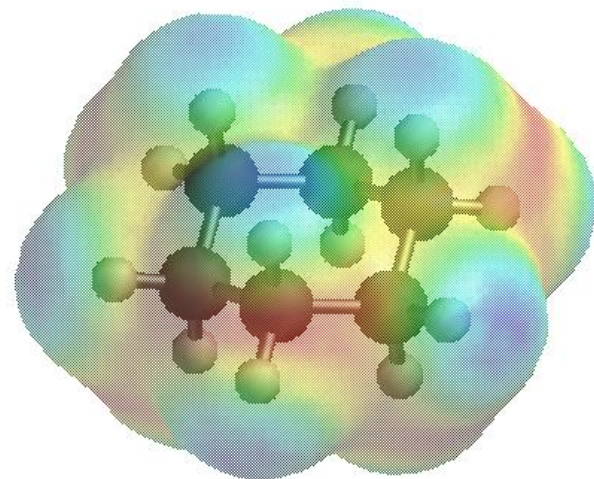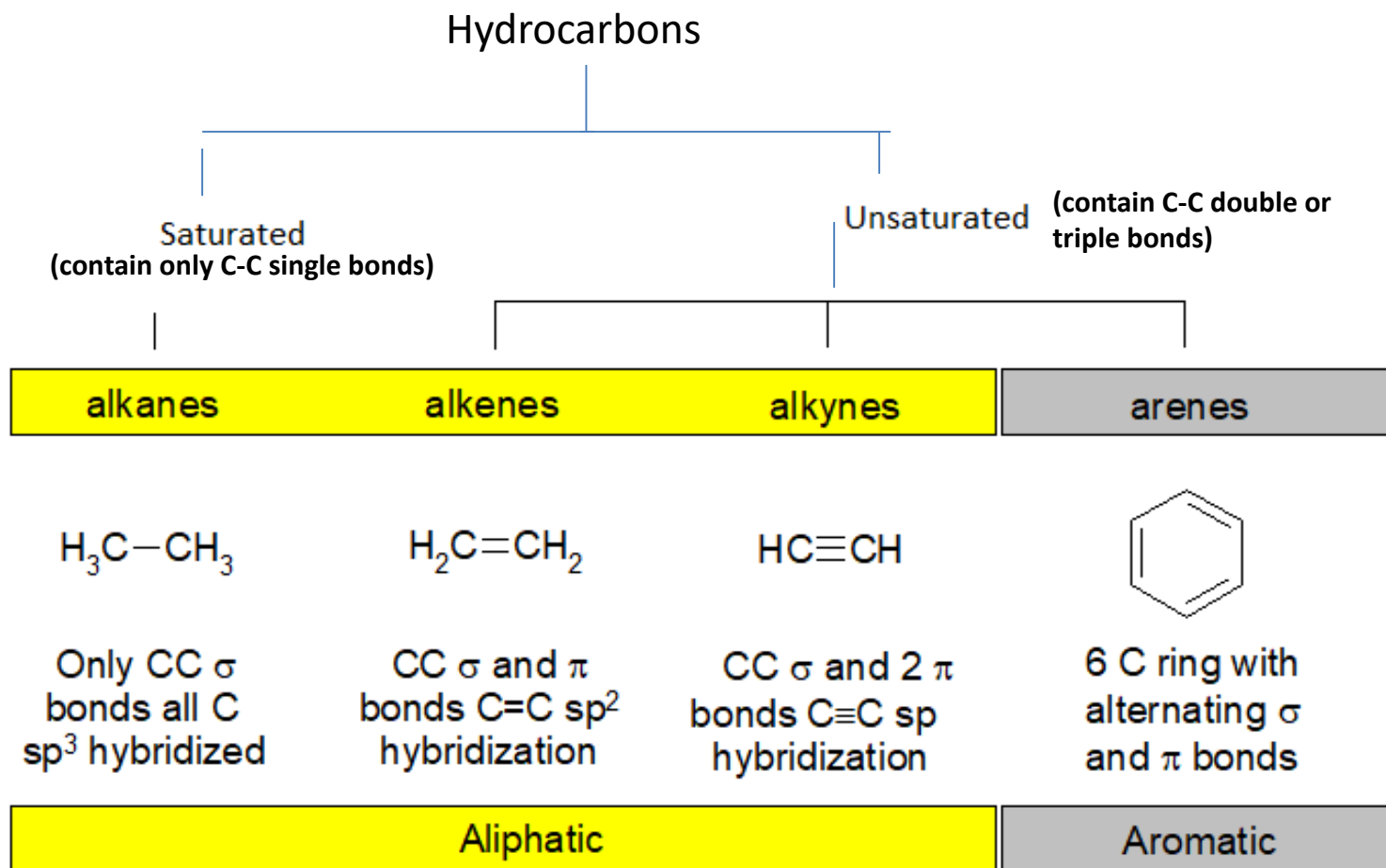# *Chapter 2: Alkanes and Cycloalkanes: Conformational and Geometric Isomers*

Types of Hydrocarbons

Hydrocarbons are compounds that only contain C and H atoms.

Hydrocarbons

Saturated
(contain only C-C single bonds)

Unsaturated **(contain C-C double or triple bonds)**

| alkanes	alkenes	alkynes	arenes
H_3C-CH_3	$H_2C=CH_2$	$HC\equiv CH$	
Only CC σ bonds all C sp^3 hybridized	CC σ and π bonds C=C sp^2 hybridization	CC σ and 2 π bonds C$\equiv$C sp hybridization	6 C ring with alternating σ and π bonds
Aliphatic			Aromatic

Structure of Alkanes

Alkanes are saturated hydrocarbons, that is they contain the maximum number of H atoms possible for the number of C atoms present.
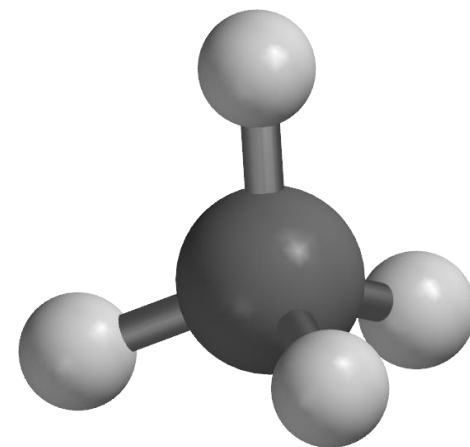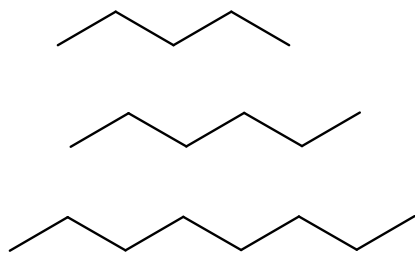
The generic formula for an alkane is: C_nH_{2n+2}
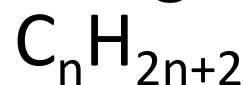
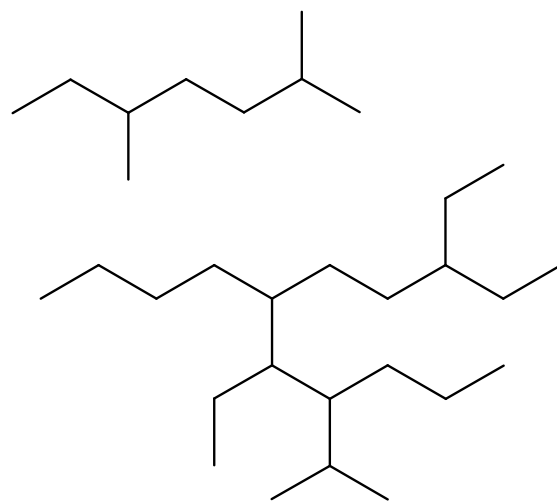This means every C atom is sp^3 hybridized with bond angles of ~109.5°
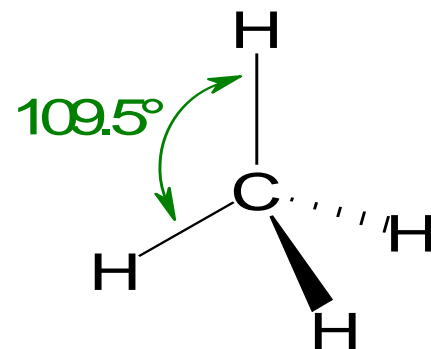
Structure of Alkanes (cont'd)

Alkanes can come in two forms, normal (or linear) and branched. Branched alkanes can have branched branches. Therefore the number of isomers possible growths quickly
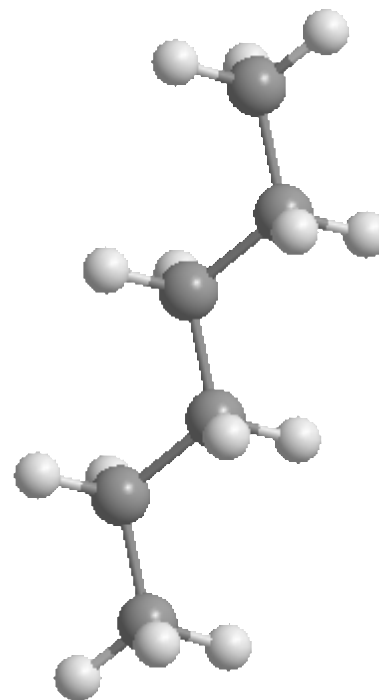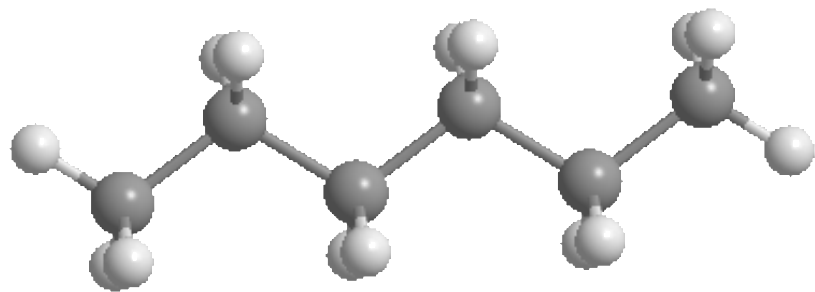

Normal, unbranched (or linear)

branched

Nomenclature of Organic Compounds

A. Common names: In the early days of organic chemistry, each new compound was given a name that was usually based on its source or use.

B. IUPAC :

The IUPAC name of any compound contains **3 parts :**

$$\text{IUPAC name= Prefix + parent + suffix}$$

Prefix :What and where substituents.

Parent (Root) : longest chain

Suffix : functional group.

Table 2.1 ◢ **Names and Formulas of the First Ten Unbranched Alkanes**

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

Note: The repeating group is $(-CH_2-)$ is Methylene group

IUPAC Rules for Naming Alkanes

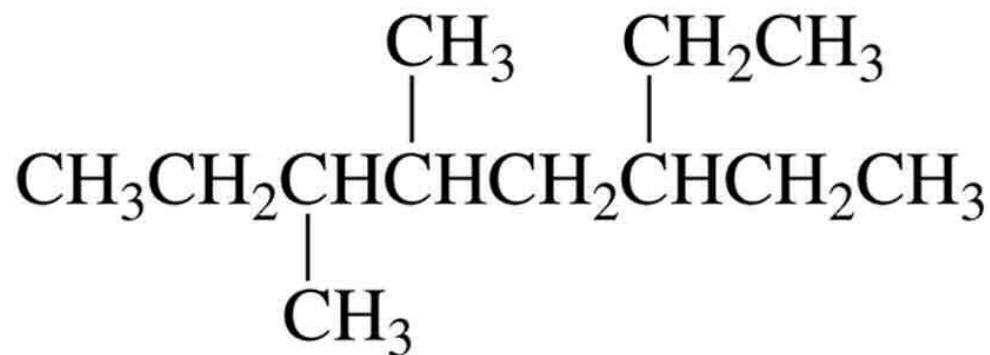## 1. First identify the longest continuous chain (parent name)
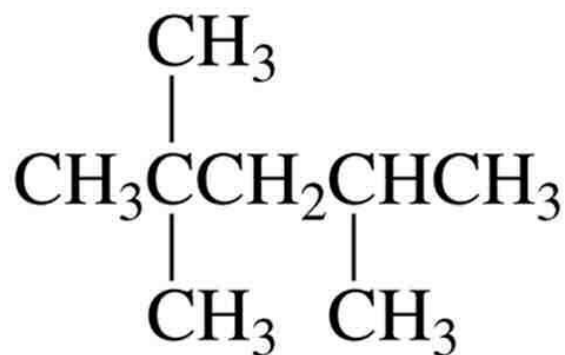
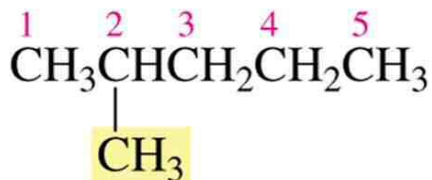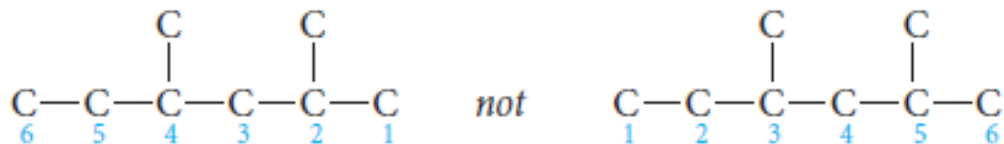2,2,4-trimethylpentane
not
2,4,4-trimethylpentane
because 2 < 4

6-ethyl-3,4-dimethyloctane
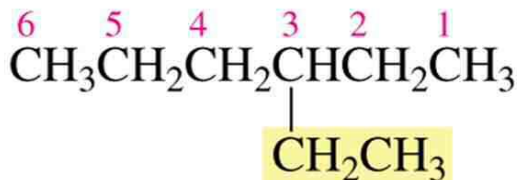**not**
3-ethyl-5,6-dimethyloctane
because 4 < 5

2. Number the chain in the direction that gives the substituent as low a number as possible

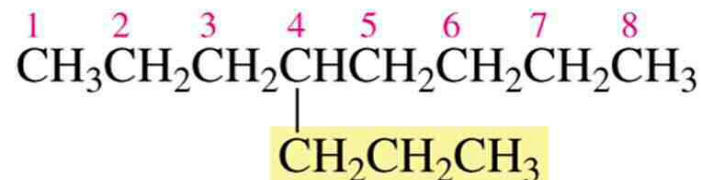$$\underset{6}{C}-\underset{5}{C}-\underset{4}{C}-\underset{3}{C}-\underset{2}{C}-\underset{1}{C} \quad not \quad \underset{1}{C}-\underset{2}{C}-\underset{3}{C}-\underset{4}{C}-\underset{5}{C}-\underset{6}{C}$$

$$\underset{1}{CH_3}\underset{2}{CH}\underset{3}{CH_2}\underset{4}{CH_2}\underset{5}{CH_3}$$
CH_3
2-methylpentane
not
4-methylpentane

$$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH}\underset{2}{CH_2}\underset{1}{CH_3}$$
CH_2CH_3
3-ethylhexane
not
4-ethylhexane

$$\underset{1}{CH_3}\underset{2}{CH_2}\underset{3}{CH_2}\underset{4}{CH}\underset{5}{CH_2}\underset{6}{CH_2}\underset{7}{CH_2}\underset{8}{CH_3}$$
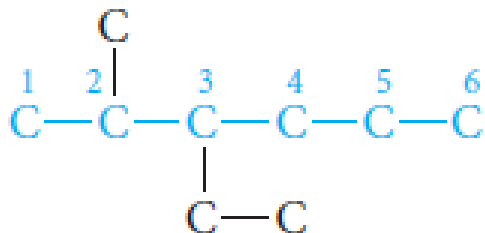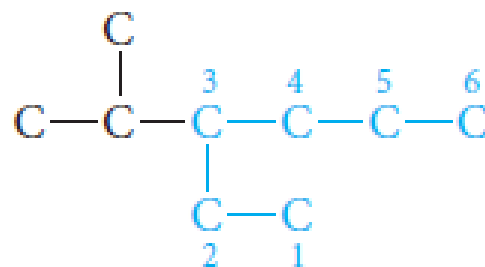$CH_2CH_2CH_3$
4-propyloctane
not
5-propyloctane

Note: If there are two equally long continuous chains, select the one with the most branches. For example:
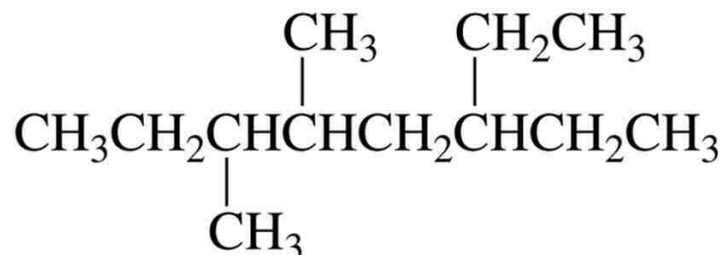
two branches

not

one branch

If there is a branch equidistant from each end of the longest chain, begin numbering nearest to a third branch

2,3,6-trimethylheptane   *not*   2,5,6-trimethylheptane

- **How to name a substituent?**
- **It can be a branch In the chain**
- **A branch (alkyl substituent): is (Alkane – H)**

Replace "ane" of alkane with "yl.
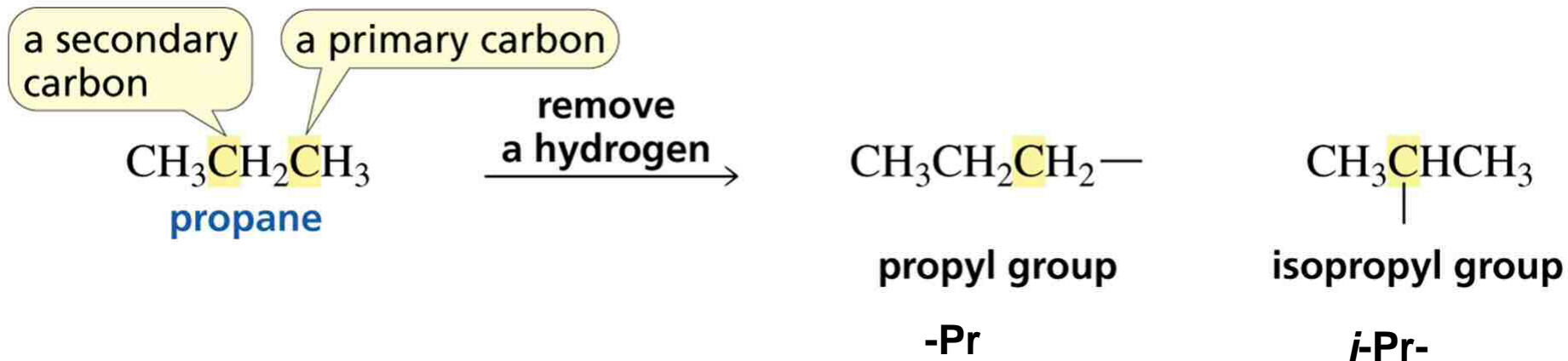
CH_3-
methyl group

CH_3CH_2-
ethyl group

$CH_3CH_2CH_2-$
propyl group

$CH_3CH_2CH_2CH_2-$
butyl group

$CH_3CH_2CH_2CH_2CH_2-$
pentyl group

$R-$
any alkyl group

-There are two propyl Groups

a secondary carbon

a primary carbon

$CH_3CH_2CH_3$

propane

remove a hydrogen →

$CH_3CH_2CH_2-$

propyl group

-Pr

CH_3CHCH_3

isopropyl group

i-Pr-

-There are Four Butyl Groups

primary carbon

$CH_3CH_2CH_2CH_2-$

butyl group

primary carbon

CH_3CHCH_2-
|
CH_3

isobutyl group

secondary carbon

CH_3CH_2CH-
|
CH_3

sec-butyl group

tertiary carbon CH_3

CH_3C-
|
CH_3

tert-butyl group
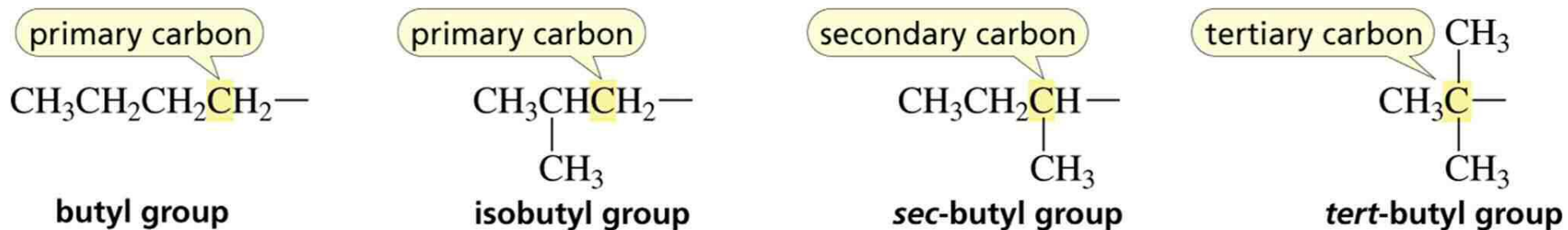
Note: These names for the alkyl groups with up to four carbon atoms are very commonly used, so you should memorize them.
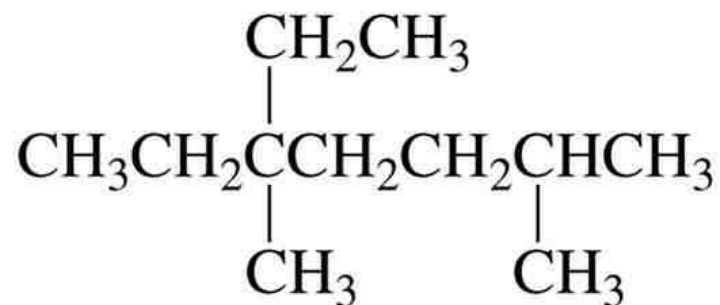
Examples:

$$CH_3CH_2CHCH_2CHCH_3$$

$$CH_3 \quad CH_3$$

2,4-dimethylhexane

$$CH_2CH_3$$

$$CH_3CH_2CCH_2CH_2CHCH_3$$

$$CH_3 \quad CH_3$$
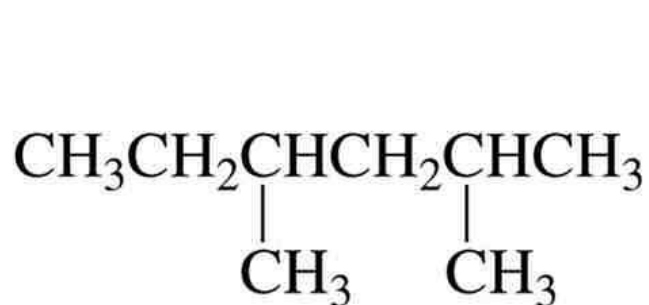
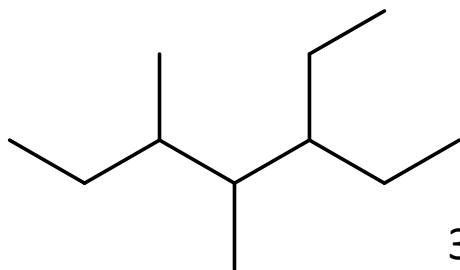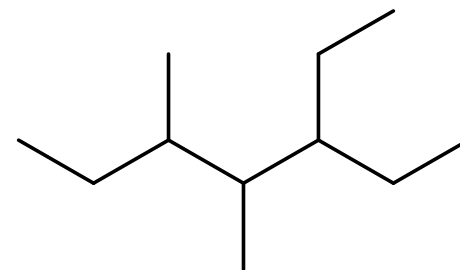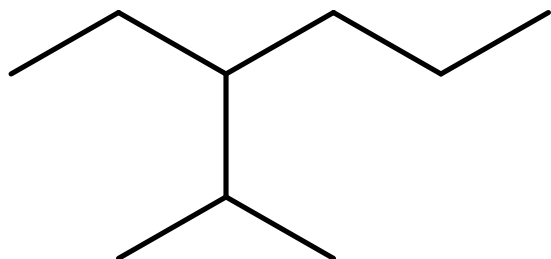**5-ethyl-2,5-dimethylheptane**

numbers are separated by a comma;
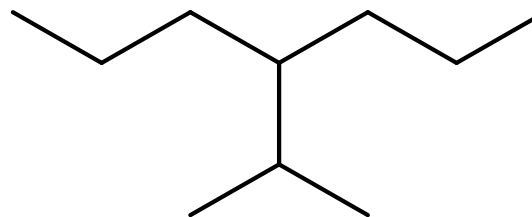a number and a word are separated by a hyphen

3-ethyl-4,5-dimethylheptane
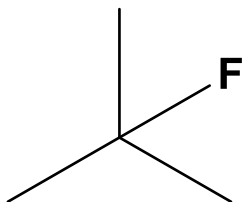
Examples

3-ethyl-2-methylhexane

4-isopropylheptane

2.4: Alkyl and Halogen Substituents (R-X)

Common name : Alkyl halide
eg. CH_3CH_2Br Ethyl bromide

***tert*-butyl fluoride**
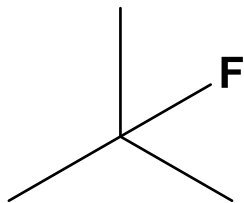
IUPAC:
Halogen substituents are named by changing the *-ine* ending of the element to *-o*.

F: fluoro   Cl: chloro   Br: bromo   I: iodo-

2-fluoro-2-methylpropane

Sources of Hydrocarbons

Hydrocarbons are found in crude oil and natural gas. Both are mixtures of different hydrocarbons and they are separated by "fractional distillation" a process where the different compounds are separated in a long distilling column based on their boiling points. Heavy fractions can be "cracked" into small lighter, hydrocarbons using heat and/or catalysts.

2.7: Physical Properties of Alkanes and Nonbonding Intermolecular Interactions

A physical property is any property of matter or energy that can be measured. When it changes, the chemical composition of the object does not change

Alkanes *are insoluble in water*. This is because water molecules are *polar,* whereas alkanes are *nonpolar* (Like dissolves like: Polar/ionic solvents **dissolve** polar/ionic solutes and non-polar solvents **dissolve** non-polar solutes)

Alkanes *have lower boiling points for a given molecular weight than most other organic compounds.* This is because they are nonpolar molecules.

The physical properties of molecules are in part dependent on the type's of intermolecular forces (IMF) present.

attraction
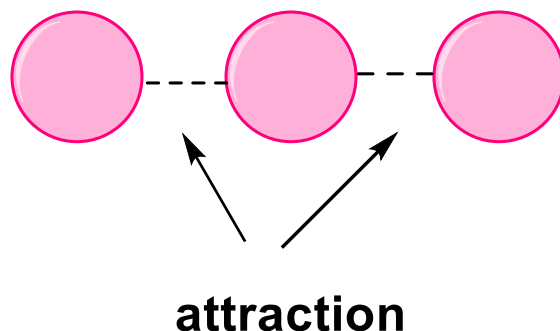
Intermolecular Forces

The physical properties of molecules are in part dependent on the type's of intermolecular forces (IMF) present.

Boiling points (BP) are also dependent on the **mass of the molecule.**

Solubility, the ability to dissolve into a solvent is dependent on IMFs.

The strength of the interaction between molecules is also dependent on the **overall shape** of the molecule.

Intermolecular Forces

There are 3 types of IMFs, by decreasing strength they are:

1) Hydrogen bonding
2) Dipole-dipole
3) Van der Waals or London Dispersion

Dipole-dipole

Dipole-dipole forces arise from the attraction of oppositely charged atoms (other than H) in molecules. These molecules may have a **permanent** dipole moment. Generally in organic molecules they results from the presence of C-X bonds where X is more electronegative that C.

These are generally weaker than H-bonding, ranging from about 5-10 kJ/mol.

Dipole-dipole
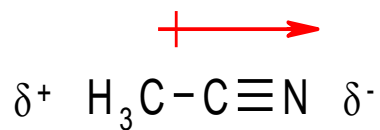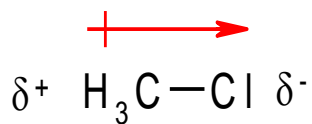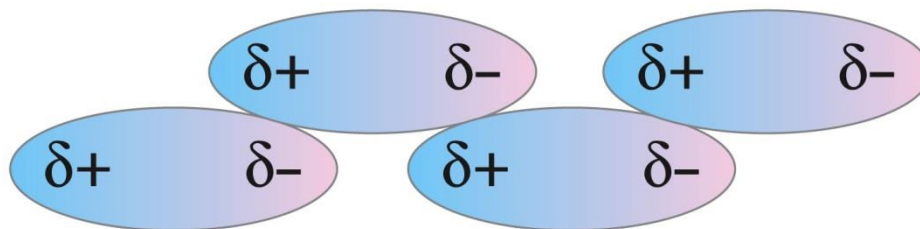
Hydrogen Bonding

Hydrogen bonding is a complex interaction that includes dipole-dipole, as well as orbital interactions and the transfer of electron density between molecules.

These are the strongest of the IMFs and range from 5 – 25 kJ/mol
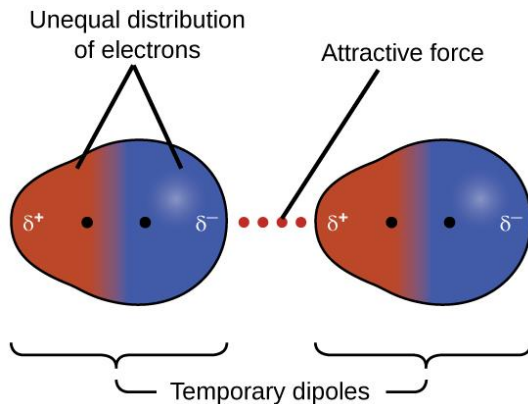
Hydrogen Bonding

Occur primarily between OH, NH and FH. The more EN the atom the stronger the interaction. (The atom H is attached to usually has a lone pair of e$^-$)

Geometry: X-H ----:X-
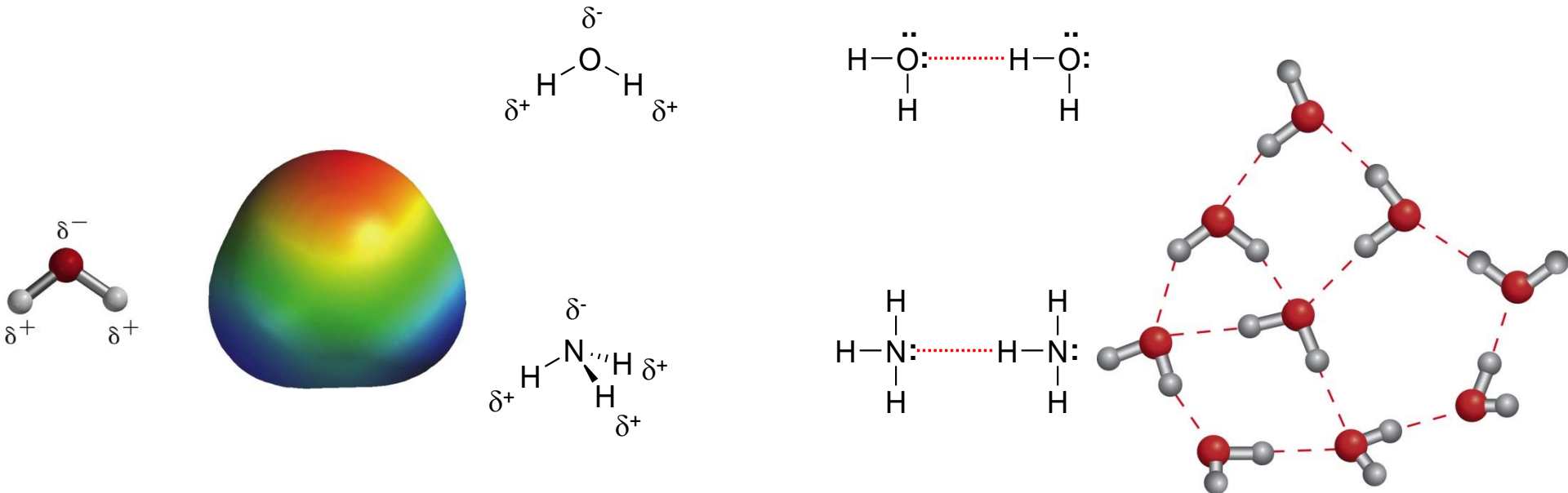
Van der Waals or (London) *dispersion* forces arise from the movement of electrons within a molecule. This natural motion can produce an uneven distribution of the electrons (polarization of the distribution) resulting in a **temporary dipole moment** in the molecule. This will induce the movement of electrons in adjacent molecules producing a dipole moment in them. These "induced" dipole moments are very brief as they disappear when the electrons move to new locations within the molecule, so they forces are very brief and weak, only 2-5 kJ/mol.

Unequal distribution
of electrons

Attractive force

Very Weak attraction

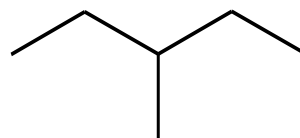δ^+ δ^- δ^+ δ^-

Temporary dipoles

London dispersion, $<$ *dipole-dipole,* $<$ *Hydrogen bonding*

Effects on Physical Properties (cont'd)

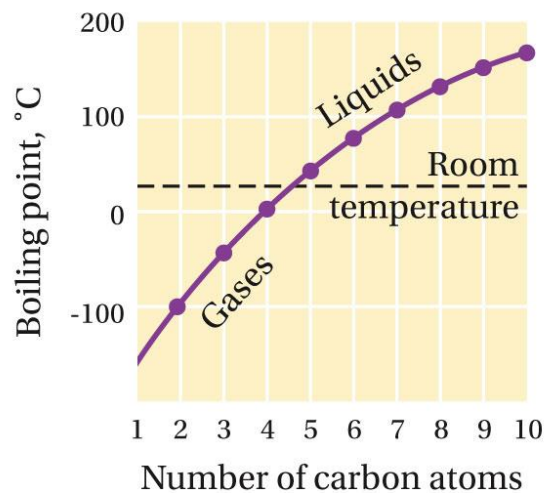Dipole forces: much strong IMFs so the BP is higher when dipole-dipole interactions are present, i.e.
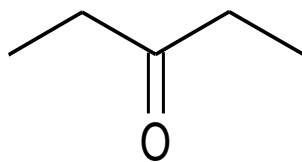
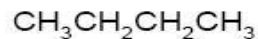mass = 86 amu
BP = 101.7 °C

mass = 86 amu
BP = 63.3 °C

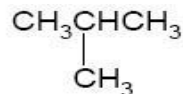Alkanes: no H-bonding or dipole moment (C & H have nearly the same EN ∴ not polar).

Name	Formula	Boiling point, °C
pentane	$CH_3CH_2CH_2CH_2CH_3$	36
2-methylbutane (isopentane)	$CH_3CHCH_2CH_3$ with CH_3 branch	28
2,2-dimethyl-propane (neopentane)	$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$	10

- Boiling point for alkanes increases with increasing size (mass)
- Boiling point for alkanes decreases with increasing branching

Example:

$CH_3CH_2CH_2CH_3$
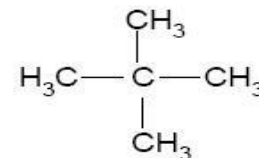
n-butane, 0° C

CH_3CHCH_3 with CH_3 branch

Isobutane , -12° C

$CH_3CH_2CH_2CH_2CH_3$

n-pentane, 36°C

$CH_3CHCH_2CH_3$ with CH_3 branch

Isopentane, 28°C

$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$
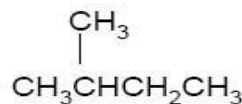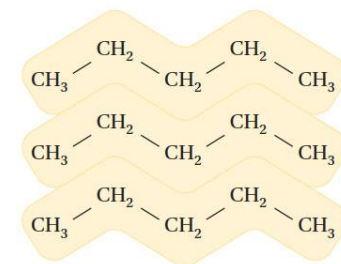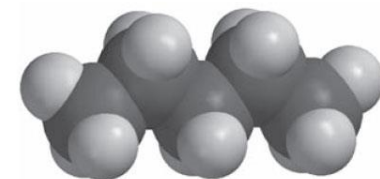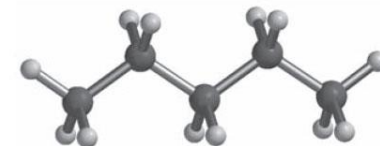
Neopentane, 9.5°C

Structural Effects on IMFs

The strength of the IMFs depend on the amount of contact between the molecules, especially for dispersion forces. Hence the shape of the molecule can affect the **surface area of contact,** long thin molecules have more surface in contact than spherical molecules.
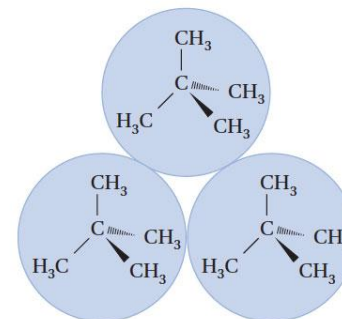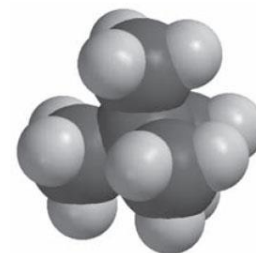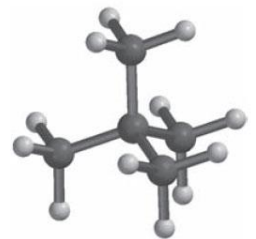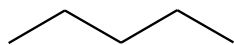

2,2-dimethylpropane
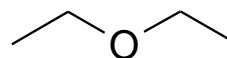bp 10°C

(a)

pentane
bp 36°C
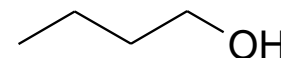
(b)

Effects on Physical Properties (cont'd)

Hydrogen bonding: strongest intermolecular forces so BP are very high for equivalent MW compounds, i.e.
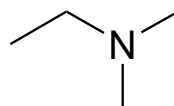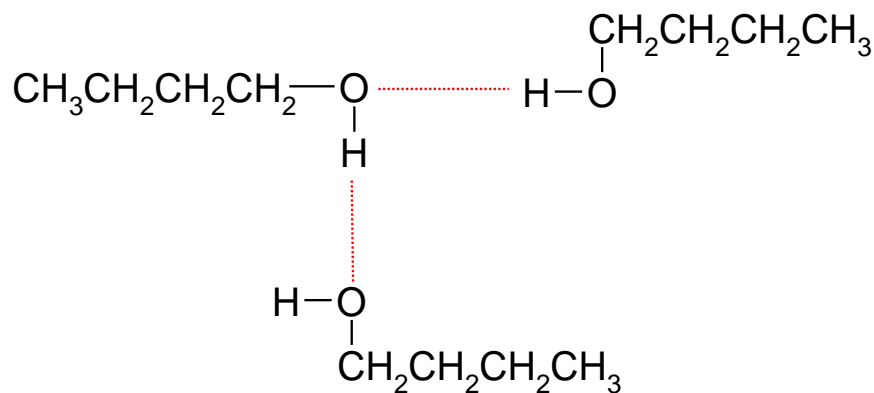
mass = 72 amu
BP = 36.1 °C

mass = 74 amu
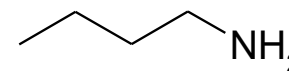BP = 35 °C

mass = 74 amu
BP = 117 °C

$CH_3CH_2CH_2CH_2$—O ∙∙∙∙∙∙∙∙∙∙ H—O

$CH_2CH_2CH_2CH_3$

H

H—O

$CH_2CH_2CH_2CH_3$

mass = 73 amu
BP = 36 °C

mass = 73 amu
BP = 78 °C

Conformational Isomers

Conformational isomers (rotamers or conformers) are compounds with the same constitution (atoms are bonded in the same order) but the atoms are located in different places in space.

This is achieved by rotating about C-C single (s) bonds or the dihedral (or torsion) angle (q).

Rotation about a **single bond** occurs easily because the amount of overlap of the $sp3$ orbitals on the two carbon atoms is unaffected by rotation about the sigma bond
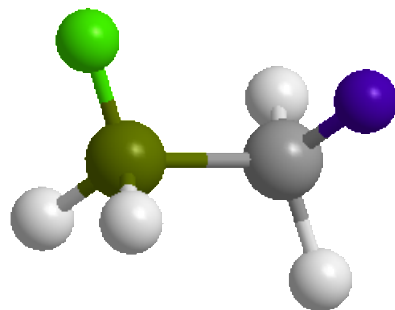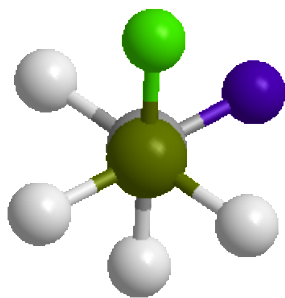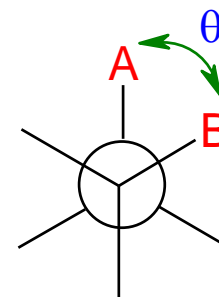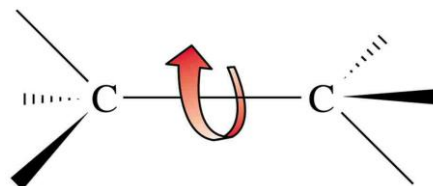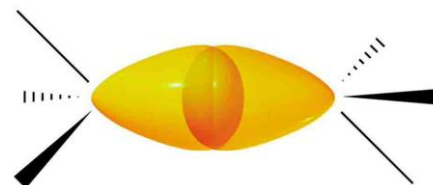
Conformational Isomers (cont'd)

Two extremes exist for ethane: staggered & eclipsed

staggered

"dash-wedge"   "sawhorse"   Newman

eclipsed

"dash-wedge"   "sawhorse"   Newman
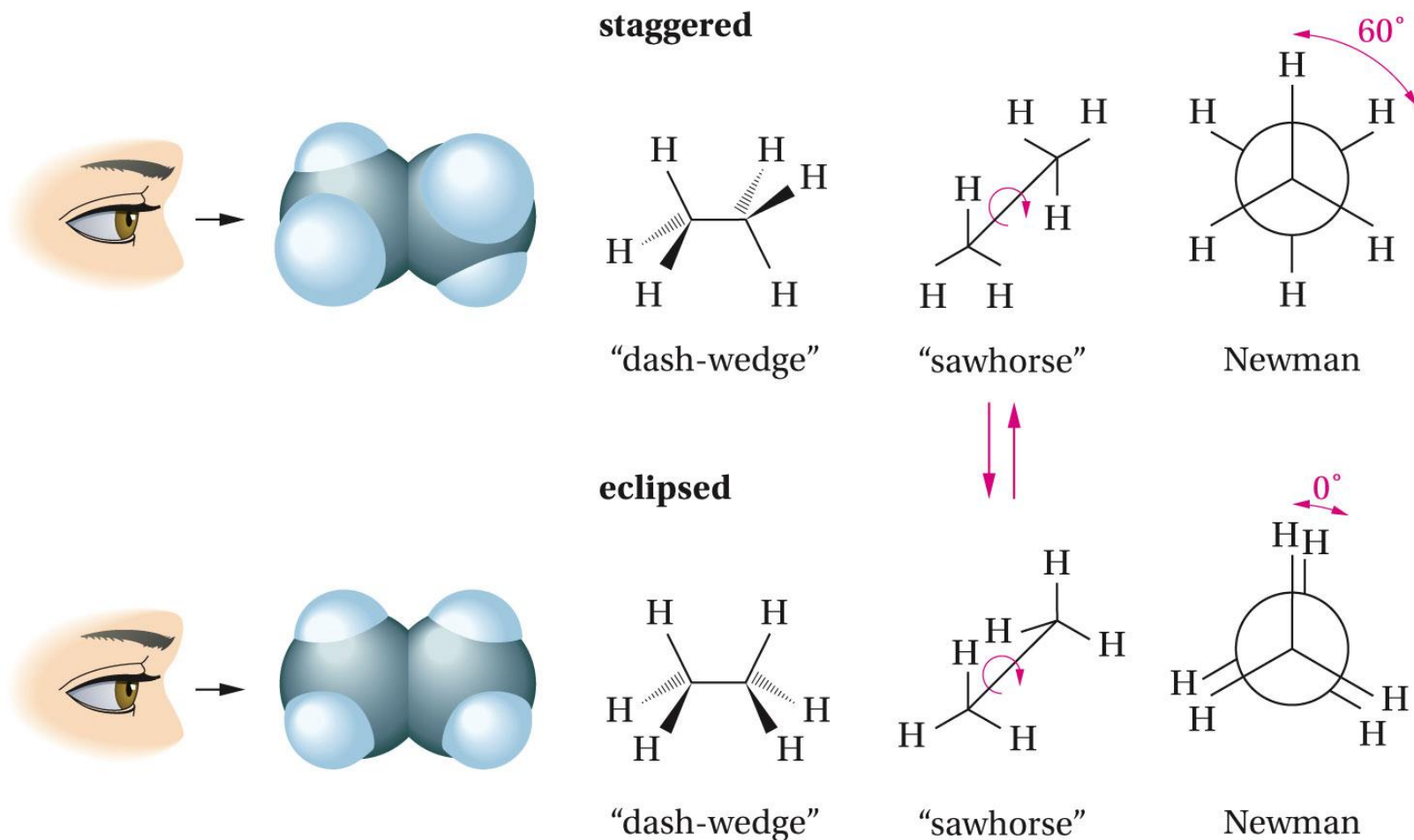
Conformational Isomers (cont'd)

These two extremes represent high and low energy "conformations" of ethane. The "high" E is the eclipsed and low E the staggered.
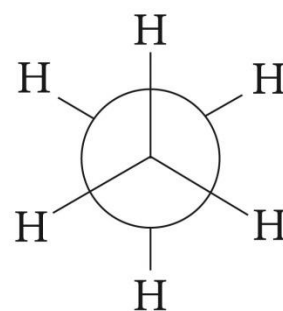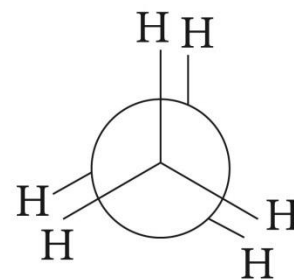
staggered   eclipsed
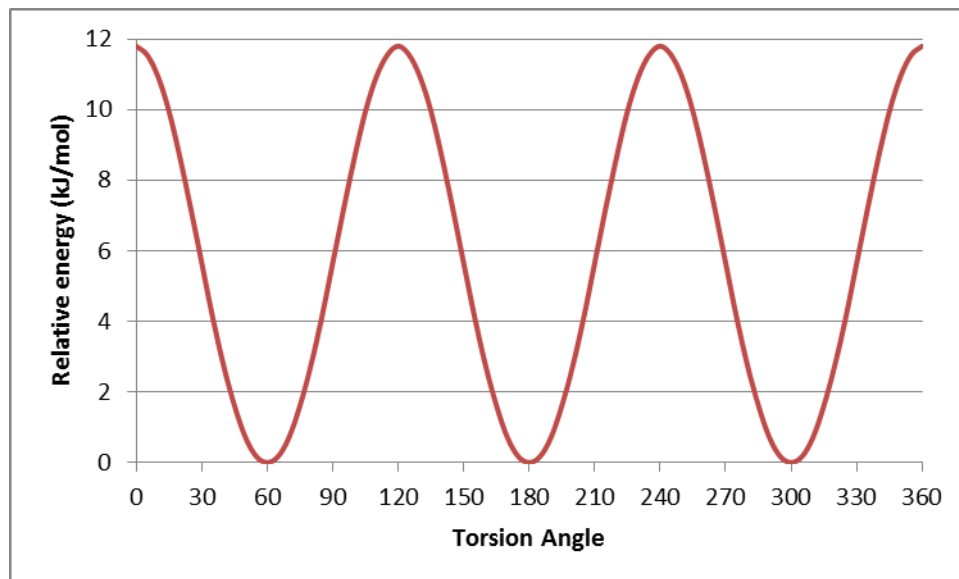
Conformational Isomers (cont'd)

The difference in energy is caused by "steric" interactions between the H atoms. Steric interactions are repulsions caused when two atoms are too close together in space and their valence shell electrons repel each other.

Rotating one carbon 60°

3.0 Kcal/mol

Torsional strain
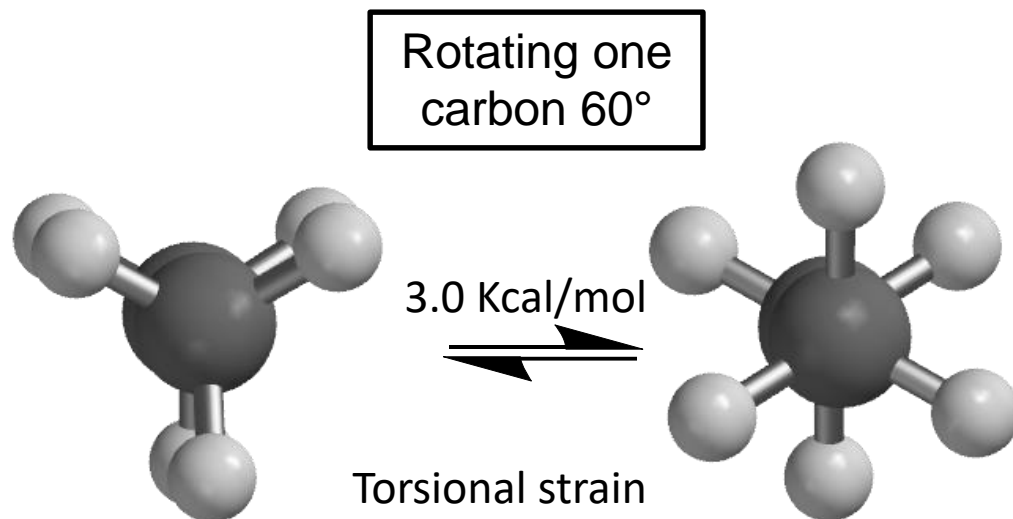
The H – H distance in the eclipsed is 2.36 Å and 2.54 Å in the staggered.

Conformational Isomers (cont'd)

The problem is worse in propane as a methyl group is larger than a H atom. The eclipsed is on the left in both sets of images.
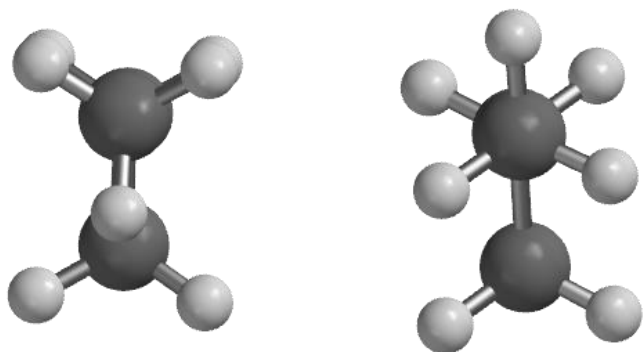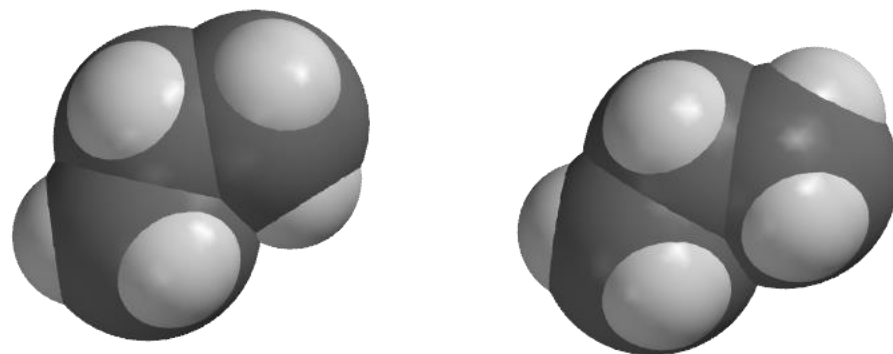
ball & stick   space filling
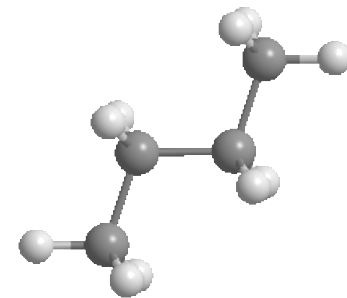
Steric effects reach their maximum in butane:
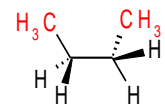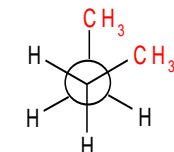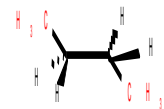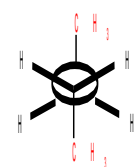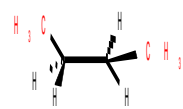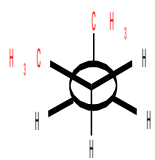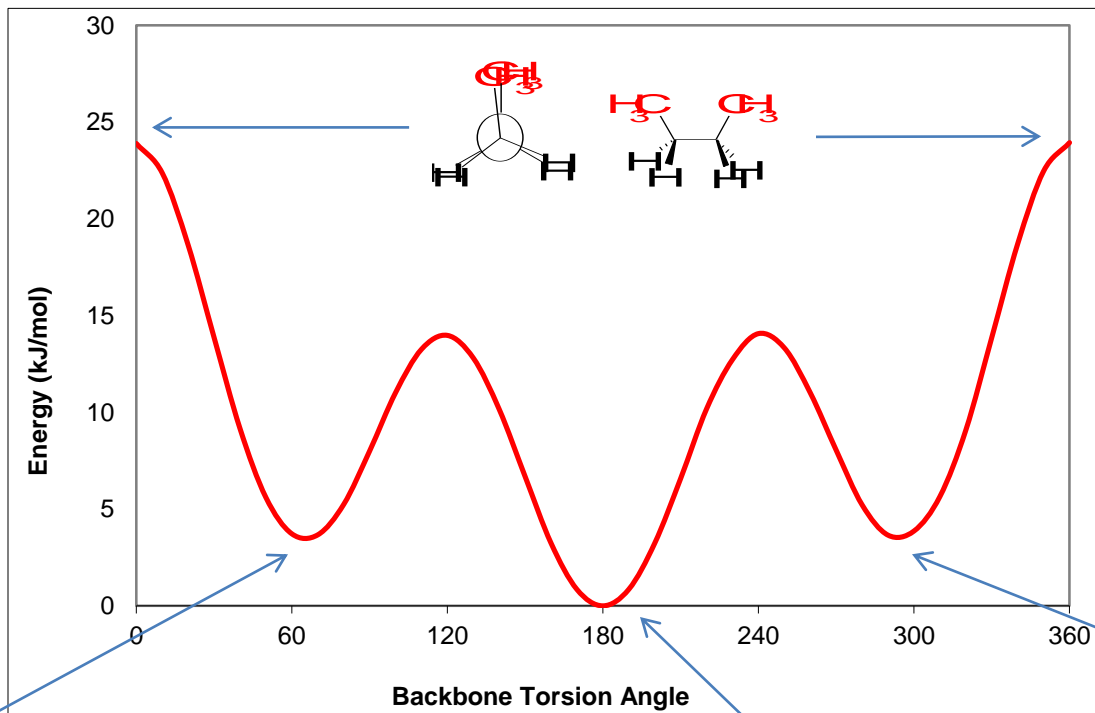
2.9 Cycloalkane Nomenclature and Conformation

Cycloalkanes are saturated hydrocarbons that have at least one ring of carbon atoms. The general formula is CnH2n.

$$CH_2$$
$$H_2C-CH_2$$
cyclopropane

$$H_2C-CH_2$$
$$H_2C-CH_2$$
cyclobutane

$$CH_2$$
$$H_2C \qquad CH_2$$
$$H_2C-CH_2$$
cyclopentane

$$CH_2$$
$$H_2C \qquad CH_2$$
$$H_2C \qquad CH_2$$
$$CH_2$$
cyclohexane

cyclopropane

cyclobutane

cyclopentane

cyclohexane
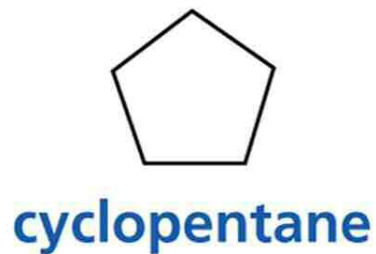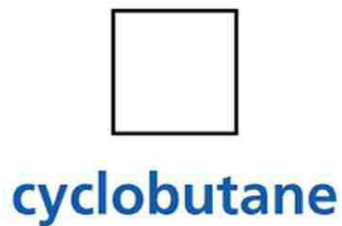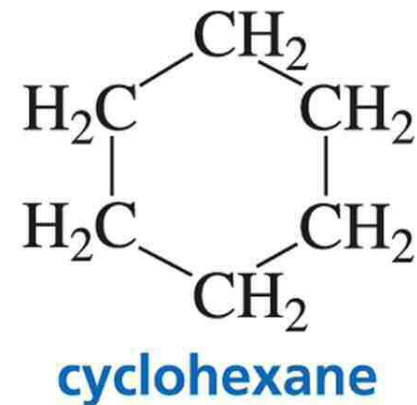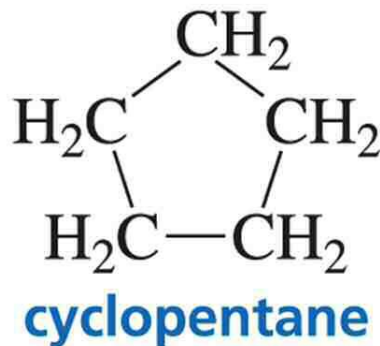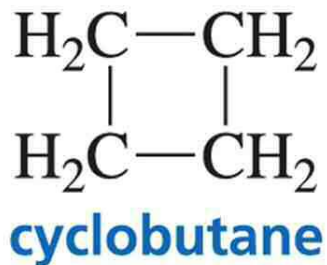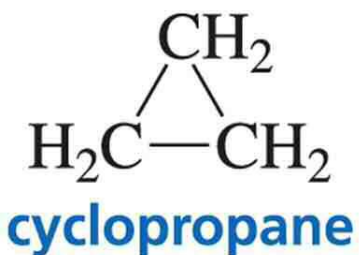
Cycloalkane Nomenclature

- **One substituent** is always located at ring carbon number 1. A number is not needed.

CH$_3$

=

CH$_3$
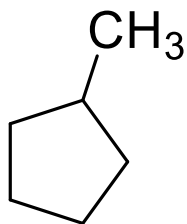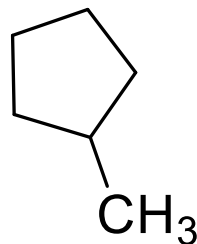
methylcyclopentane

methylcyclopentane

Two substituents : Substituents are stated in alphabetical order. #1 goes to the first-listed substituent
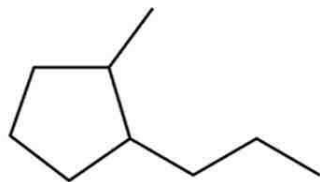
1-methyl-2-propylcyclopentane   **1-ethyl-3-methylcyclopentane**   **1,3-dimethylcyclohexane**
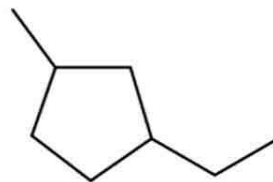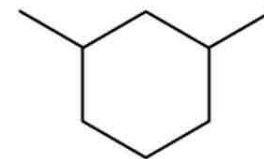
CH$_3$
CH$_3$
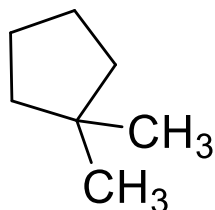
Cycloalkanes: cyclopropane – is the smallest ring structure possible.

- It is rigid and very highly **strained** as the bond angles (60°) are distorted from ideals (109.5°)

- It is more reactive than a linear alkane as the strained C-C bonds are easier to break

Eclipsed Hydrogens

a.

b.
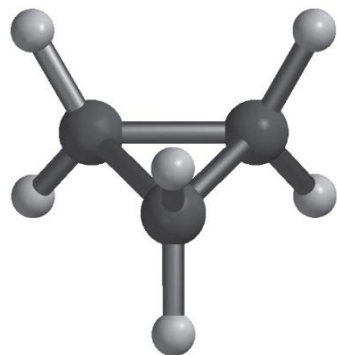
good overlap
strong bond

tetrahedral bond angle = 109.5°
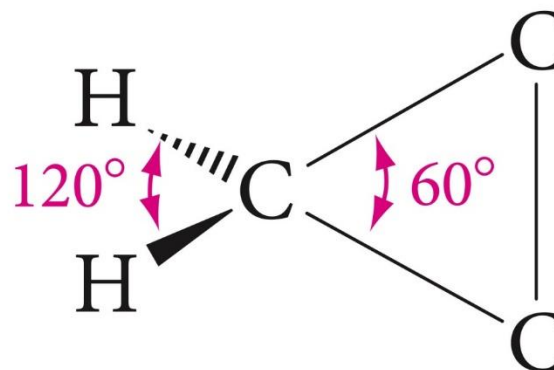
poor overlap
weak bond

bond angle < 109.5°

Angle strain results from poor orbital–orbital overlap because bonds have to deviate from the ideal (109.5°) bond angle

Cyclobutane

Cycloalkanes: cyclobutane – "puckered" conformation

- It is more flexible than cyclopropane and is not flat although it is commonly drawn that way.

- It is more reactive than a linear alkane as the strained C-C bonds are easier to break, bond angle ~90°
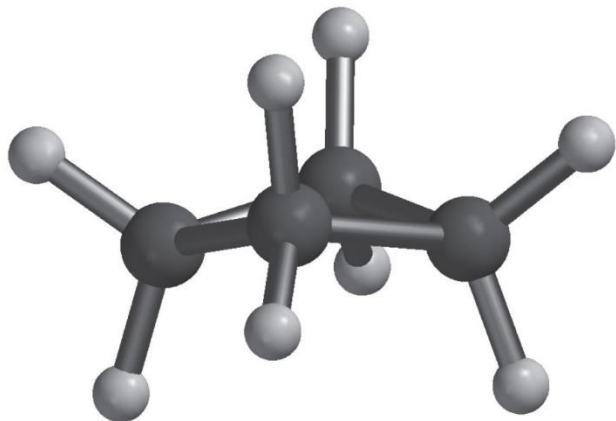
common
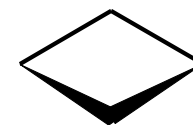
better

Molecules twist out of a planar arrangement to minimize angle strain and the number of eclipsed hydrogens

cyclopentane

Cycloalkanes: cyclopentane – "envelope" conformation

- It is more flexible than cyclobutane and bond angle are ~105°, and less strained
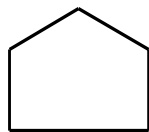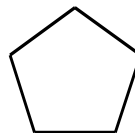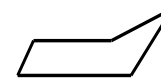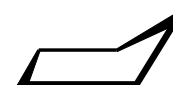
poor   better   good   best
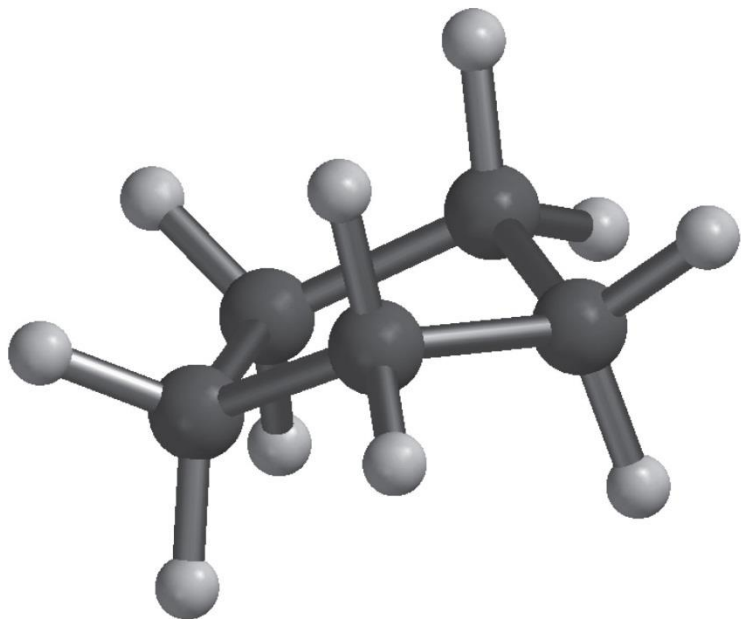
Molecules twist out of a planar
Arrangement to minimize angle strain and
the number of eclipsed hydrogens.

cyclohexane

Cycloalkanes: cyclohexane – "chair"

- It is highly flexible and can adopt a **strain free** non-planar conformation with bond angle of 109.5°

- It is very common in nature so understanding its conformations is important.

Although commonly drawn as a hexagon, implying a flat six-membered ring this is not the common conformation seen.
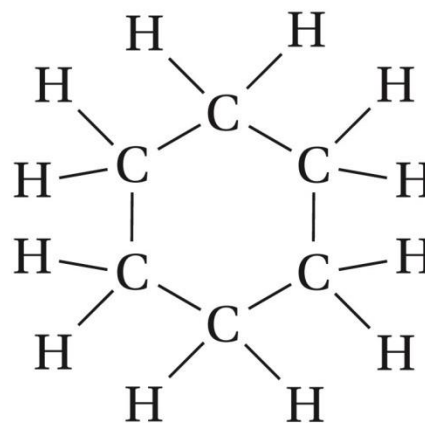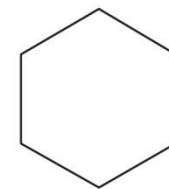
Structural and abbreviated structural formulas for cyclohexane

Conformational Isomers (cont'd)

Cyclohexane cont'd:

The most common conformation of cyclohexane is the "chair" conformation. In this geometry the C bonds are all ~109.5° as opposed to the 120° in a planar structure.

axial
equatorial
axial
ball-and-stick model

axial
equatorial
axial
space-filling model

chair framework
(has a chair shape)
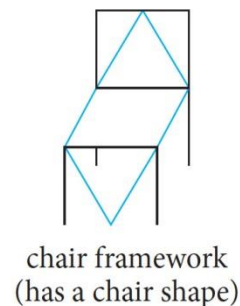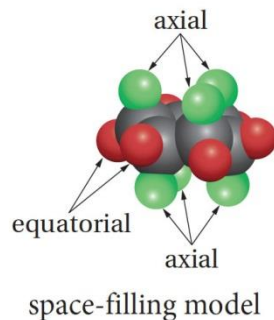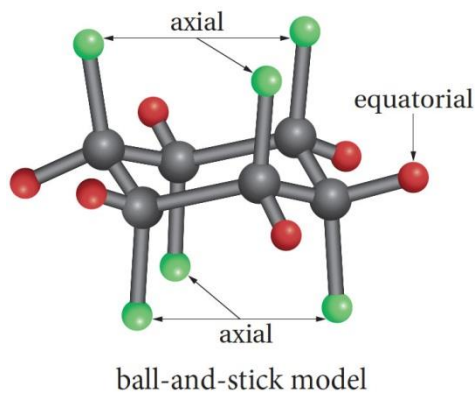
This structure creates two subsets of hydrogen atoms, those lying in the same plane as the C atoms, the equatorial H and those lying above and below that plane, the axial H atoms

Cyclohexane interconverts between two chair conformers.

Cyclohexane cont'd:

Since the C-C bonds are all single (σ) bonds, it is possible to rotate about these bonds. This process in known as **a ring inversion** or a "chair-chair" **flip**. In the process of the inversion **all equatorial H become axial and axial become equatorial.**
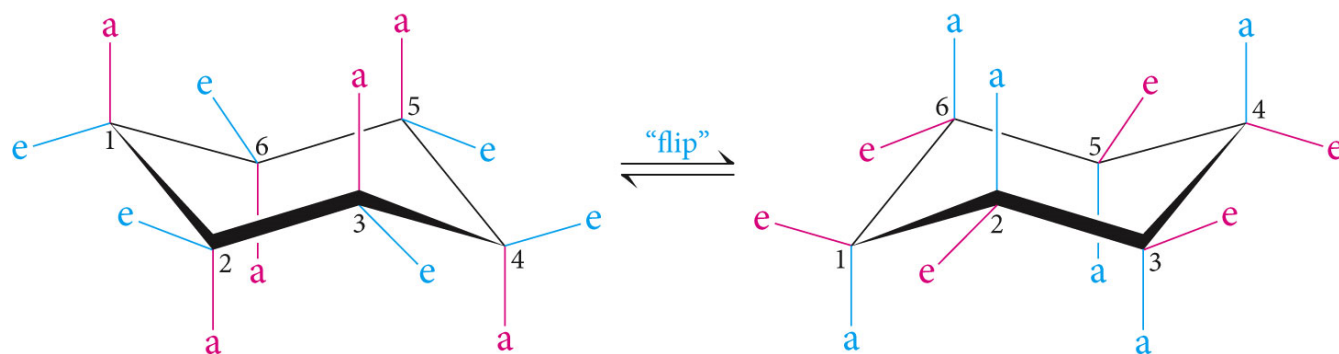
Axial bonds (red) in the left structure become equatorial bonds (red) in the right structure when the ring "flips."

Cis and Trans Isomers

two methyl groups are on the same side of the ring
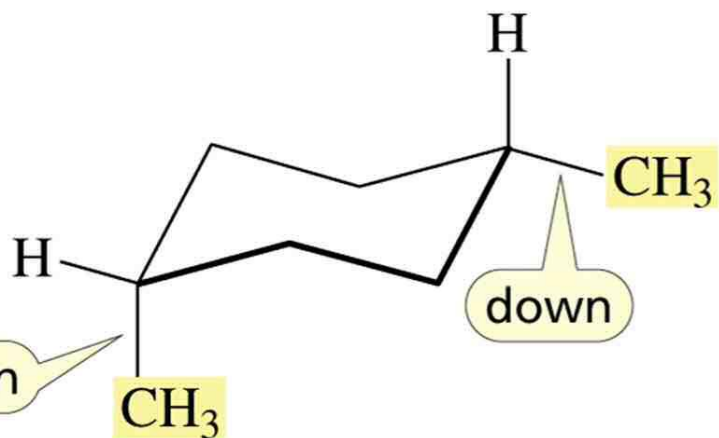
cis-1,4-dimethylcyclohexane

two methyl groups are on opposite sides of the ring
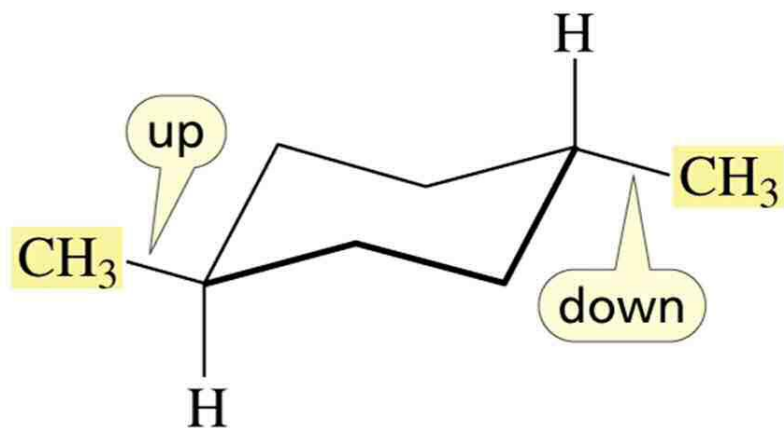
trans-1,4-dimethylcyclohexane

Conformational Isomers (cont'd)

Cyclohexane cont'd:

Other conformations of cyclohexane are possible but they are higher in energy and less stable, i.e. the "boat" conformation
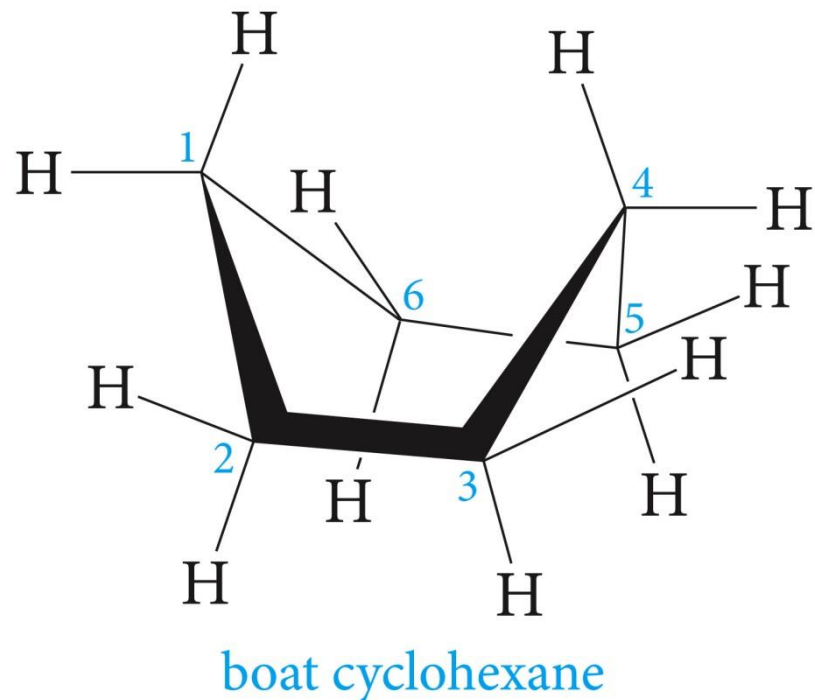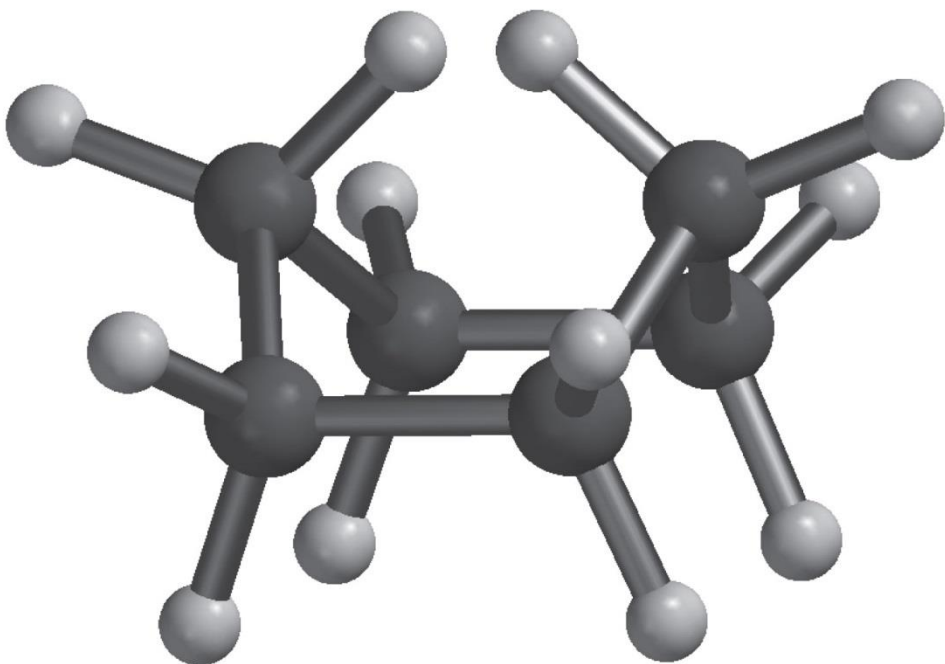
boat cyclohexane

- Substituted cyclohexane: (**1,3-Diaxial Interactions)**

The addition of a methyl group on cyclohexane (methylcyclohexane) can have two conformations, the methyl can be axial or equatorial, i.e.

methyl axial
5%

"flip"

methyl equatorial
95%

a 1,3-diaxial interaction

CH_3 H

H

H

H CH_3

this chair conformer has four 1,3-diaxial interactions
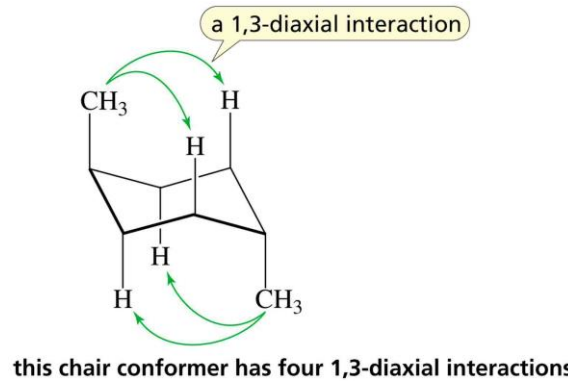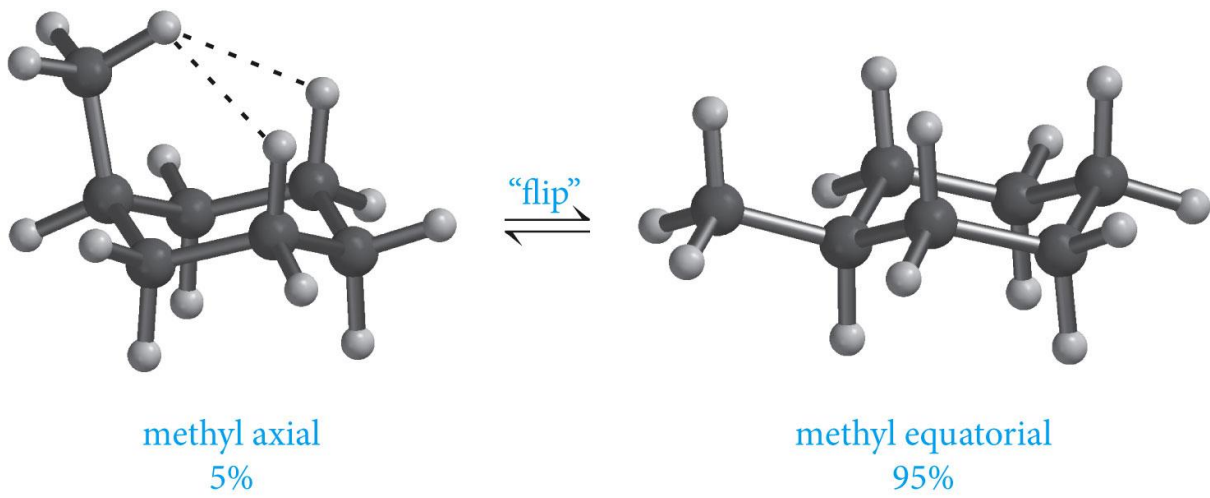
The equatorial is preferred as there is significantly less steric interactions than when in the axial position. This will be true for any group on a cyclohexane ring and has implications for the chemical reactivity of the compound.

1,3-diaxial interactions

H   H—C⋯H

H   H

H   H

H

H

H   H

H   H
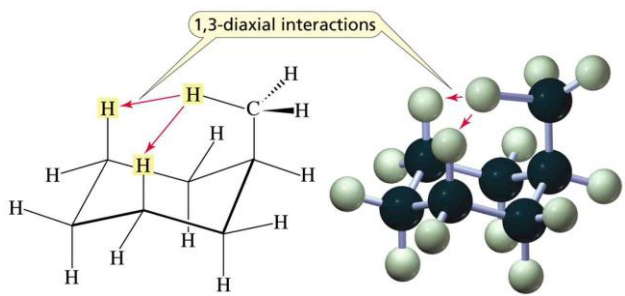
Note: The larger the substituent, the more the equatorial-substituted conformer is favored.

Geometric Isomers (*Cis–trans isomerism*)

Geometric isomers (or **configurational** isomers, a subset of stereoisomers) are molecules which have the same chemical formula, the atoms are bonded in the same order, but located in different positions in space. Unlike conformational isomers, where the atoms are located in different location in space due to rotation about C-C single (σ) bonds, geometric isomers are not related by rotation about σ bonds. This situation arises with cyclic structures.

An example of this is 1,2-dimethylcyclopentane

This structures can not interconvert without breaking a C-C bond.

cis-1,2-dimethylcyclopentane
bp 99°C

trans-1,2-dimethylcyclopentane
bp 92°C
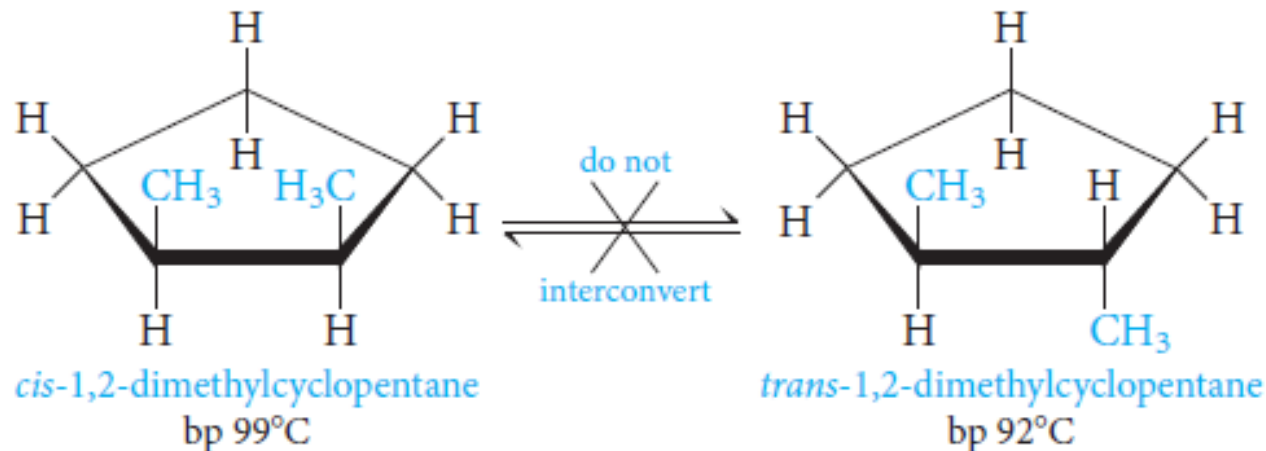
- The two methyl groups may be on the same side of thering plane (*cis*)
- or they may be on the opposite sides (*trans*)

- Cis–trans isomers differ from one another only in the way that the atoms or groups are positioned in space. Yet this difference is sufficient to give them different physical and chemical properties
- *Cis–trans* isomers can be separated from each other and kept separate

Summary of Isomers (to date)

Isomers

different bonding pattern → structural (or constitutional) isomers

same bonding pattern → stereoisomers

stereoisomers:

interconvertable by single bond rotation → conformational (rotamers) isomers

NOT interconvertable by single bond rotation → configurational isomers
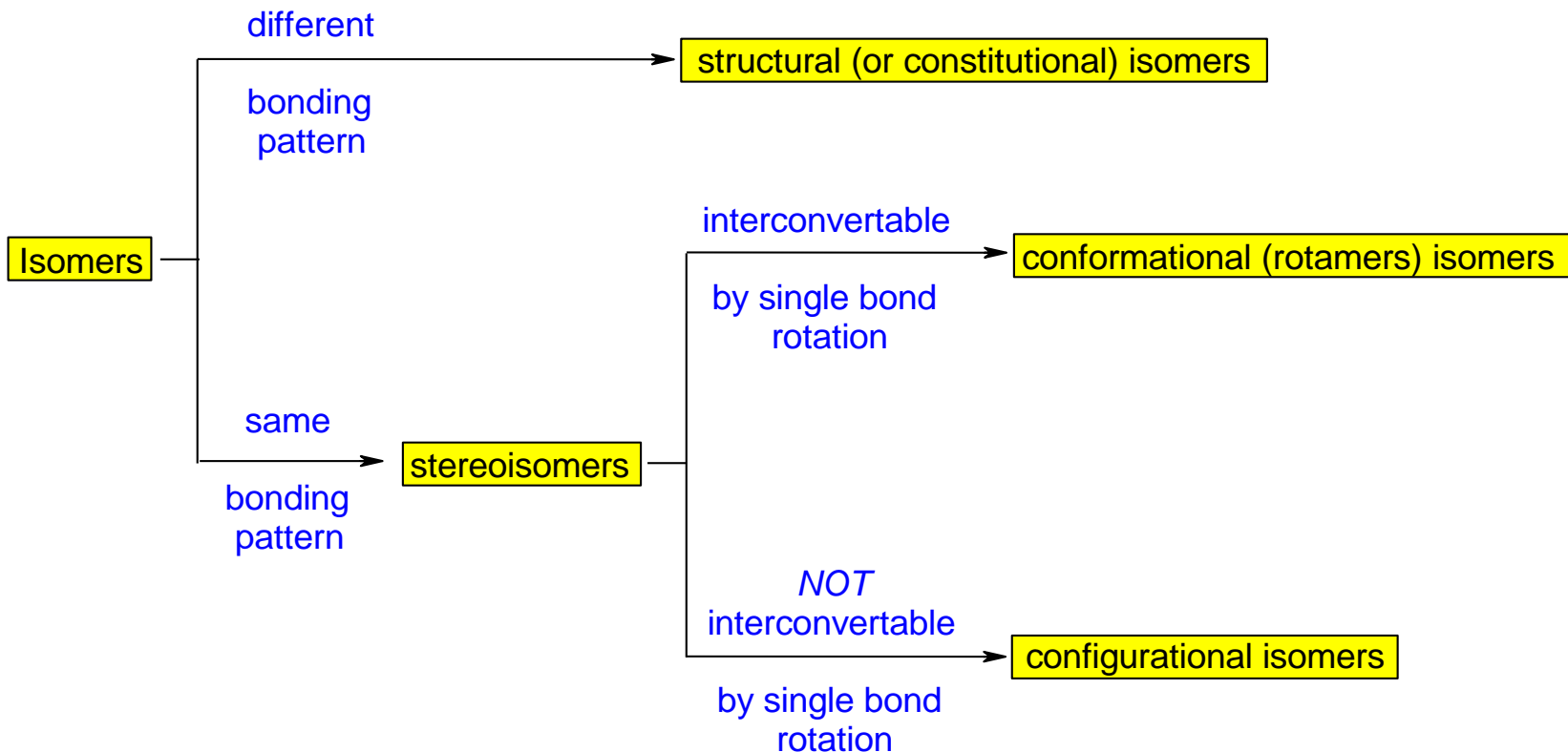
Chemical Reactions of Alkanes

In general, because of their strong non-polar covalent bonds alkanes are fairly inert. They do not react with most common acids, bases, oxidizing or reducing reagents. They means they do make good solvents for extraction, recrystallization or as a reaction solvent. They do however have two substances they react with; molecular oxygen and halogens.

Oxidation Reactions

All chemical processes are redox (oxidation / reduction) reactions. Formally oxidation is the loss of electrons (increase in oxidation sate) and reduction the gain of electrons (decrease in oxidation sate). The two processes are coupled since whatever gains the electrons must gain them from somewhere and whatever loses the electrons must lose them to somewhere.

Oxidation Reactions (cont'd)

For the C atom, oxidation involves increasing the number of C-O (or other atoms more EN than C) bonds and/or decreasing the number of C-H bonds.

Reduction will be the opposite, a decrease in the number of C-O bonds or increase in the number of C-H bonds.

Oxidation Reactions (cont'd)

To determine the oxidation state:

- each bond to a C atom counts: 0
- each bond to a H atom counts +1
- Each (single) bond to a more EN atom count -1, i.e.
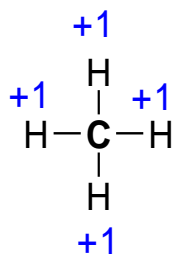
$$\begin{array}{c} +1 \\ H \\ | \\ +1 \; H-\mathbf{C}-H \; +1 \\ | \\ H \\ +1 \end{array}$$
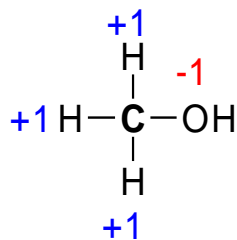
C = -(+1+1+1+1)
   = -4

$$\begin{array}{c} +1 \\ H \quad -1 \\ | \\ +1 \; H-\mathbf{C}-OH \\ | \\ H \\ +1 \end{array}$$

C = -(+1+1+1-1)
   = -2

$$\begin{array}{c} +1 \\ H \quad -1 \\ | \\ +1 \; H-\mathbf{C}-Cl \\ | \\ H \\ +1 \end{array}$$

C = -(+1+1+1-1)
   = -2

$$\begin{array}{c} +1 \\ H \quad -1 \\ | \\ +1 \; H-\mathbf{C}-NH_2 \\ | \\ H \\ +1 \end{array}$$

C = -(+1+1+1-1)
   = -2

Oxidation Reactions (cont'd)

More examples:

+1 H—**C**≡C—H
0

C = -(0+1)
= -1

+1 H—**C**=C 0 (with H's)

C = -(0+1+1)
= -2

+1 H—**C**—C—H (with H's)
0

C = -(0+1+1+1)
= -3

-2 O=**C**=O -2

C = -(-2-2)
= +4

-2 O
 H—**C**—OH
 +1   -1

C = -(-2-1+1)
= +2

-2 O
 H—**C**—H
 +1   +1

C = -(-2+1+1)
= 0

+1 H—**C**—OH -1 (with H's)

C = -(+1+1+1-1)
= -2

+1 H—**C**—H (with H's) +1

C = -(+1+1+1+1)
= -4

Most C-O bonds

Reduction →

← Oxidation

Most C-H bonds
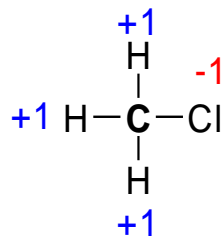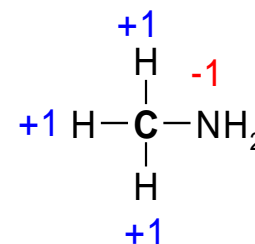
Oxidation Reactions (cont'd)

The most import use of alkanes is as a fuel. The light weight ones are gases and intermediate weight liquids which makes them handy for storage and transportation. Natural gas is composed primarily of methane with varying amounts of ethane, propane and butanes. It is commonly used to heat homes. The liquid hydrocarbons are used as gasoline, kerosene and jet fuels.

Oxidation Reactions (cont'd)

The energy of the hydrocarbon is released when combusted or burned. This is an oxidation process and requires atmospheric oxygen. The final oxidation product (assuming sufficient oxygen) is carbon dioxide. If insufficient oxygen is present then partial oxidation products such as carbon monoxide, formaldehyde or formic acid may be formed.

Halogenation of Alkanes

Besides combustion, the only other useful chemical reaction that alkanes undergo is halogenation.

This is a free radical process in which heat or light is used to break a halide-halide bond forming two halide free radicals.

Halogenation of Alkanes (cont'd)

This type of reaction is a *substitution reaction* where a halide atom is substituted for a H atom in the alkane.

$$R-H + X_2 \xrightarrow[\text{or light}]{\text{heat}} R-X + H-X \quad (X = Cl, Br)$$

The two common halides used are chlorine and bromine.

Halogenation of Alkanes (cont'd)

The process involves three steps:

1. initiation: this is where the free radical is formed: note we generate 2 free radical atoms in this process.
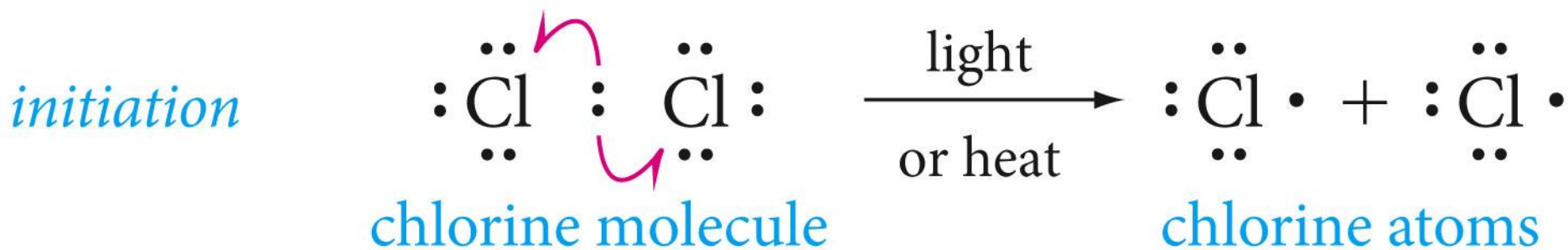
Halogenation of Alkanes (cont'd)

2. Propagation: this is where the halide free radical reacts with the hydrocarbon, extracting a H atom, generating an intermediate C radical, and then adding a halide atom. This process can repeat many times depending on the amount of halide radical available.

propagation

$$R—H + \cdot \ddot{C}l\colon \longrightarrow R\cdot + H—Cl$$

alkyl
radical

$$R\cdot + Cl—Cl \longrightarrow R—Cl + \cdot \ddot{C}l\colon$$

alkyl
chloride
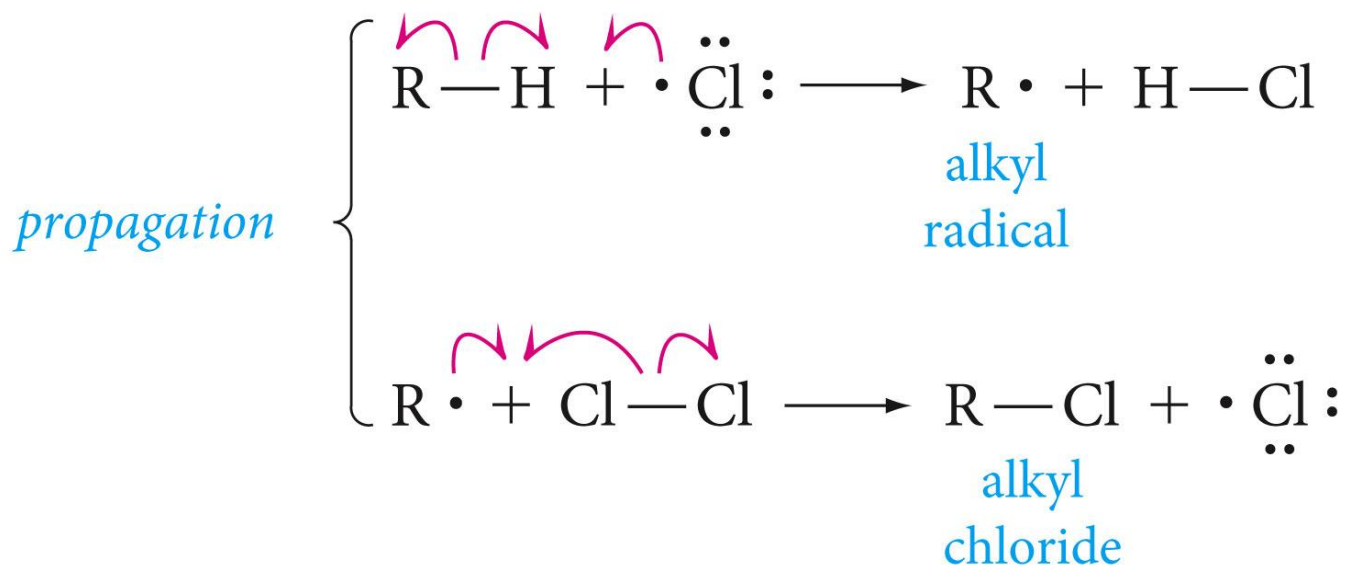
Halogenation of Alkanes (cont'd)

3. Termination: this is the final step where the remaining free radicals are consumed. It can involve the halide radical reacting with another halide radical, a carbon radical or two carbon radicals combining.

termination

$$:\ddot{C}l\cdot + \cdot\ddot{C}l: \longrightarrow Cl - Cl$$

$$R\cdot + \cdot R \longrightarrow R - R$$

$$R\cdot + \cdot\ddot{C}l\cdot \longrightarrow R - Cl$$
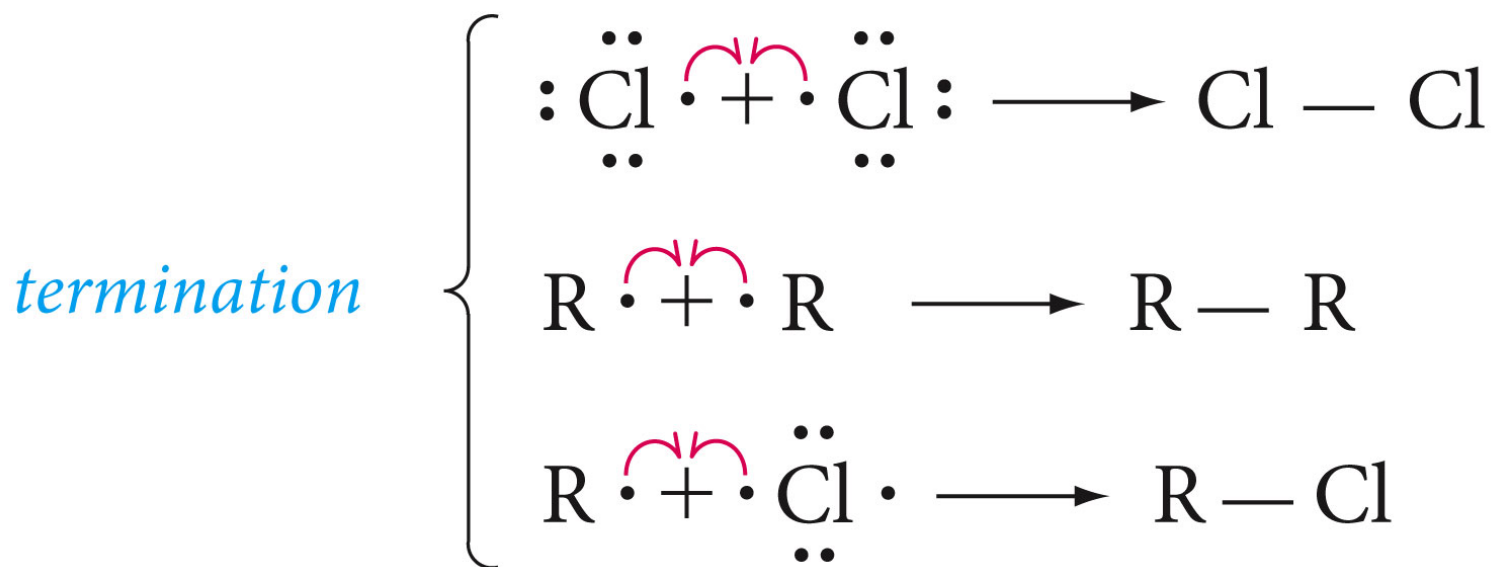
Halogenation of Alkanes (cont'd)

A single alkane molecule can undergo several substitution steps depending on the concentration of the halide radical, i.e.

$$CH_3Cl \xrightarrow{\ Cl_2\ } CH_2Cl_2 \xrightarrow{\ Cl_2\ } CHCl_3 \xrightarrow{\ Cl_2\ } CCl_4$$

dichloromethane	trichloromethane	tetrachloromethane
(methylene chloride)	(chloroform)	(carbon tetrachloride)
bp 40°C	bp 61.7°C	bp 76.5°C
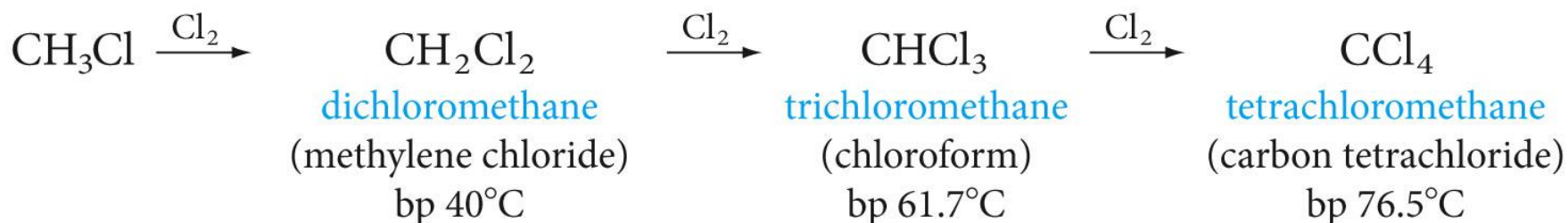
As a matter of fact, unless the concentration of chlorine is kept quite low there will be a mixture of these produces.

Halogenation of Alkanes (cont'd)

What about longer chain hydrocarbons? All of the H atoms in a hydrocarbon are susceptible to substitution, but not equally. The process involves the formation of a carbon radical as an intermediate. Not all carbon radicals are created equal. As a matter of fact there is a predictable trend in their stability:
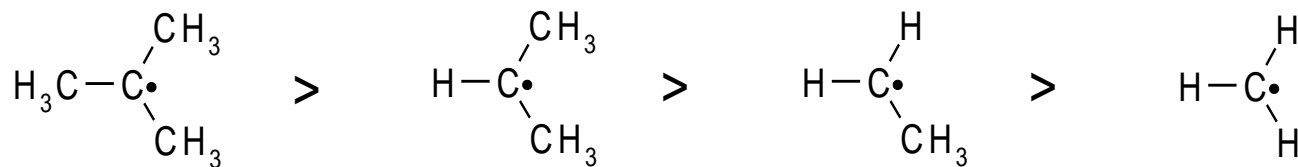
		3°	2°	1°	methyl
bond dissociation	kJ/mol	380	397	410	435
energies	kcal/mol	91	95	98	104

Halogenation of Alkanes (cont'd)

In addition the halide free radicals are different. Bromine radicals are less reactive than chlorine radicals. This means that Br· tend to be more selective in its reactions and prefers to react with weaker C-H bonds. As a results the halides have different reactivities to each other and to different types of C-Hs, i.e.

$$\% P_i = \frac{100 * nH_i * R_i}{\sum_i nH_i * R_i}$$

Reactivity factors R_i		
	Br	Cl
1°	1	1
2°	82	3.9
3°	1640	5.2

$\%P_i$ = %yield of product i
nH_i = number of H of type i
R_i = reactivity factor for type i
$\sum_i$ = sum of all types

Halogenation of Alkanes (cont'd)

With this information we can now determine the product distributions. For example for propane, there are two 2° H and 6 1° H, so for chlorination:

%1° = 100x(6x1) / (6x1 + 2x3.9) = 600/13.8 = 43.5%

%2° = 100x(2x3.9)/(6x1 + 2x3.9) = 780/13.8 = 56.5%

Or for bromination:

%1° = 100x(6x1) / (6x1 + 2x82) = 600/170 = 3.53%

%2° = 100x(2x82)/(6x1 + 2x82) = 16400/170 = 96.47%

Halogenation of Alkanes (cont'd)

The bottom line is fairly simple here.

If you want a 3° halide use bromine since it is 1640 times more likely than a 1°, and 20 times more likely than a 2°.

If you want a 2°, if no 3° present use bromine, other wise use chlorine.

If you want a 1° use chlorine and accept the fact you will have a mixture of products.