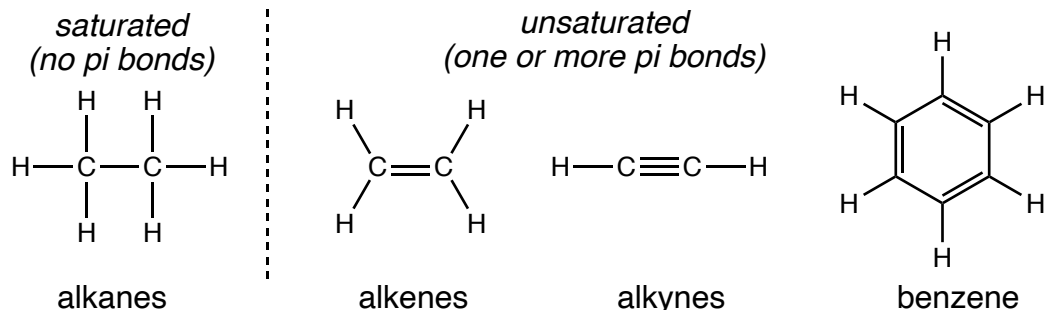


Chapter 4: Alkanes and Cycloalkanes

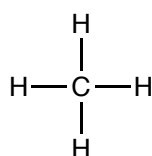
[Sections: 4.1-4.14]

Basic Organic Compound Nomenclature

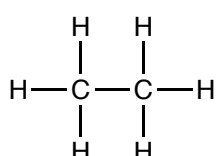
hydrocarbons: comprised of just carbon and hydrogen



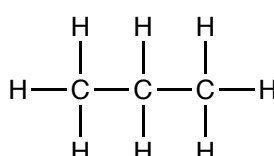
naming alkanes



CH₄
methane



C₂H₆
ethane



C₃H₈
propane

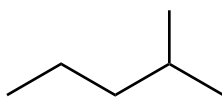
C ₄ H ₁₀	butane
C ₅ H ₁₂	pentane
C ₆ H ₁₄	hexane
C ₇ H ₁₆	heptane
C ₈ H ₁₈	octane
C ₉ H ₂₀	nonane
C ₁₀ H ₂₂	decane

general molecular formula for alkanes:
C_nH_{2n+2}

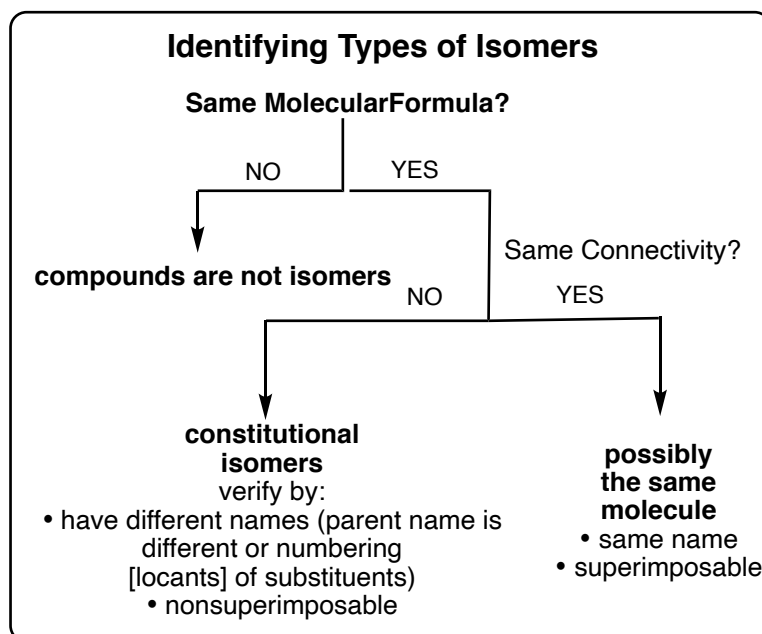
name:



molecular formula?

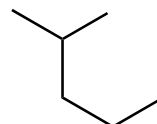
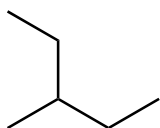
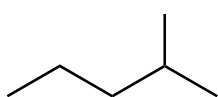


relationship?



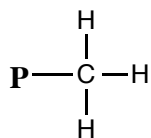
Naming Organic Compounds According to IUPAC (International Union of Pure and Applied Chemistry) Rules

- identify the parent chain and all substituents
- parent chain: longest continuous carbon chain
- substituent: anything not part of the parent chain
- number the parent chain (i.e., assign locant values)
- locants should be minimized for the first substituents on the parent chain from either end
- if there is a tie, minimize the locant for the second substituent
- if the locants are the same in either direction, the first substituent alphabetically is assigned the lower locant (this is used ONLY if the locant values cannot prioritize the substituents!!)



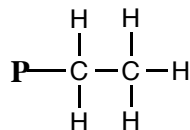
alkyl groups

P = parent chain



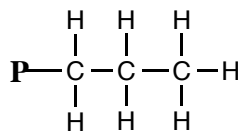
-CH₃

methyl group



-CH₂CH₃

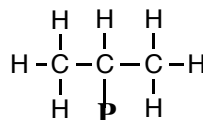
ethyl group



"propyl group"

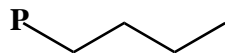
1-propyl group

n-propyl group

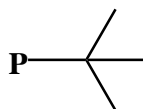


2-propyl group

isopropyl group



n-butyl



tert-butyl



halogens



fluoro



chloro



bromo

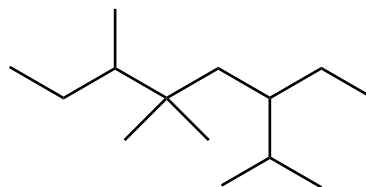
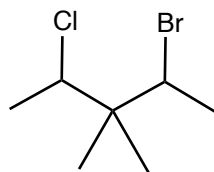
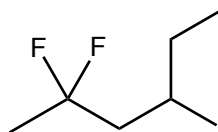
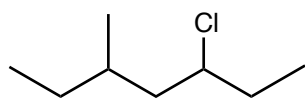
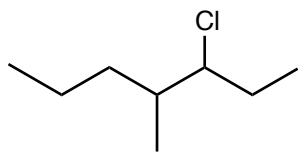


iodo

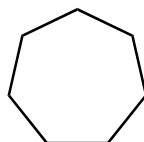
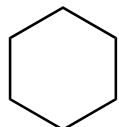
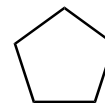




- identify the parent chain and all substituents
- if there are two longest chains of the same length, select the one with more substituents
- properly assign locants to all substituents
- alphabetize substituents and place before name of parent chain along with locant values
- use di, tri, tetra, etc. for substituents if necessary (these are not used for alphabetizing)

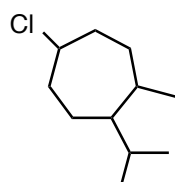
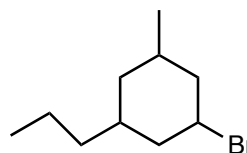
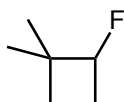
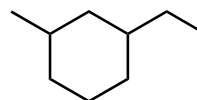
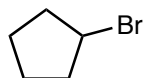


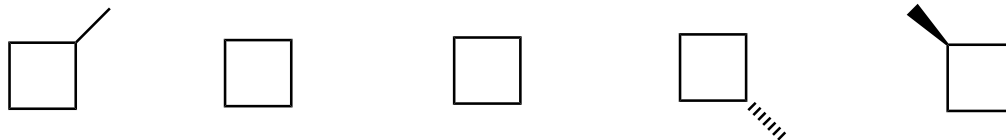
Cycloalkanes



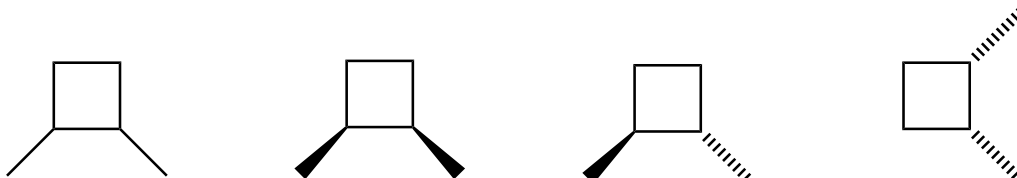
Naming Cycloalkanes According to IUPAC rules

- identify the parent cycloalkane
- if there is one substituent, it is automatically at the "1" position
- for two substituents, minimize the locant values, prioritize based on alphabetizing
- if more than two substituents, minimize locants
- if there is more than one way to count around the ring while still minimizing locant values, prioritize based on alphabetizing (ONLY if the locant values cannot prioritize the substituents!!)
- use di, tri, tetra, etc. for substituents if necessary
- alphabetize substituents and place before name of parent cycloalkane along with locant values





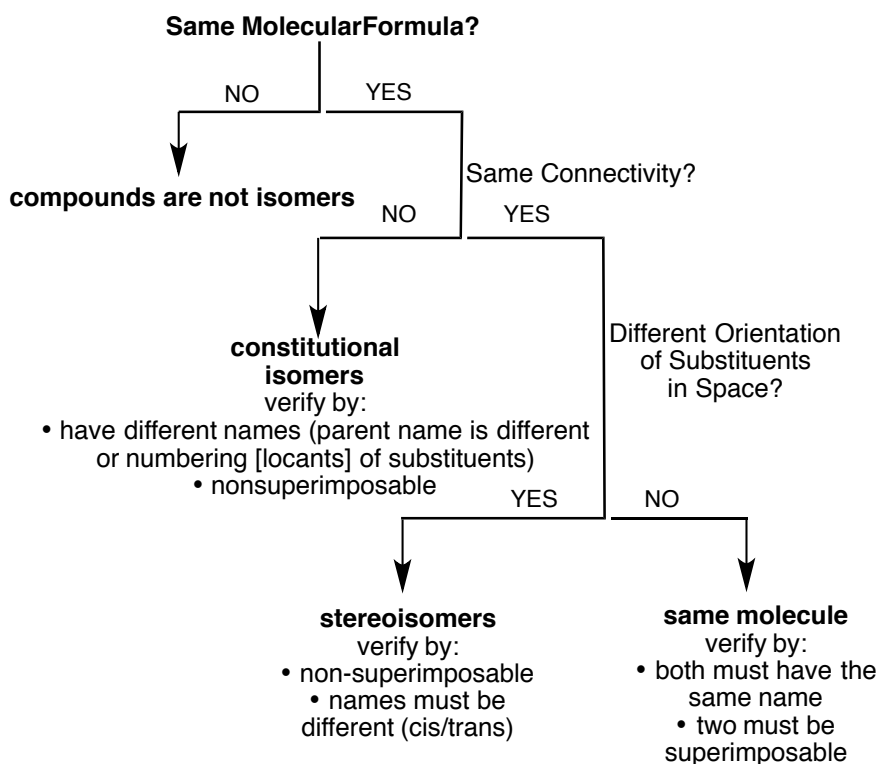
name?
relationship?



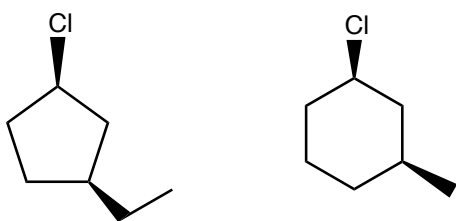
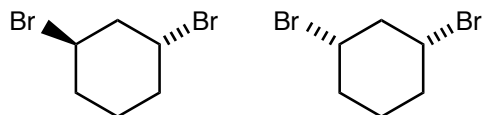
name?
relationship?



1. Identifying Types of Isomers

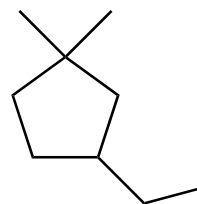
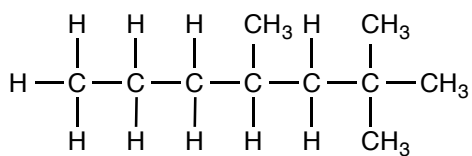


Determine the relationship between the following pairs of molecules:



Problems: 2,3,5,8

Carbon and Proton Types



Types of carbons

- 1° carbon = a carbon attached to one other carbon
- 2° carbon = a carbon attached to two other carbons
- 3° carbon = a carbon attached to three other carbons
- 4° carbon = a carbon attached to four other carbons

Types of hydrogens

- 1° hydrogen = a hydrogen attached to a 1° carbon
- 2° hydrogen = a hydrogen attached to a 2° carbon
- 3° hydrogen = a hydrogen attached to a 3° carbon

carbon <u>type</u>	no.	hydrogen <u>type</u>	no.
4°		3°	
3°		2°	
2°		1°	
1°			

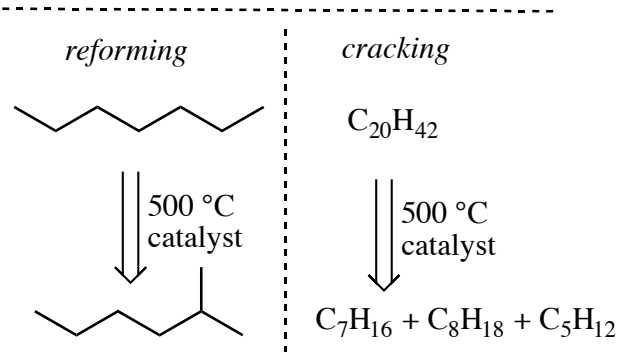
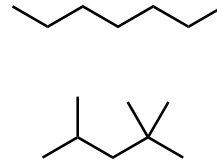
Problems: 4,6,7

Sources of Common Alkanes

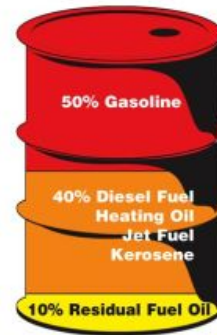
- methane
- ethane
- propane
- butane

- pentane
- hexane
- heptane
- octane
- nonane
- decane
- C₁₁-C₁₅

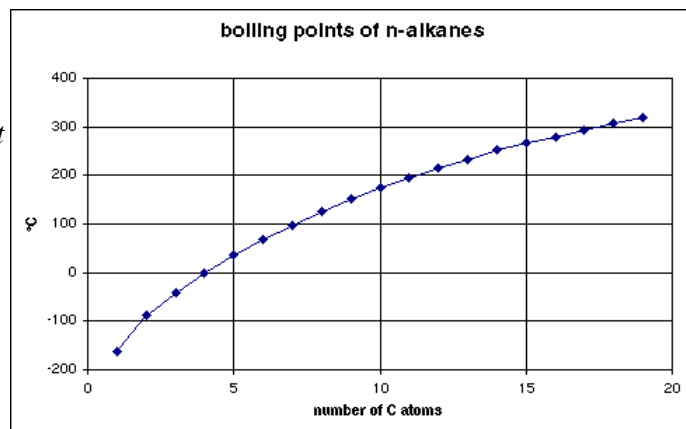
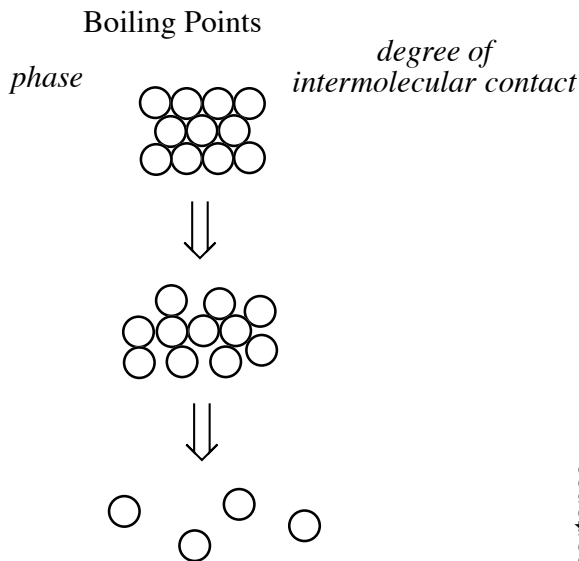
- >C₂₅



Typical U.S. Refinery Yield from a Barrel of Crude Oil



4. Alkane (and Cycloalkane) Properties

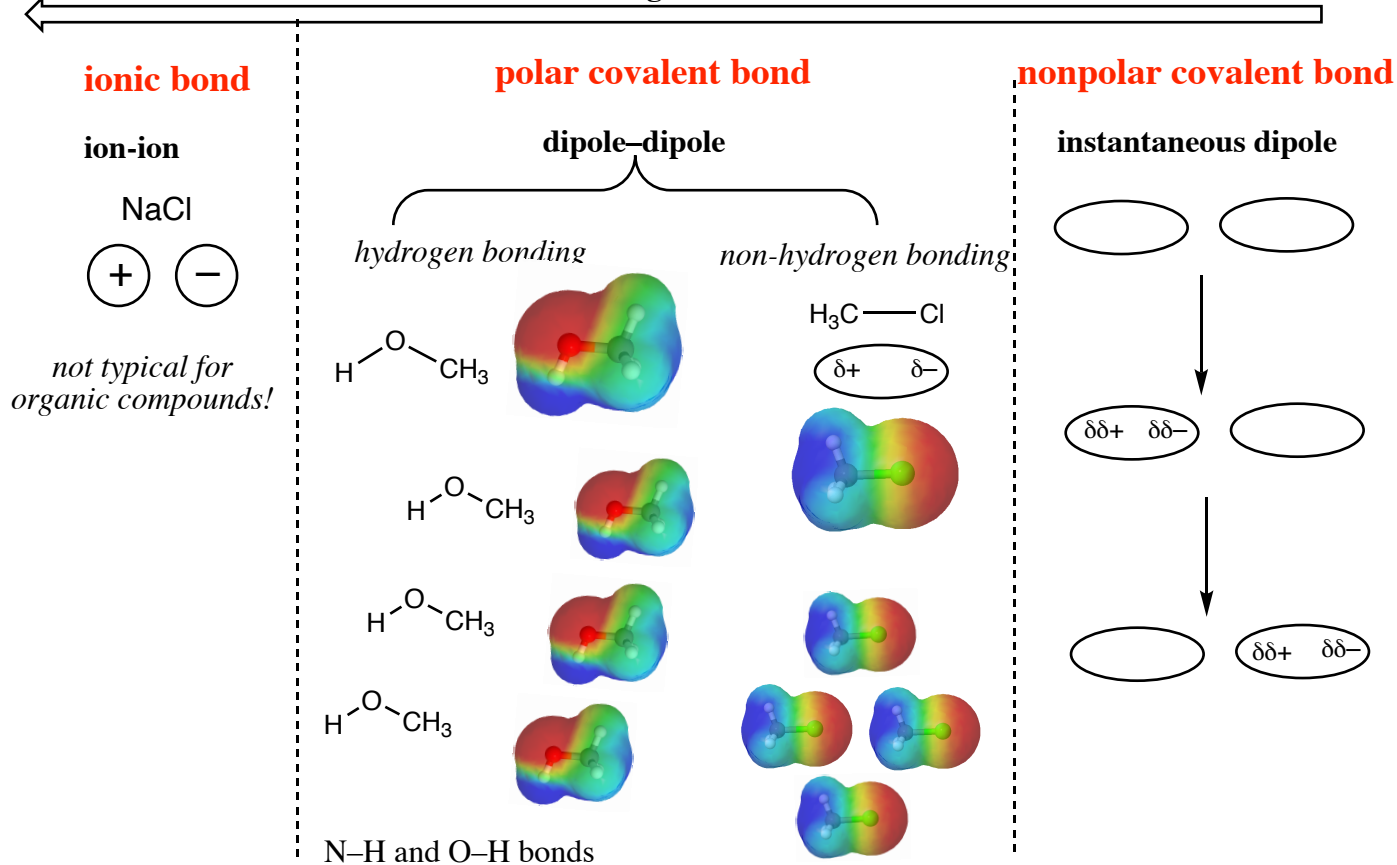


Boiling points are dependent upon:

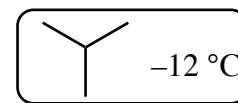
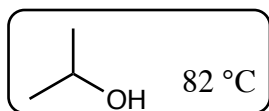
- importance ↑
- **Molecular Weight:** Generally as molecular weight increases, boiling point increases.
 - **Intermolecular Forces** (forces of attraction between molecules): Stronger intermolecular forces mean higher boiling points.

types of intermolecular forces: forces of attraction between individual molecules

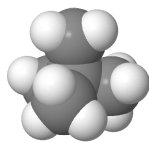
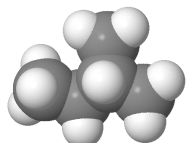
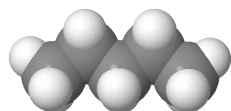
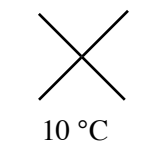
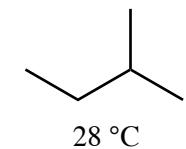
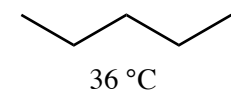
~strength~



Examples compound	NaCl			
mol. wt.	58	60	64	58
b.p.	1400 °C	97 °C	12 °C	-0.5 °C



Effect of branching



Summary of BP Factors

- importance ↑
1. higher MW > lower MW
 2. polar H-bonding > polar > nonpolar
 3. unbranched > branched

• branching decreases boiling points due to decrease in surface area and therefore decrease in the extent of intermolecular forces

Predicting Solubility



- *measure of how well one organic compound dissolves in another*
- *soluble: the two compounds mix well to form a homogeneous mixture*
- *insoluble: the two compounds do not mix well*
- *general rule of thumb: like dissolves like*

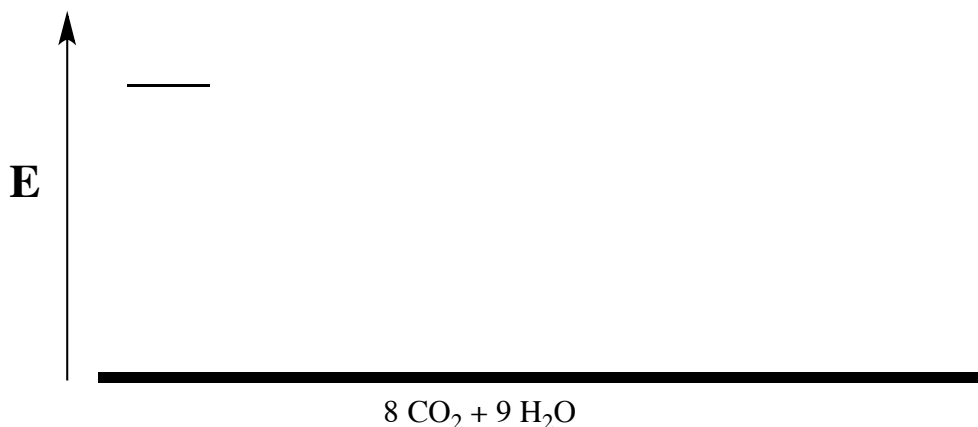
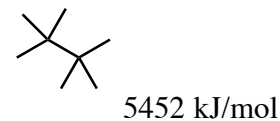
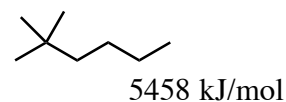
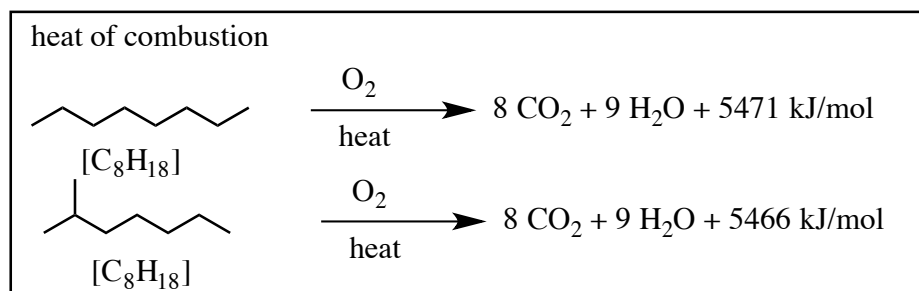
CH₃OH / H₂O

hexane / H₂O

hexane / CH₃OH

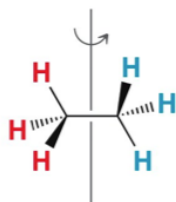
hexane / 1-hexanol

Relative Thermodynamic Stability of Isomers

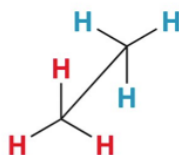


Problems: 9–15

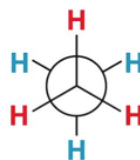
Acyclic Alkanes: Newman Projections



Wedge and dash



Sawhorse



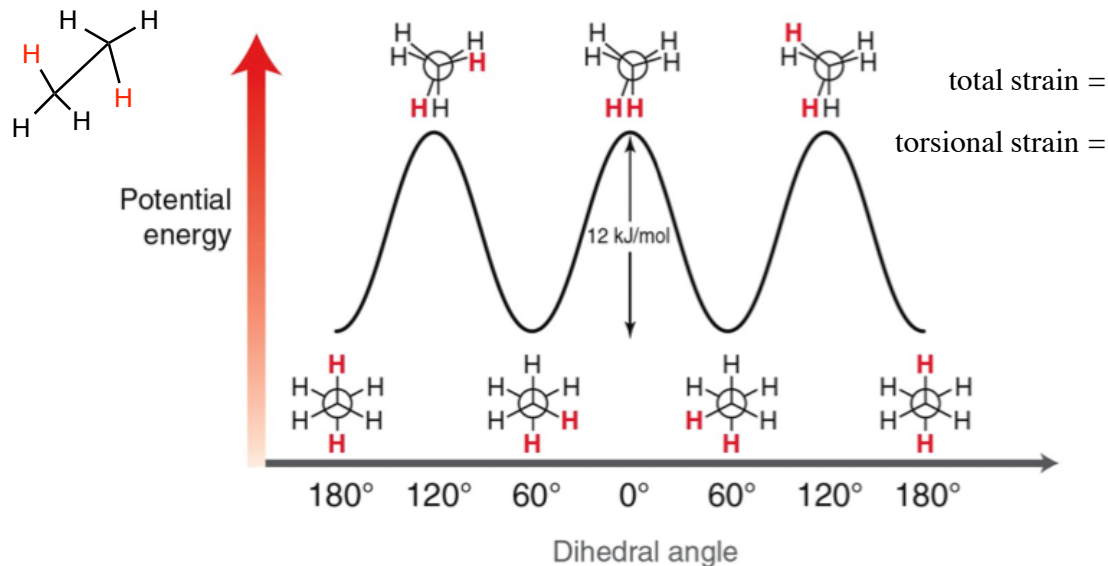
Newman projection



Melvin Newman
1908-1993

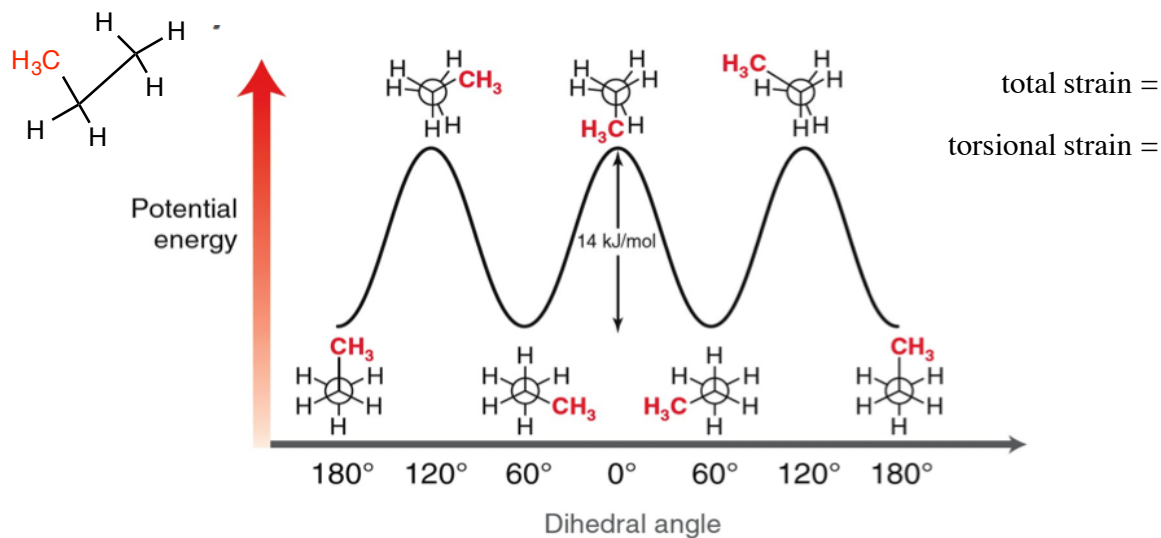
Analyzing Conformations of Simple Alkanes

consider ethane



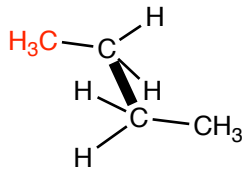
- there are two major conformations for ethane: eclipsed and staggered
- conformation: change in shape of a molecule due to bond rotation
- molecular strain: a force that results in a molecule being at a higher E state than its minimum
- torsional strain: molecular strain induced by electron-electron repulsion of overlapping bonds

consider propane

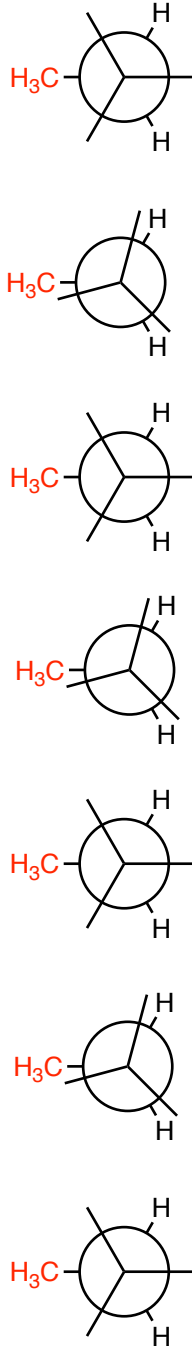


- steric strain: molecular strain induced by atoms or groups of atoms trying to occupy the same physical space

consider butane



Energy



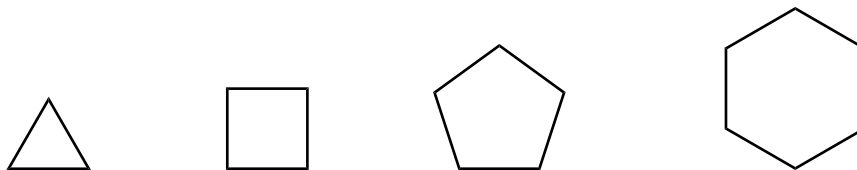
torsional strain E?

steric strain E?

conformer name?

Conformations of Cycloalkanes

If cycloalkanes were planar



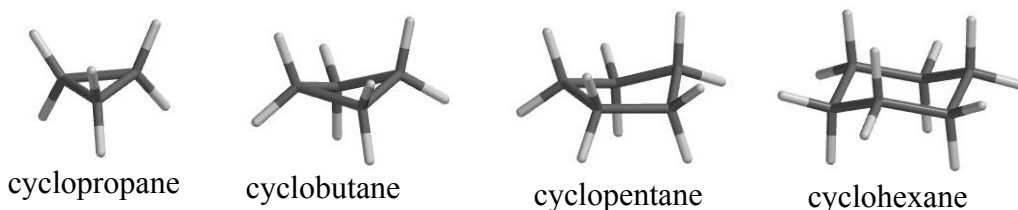
torsional strain?

angle strain?

total strain:

- there would be considerable torsional strain caused by eclipsing of neighboring C–H bonds (view cyclopropane in CheMagic)
- a new type of strain energy, angle strain, would be prevalent, especially, in small cycloalkanes
- angle strain results when atoms in a molecule have to adopt a bond angle that deviates (either greater or less) from the "ideal" bond angle for an atom of a specific hybridization

Cycloalkanes attempt to minimize strain by adopting non-planar conformations



name

torsional strain?

angle strain?

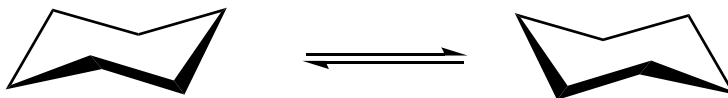
total strain:

- non-planar conformations minimize overall strain energy in cycloalkanes (caused by a combination of angle and torsional)
- the exception is cyclopropane that cannot adopt a non-planar structure
- cyclohexane is the only cycloalkane free of angle AND torsional strain



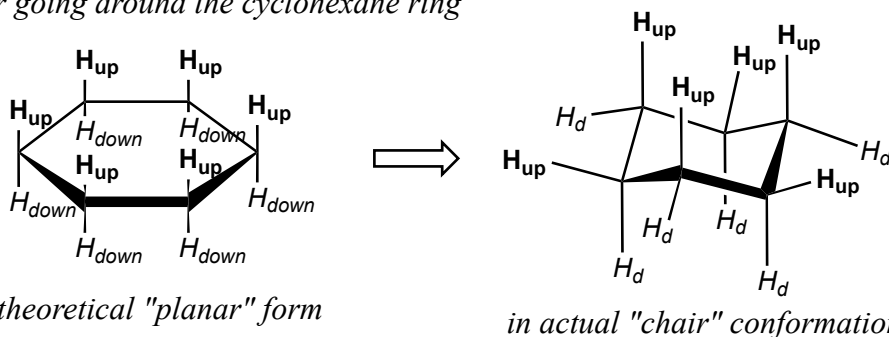
A Closer Look at Cyclohexanes

Drawing chair conformations

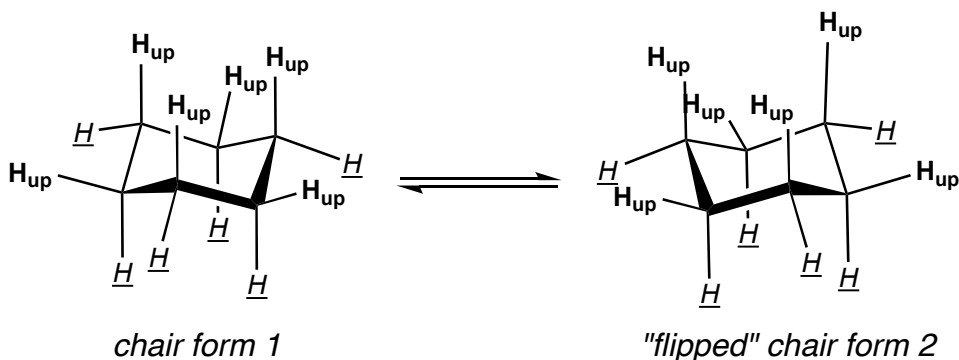


implications of the chair-chair flip

- *Cis positions ("up" or "down") alternate axial/equatorial positions as you move from one atom to another going around the cyclohexane ring*

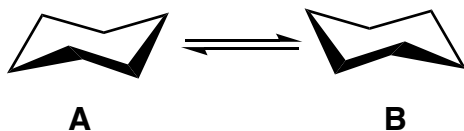


- *All of the substituents occupying the axial position in one chair form adopt the equatorial position in the other chair conformation (after the chair/chair flip) and vice versa*

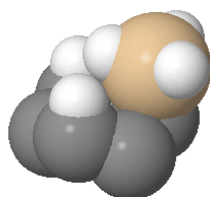
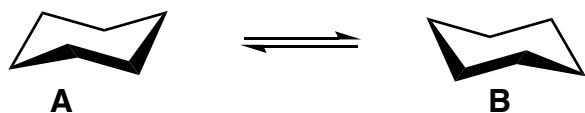


11. Energy Considerations

consider unsubstituted cyclohexane



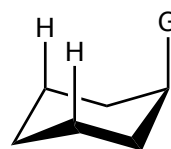
consider methylcyclohexane



- chair-flip conformations of substituted cyclohexanes often have different energies
- **substituents prefer the equatorial orientation** to prevent 1,3-diaxial interactions which lead to steric strain

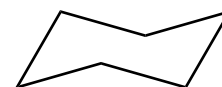
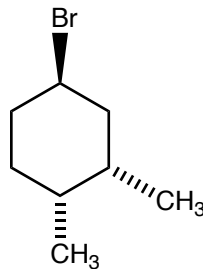
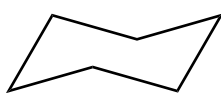
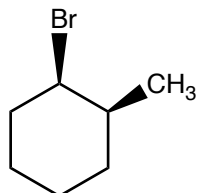
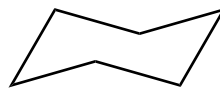
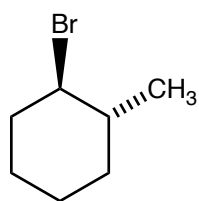
*only 1,3-diaxial hydrogens shown

SUBSTITUENT	STERIC HINDRANCE FROM 1,3-DIAXIAL INTERACTIONS (KJ/MOL)	AXIAL-EQUATORIAL RATIO (AT EQUILIBRIUM)
-Cl	2.0	70 : 30
-OH	4.2	83 : 17
-CH ₃	7.6	95 : 5
-CH ₂ CH ₃	8.0	96 : 4
-CH(CH ₃) ₂	9.2	97 : 3
-C(CH ₃) ₃	22.8	9999 : 1



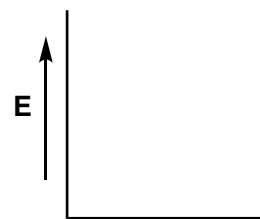
• In general, the larger the substituent, the worse the steric strain due to 1,3-diaxial interactions, and the greater preference for the substituent to occupy the equatorial position

Drawing Chair Conformations of Disubstituted Cycloalkanes

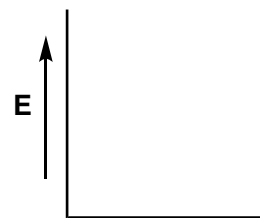
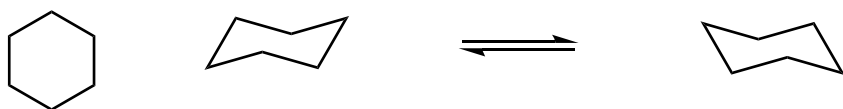


Chair Conformations of Disubstituted Cycloalkanes

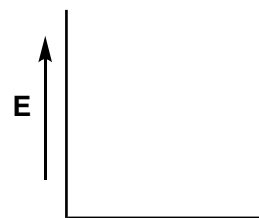
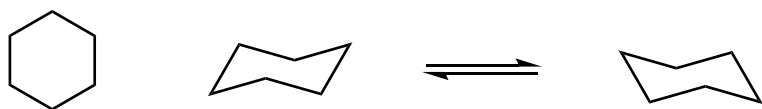
consider trans-1,2-dimethylcyclohexane



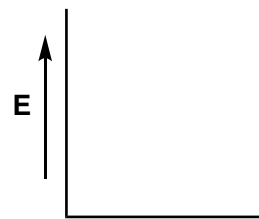
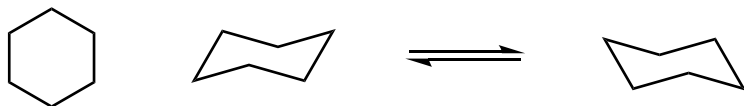
compare to cis-1,2-dimethylcyclohexane



consider cis-1-ethyl-4-methylcyclohexane

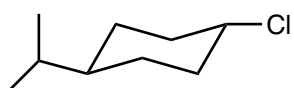


consider trans-1-chloro-3-bromocyclohexane

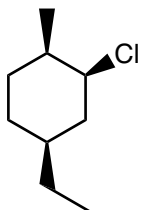


- *NOTE: both chair conformations are the same molecule in all cases. They are simply conformations!*
- *DO NOT transform cis- to trans- via a chair chair flip! This does NOT happen!*

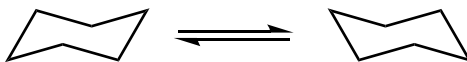
name:



consider the following molecule:

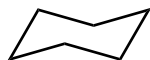


A. Draw the two chair conformations for this molecule



B. Which chair form is most stable?

C. Draw the chair form (and the flat structure) corresponding to the most thermodynamically stable isomer of this compound:



Chapter 4 *Essential Concepts*

1. Recognize saturated and unsaturated bonds.
2. Given a structure, be able to assign an IUPAC name to cyclic and acyclic alkanes and haloalkanes (including stereochemistry for cyclic structures, where relevant).
3. Given an IUPAC name, be able to draw a structure.
4. Be able to assign a provided pair of compounds as being unrelated, identical, constitutional isomers, or stereoisomers.
5. Understand and be able to identify the various types of carbon and hydrogen atoms in a structure (i.e., 1°, 2° etc.).
6. Know the common uses of alkanes; understand octane ratings and methods of refining gasoline. Know how branching affects octane ratings.
7. Understand how molecular weight, intermolecular forces and branching affect boiling points.
8. Be able to identify the types of intermolecular forces active for a given type of molecule.
9. Understand how solubility is affected by structure.
10. Understand how heat of combustion can be used to determine relative stabilities of alkanes.
11. Know how branching affects the stability of isomeric alkanes.
12. Understand how potential energy curves are used to determine relative energies of conformers and be able to identify (and define) torsional and steric strain energy.
13. Know how to use Newman projections and understand the difference between staggered and eclipsed conformations and how their structures generally determine stability.
14. Given several conformations of a compound, be able to order them according to relative energies based on the types of strain energies discussed.
15. Know the structures and names for the nonplanar conformations adopted for cyclobutene, cyclopentane and cyclohexane.
16. Know how angle strain, torsional strain and steric strain are important to cycloalkane stability.
17. Know the changes that take place upon flipping cyclohexane chair forms and the energetic consequences. Be able to draw both chair forms and identify which is more stable.
18. Be able to identify responsible 1,3-diaxial interactions in chair forms.
19. Be able to transform a provided “planar” cyclohexane structure (or provided IUPAC name) into its two chair forms and the reverse.