Chemistry 1b

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chemweb.caltech.edu/chem1ab

Course website: http://chem1.che.caltech.edu/

Syllabus: All the important details

You must hand in all work to pass the course!

Textbooks:

Oxtoby, Gillis & Campion "Principles of Modern Chemistry"

Roberts & Caserio "Basic Principles of Organic Chemistry"

http://authors.library.caltech.edu/25034/

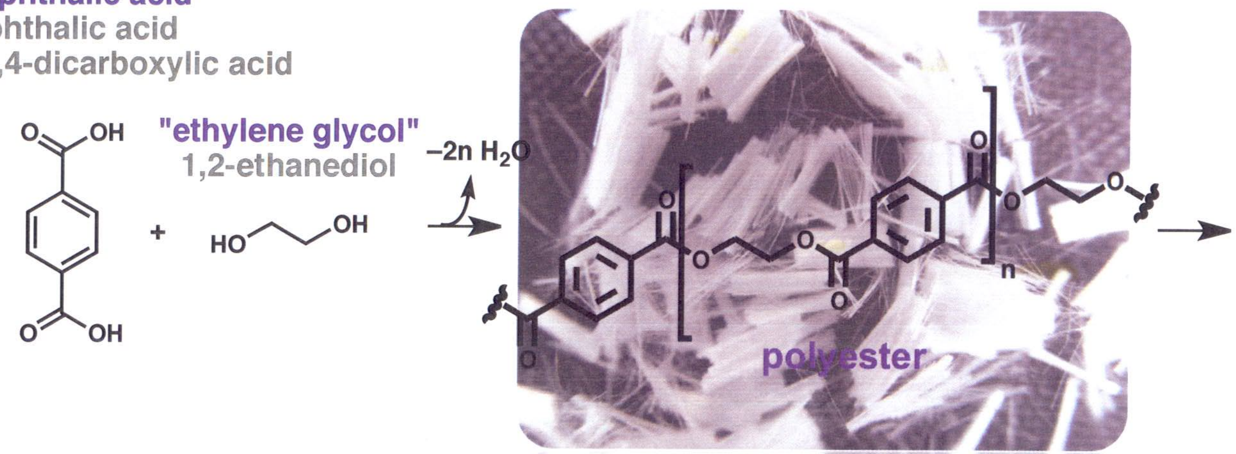
Chemistry 1b - Calendar

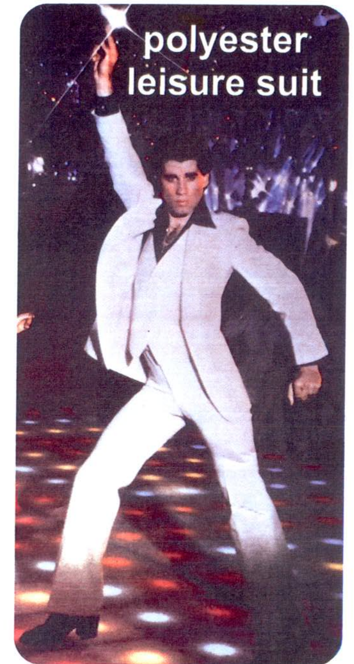
Week	Monday	Tuesday	Thursday	Friday
Week 1	7-Jan-2012 (First Lecture) SER Organic Structures and Naming PS1 Out	8-Jan-2012 SER Organic Structures and Naming Conjugation and Aromaticity	10-Jan SER Functional Groups and Dipoles	11-Jan PS1 Due (4PM) PS2 Out
Week 2	14-Jan SER Introduction to Organic Reactions Curved Arrows PS1 Out	15-Jan SER Introduction to Organic Reactions Nucleophiles and Electrophiles	17-Jan GAB Introduction to spectroscopy	18-Jan PS2 Due (4PM) PS3 Out
Week 3	21-Jan MLK Day (No Class)	22-Jan GAB Vibrational spectroscopy	24-Jan GAB Optical spectroscopy	25-Jan Quiz 1 Out (4PM), PS4 Out PS3 Due (4PM)
Week 4	28-Jan GAB NMR spectroscopy	29-Jan GAB Kinetic theory Quiz 1 Due (8 PM)	31-Jan GAB Ideal gases	1-Feb PS4 Due (4PM) PS5 Out
Week 5	4-Feb GAB Thermodynamics: 1st law	5-Feb GAB Reversible/irreversible processes	7-Feb GAB Entropy and the 2nd law	8-Feb Midterm Out (4PM) PS5 Due (4PM)
Week 6	11-Feb GAB Spontaneous processes	12-Feb GAB Equilibrium and free energy Midterm Due (8PM)	14-Feb GAB Acids and bases	15-Feb PS6 Out
Week 7	18-Feb President's Day (No Class)	19-Feb SER Organic Acids and Bases	21-Feb GAB Thermo. of oxidation- reduction reactions	22-Feb Quiz 2 Out (4PM), PS7 Out PS6 Due (4PM)
Week 8	25-Feb SER Kinetics OGC: 18	26-Feb SER Kinetics Quiz 2 Due (8PM)	28-Feb SER Addition of Organometallic Reagents to the Carbonyl	1-Mar PS7 Due (4PM) PS8 Out
Week 9	4-Mar SER Nucleophilic Substitution at the Carbonyl	5-Mar SER The Polyketide Synthesis and 6-deoxyerythronolide B	7-Mar SER Peptide Synthesis and Proteins	8-Mar
Week 10	11-Mar DEMO DAY	12-Mar SER (last lecture) Polymerization Reactions	14-Mar 13-Mar End of Term PS8 Due (Wed 3/13, 4PM)	15-Mar
Week 11	18-Mar Final Out (12 PM)	19-Mar	21-Mar Final Exam Due (Wed 3/20, 4 PM)	

Learning and Studying Chemical Reactions

Chemical reactions – the key to making STUFF

"terephthalic acid"
p-phthalic acid
benzene-1,4-dicarboxylic acid





What you will learn:

- Chemical reactions of organic molecules
- Arrow pushing – a formalism for thinking about reaction mechanisms
- Spectroscopy – how do we detect molecules and determine their structures or their energies?
- Gas laws – how do molecules behave in an ideal state? How do they behave when they interact?
- Thermodynamics, enthalpy, entropy, and equilibria – why do reactions "go"?
- Kinetics – how fast is a given chemical reaction? What governs the rate?

Carbons form bonds through sp^3, sp^2, and sp hybridized orbitals (remember Ch1a)

methane (CH_4)

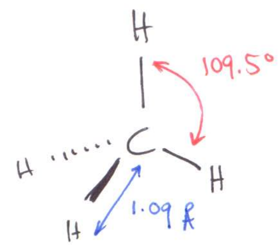
- tetrahedral carbon
- sp^3 hybridized
- $\sigma_{C\text{-}H}$ bond

important numbers:

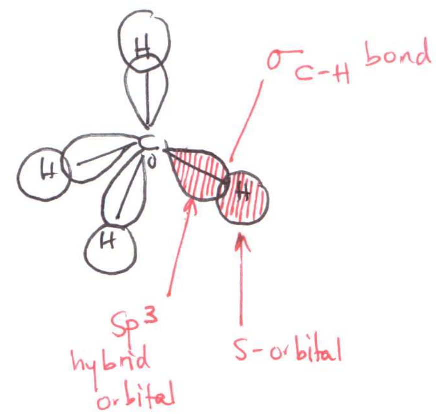
bond angle: 109.5°

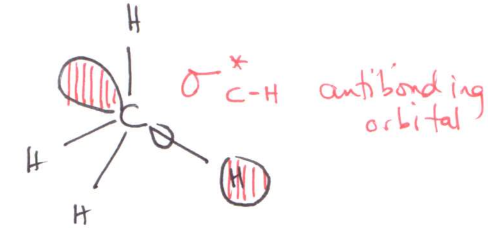
C–C bond length: 1.54 Å

C–H bond length: 1.09 Å



H's are at the vertices of a tetrahedron



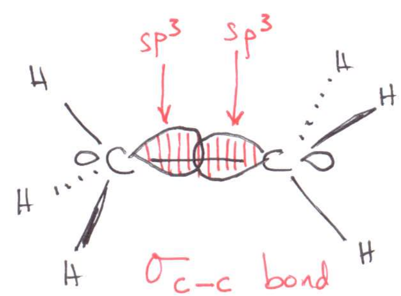


remember, for each bonding orbital, there is an antibonding orbital (LCAO)

ethane (C_2H_6)

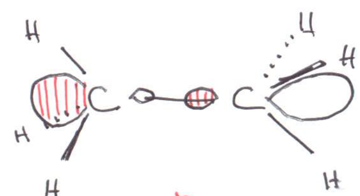
- C–C single bond, $\sigma_{C\text{-}C}$ bond
- generic name: alk<u>ane</u>

suffix



σ_{C-C} bond

~1.54 Å



σ^*_{C-C} antibonding orbital

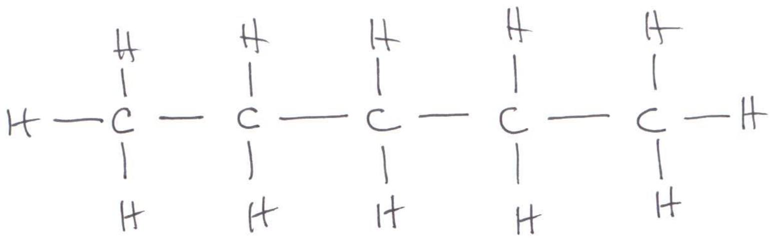
- alkanes have free rotation around C–C and C–H bonds

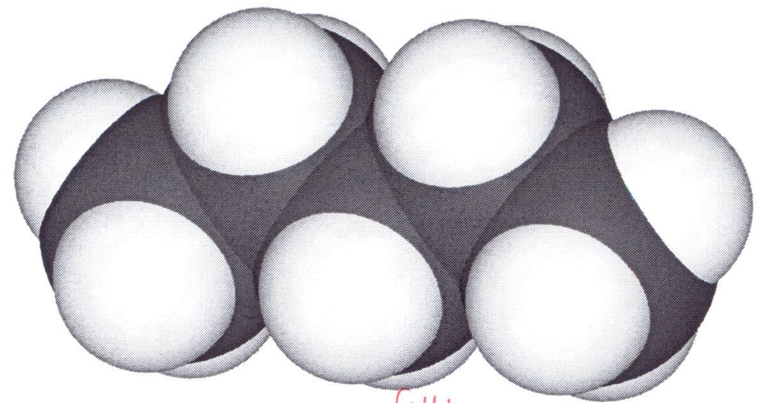
for a refresher on chemical bonding and molecular structure, read Chapter 3 of OGC

Representing Molecular Structures

Chemists have many different ways of representing the same structure.

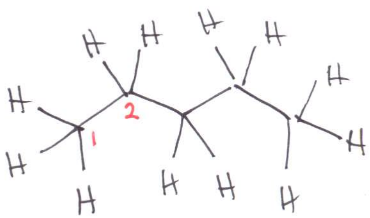
C_5H_{12}



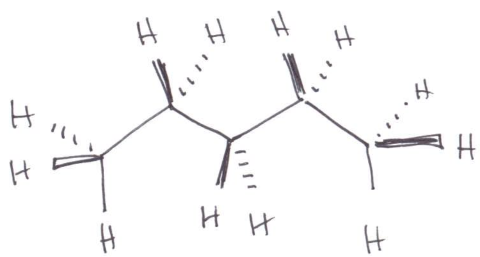


space filling

$CH_3\ CH_2\ CH_2\ CH_2\ CH_3$



carbons are at the vertices

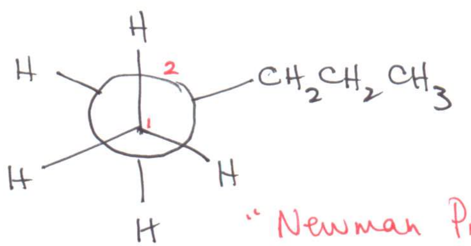


"wedges and dashes"
we will use these frequently

H's omitted for clarity

"skeleton"

H's are assumed to fill the carbon valence, carbons at each vacency



"Newman Projection"

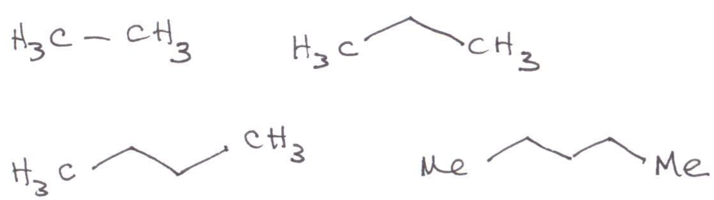
I will mainly use the skeleton version and wedge and dash.

Naming Organic Compounds: Hydrocarbons

Saturated hydrocarbons: alk<u>anes</u> consisting of carbon and hydrogen.

- generic formula: C_nH_{2n+2}
- **prefix** indicates number of carbons in longest chain
- Chains with no branches are "normal" alkanes, e.g. *n*-hexane

# carbons	n-alkane	name	substituent name
1	CH_4	methane	methyl
2	C_2H_6	ethane	ethyl
3	C_3H_8	propane	propyl
4	C_4H_{10}	butane	butyl
5	C_5H_{12}	pentane	pentyl
6	C_6H_{14}	hexane	hexyl
7	C_7H_{16}	heptane	heptyl
8	C_8H_{18}	octane	octyl
9	C_9H_{20}	nonane	nonyl
10	$C_{10}H_{22}$	decane	decyl
20	$C_{20}H_{44}$	eicosane	eicosyl



normal alkanes - each carbon is attached one after another in a straight chain

For more info, see RC, Ch 3 or http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/nomen1.htm

Naming Organic Compounds: Hydrocarbons

Saturated hydrocarbons: alkanes consisting of carbon and hydrogen.

Constitutional Isomers: molecules with the same molecular formula but different connectivity of atoms

- term first proposed by J.J. Berzelius in 1832 to describe compounds with the same composition but different physical properties

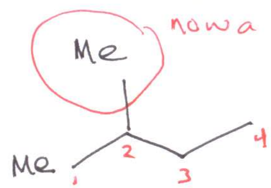
Naming:
- identify longest chain
- number the carbons
- assign number locators to the substituent
- list alphabetically

Not all hydrocarbons are straight chains.

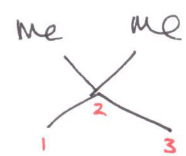
Consider C_5H_{12}

now a "substituent"

n-pentane

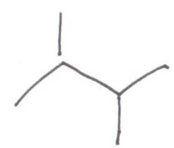


2-methylbutane



2,2-dimethylpropane

Draw all the isomers of hexane:

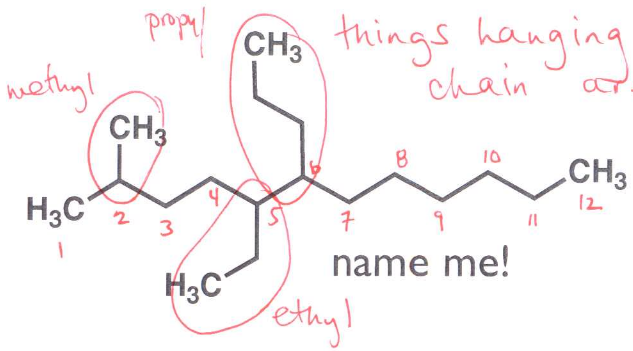


For more info, see RC, Ch 3 or http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/nomen1.htm

Naming Branched Alkanes

- Identify the parent hydrocarbon (the longest straight chain)
- Number the carbons of the parent hydrocarbon, minimizing the sum of the substituent #' s
- List the sidechain fragments in alphabetical order, use numbers to indicate position attached to main chain

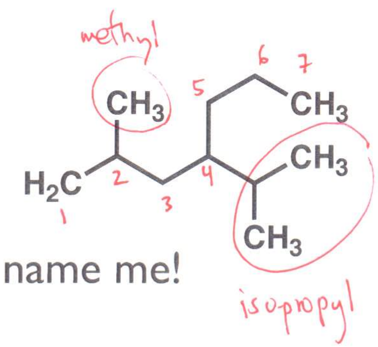
things hanging off the main chain are called "substituents"



name me!

parent chain: dodecane = 12 carbons

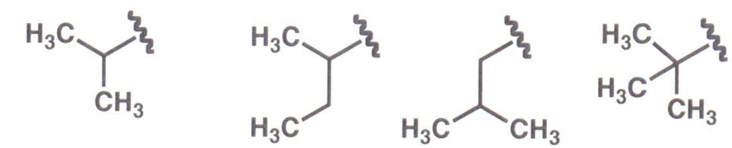
5-ethyl-2-methyl-6-propyldodecane



name me!

4-isopropyl-2-methyl heptane

common alkyl substituents:



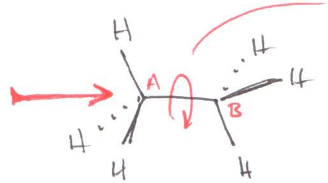
iso-propyl (*i*-Pr) | *sec*-butyl (*s*-Bu) | *iso*-butyl (*i*-Bu) | *tert*-butyl (*t*-Bu)

Conformations of Alkanes

Conformational isomers: two isomers of a molecule which differ only in the spatial arrangement of the atoms; conformations can be interconverted by rotation about single bonds.

- Not all conformations are created equal

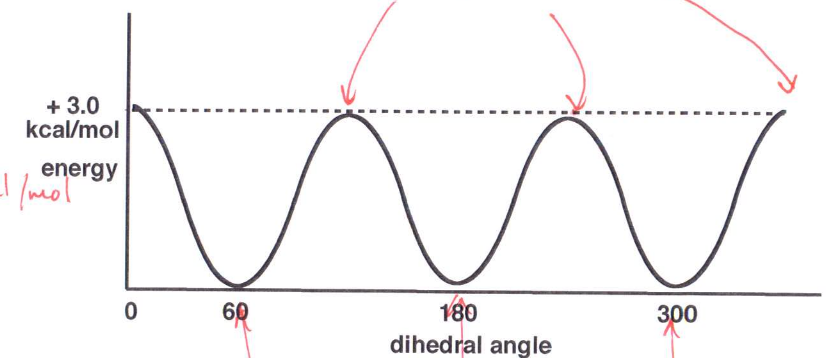
consider ethane



what happens to the energy profile as we rotate around this bond

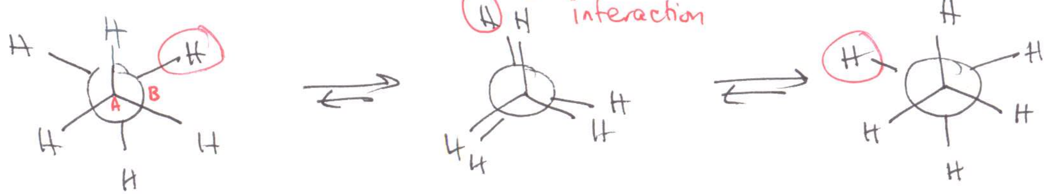
3×1 kcal/mol $= +3$ kcal/mol.

eclipsed



staggered

eclipsing C–H/C–H interaction } destabilizing; + 1 kcal/mol



Staggered ⇌ eclipsed ⇌ staggered

How big is 3 kcal/mol? Rate constant at 298 K for rotation 120°c $= 6 \times 10^{10}\ s^{-1}$

very fast!

calculated from Arrhenius eqn $k = Ae^{-Ea/RT}$

$A = 10^{13}$ (common for unimolecular processes)

} half-life of a staggered conformer $t_{1/2} = 10$ picoseconds