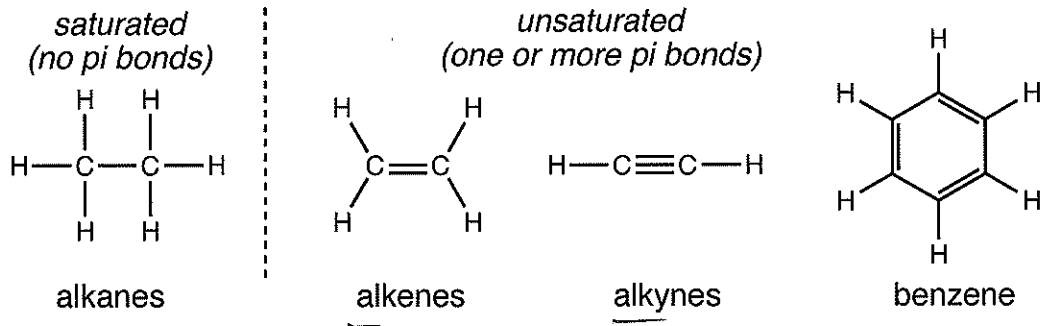


# Chapter 4: Alkanes and Cycloalkanes

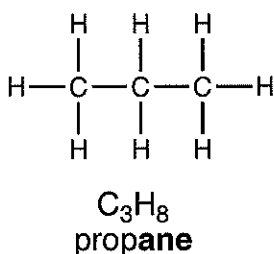
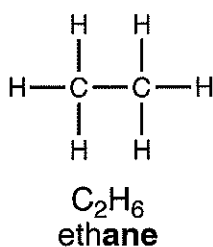
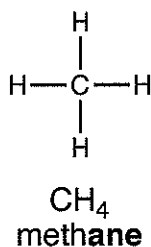
[Sections: 4.1-4.14]

## Basic Organic Compound Nomenclature

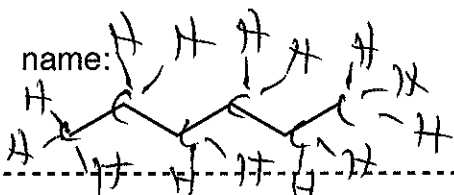
hydrocarbons: comprised of just carbon and hydrogen



### naming alkanes



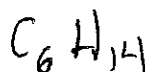
$\text{C}_4\text{H}_{10}$	butane
$\text{C}_5\text{H}_{12}$	pentane
$\text{C}_6\text{H}_{14}$	hexane
$\text{C}_7\text{H}_{16}$	heptane
$\text{C}_8\text{H}_{18}$	octane
$\text{C}_9\text{H}_{20}$	nonane
$\text{C}_{10}\text{H}_{22}$	decane



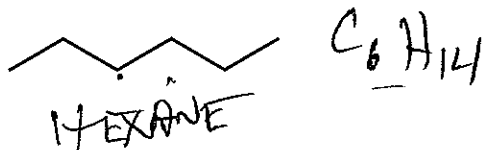
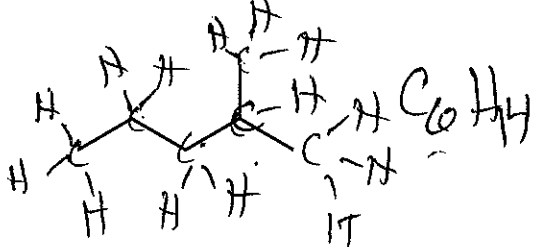
HEXANE

general molecular formula for alkanes:

$$\text{C}_n\text{H}_{2n+2}$$

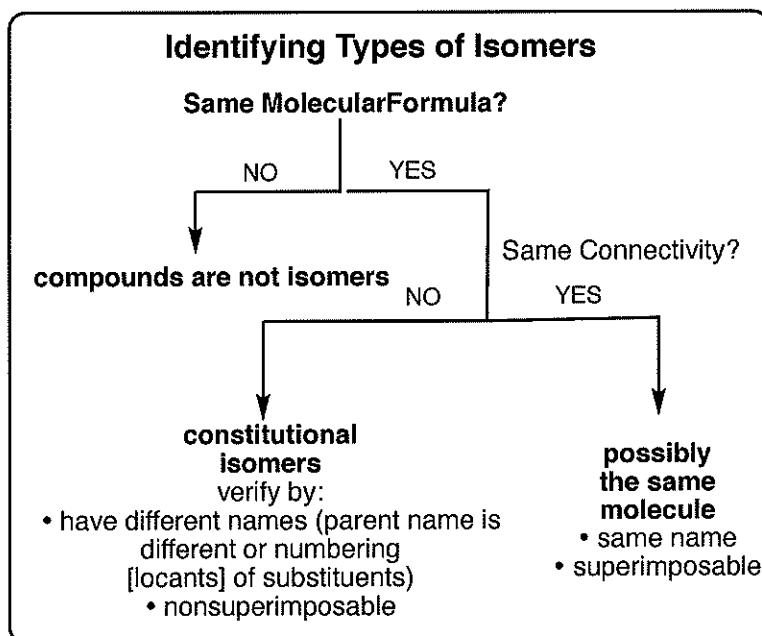


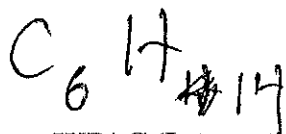
molecular formula?



relationship?

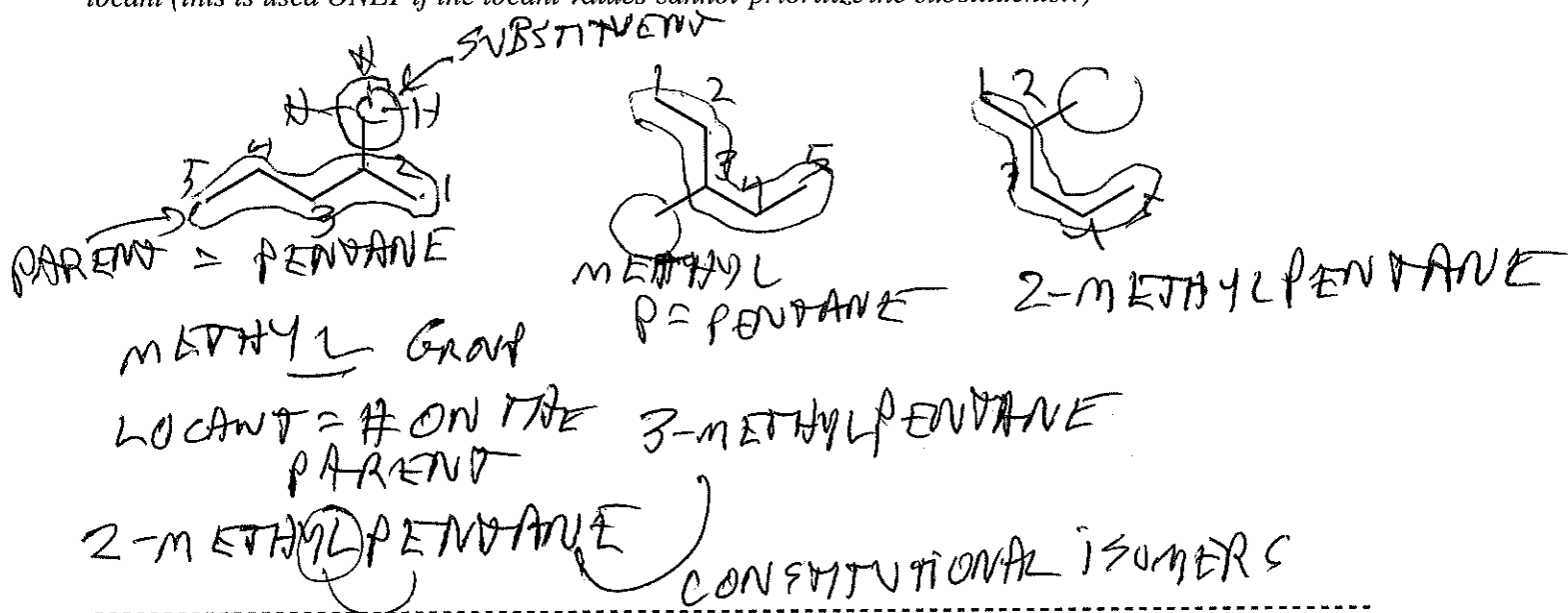
CONSTITUTIONAL ISOMERS





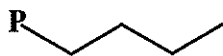
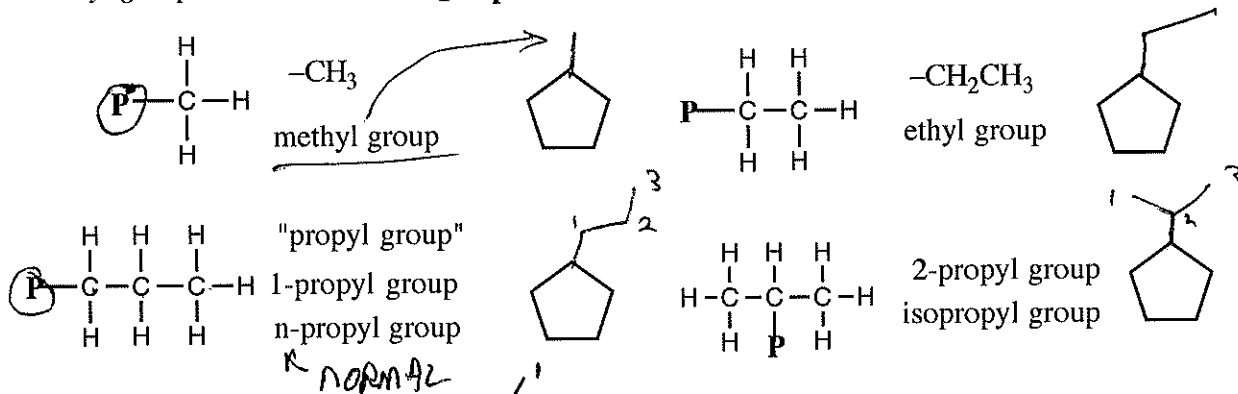
## Naming Organic Compounds According to IUPAC (International Union of Pure and Applied Chemistry) Rules

- 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!!)

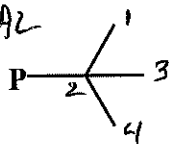


alkyl groups

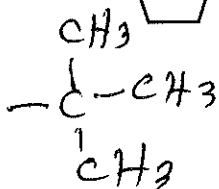
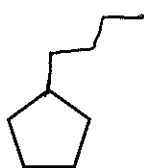
P = parent chain



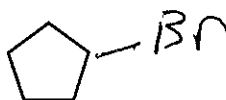
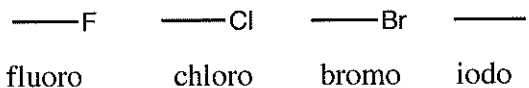
n-butyl



tert-butyl



halogens

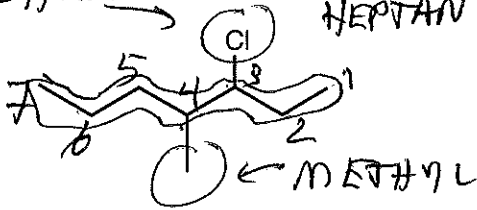


- identify the parent chain and all substituents
- if there are two longest chains of the same length, select the one with more substituents
- properly assign locants to all substituents
- alphabetize substituents and place before name of parent chain along with locant values
- use di, tri, tetra, etc.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



CHLORO

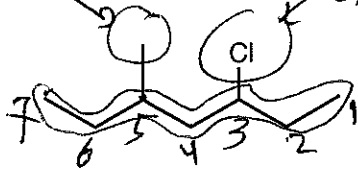
HEPTANE



3-CHLORO-4-METHYLHEPTANE

METHYL

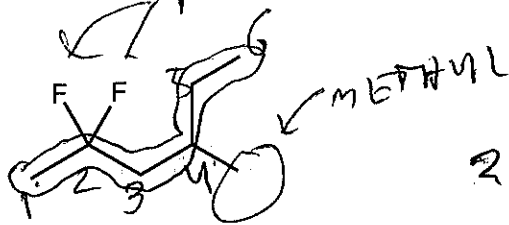
CHLORO



3-CHLORO-5-METHYLHEPTANE

CONSTITUTIONAL ISOMERS

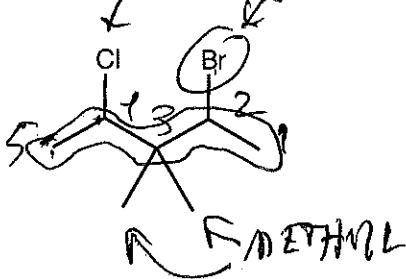
FLUORO



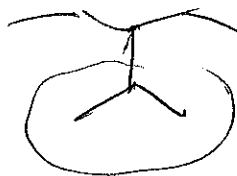
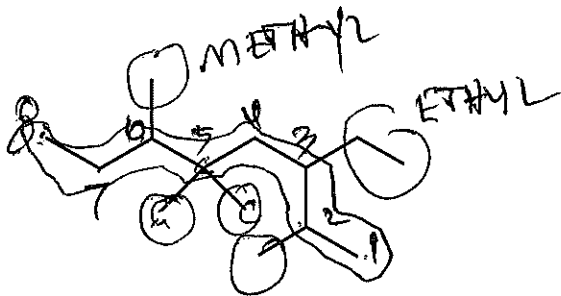
2,2-DIFLUORO-4-METHYLHEXANE

CHLORO

BROMO

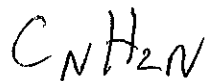


2-BROMO-4-CHLORO-3,3-DIMETHYLPENTANE



3-ETHYL-2,5,5,6-TETRAMETHYLOCTANE

CYCLIC MOLECULES  
ACYCLIC



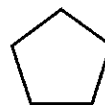
Cycloalkanes



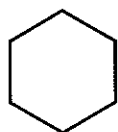
CYCLOPROPANE



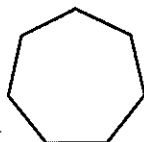
CYCLOBUTANE



CYCLOPENTANE



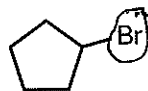
CYCLOHEXANE



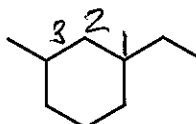
CYCLOHEPTANE

**Naming Cycloalkanes According to IUPAC rules**

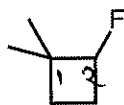
- identify the parent cycloalkane
- if there is one substituent, it is automatically at the "1" position
- for two substituents, minimize the locant values, prioritize based on alphabetizing
- if more than two substituents, minimize locants
- if there is more than one way to count around the ring while 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



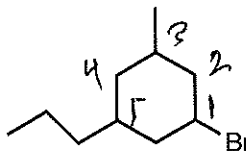
BROMOCYCLOPENTANE



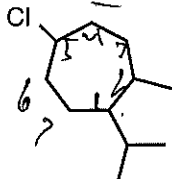
1-ETHYL-3-METHYLCYCLOHEXANE



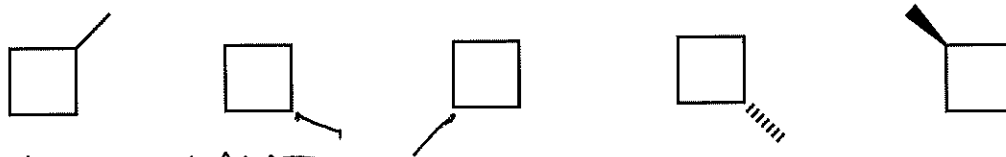
2-FLUORO-1,1-DIMETHYLCYCLOBUTANE



1-BROMO-3-METHYL-5-PROPYLCYCLOHEXANE

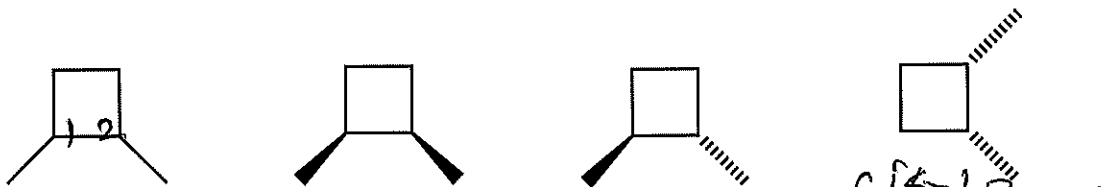


5-CHLORO-1-PROPYL-2-METHYLCYCLOHEPTANE



name? METHYLCYCLOBUTANE  
 relationship?

IDENTICAL



name? 1,2-DIMETHYLCYCLOBUTANE TRANS-1,2-

relationship?

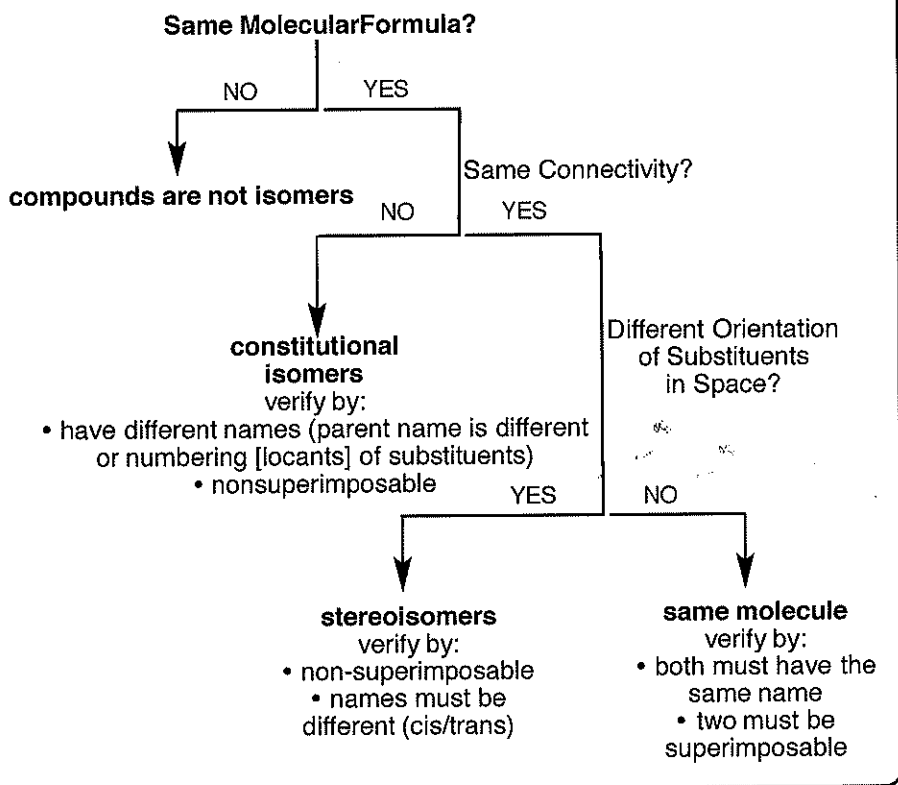
CIS-1,2-DIMETHYLCYCLOBUTANE

STEREISOMERS

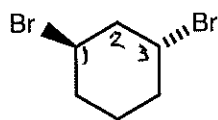
CIS + TRANS - 1,2-DIMETHYLCYCLOBUTANE



### 1. Identifying Types of Isomers



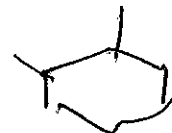
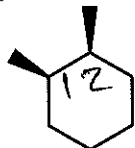
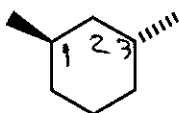
Determine the relationship between the following pairs of molecules:



STEREOMERS

TRANS-1,3-DIBROMOCYCLOHEXANE

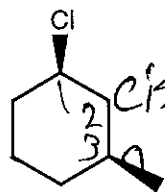
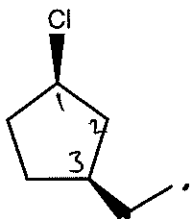
CIS-1,3-DIBROMOCYCLOHEXANE



CONSTITUTIONAL ISOMERS

TRANS-1,3-DIMETHYLCYCLOHEXANE

CIS-1,2-DIMETHYLCYCLOHEXANE



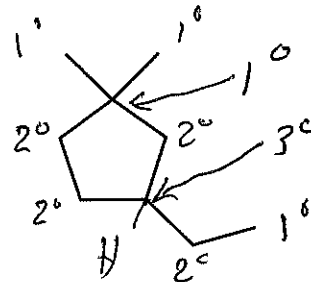
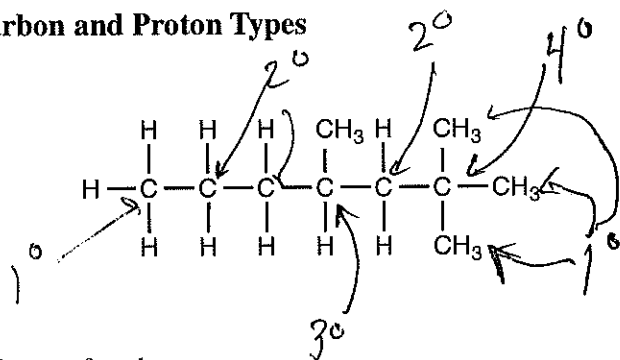
CONSTITUTIONAL ISOMERS

CIS-1-CHLORO-3-METHYLCYCLOHEXANE

CIS-1-CHLORO-3-ETHYLCYCLOPENTANE

Problems: 2,3,5,8

**Carbon and Proton Types**



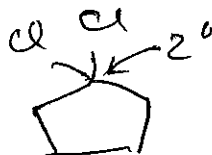
**Types of carbons**

- 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**

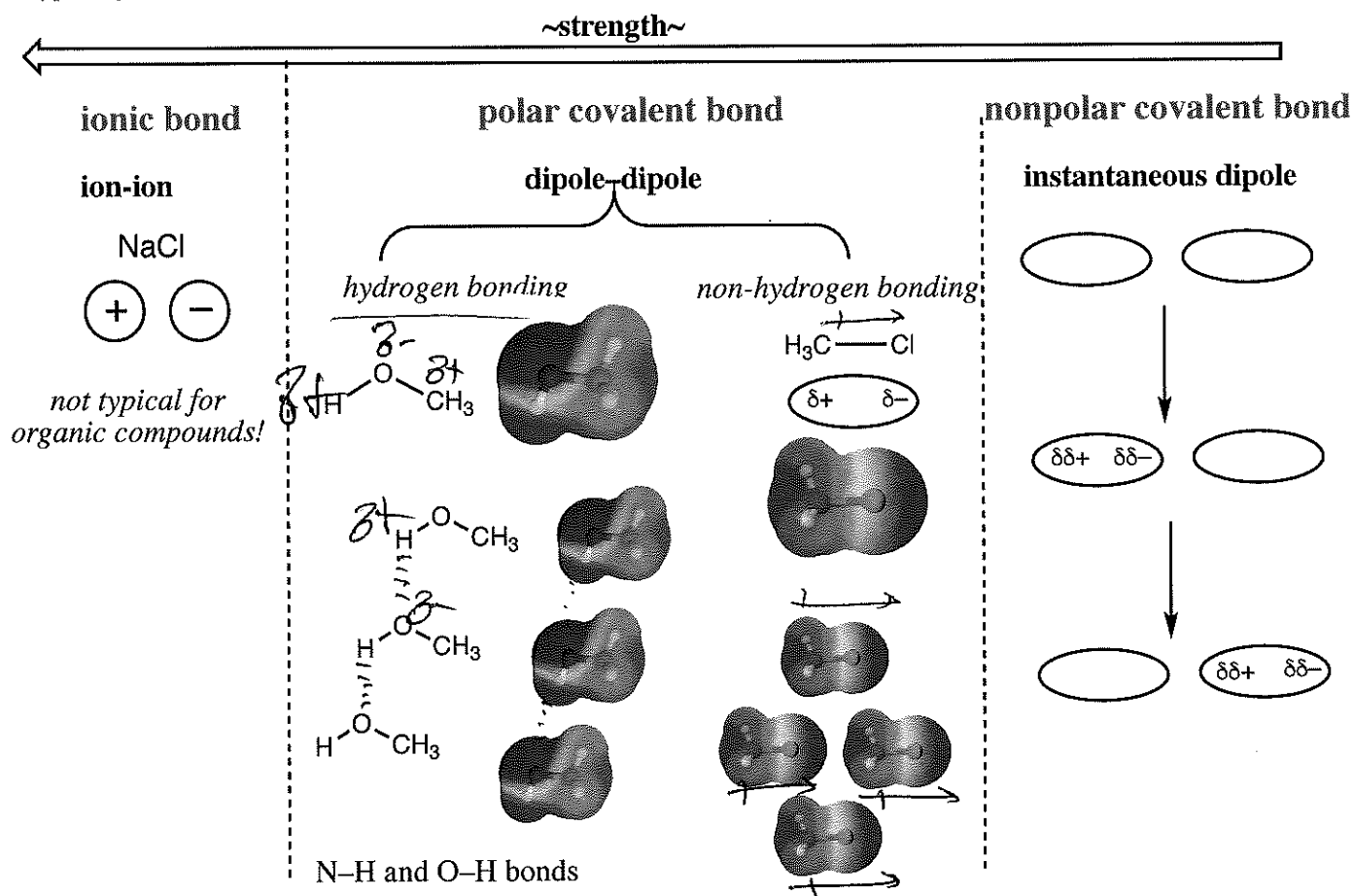
- 1° hydrogen = a hydrogen attached to a 1° carbon
- 2° hydrogen = a hydrogen attached to a 2° carbon
- 3° hydrogen = a hydrogen attached to a 3° carbon

carbon		hydrogen	
type	no.	type	no.
4°	1	3°	1
3°	1	2°	8
2°	4	1°	9
1°	3		



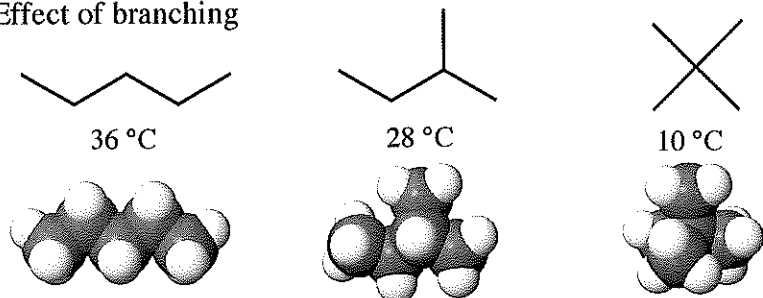
Problems: 4,6,7

types of intermolecular forces: forces of attraction between individual molecules



Examples compound	NaCl	<chem>CCCC(O)C</chem>	<chem>CC(C)Cl</chem>	<chem>CCCC</chem>
mol. wt.	58	60	64	58
b.p.	1400 °C	97 °C • POLAR AND • H-BONDING	12 °C • POLAR	-0.5 °C • NONPOLAR
		<chem>CC(C)O</chem> 82 °C		<chem>CC(C)C</chem> -12 °C

Effect of branching

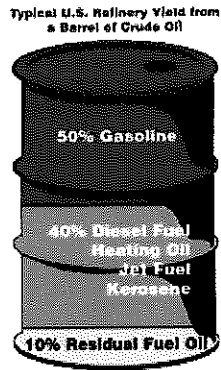
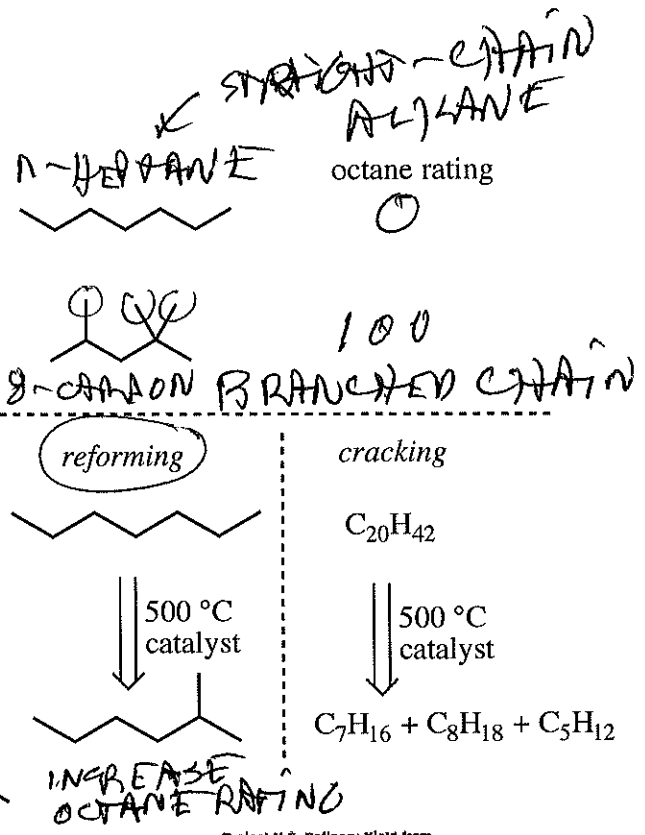
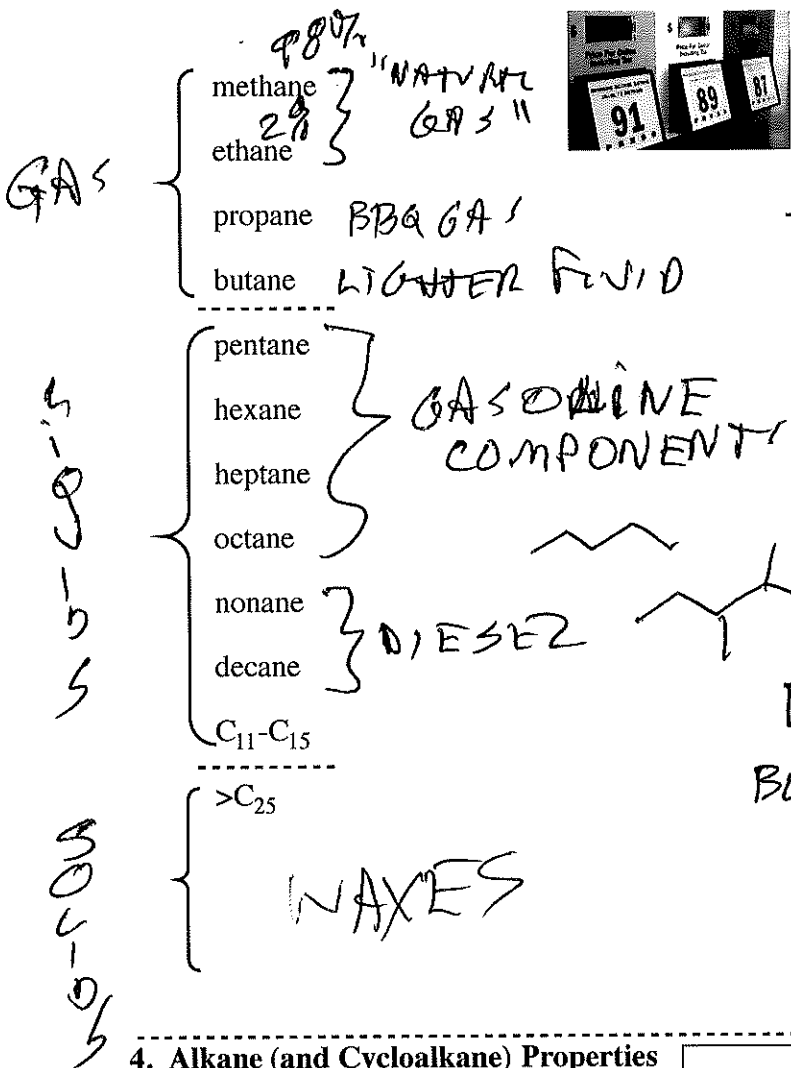


Summary of BP Factors

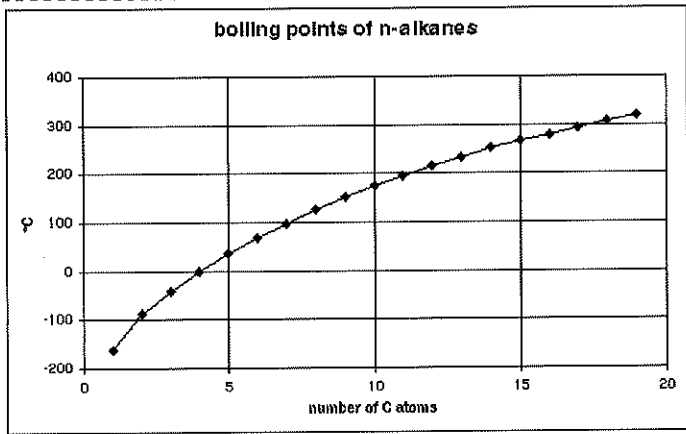
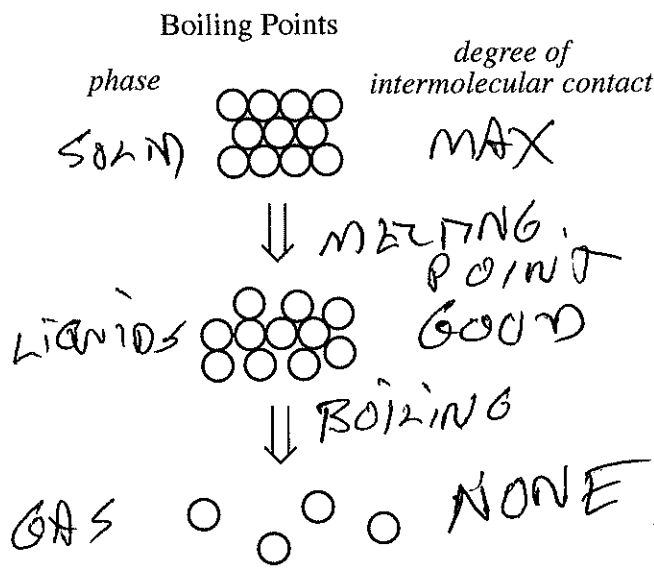
- importance ↑
1. higher MW > lower MW
  2. polar H-bonding > polar > nonpolar
  3. unbranched > branched
- ↓  
MW  
↑  
BP

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

Sources of Common Alkanes



4. Alkane (and Cycloalkane) Properties



Boiling points are dependent upon:

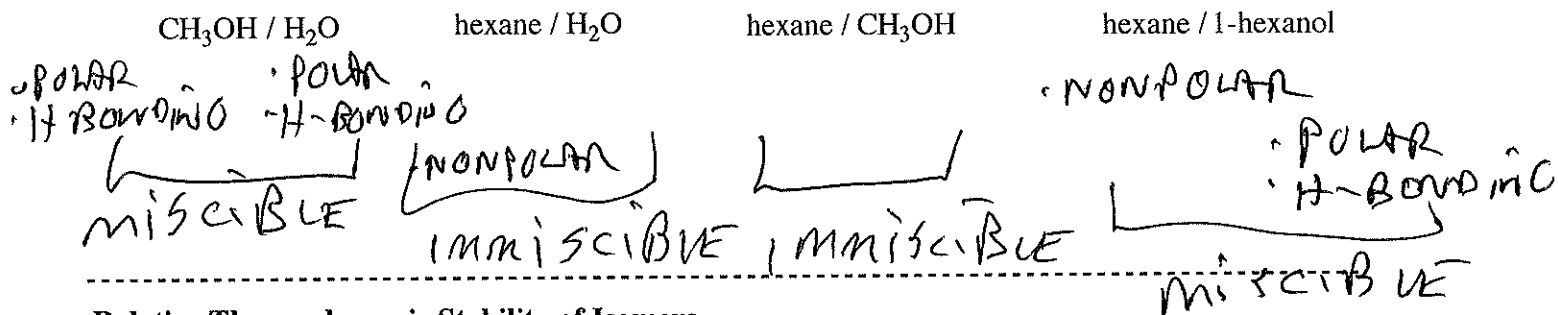
- Molecular Weight: Generally as molecular weight increases, boiling point increases.
- Intermolecular Forces (forces of attraction between molecules): Stronger intermolecular forces mean higher boiling points.



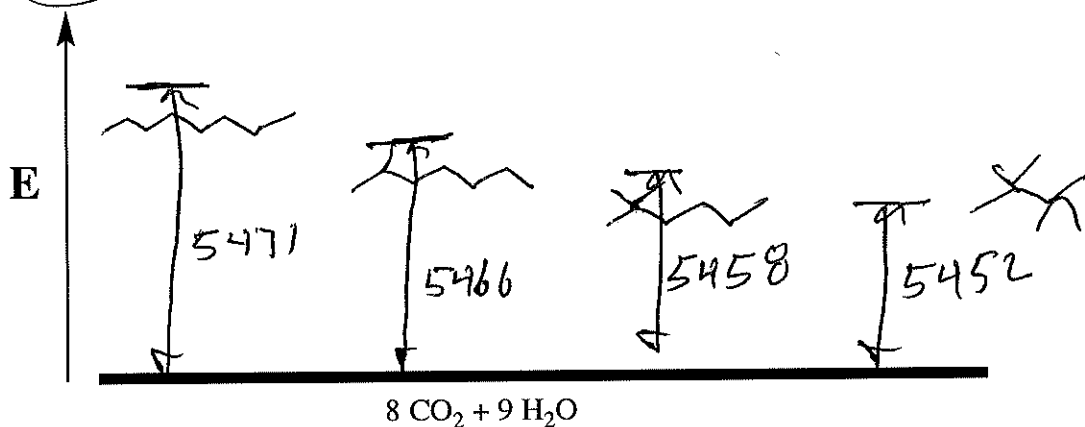
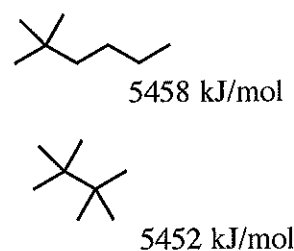
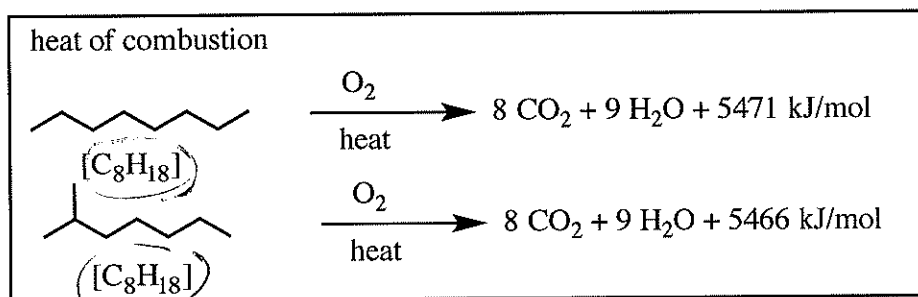
## Predicting Solubility



- 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

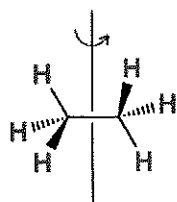


## Relative Thermodynamic Stability of Isomers

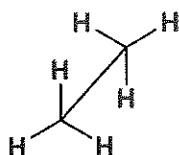


Problems: 9-15

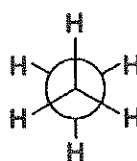
## Acyclic Alkanes: Newman Projections



Wedge and dash



Sawhorse



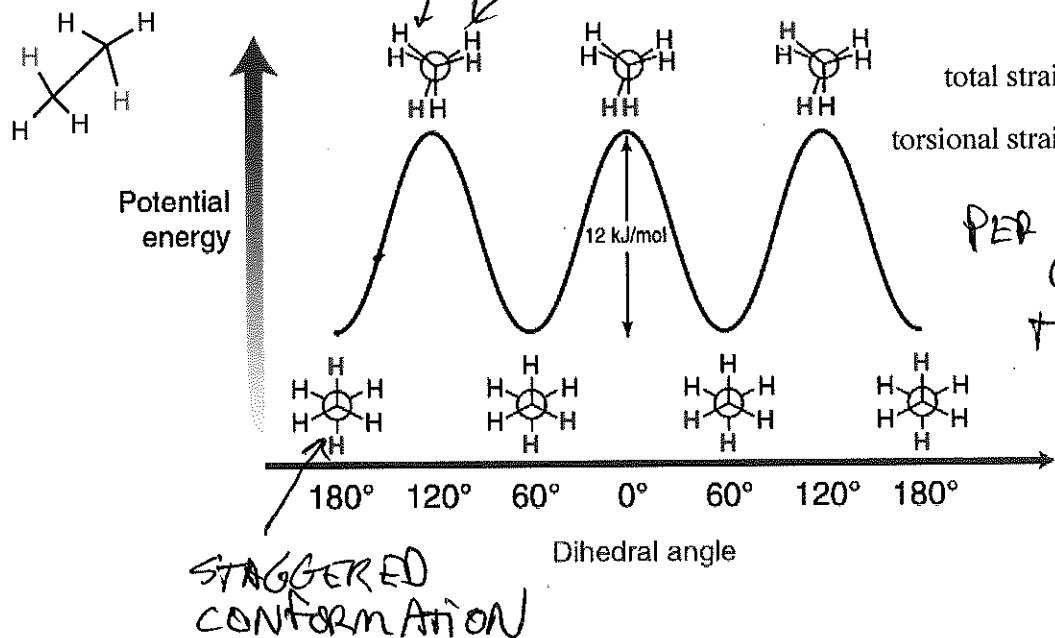
Newman projection



Melvin Newman  
1908-1993

## Analyzing Conformations of Simple Alkanes

consider ethane



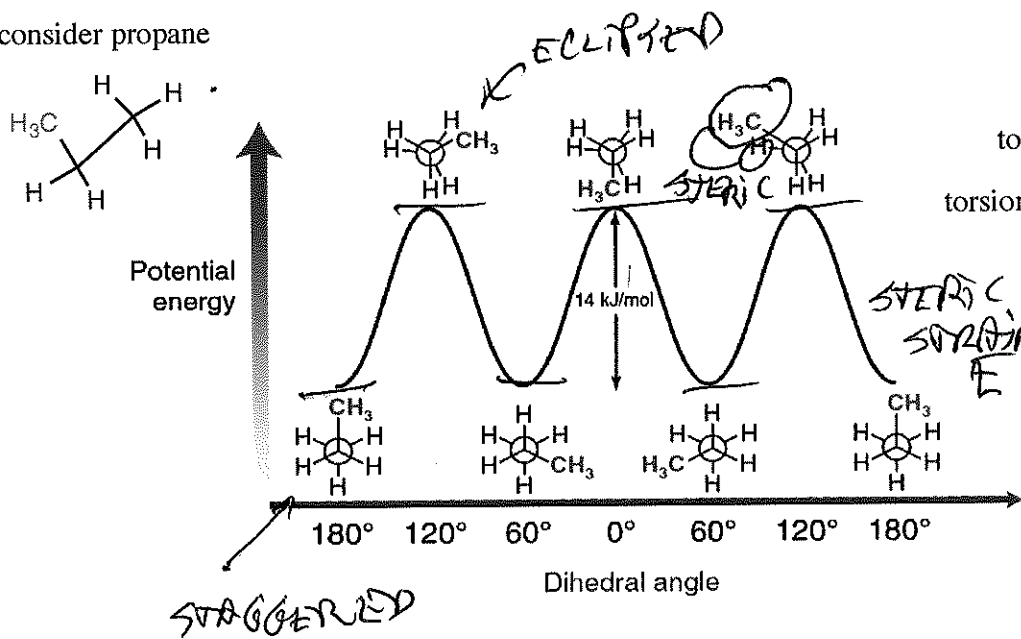
total strain = 12 kJ/mol  
torsional strain = 12 kJ/mol

PER ECLIPSED CH BOND TORSIONAL  
SO, E = 4 kJ/mol

STAGGERED CONFORMATION

- 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



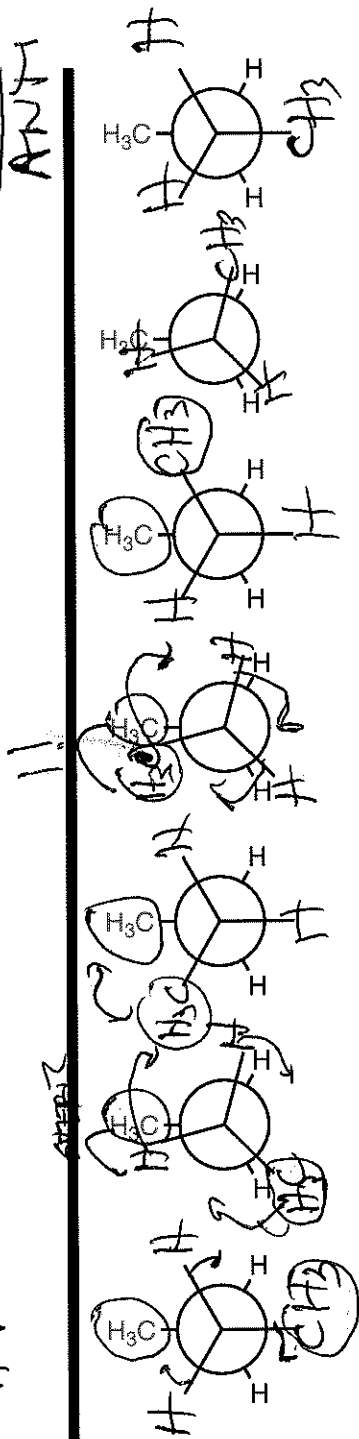
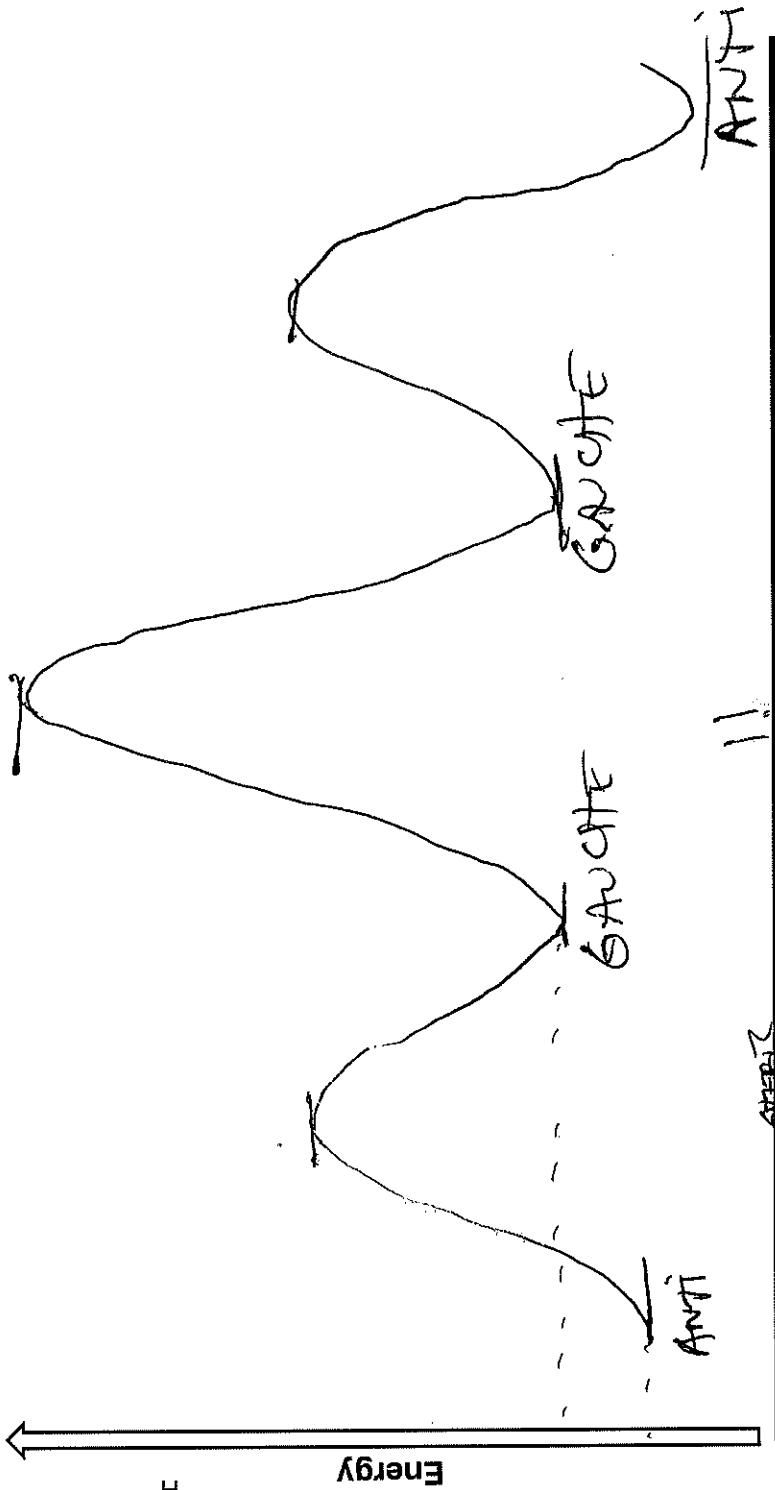
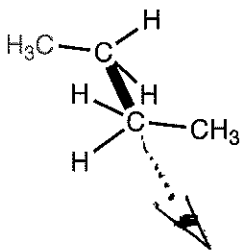
total strain = 14 kJ/mol  
torsional strain = 12 kJ/mol

STERIC STRAIN = 2 kJ/mol

STAGGERED

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

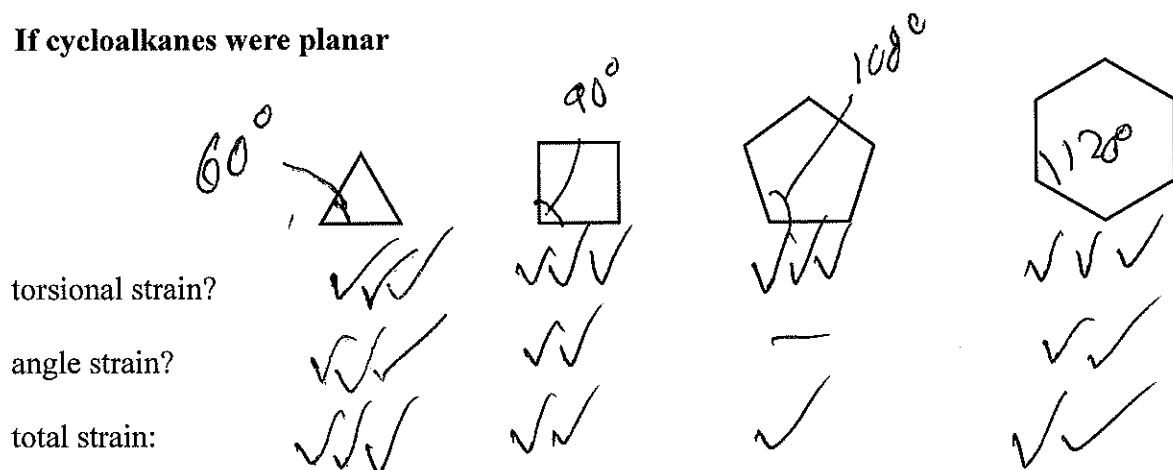
consider butane



torsional strain E?	X	X	✓	✓	✓	X	X
steric strain E?	X	X	✓	✓	✓	✓	X
conformer name?	ANTI	ANTI	GAUCHE	ANTI	GAUCHE	GAUCHE	ANTI

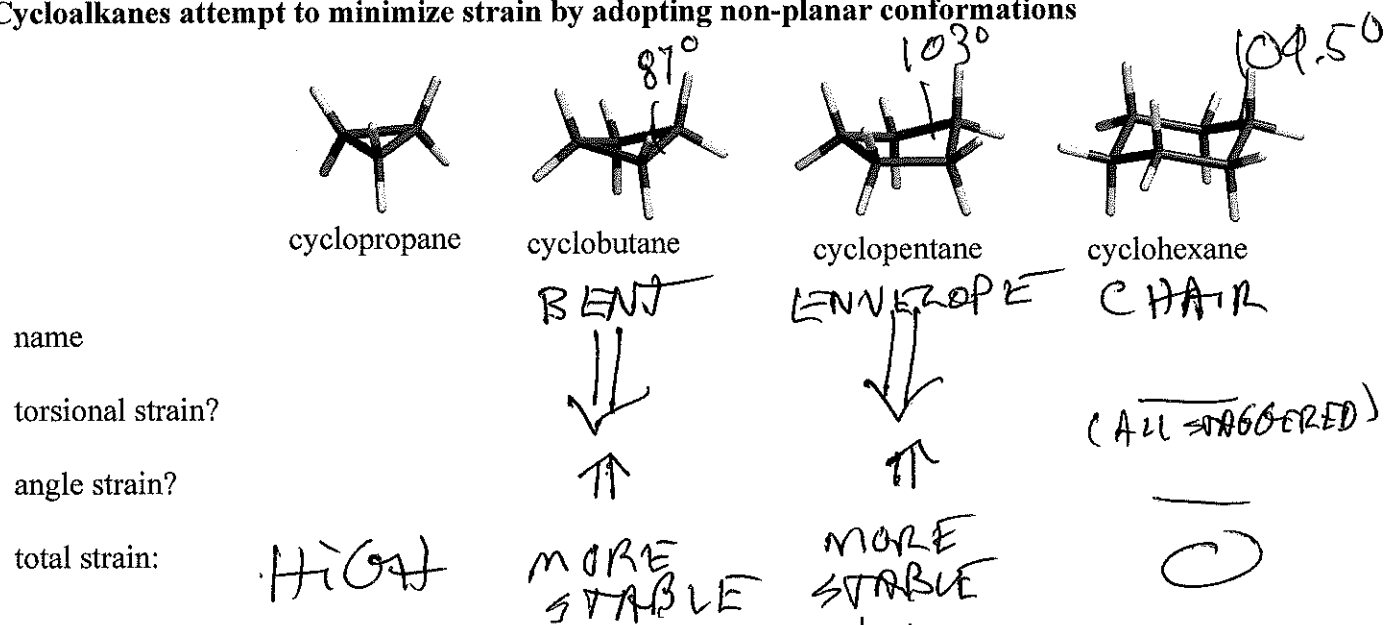
## Conformations of Cycloalkanes

If cycloalkanes were planar

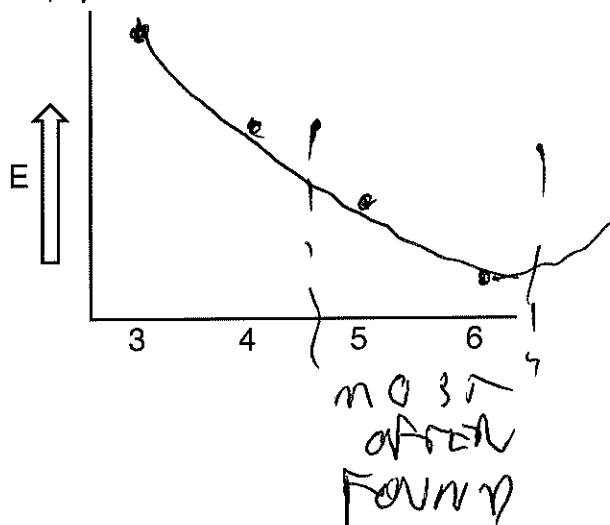


- there would be considerable torsional strain caused by eclipsing of neighboring C-H bonds (view cyclopropane in Chemagic)
- a new type of strain energy, angle strain, would be prevalent, especially, in small cycloalkanes
- angle strain results when atoms in a molecule have to adopt a bond angle that 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

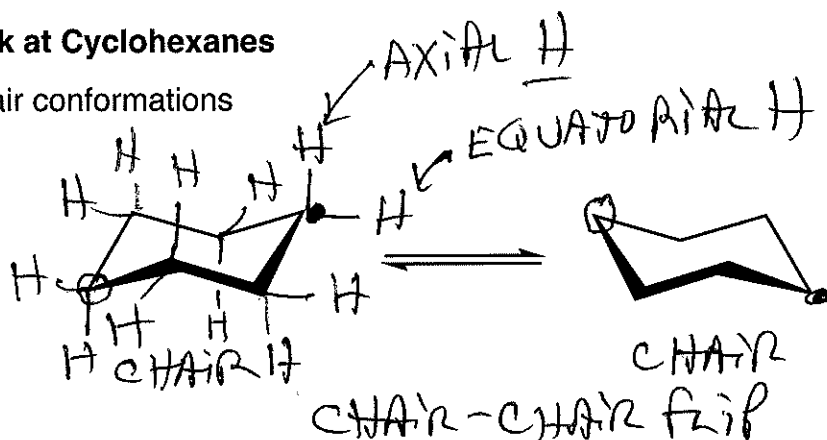


- non-planar conformations minimize overall strain energy in cycloalkanes (caused by a combination of angle and torsional)
- the exception is cyclopropane that cannot adopt a non-planar structure
- cyclohexane is the only cycloalkane free of angle AND torsional strain



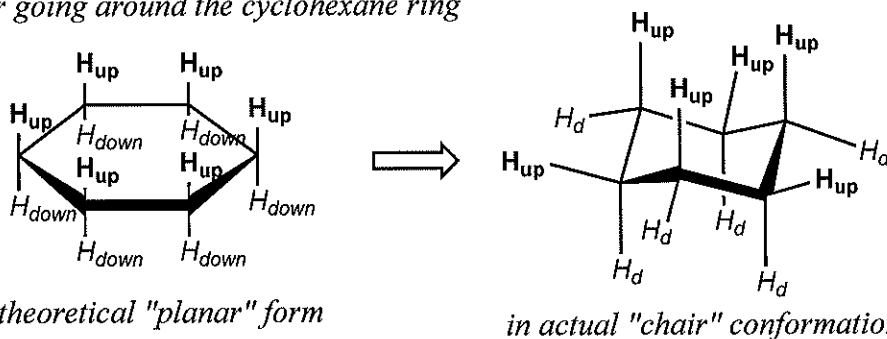
## A Closer Look at Cyclohexanes

Drawing chair conformations

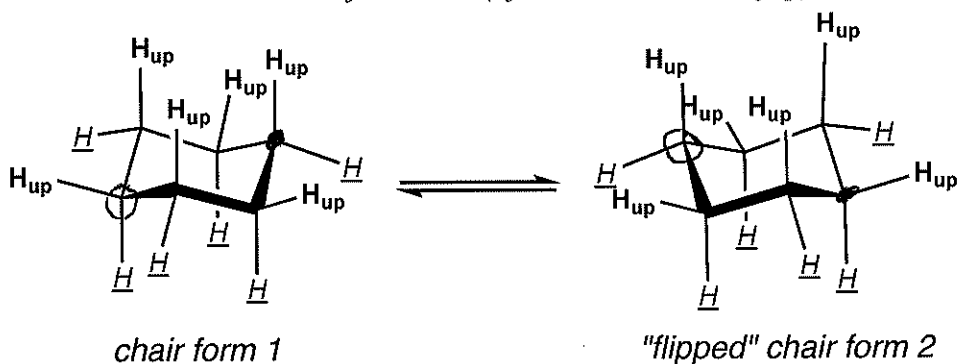


implications of the chair-chair flip

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

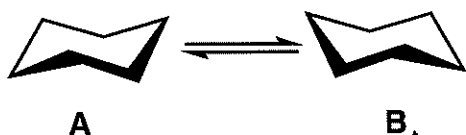


- All of the substituents occupying the axial position in one chair form adopt the equatorial position in the other chair conformation (after the chair/chair flip) and vice versa

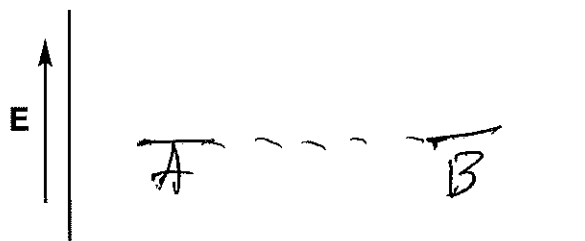


## 11. Energy Considerations

consider unsubstituted cyclohexane

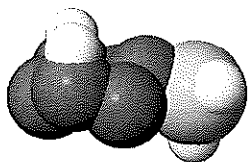
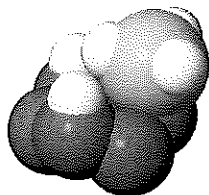
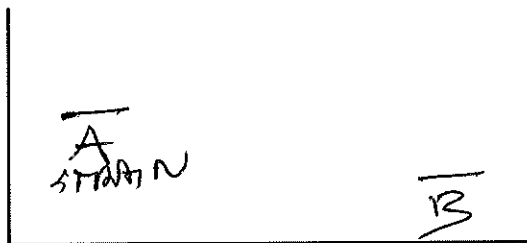
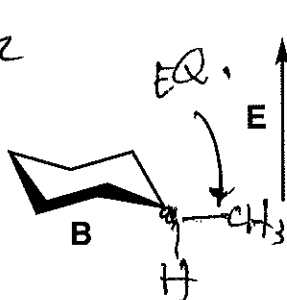
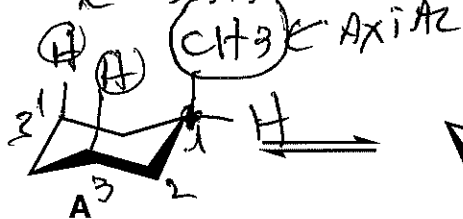


EQUIVALENT  
ENERGIES



# STERIC 2X 1,3-DIAXIAL INTERACTION

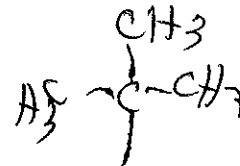
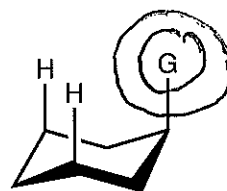
consider methylcyclohexane



- 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

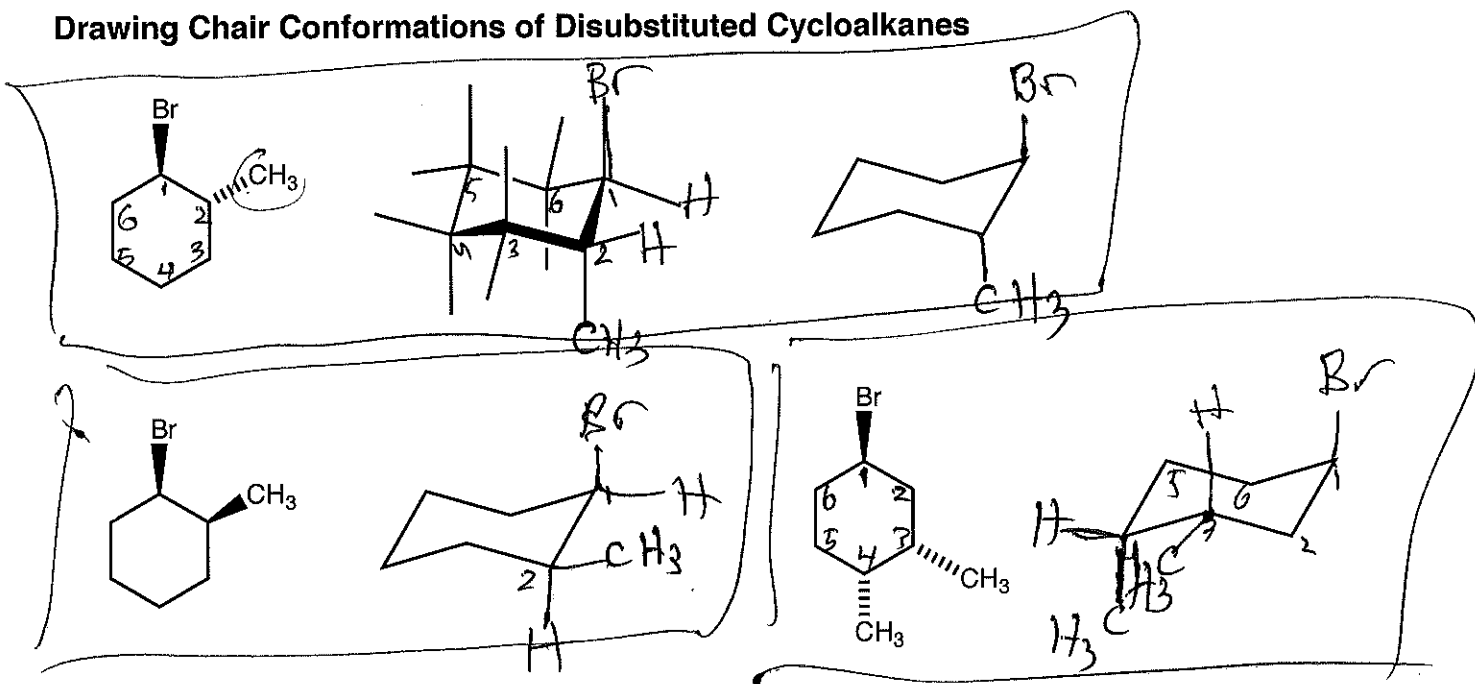
\*only 1,3-diaxial hydrogens shown

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 <sub>3</sub>	7.6	95 : 5
-CH <sub>2</sub> CH <sub>3</sub>	8.0	96 : 4
-CH(CH <sub>3</sub> ) <sub>2</sub>	9.2	97 : 3
-C(CH <sub>3</sub> ) <sub>3</sub>	22.8	9999 : 1



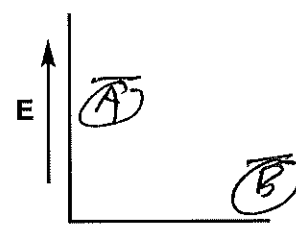
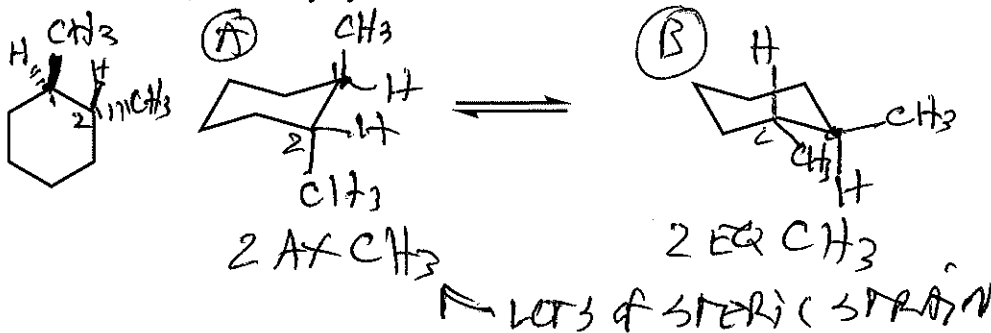
• In general, the larger the substituent, the worse the steric strain due to 1,3-diaxial interactions, and the greater preference for the substituent to occupy the equatorial position

## Drawing Chair Conformations of Disubstituted Cycloalkanes

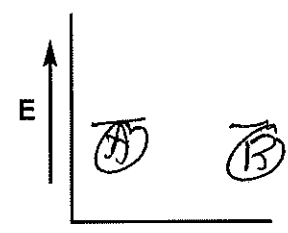
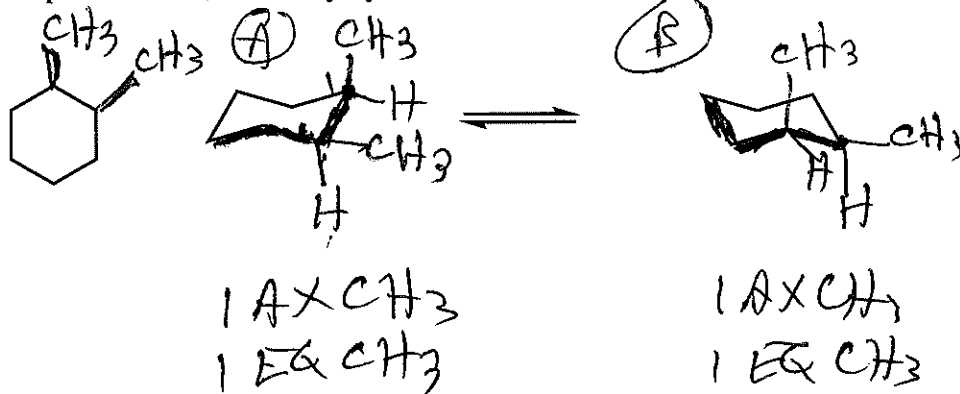


# Chair Conformations of Disubstituted Cycloalkanes

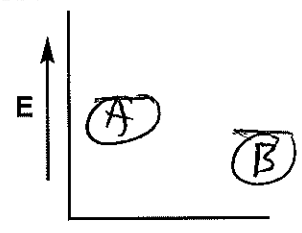
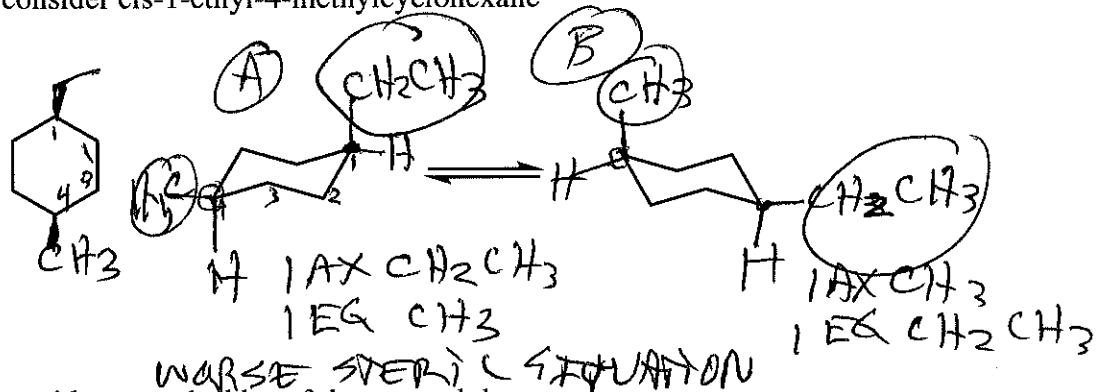
consider trans-1,2-dimethylcyclohexane



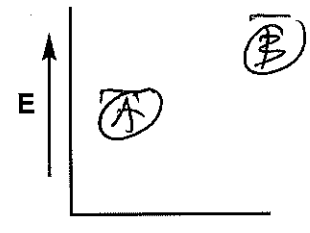
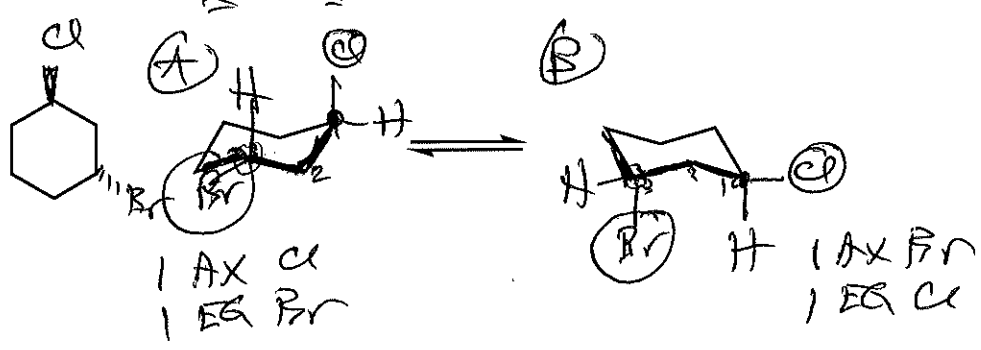
compare to cis-1,2-dimethylcyclohexane



consider cis-1-ethyl-4-methylcyclohexane

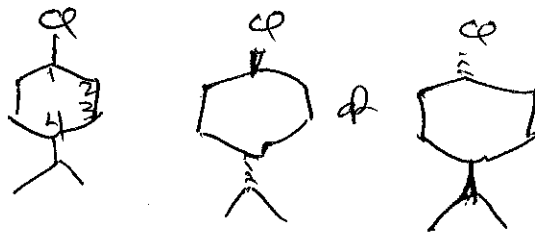
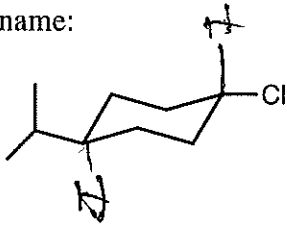


consider trans-1-chloro-3-bromocyclohexane



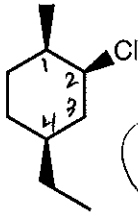
- NOTE: both chair conformations are the same molecule in all cases. They are simply conformations!
- DO NOT transform cis- to trans- via a chair chair flip! This does NOT happen!

name:

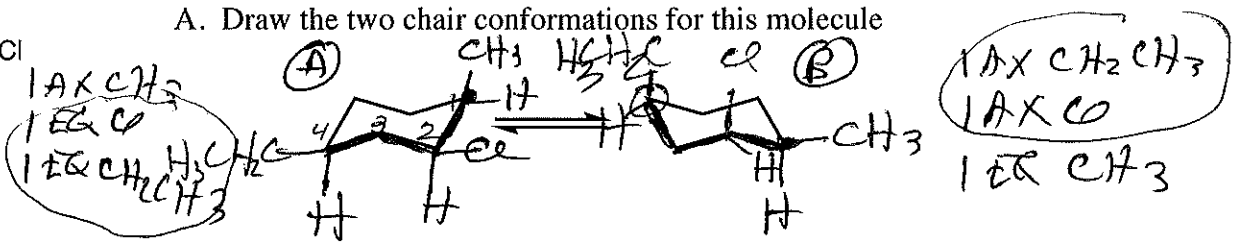


~~TRANS-1-CHLORO-4-ISOPROPYLCYCLOHEXANE~~

consider the following molecule:

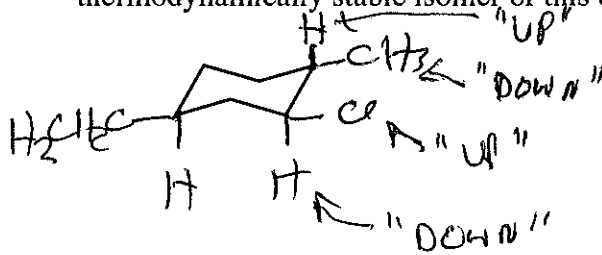
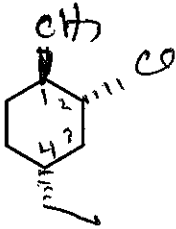


A. Draw the two chair conformations for this molecule



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:



Problems: 20-26