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

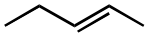
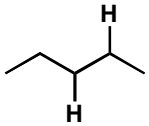
$$C_nH_{2n+2}$$

(sp^3, 109.5° bond angles, □ bonds)

$C_{11}H_{24}$ 

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

saturated  H_2, cat. → no reaction

unsaturated  H_2, cat. → 

"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

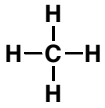
$$CH_4 + Cl_2 \xrightarrow{h\square} CH_3Cl + HCl$$

2. Combustion

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{heat}$$

C. Uses

1. Energy Source (natural gas & petroleum)

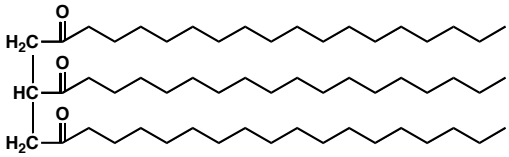


methane = 75% world's natural gas (20% from animals!)

2. Parts of Other Molecules

a. Waxes

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



"burn fat" - covert alkane to CO_2 (exhale) and H_2O (urine)

9 kcal released per fat gram

Re-Moo-able Energy

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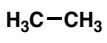
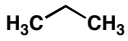
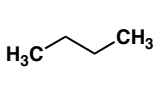
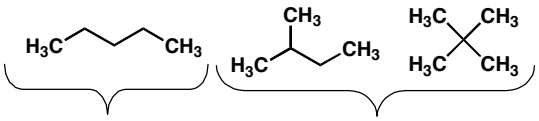
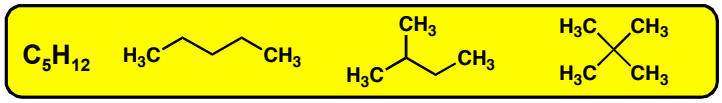
D. Structure

# Carbon	C_nH_{2n+2}	Structure
1	CH_4	
2	C_2H_6	
3	C_3H_8	
4	C_4H_{10}	
5	C_5H_{12}	

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

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!

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

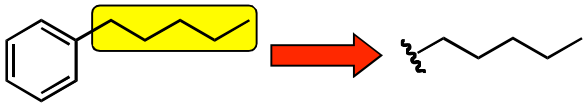
Alkane: suffix "**-ane**"

C_nH_{2n+2}	***n*-Alkane**	C_nH_{2n+2}	***n*-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



"Pentyl"

Pentane with 1 hydrogen atom removed

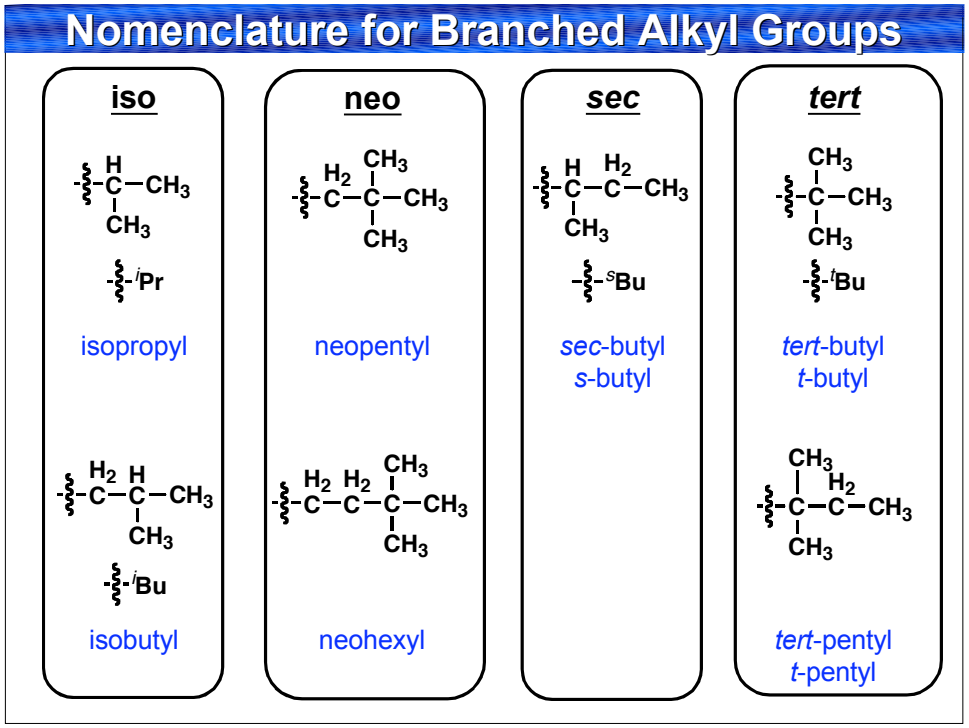
To name: replace "-ane" with "yl"

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}	*n*-Alkane	Alkyl Subst.	Alkyl Name
CH_4	methane	$-CH_3$ (-Me)	methyl
C_2H_6	ethane	$-C_2H_5$ (-Et)	ethyl
C_3H_8	propane	$-C_3H_7$ ($-^nPr$)	propyl
C_4H_{10}	butane	$-C_4H_9$ ($-^nBu$)	butyl
C_5H_{12}	pentane	$-C_5H_{11}$	pentyl
C_6H_{14}	hexane	$-C_6H_{13}$	hexyl
C_7H_{16}	heptane	$-C_7H_{15}$	heptyl
C_8H_{18}	octane	$-C_8H_{17}$	octyl
C_9H_{20}	nonane	$-C_9H_{19}$	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



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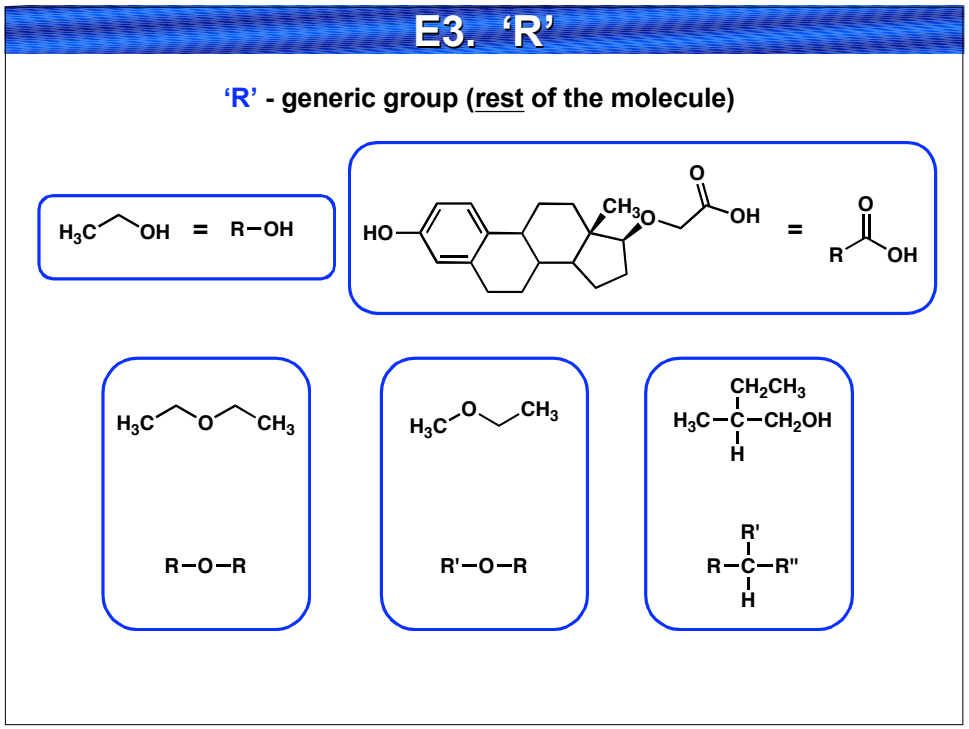
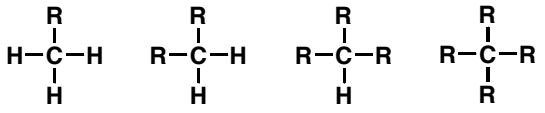
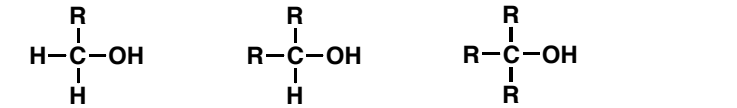


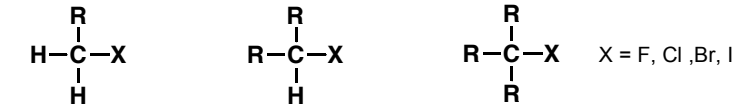
E4. Classifying sp^3 Atoms by Connectivity I

sp^3 C by C-C connectivity



alcohols and halides by C-C connectivity





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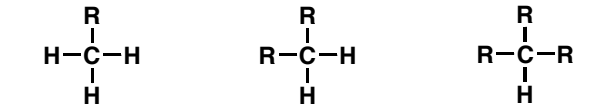
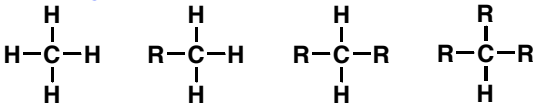
E4. Classifying sp^3 atoms by Connectivity II

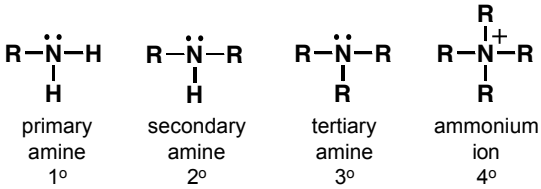
H by C-C connectivity



sp^3 C by C-H connectivity



sp^3 N by C-N connectivity



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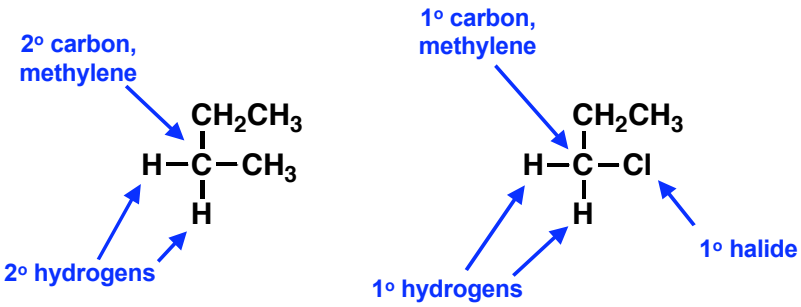
E4. Examples of Classifying Atoms



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 substitutents 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 ($\Delta G^{\neq}$).

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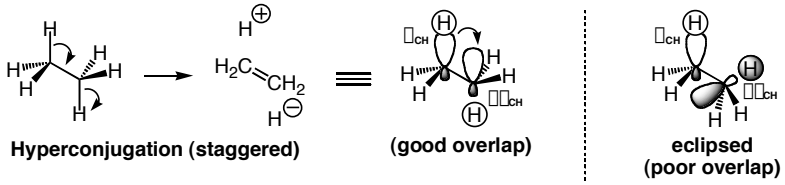
Barrier to rotation = $E_{highest}$ - E_{lowest} = 2.9 kcal/mol

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



Hyperconjugation (staggered) **(good overlap)** **eclipsed (poor overlap)**

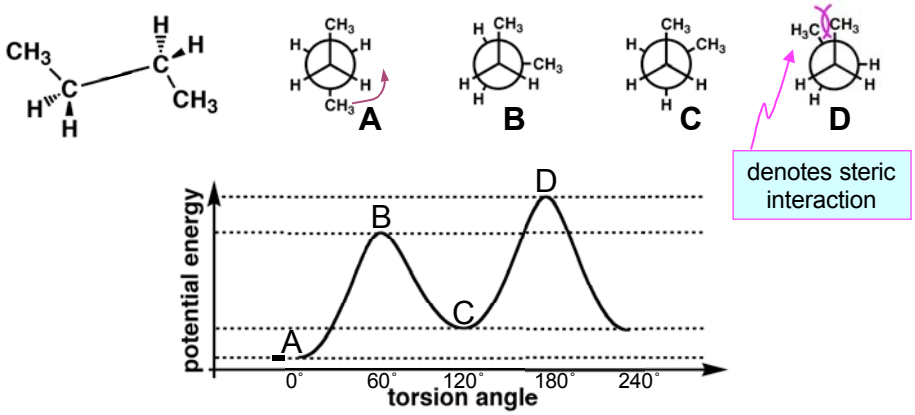
A second explanation for the lower energy of the staggered ethane conformer is that **electron-electron repulsion** between the C-H bonds is occurring in the eclipsed conformer (same principles as VSEPR theory), which destabilizes it.

Please see the following articles for further information:

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