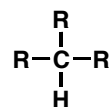
H by C-C connectivity



primary hydrogens
 1°

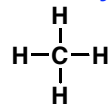


secondary hydrogens
 2°

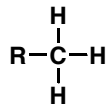


tertiary hydrogen
 3°

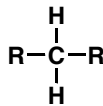
sp^3 C by C-H connectivity



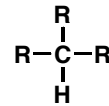
methane



methyl

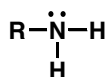


methylene

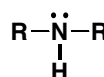


methine

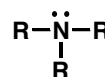
sp^3 N by C-N connectivity



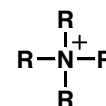
primary amine
 1°



secondary amine
 2°



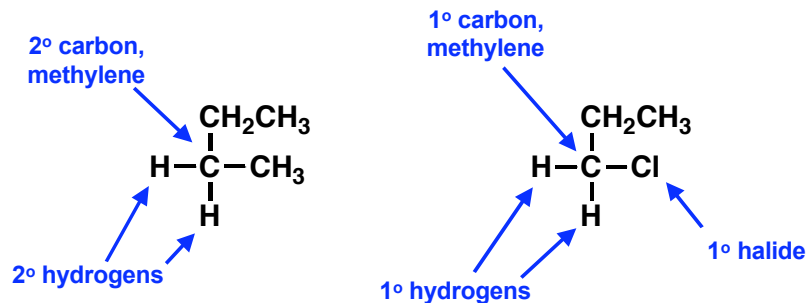
tertiary amine
 3°



ammonium ion
 4°

Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign. Used with permission. Adapted by Kimberly Berkowski.

E4. Examples of Classifying Atoms



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.

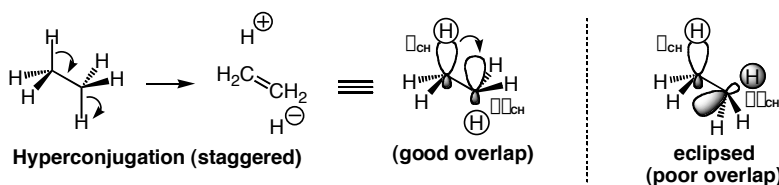
The length of time that a molecule resides in one conformational minimum is determined by the barrier height (ΔG^\ddagger).

Figure removed due to copyright reasons.

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

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 σ_{CH} and σ_{CH}^* orbitals that does not occur in the eclipsed conformer).



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:

Weinhold, F. *Nature* **2001**, 411, 539-541.

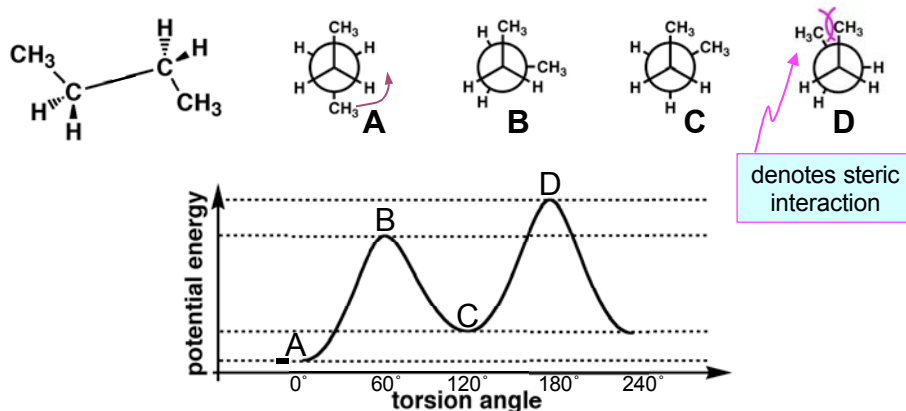
Bickelhaupt F. M.; Baerends, E. V. *Angew. Chem. Int. Ed.* **2003**, 42, 4183-4188. (rebuttal)

Weinhold, F. *Angew. Chem. Int. Ed.* **2003**, 42, 4188-4194. (re-rebuttal)

and others . . .

F2c. Conformational Energy of Butane

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 |