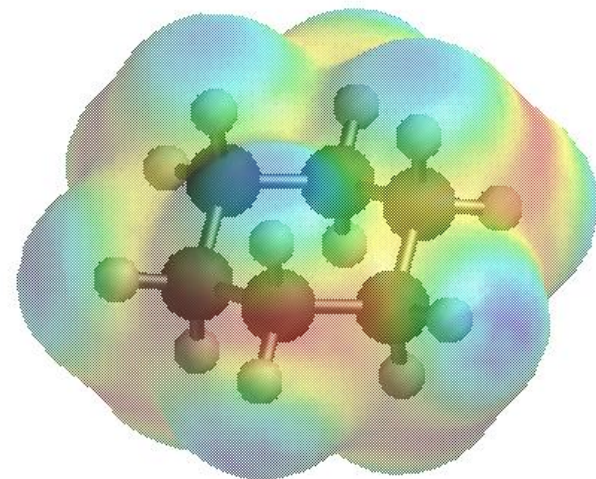


Chapter 2: Alkanes and Cycloalkanes: Conformational and Geometric Isomers

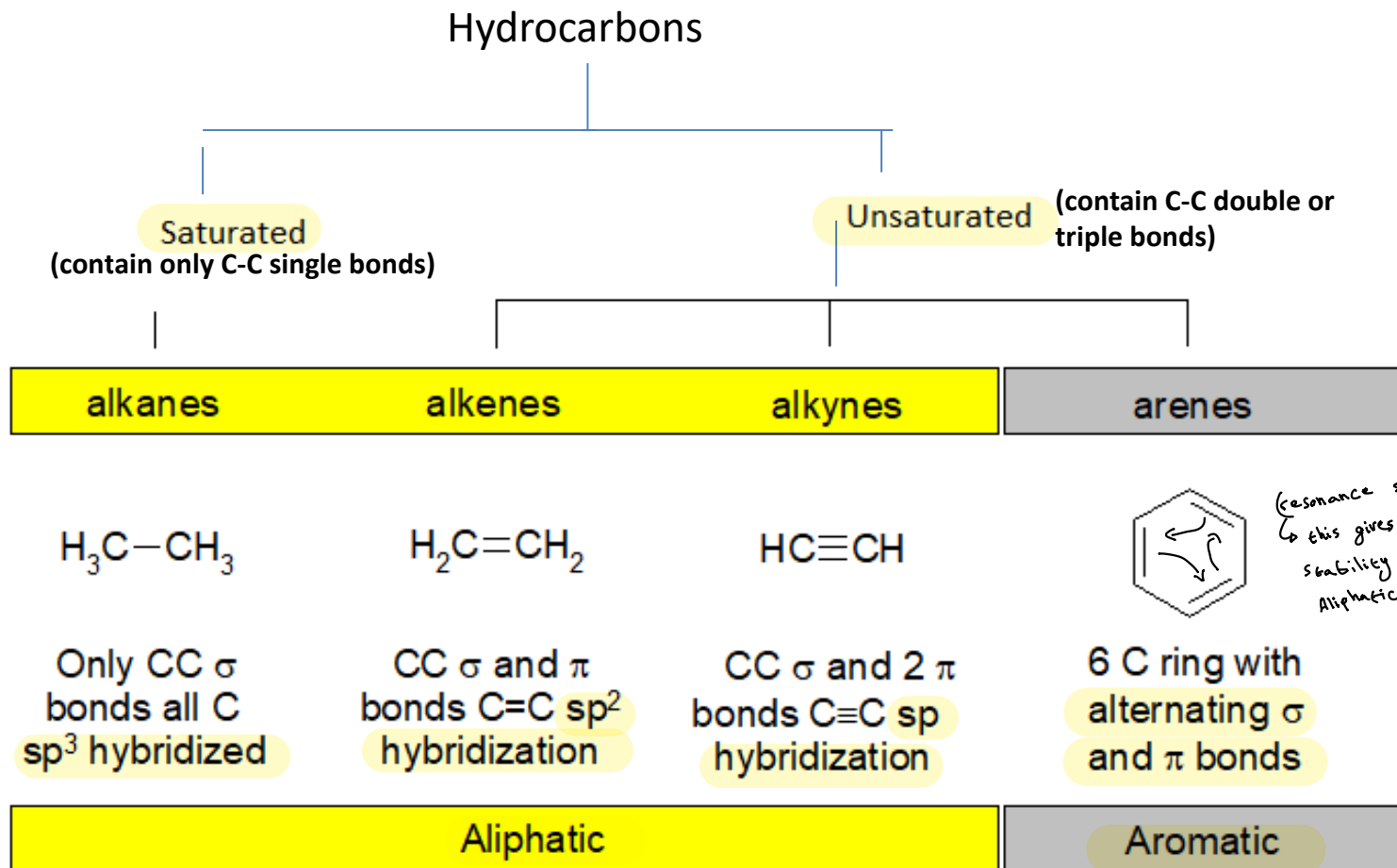


Done By : Sad Melhem



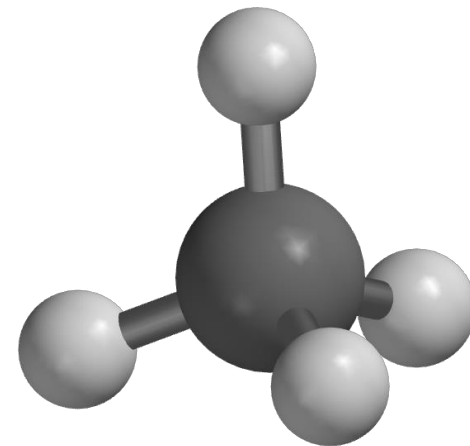
Types of Hydrocarbons

Hydrocarbons are compounds that only contain C and H atoms.

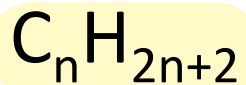


Structure of Alkanes

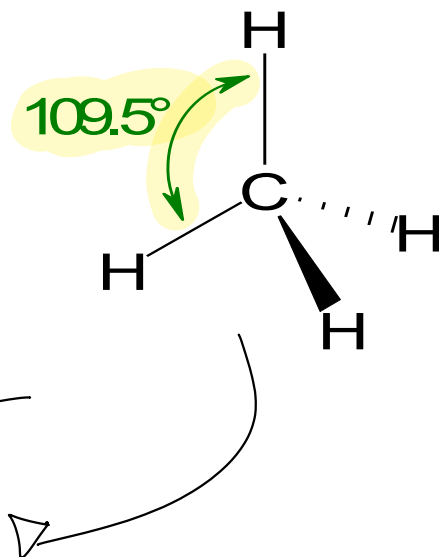
Alkanes are saturated hydrocarbons, that is they contain the **maximum number of H atoms possible** for the number of C atoms present.



The generic formula for an alkane is:



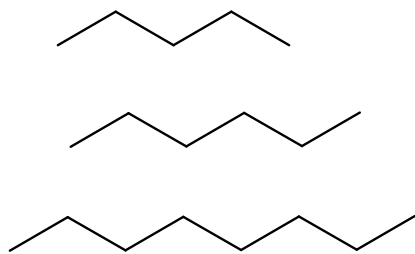
This means every C atom is **sp³ hybridized** with **bond angles of ~109.5°**



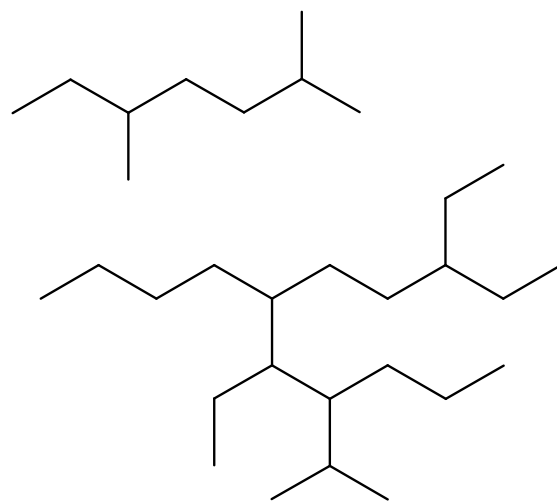
geometry : tetrahedral

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 grows quickly



Normal, unbranched (or linear)

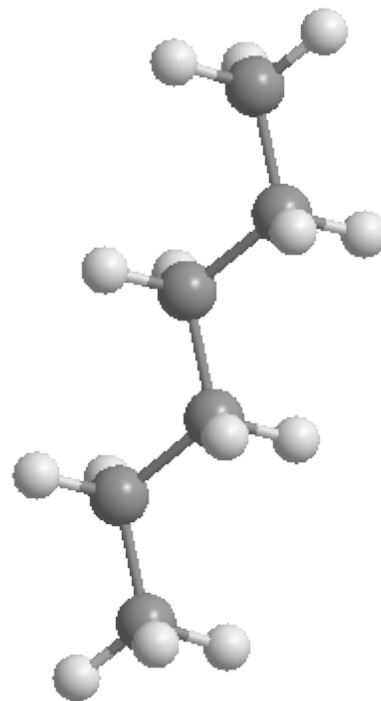
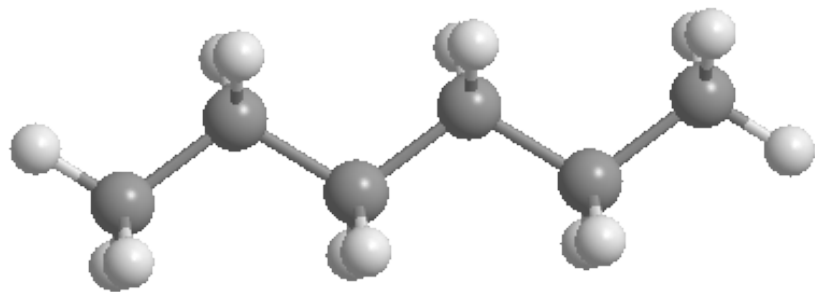


branched

Structure of Alkanes (cont'd)

6 C

14 H



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** :

IUPAC name = Prefix + parent + suffix

Prefix : What and where substituents.

Parent (Root) : longest chain

Suffix : functional group.

branches

(root)

(longest chain)

→ function group

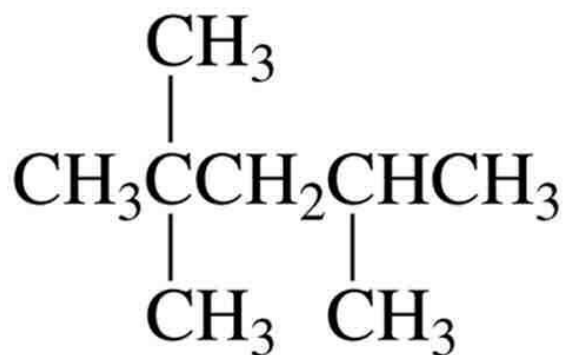
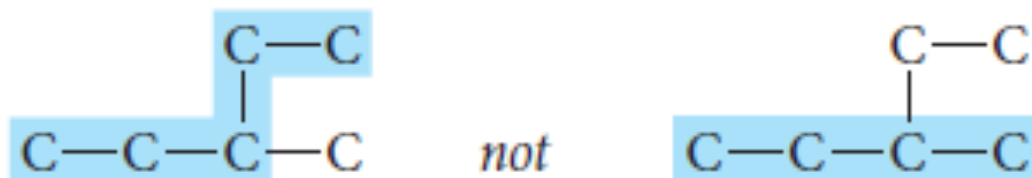
Table 2.1 ▀ **Names and Formulas of the First Ten Unbranched Alkanes**

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH ₄	CH ₄	1
ethane	2	C ₂ H ₆	CH ₃ CH ₃	1
propane	3	C ₃ H ₈	CH ₃ CH ₂ CH ₃	1
butane	4	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	2
pentane	5	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	3
hexane	6	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	5
heptane	7	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	9
octane	8	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	18
nonane	9	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	35
decane	10	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	75

Note: The repeating group is (-CH₂-) is Methylene group

IUPAC Rules for Naming Alkanes

1. First identify the longest continuous chain (parent name)

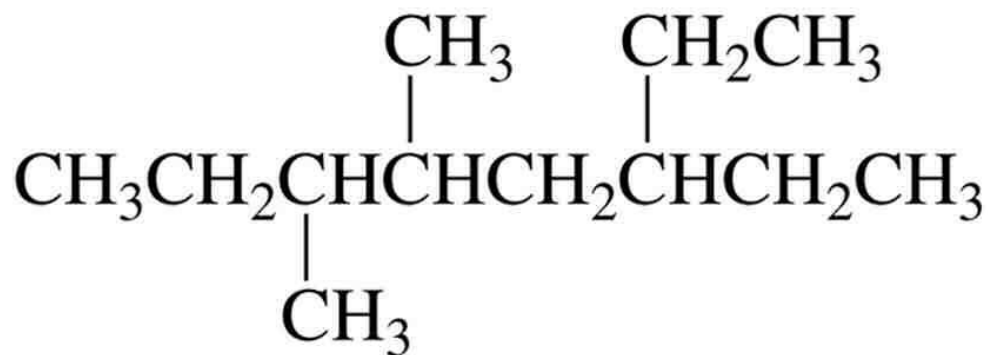


2,2,4-trimethylpentane

not

2,4,4-trimethylpentane

because $2 < 4$



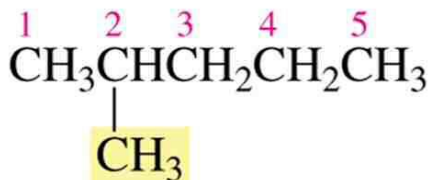
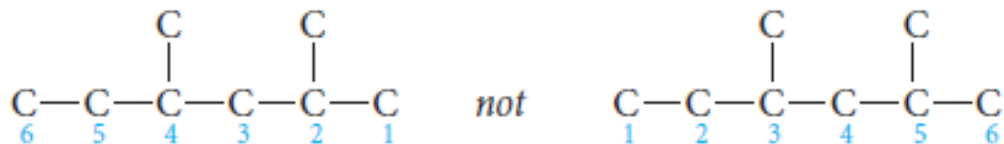
6-ethyl-3,4-dimethyloctane

not

3-ethyl-5,6-dimethyloctane

because $4 < 5$

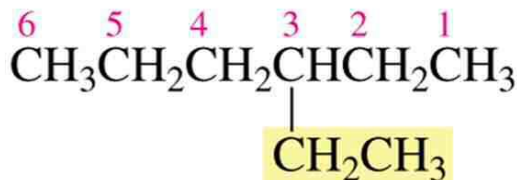
2. Number the chain in the direction that gives the substituent as low a number as possible



2-methylpentane

not

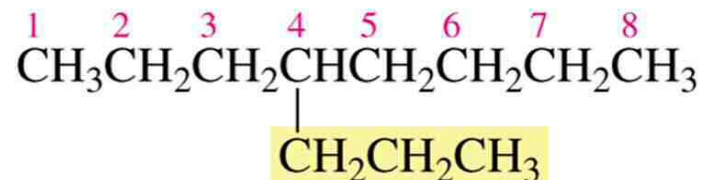
4-methylpentane



3-ethylhexane

not

4-ethylhexane

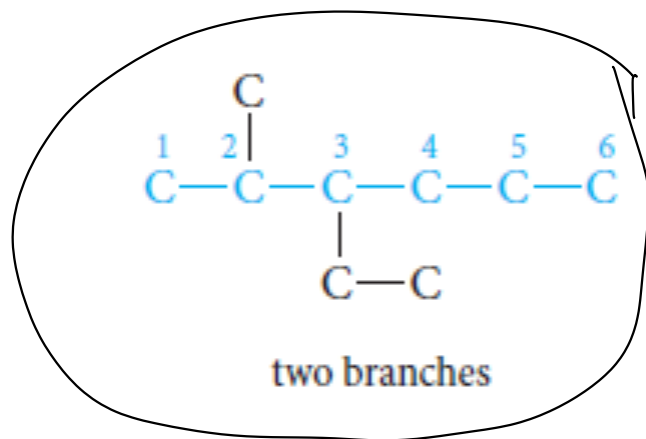


4-propyloctane

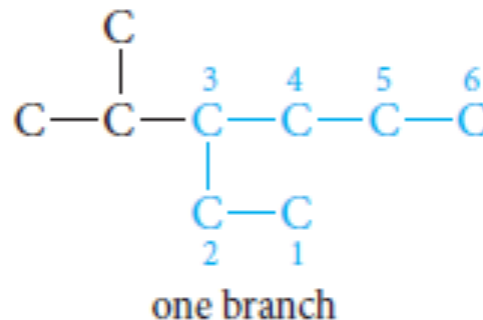
not

5-propyloctane

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



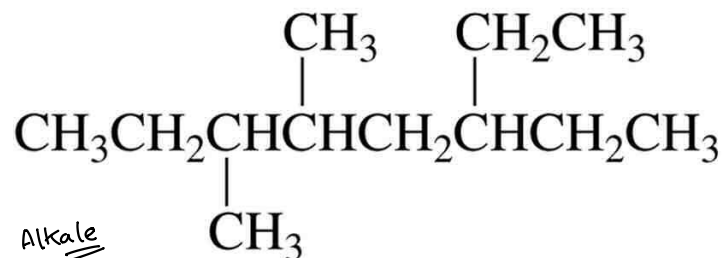
not



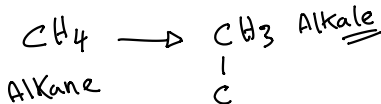
If there is a branch equidistant from each end of the longest chain, begin numbering nearest to a third branch



- 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

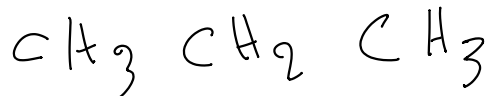
CH_3CH_2-
ethyl group

$\text{CH}_3\text{CH}_2\text{CH}_2-$
propyl group

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$
butyl group

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$
pentyl group

$\text{R}-$
any alkyl group



-There are two propyl Groups

a secondary carbon

a primary carbon



propane

remove
a hydrogen

(ex: it becomes a
substituent)



propyl group

(*n*-Pr) or (-Pr)



isopropyl group

(*i*-Pr-)

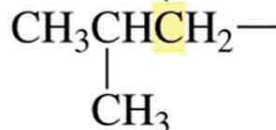
-There are Four Butyl Groups

primary carbon



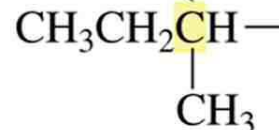
butyl group

primary carbon



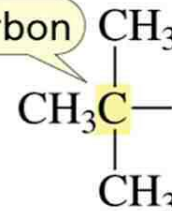
isobutyl group

secondary carbon



sec-butyl group

tertiary carbon



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.

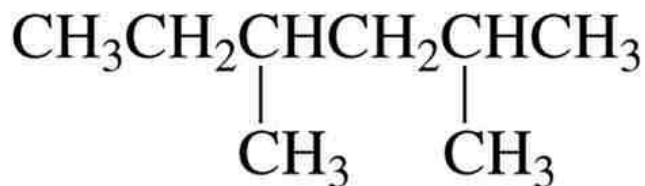
Examples:

Note 1: *di-*, *tri-*, and *tetra-* are used for the same **Multiple Substituents**

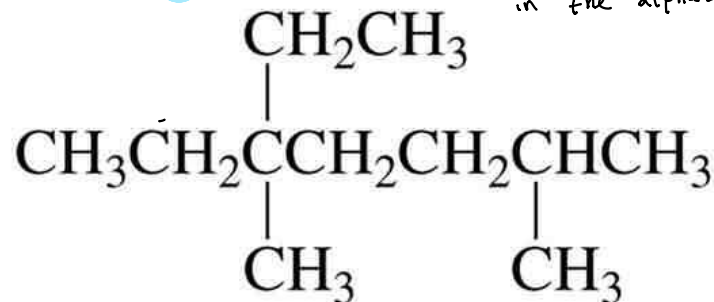
Note 2: Substituents are listed in **alphabetical order**.

(*di*, *tri*, *tetra*, *sec*, *tert* are not alphabetized) *exception!!*

↳ we count (i) in **iso** when substituents are being compared in the alphabetical order

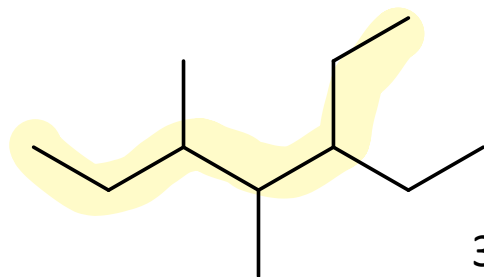


2,4-dimethylhexane



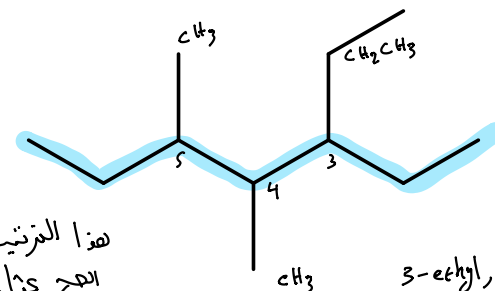
5-ethyl-2,5-dimethylheptane

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



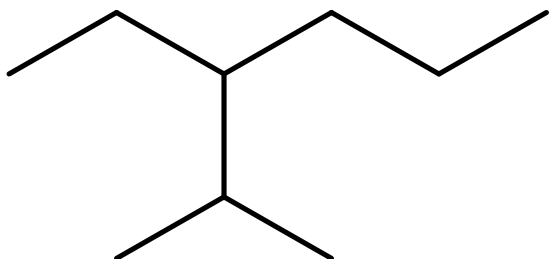
3-ethyl-4,5-dimethylheptane

هذا الترتيب
الصحيح عشان
اول خرفم 3 اقل
≡ ethyl

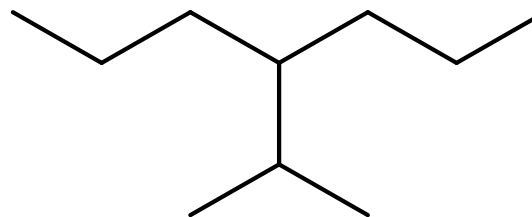


7 Cs
↳
heptan
3-ethyl, 4,5 dimethyl

Examples



3-ethyl-2-methylhexane

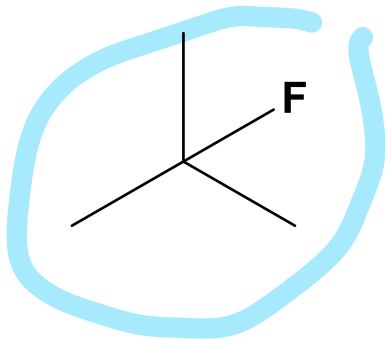


4-isopropylheptane

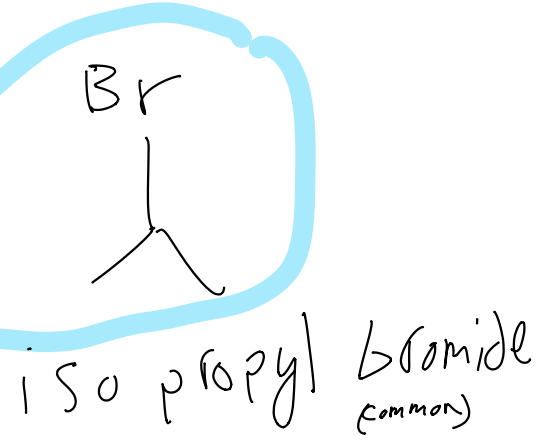
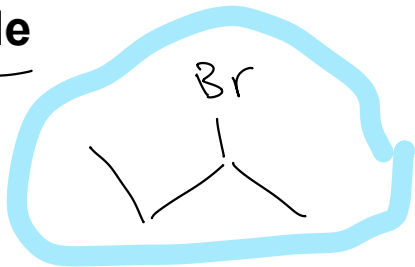
2.4: Alkyl and Halogen Substituents (R-X)

H (größt a 8)

Common name : Alkyl halide
eg. $\text{CH}_3\text{CH}_2\text{Br}$ Ethyl bromide



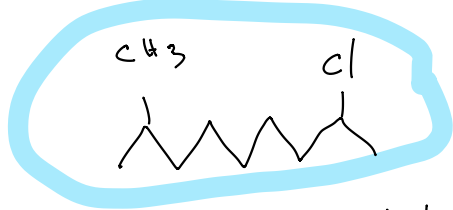
tert-butyl fluoride
(common)



sec-butyl bromide (common)

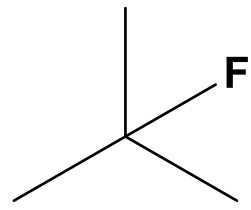
IUPAC:
Halogen substituents are named by changing the *-ine* ending of the element to *-o*.

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



2-chloro-8-methyl nonane

alphabet



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

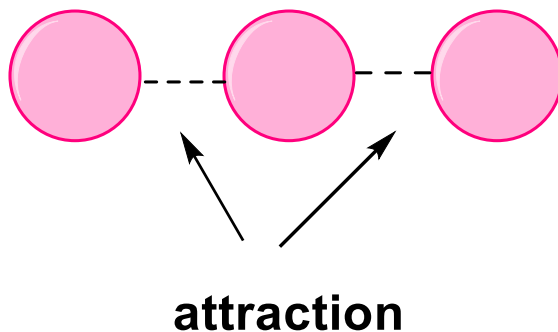
A physical property is **any property of matter or energy that can be measured.**

When it changes, the chemical composition of the object **does not change** (ice & water have the same chemical composition)

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) * solubility depends on IMF

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.



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**. *(besides its polarity)* BP is dependent on mass ⊕ polarity ⊕ branches

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:

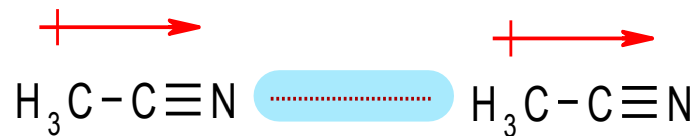
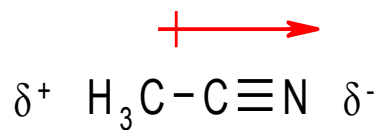
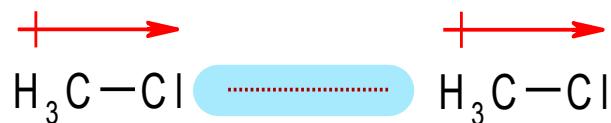
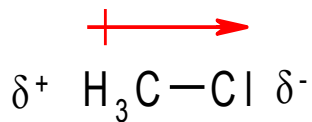
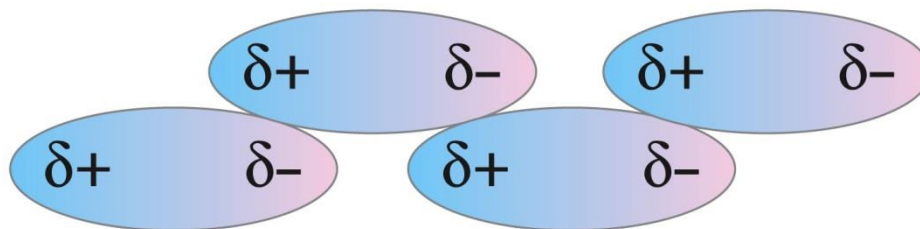
- 1) Hydrogen bonding
- 2) Dipole-dipole
- 3) Van der Waals or London Dispersion

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 result from the presence of C-X bonds where X is more electronegative than C.

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

Dipole-dipole



Hydrogen Bonding

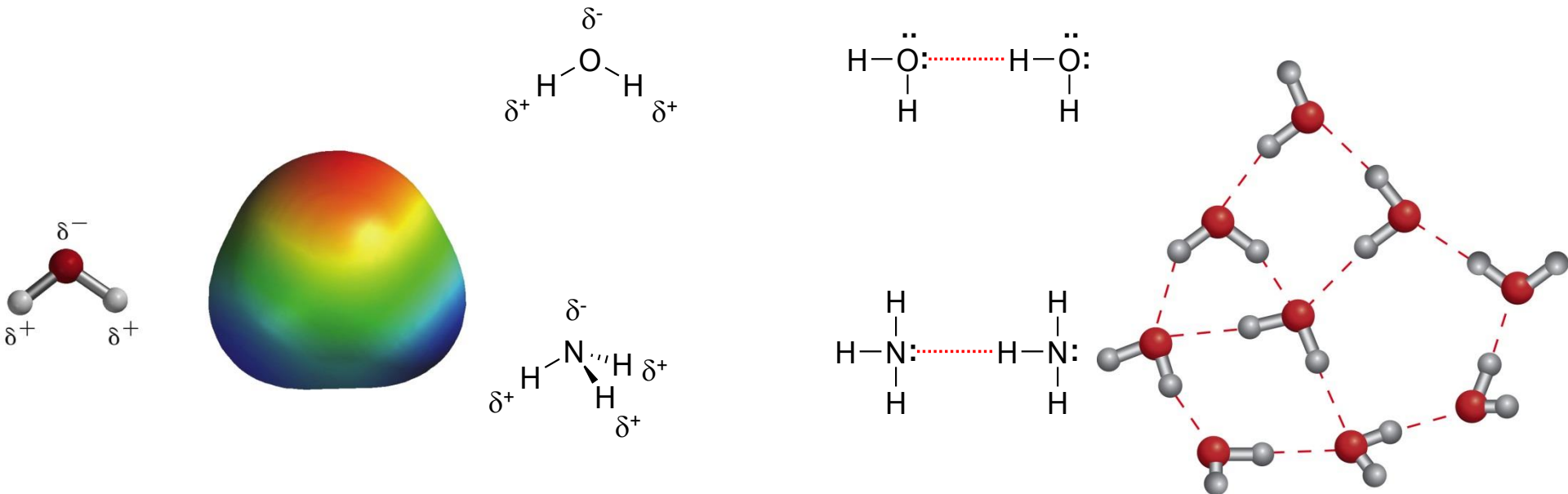
Hydrogen bonding is a complex interaction that includes dipole-dipole, as well as orbital interactions and the transfer of electron density between molecules.

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

Hydrogen Bonding

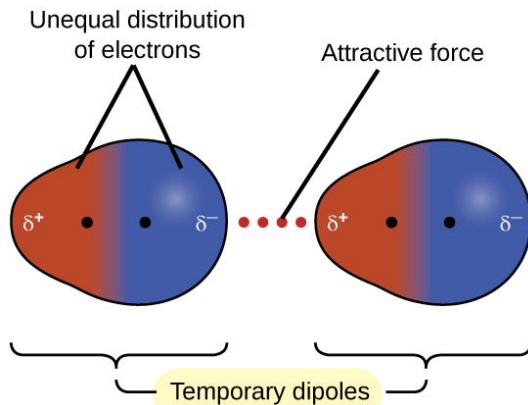
Occur primarily between OH, NH and FH. The more EN the atom the stronger the interaction. (The atom H is attached to usually has a lone pair of e⁻)

Geometry: X-H \cdots :X-



Van der Waals (dispersion)

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.

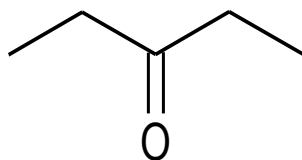


Very Weak attraction

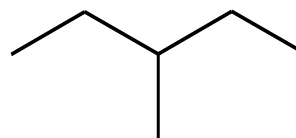
London dispersion, < dipole-dipole, < Hydrogen bonding

Effects on Physical Properties (cont'd)

Dipole forces: much strong IMFs so the BP is higher when dipole-dipole interactions are present, i.e.

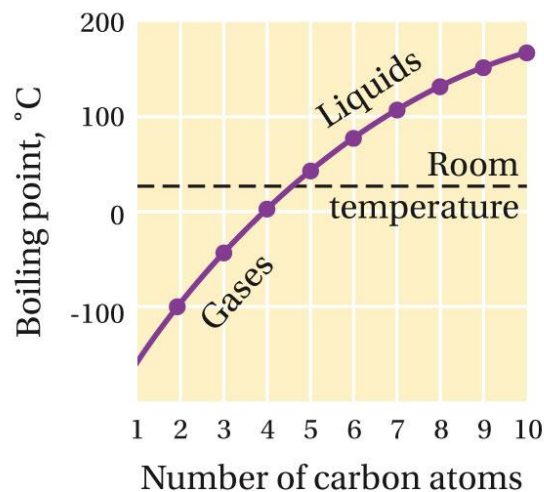


mass = 86 amu
BP = 101.7 °C



mass = 86 amu
BP = 63.3 °C

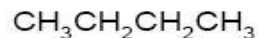
Alkanes: no H-bonding or dipole moment (C & H have nearly the same EN \therefore not polar).



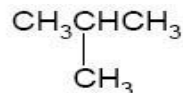
Name	Formula	Boiling point, °C
pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	36
2-methylbutane (isopentane)	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	28
2,2-dimethyl- propane (neopentane)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	10

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

Example:



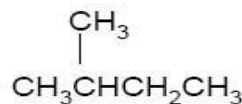
n-butane, 0°C



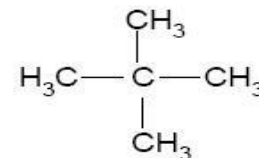
Isobutane, -12°C



n-pentane, 36°C



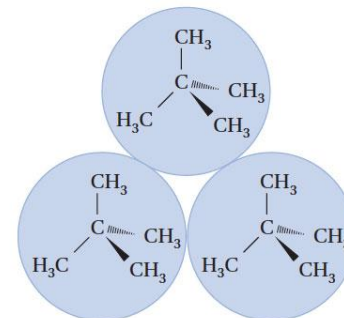
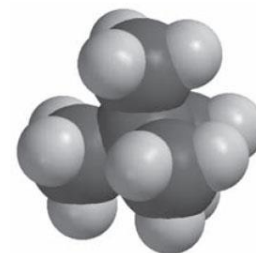
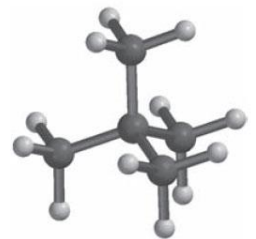
Isopentane, 28°C



Neopentane, 9.5°C

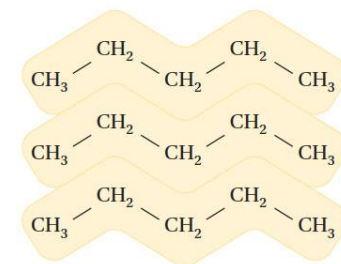
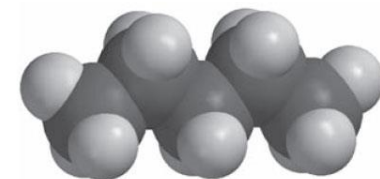
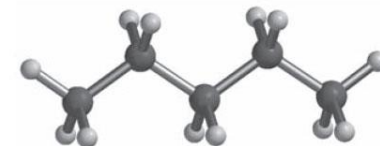
Structural Effects on IMFs

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)

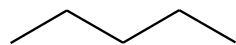


pentane
bp 36°C

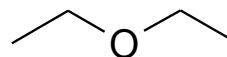
(b)

Effects on Physical Properties (cont'd)

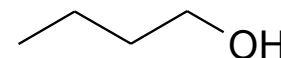
Hydrogen bonding:
strongest
intermolecular
forces so BP are
very high for
equivalent MW
compounds, i.e.



mass = 72 amu
BP = 36.1 °C

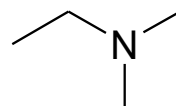
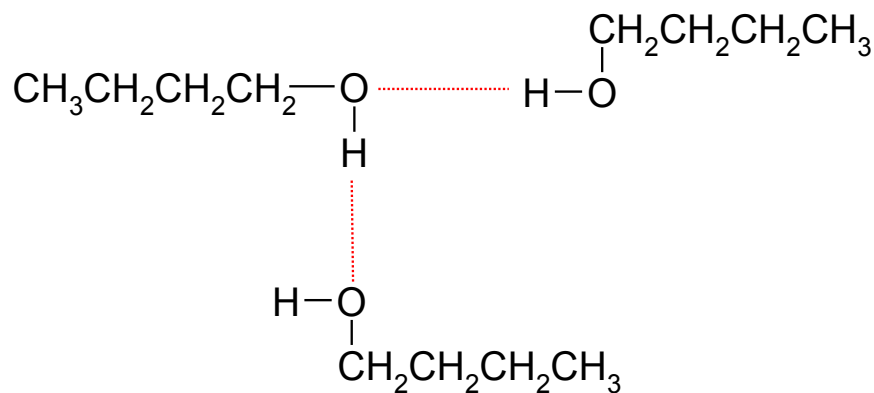


mass = 74 amu
BP = 35 °C

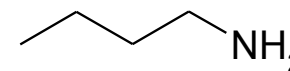


mass = 74 amu
BP = 117 °C

(look at last 10-15 mins
of lec.4)



mass = 73 amu
BP = 36 °C



mass = 73 amu
BP = 78 °C

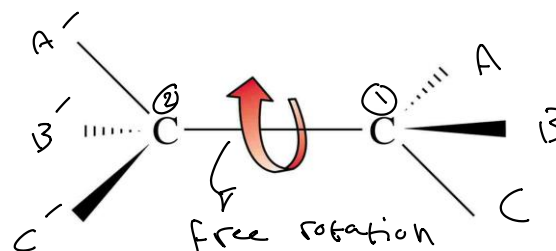
Conformational Isomers

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.

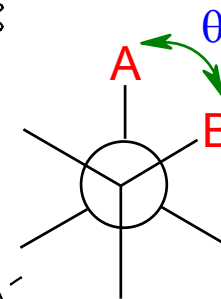
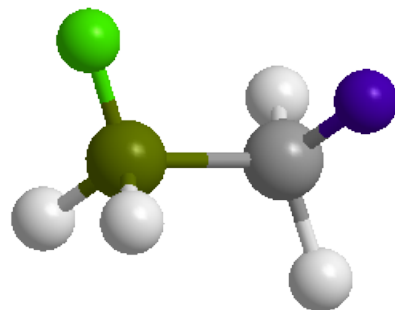
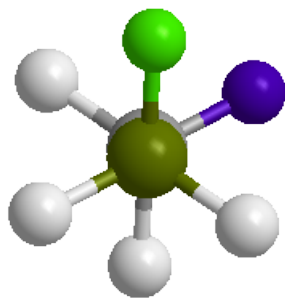
(sigma bonds)

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

Rotation about a **single bond** occurs easily because the amount of overlap of the sp^3 orbitals on the two carbon atoms is unaffected by rotation about the sigma bond



① side is sub
if we were to rotate A
the molecule would rotate creating a

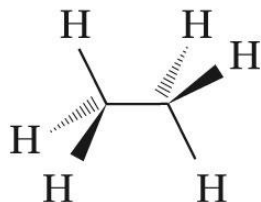
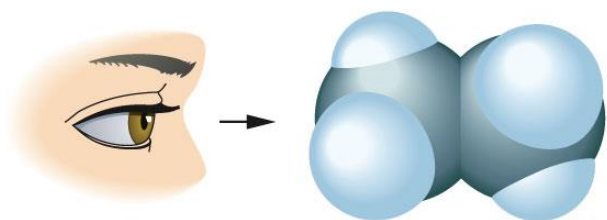


new 3D structure. the old & new structure are conformational isomers.

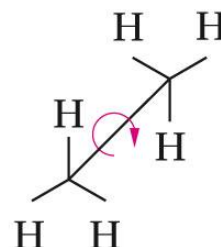
Conformational Isomers (cont'd)

Two extremes exist for **ethane**: staggered & eclipsed

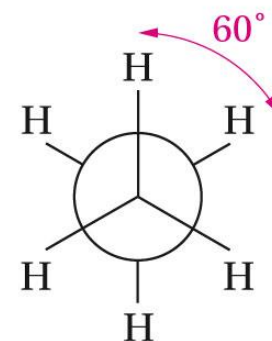
staggered



"dash-wedge"



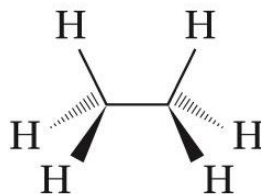
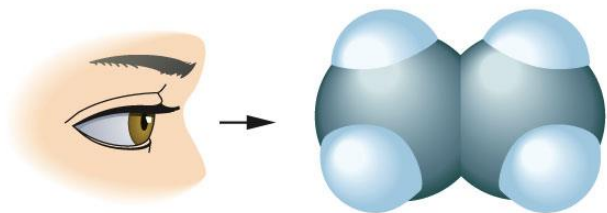
"sawhorse"



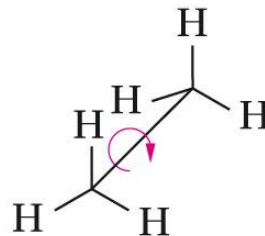
Newman

*
we will focus on the easiest projection of representing conformers
↓
new man's projection

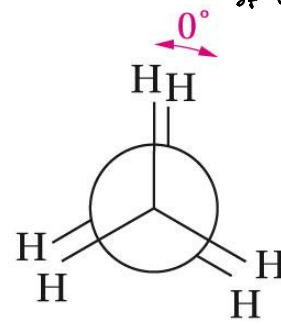
eclipsed



"dash-wedge"



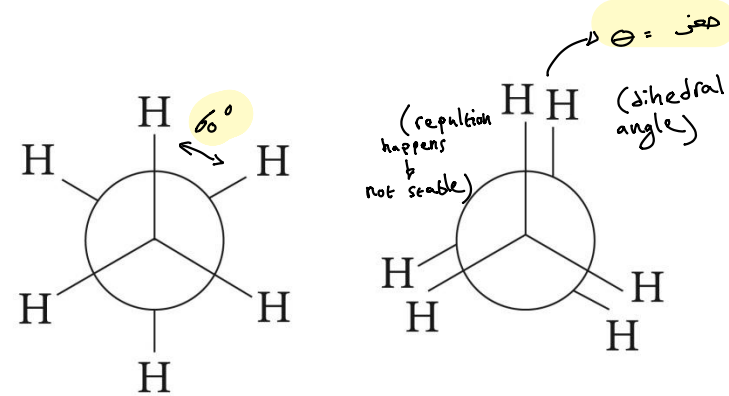
"sawhorse"



Newman

Conformational Isomers (cont'd)

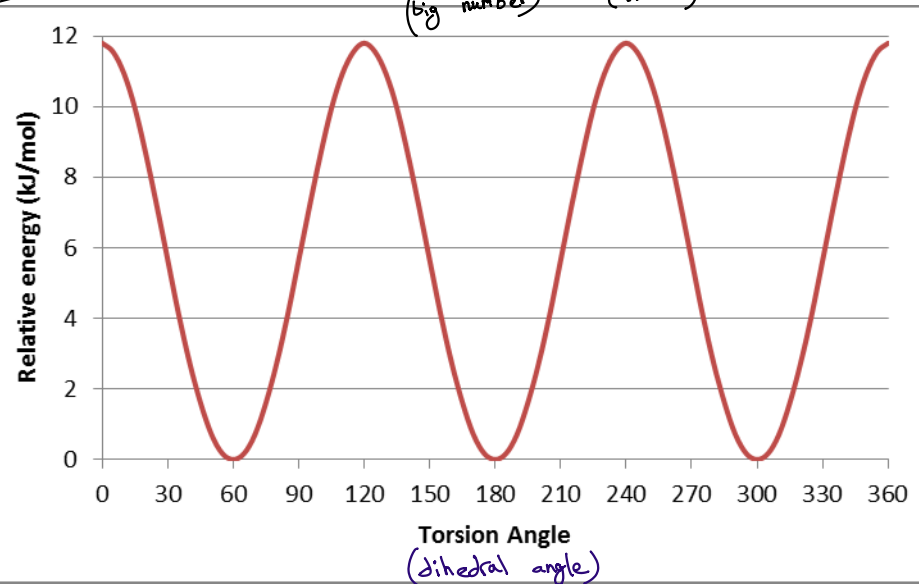
These two extremes represent high and low energy "conformations" of ethane. The "high" E is the eclipsed and low E the staggered.



(maximum dihedral angle) (least dihedral angle)
 * there is an infinite number of conformers (isomers) between 0° & 60° (big number)

* Staggered is the most stable conformer of (least energy)
 All conformers & eclipsed is the least stable (most energy)

We will focus on (staggered & eclipsed) conformers



Conformational Isomers (cont'd)

ethane

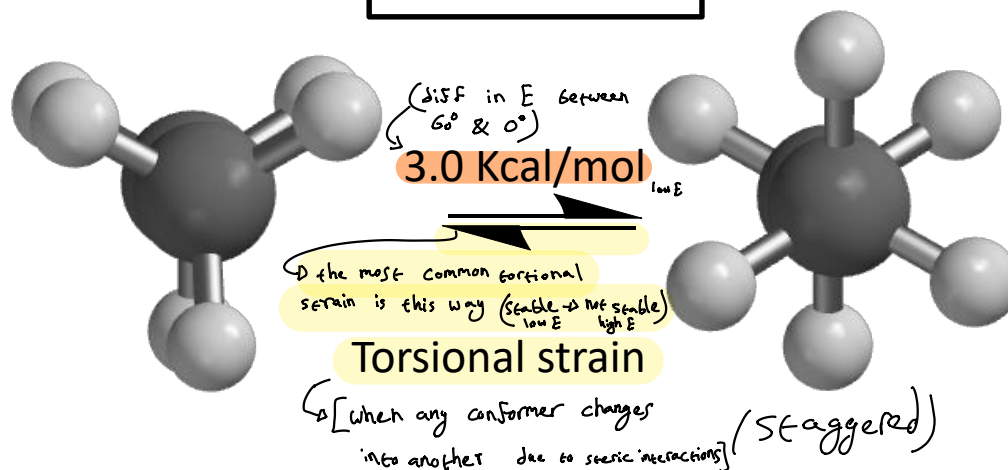
↪ between conformers

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.

two H atoms repel

(تداخل ذرات)

Rotating one carbon 60°

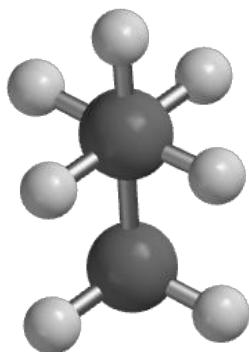
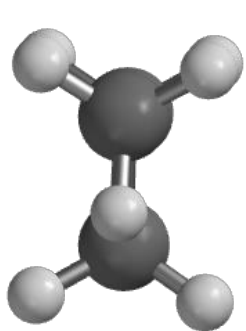


The H – H distance in the eclipsed is 2.36 Å and 2.54 Å in the staggered.

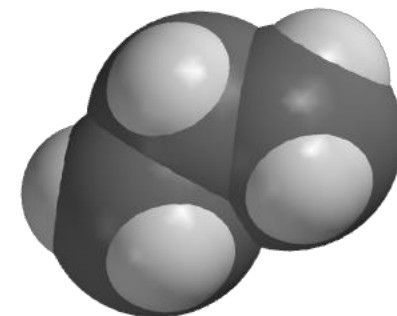
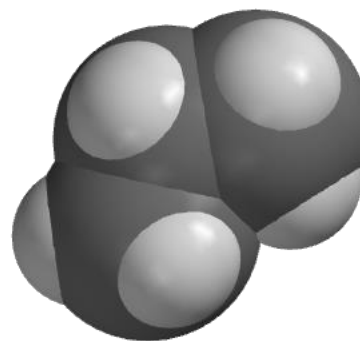
(14-27) min → → →
lec 5

Conformational Isomers (cont'd)

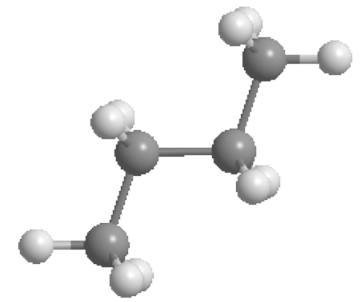
The problem is worse in propane as a methyl group is larger than a H atom. The eclipsed is on the left in both sets of images.



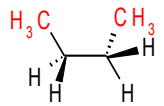
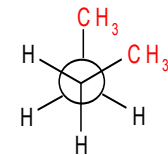
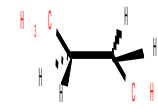
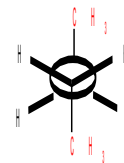
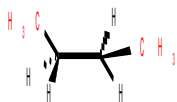
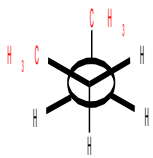
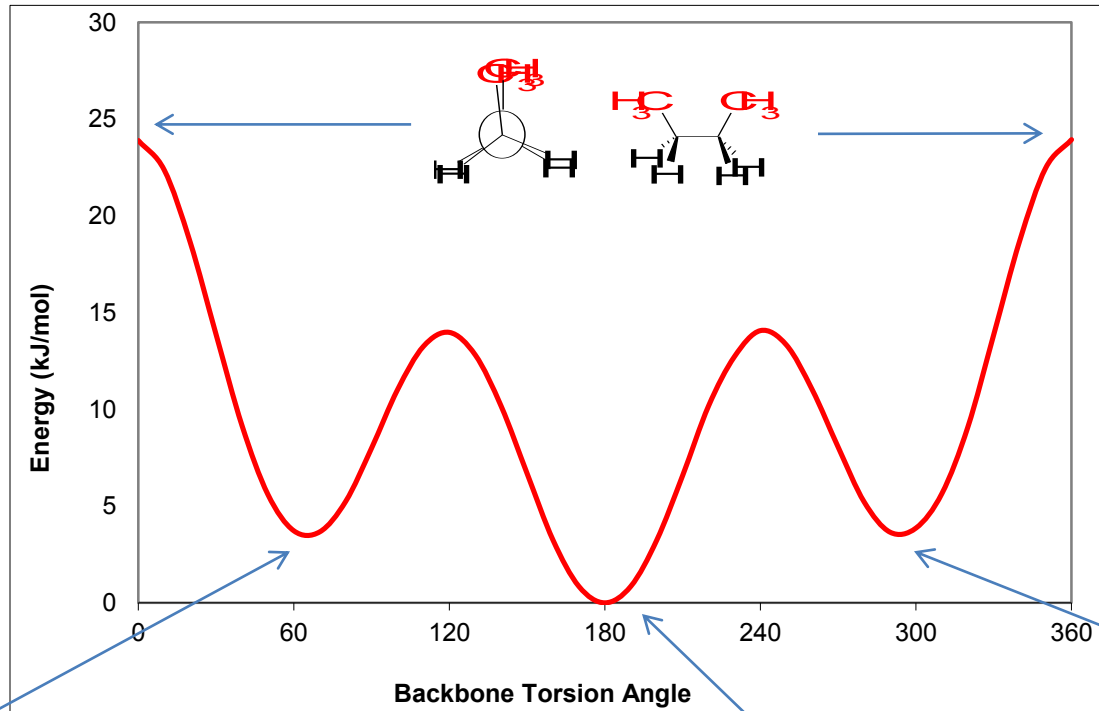
ball & stick



space filling



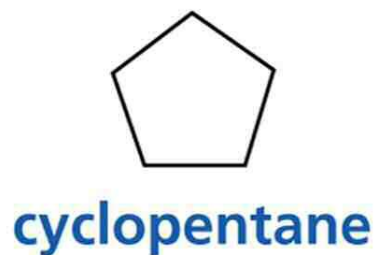
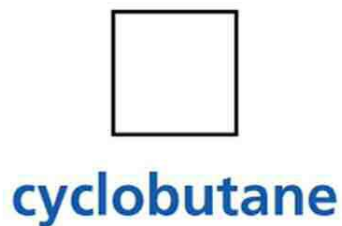
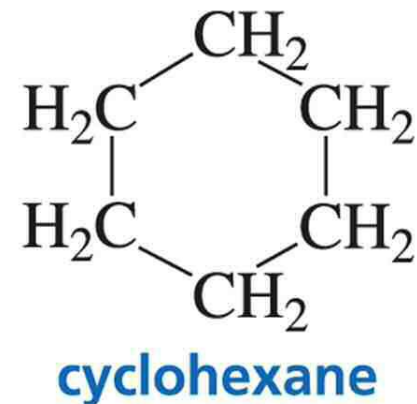
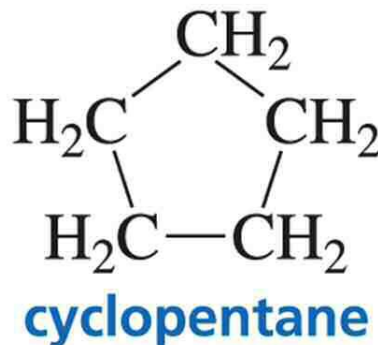
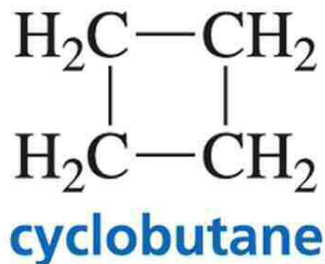
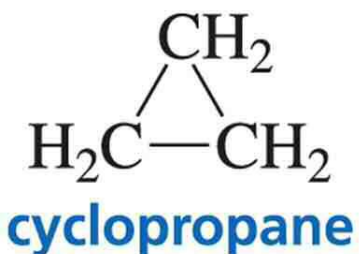
Steric effects reach their maximum in butane:



2.9 Cycloalkane Nomenclature and Conformation

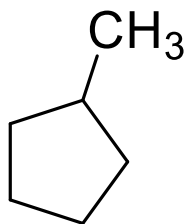
↳ the common thing between them & ^{linear} alkanes are single bonds

Cycloalkanes are saturated hydrocarbons that have at least one ring of carbon atoms. The general formula is C_nH_{2n} . linear Alkane $\rightarrow C_nH_{(2n+2)}$

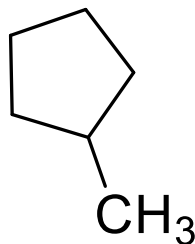


Cycloalkane Nomenclature

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

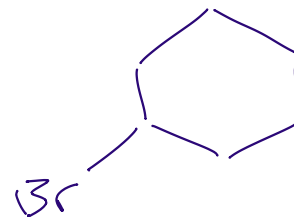


=



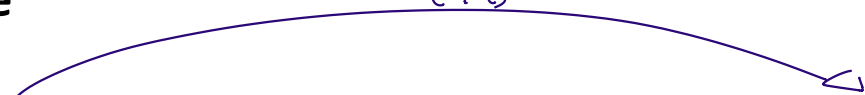
methylcyclopentane

methylcyclopentane

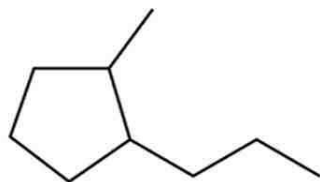


Bromo cyclohexane

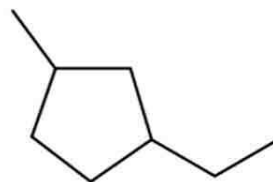
thus



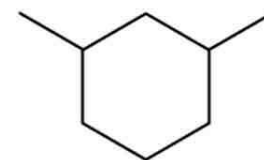
Two substituents : Substituents are stated in alphabetical order. #1 goes to the first-listed substituent (*we have to choose the shortest distance between them*)



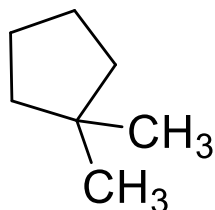
1-methyl-2-propylcyclopentane



1-ethyl-3-methylcyclopentane



1,3-dimethylcyclohexane



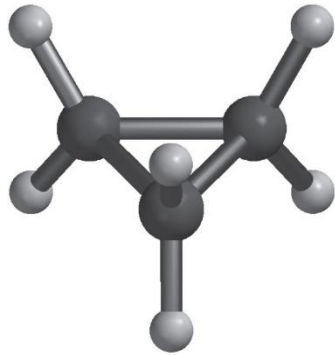
1,1-dimethylcyclopentane

Cycloalkanes: cyclopropane – is the smallest ring structure possible.

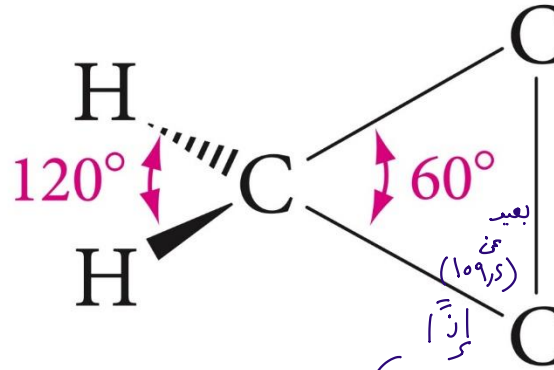
- It is rigid and very highly strained as the bond angles (60°) are distorted from ideals (109.5°) [angle strain is how far the angle is from 109.5°]
- It is more reactive than a linear alkane as the strained C-C bonds are easier to break

(Far from the wanted ideal angle)

Eclipsed Hydrogens



a.



b.

- * rigid \oplus strained angle
- * weak C-C bonds



good overlap
strong bond

poor overlap
weak bond

tetrahedral bond angle = 109.5° (ideal)
 (this exact number is because the repulsion between [e- making bonds] are at lowest/orbitals overlap the best \rightarrow strong bond)

bond angle $< 109.5^\circ$

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

remember: geometry of alkane

is tetrahedral

(109.5° has 4 carbon)

Rotation in cycloalkane is restricted (in contrast to linear alkanes)

if we were to rotate a & b the

C-C bond would break in contrast to what happens with (linear alkanes). this restriction gives us a 3-d structure that all C-H are eclipsed. (No free rotation allowed - or else - broken) \rightarrow (high torsional strain)

therefore

ring strain = angle strain \oplus torsional strain
(109 is 90) \square \square (eclipsed) \square

so, ring strain in cyclo-
-propane is most high
(compared to propane) staggered

the higher strain \rightarrow lower stability

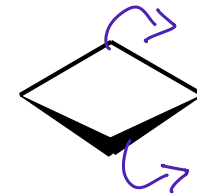
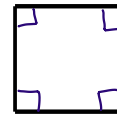
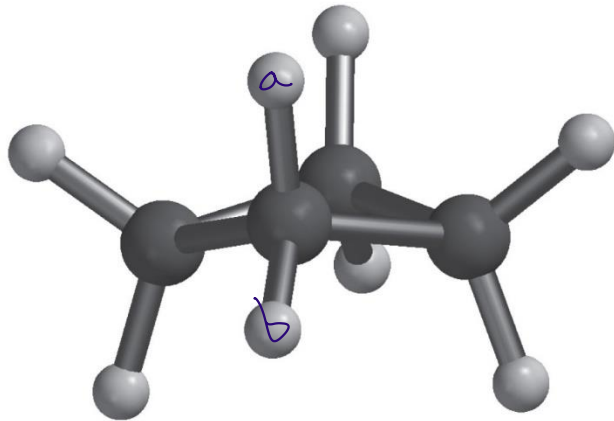
more reactive \swarrow

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 $\sim 90^\circ$

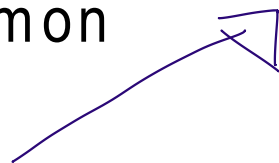
still far from 109.5 so there is angle strain but compared to cyclopropane, it's much better has more stability/less energy



- less eclipsed hydrogens
- minimize angle strain

common

better



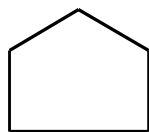
→ eclipsed form

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

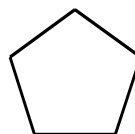
cyclopentane

Cycloalkanes: cyclopentane – “envelope” conformation

- It is more flexible than cyclobutane and bond angles are $\sim 105^\circ$, and less strained



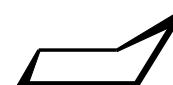
poor



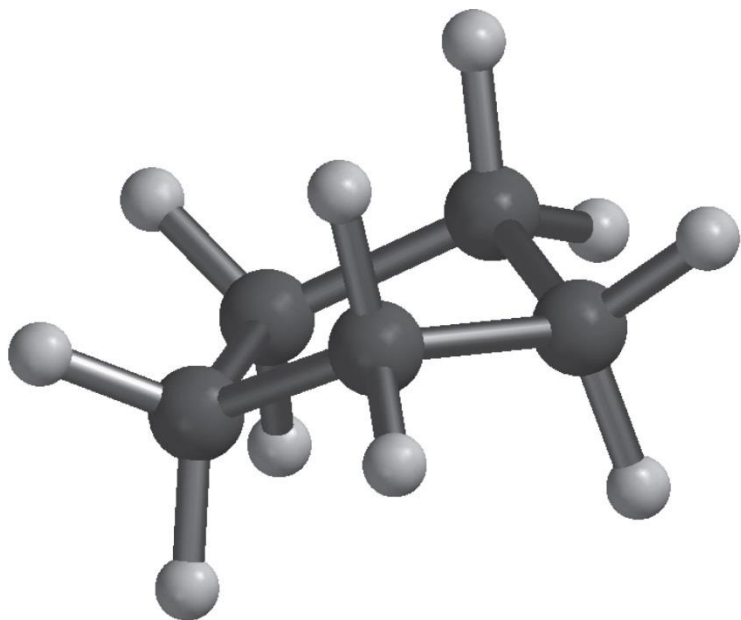
better



good



best



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

even more stable!

cyclohexane

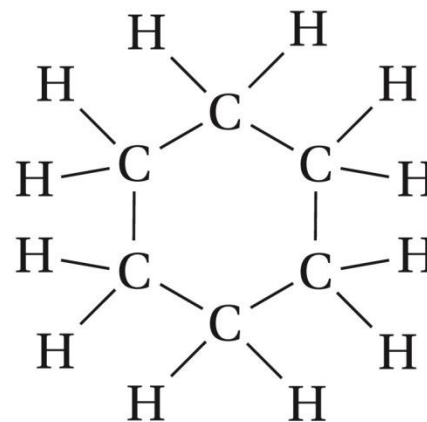
the most stable
lowest E

Cycloalkanes: cyclohexane – “chair”

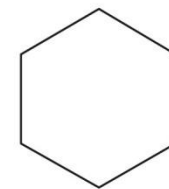
- It is highly flexible and can adopt a strain free non-planar conformation with bond angle of 109.5°
- It is very common in nature so understanding its conformations is important.

(no eclipse)

Although commonly drawn as a hexagon, implying a flat six-membered ring this is not the common conformation seen.



or

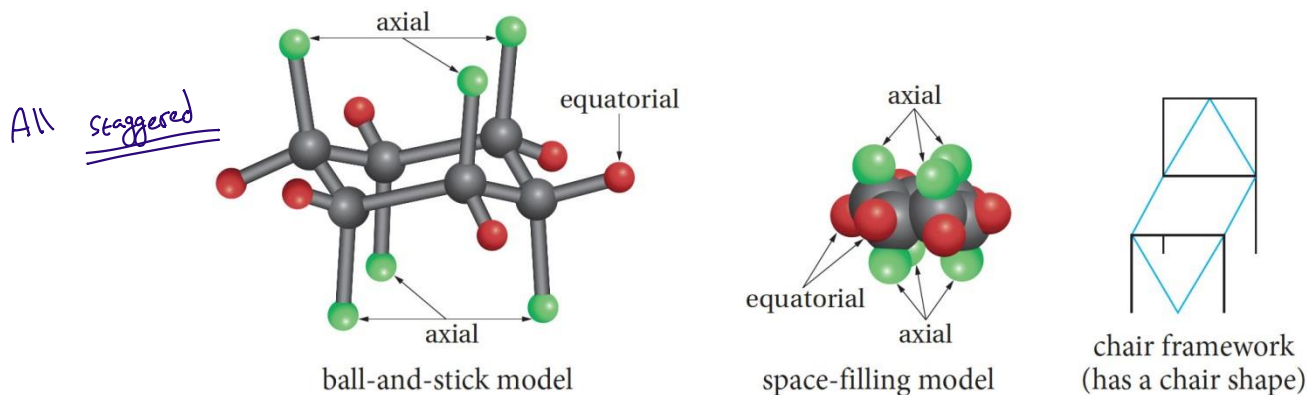


Structural and abbreviated structural formulas for cyclohexane

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 $\sim 109.5^\circ$ as opposed to the 120° in a planar structure. $\sim 109.5^\circ$

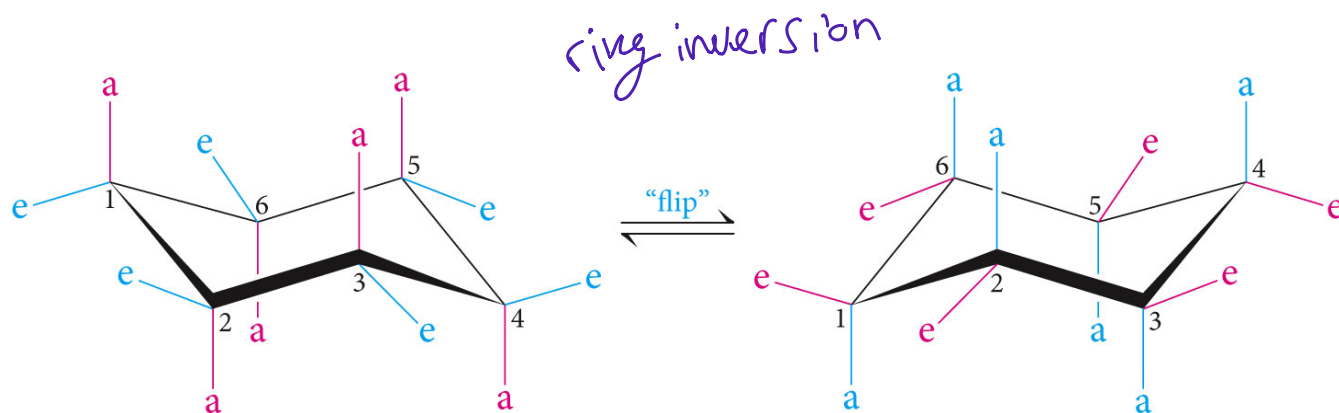


This structure creates two subsets of hydrogen atoms, those lying in the same plane as the C atoms, the equatorial H and those lying above and below that plane, the axial H atoms

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 is 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**.

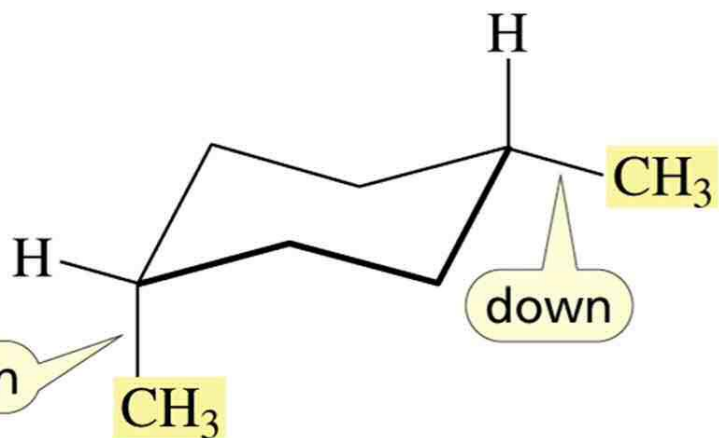


Axial bonds (red) in the left structure become equatorial bonds (red) in the right structure when the ring "flips."

every(C)atom shifts

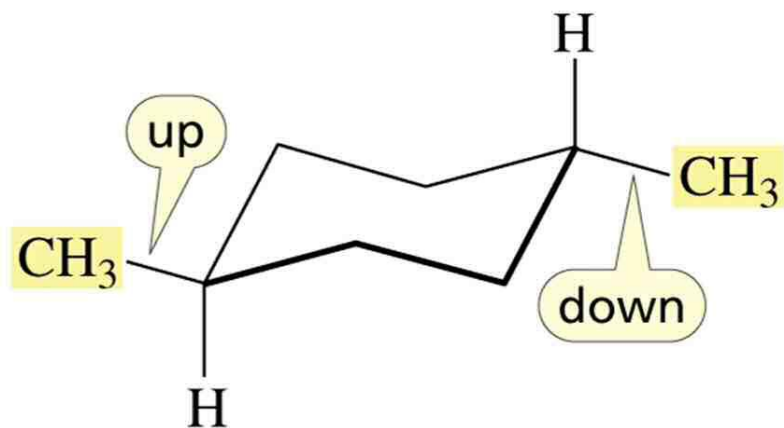
Cis and Trans Isomers

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

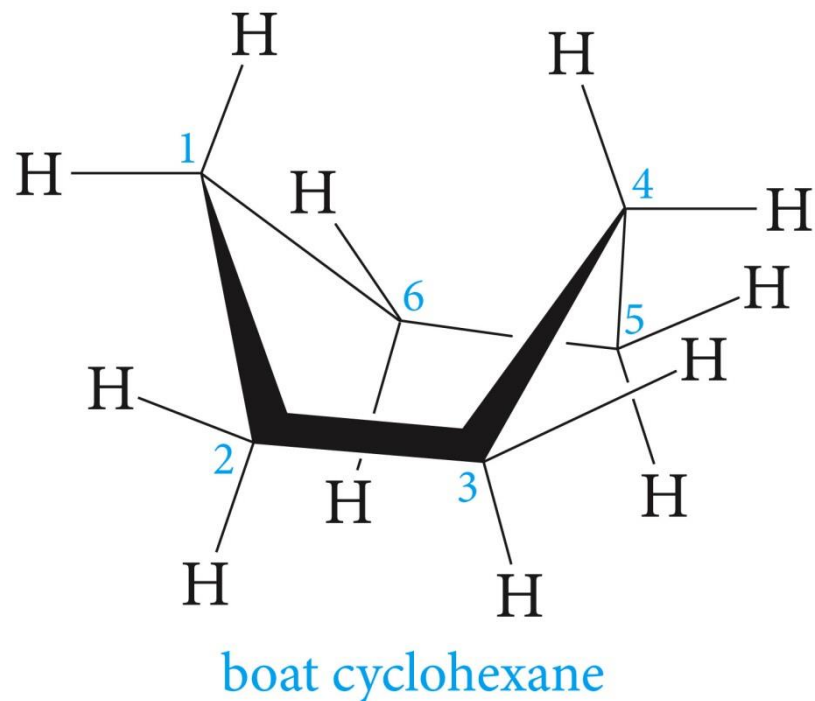
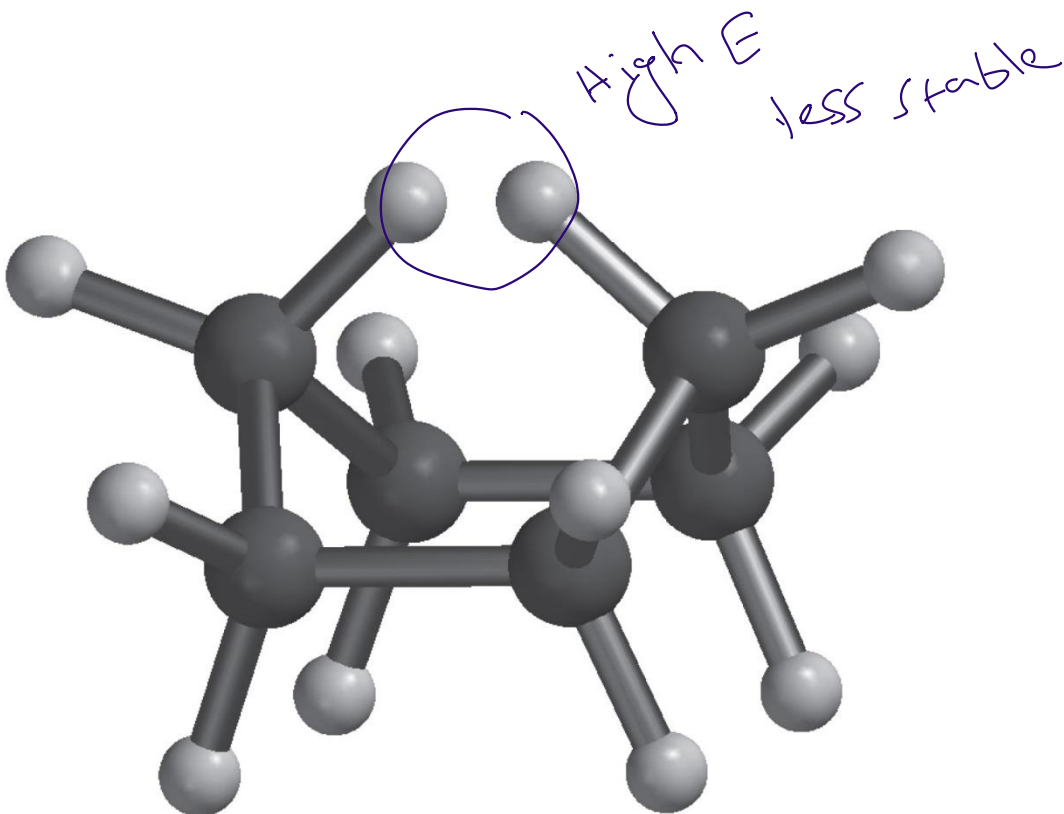


trans-1,4-dimethylcyclohexane

Conformational Isomers (cont'd)

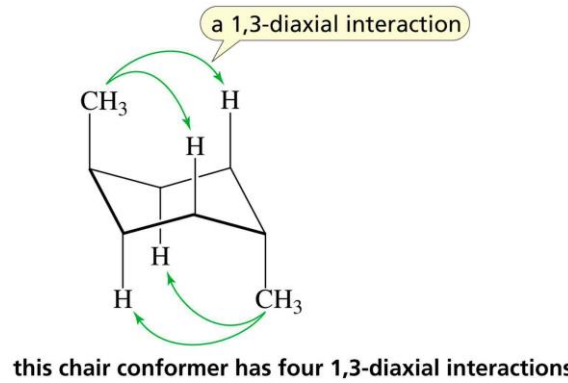
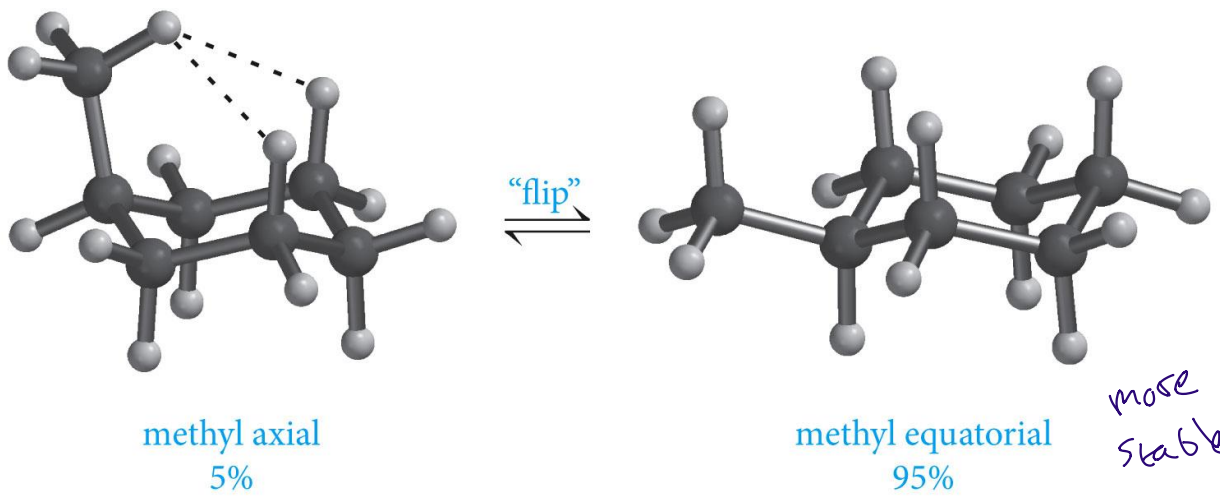
Cyclohexane cont'd:

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

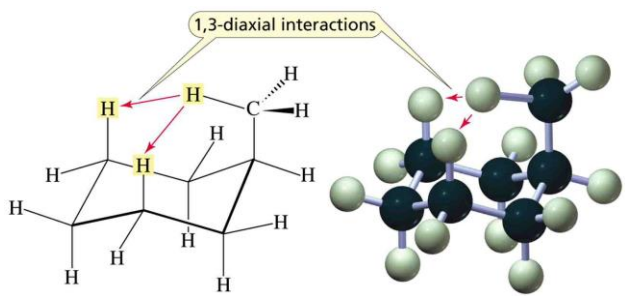


• Substituted cyclohexane: **(1,3-Diaxial Interactions)**

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



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.



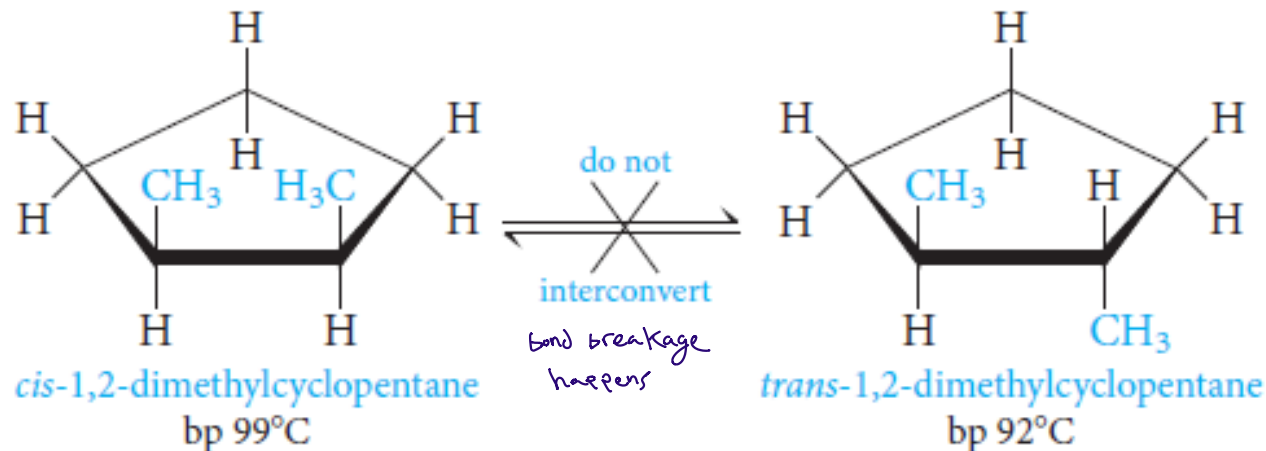
Note: The larger the substituent, the more the equatorial-substituted conformer is favored.

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.

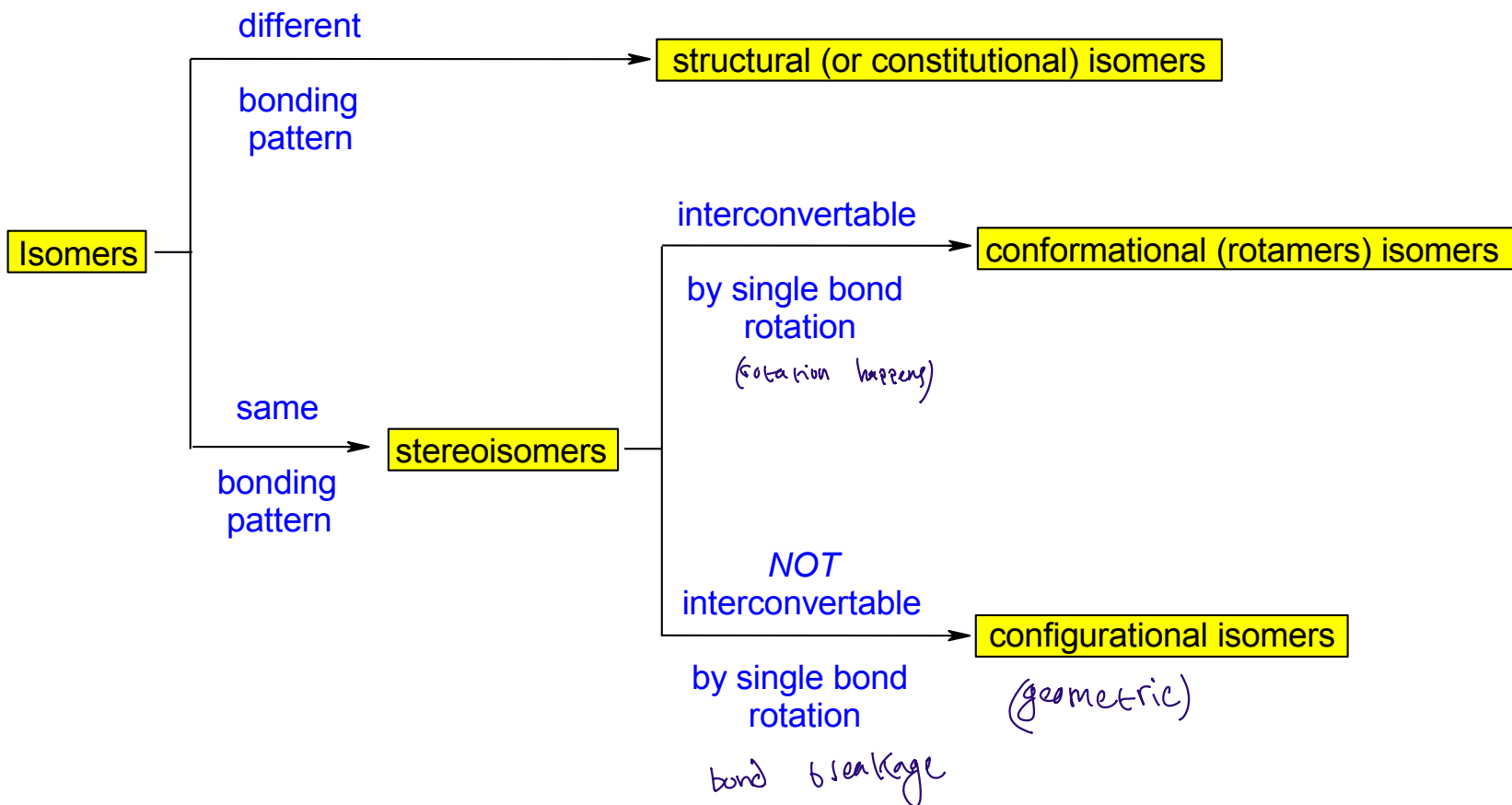
An example of this is 1,2-dimethylcyclopentane

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



- The two methyl groups may be on the same side of the ring 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)



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 state) and reduction the gain of electrons (decrease in oxidation state). 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)

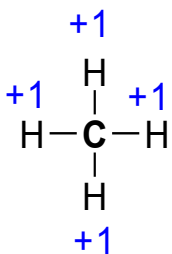
For the C atom, oxidation involves increasing the number of C-O (or other atoms more EN than C) bonds and/or decreasing the number of C-H bonds.

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

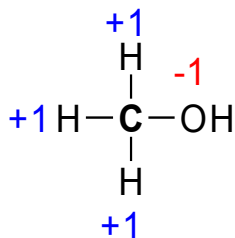
Oxidation Reactions (cont'd)

To determine the oxidation state:

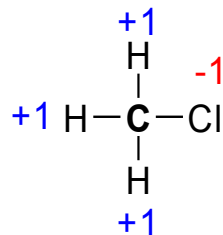
- each bond to a C atom counts: 0
- each bond to a H atom counts +1
- Each (single) bond to a more EN atom count -1, i.e.



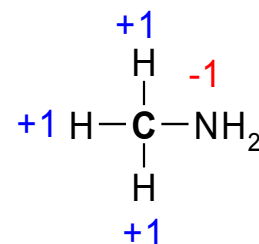
$$\begin{aligned} \text{C} &= -(+1+1+1+1) \\ &= -4 \end{aligned}$$



$$\begin{aligned} \text{C} &= -(+1+1+1-1) \\ &= -2 \end{aligned}$$



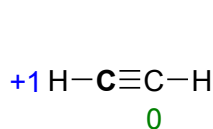
$$\begin{aligned} \text{C} &= -(+1+1+1-1) \\ &= -2 \end{aligned}$$



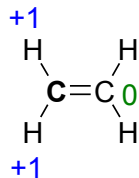
$$\begin{aligned} \text{C} &= -(+1+1+1-1) \\ &= -2 \end{aligned}$$

Oxidation Reactions (cont'd)

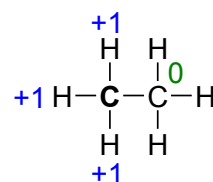
More examples:



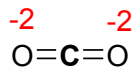
$$\begin{aligned} \text{C} &= -(0+1) \\ &= -1 \end{aligned}$$



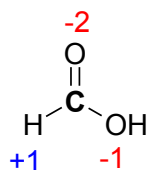
$$\begin{aligned} \text{C} &= -(0+1+1) \\ &= -2 \end{aligned}$$



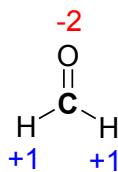
$$\begin{aligned} \text{C} &= -(0+1+1+1) \\ &= -3 \end{aligned}$$



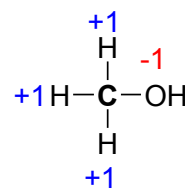
$$\begin{aligned} \text{C} &= -(-2-2) \\ &= +4 \end{aligned}$$



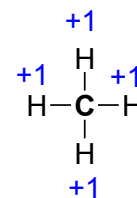
$$\begin{aligned} \text{C} &= -(-2-1+1) \\ &= +2 \end{aligned}$$



$$\begin{aligned} \text{C} &= -(-2+1+1) \\ &= 0 \end{aligned}$$

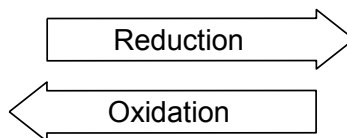


$$\begin{aligned} \text{C} &= -(+1+1+1-1) \\ &= -2 \end{aligned}$$



$$\begin{aligned} \text{C} &= -(+1+1+1+1) \\ &= -4 \end{aligned}$$

Most
C-O
bonds



Most
C-H
bonds

Oxidation Reactions (cont'd)

The most important 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.

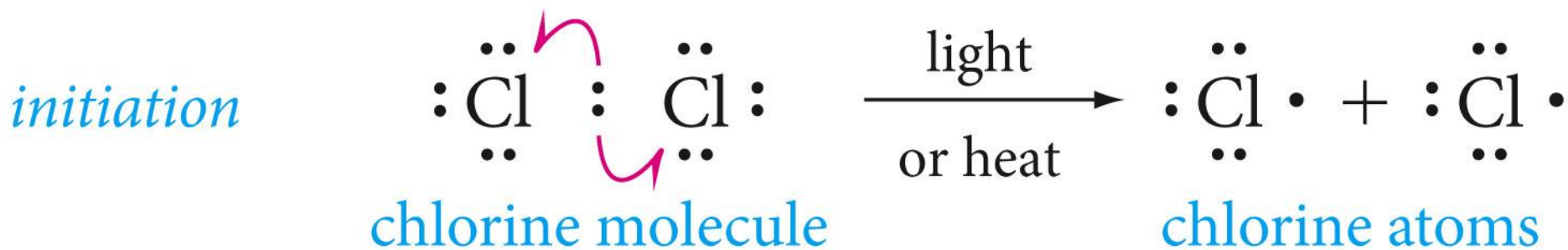


The two common halides used are chlorine and bromine.

Halogenation of Alkanes (cont'd)

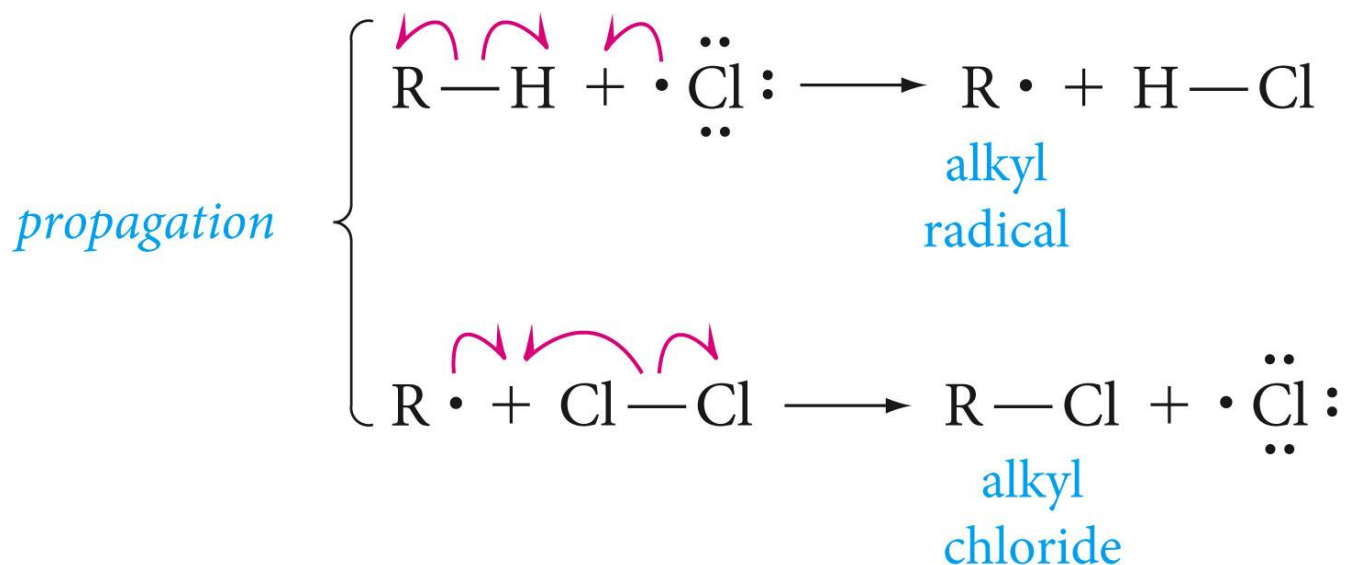
The process involves three steps:

- 1. initiation:** this is where the free radical is formed: note we generate 2 free radical atoms in this process.



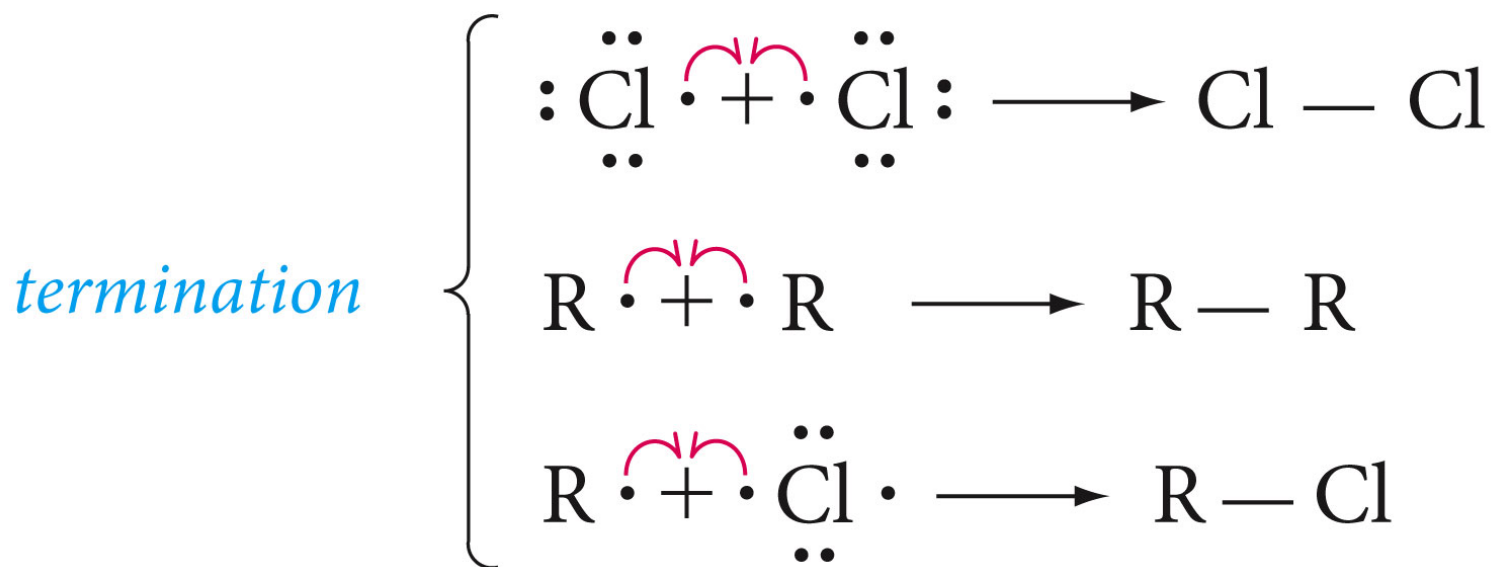
Halogenation of Alkanes (cont'd)

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.



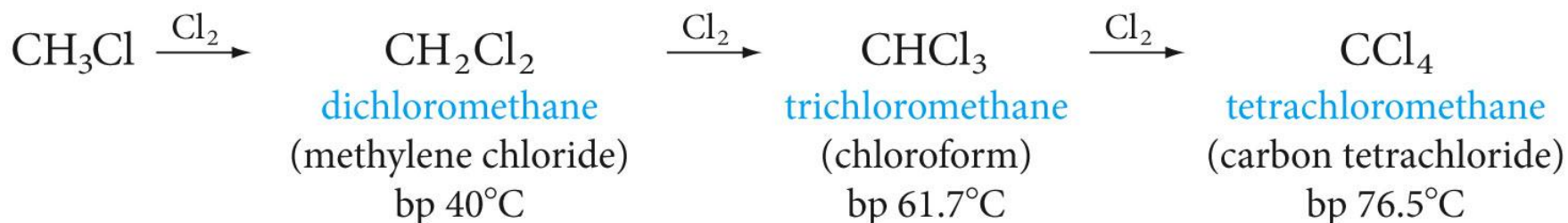
Halogenation of Alkanes (cont'd)

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.



Halogenation of Alkanes (cont'd)

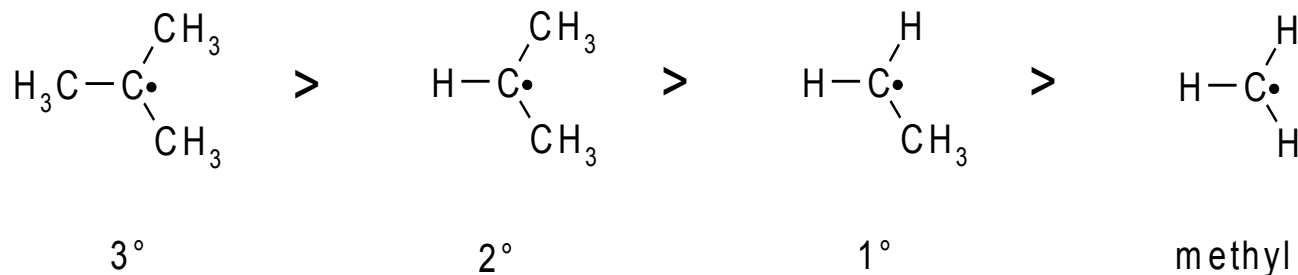
A single alkane molecule can undergo several substitution steps depending on the concentration of the halide radical, i.e.



As a matter of fact, unless the concentration of chlorine is kept quite low there will be a mixture of these products.

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:



bond dissociation energies	kJ/mol	380	397	410	435
	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.

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

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

$\%P_i$ = %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:

$$\%1^\circ = 100 \times (6 \times 1) / (6 \times 1 + 2 \times 3.9) = 600 / 13.8 = 43.5\%$$

$$\%2^\circ = 100 \times (2 \times 3.9) / (6 \times 1 + 2 \times 3.9) = 780 / 13.8 = 56.5\%$$

Or for bromination:

$$\%1^\circ = 100 \times (6 \times 1) / (6 \times 1 + 2 \times 82) = 600 / 170 = 3.53\%$$

$$\%2^\circ = 100 \times (2 \times 82) / (6 \times 1 + 2 \times 82) = 16400 / 170 = 96.47\%$$

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.