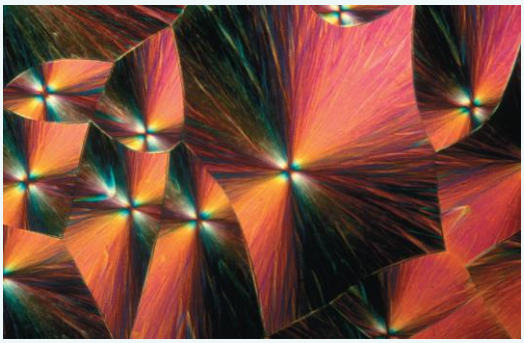
Chapter 3



An Introduction to Organic Compounds

Nomenclature, Physical Properties, and Representation of Structure

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Alkanes are Hydrocarbons that contain only single Bonds general Molecular Formula: C_nH_{2n+2}

Table 3.1 Nomenclature and Physical Properties of Straight-Chain Alkanes

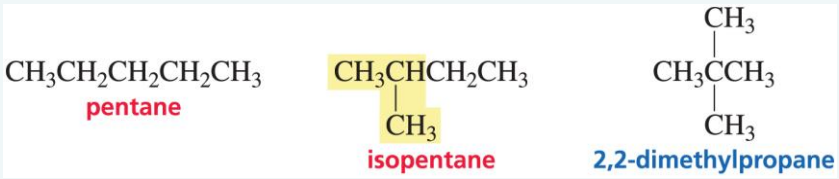
Number of carbons	Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Density[a] (g/mL)
1	CH_4	methane	CH_4	−167.7	−182.5	
2	C_2H_6	ethane	CH_3CH_3	−88.6	−183.3	
3	C_3H_8	propane	$CH_3CH_2CH_3$	−42.1	−187.7	
4	C_4H_{10}	butane	$CH_3CH_2CH_2CH_3$	−0.5	−138.3	
5	C_5H_{12}	pentane	$CH_3(CH_2)_3CH_3$	36.1	−129.8	0.5572
6	C_6H_{14}	hexane	$CH_3(CH_2)_4CH_3$	68.7	−95.3	0.6603
7	C_7H_{16}	heptane	$CH_3(CH_2)_5CH_3$	98.4	−90.6	0.6837
8	C_8H_{18}	octane	$CH_3(CH_2)_6CH_3$	125.7	−56.8	0.7026
9	C_9H_{20}	nonane	$CH_3(CH_2)_7CH_3$	150.8	−53.5	0.7177
10	$C_{10}H_{22}$	decane	$CH_3(CH_2)_8CH_3$	174.0	−29.7	0.7299

[a]Density is temperature dependent. The densities given are those determined at 20 °C ($d^{20°}$).

Nomenclature of Alkanes

C_4H_8 can be arranged in two ways:

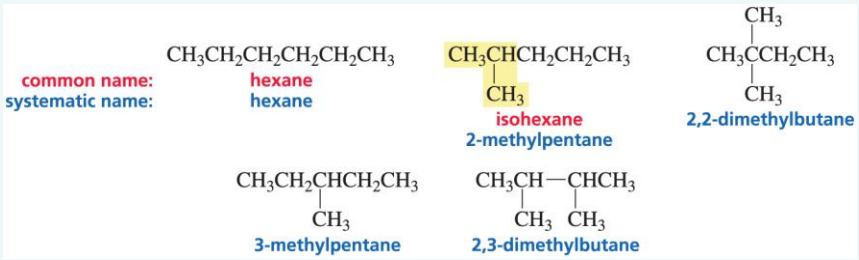
C_5H_{10} can be arranged in three ways:



These are constitutional isomers:
the same molecular formula but the atoms are linked differently.

Nomenclature of Alkanes

C_6H_{14} can be arranged in five ways:

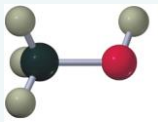


Alkyl Substituents

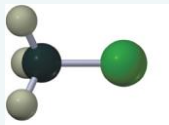
Removing a hydrogen from an alkane results in an alkyl substituent.

CH_3—	CH_3CH_2—	$CH_3CH_2CH_2$—	$CH_3CH_2CH_2CH_2$—
a methyl group	an ethyl group	a propyl group	a butyl group

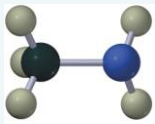
$CH_3CH_2CH_2CH_2CH_2$—	R—
a pentyl group	any alkyl group



methyl alcohol



methyl chloride



methylamine

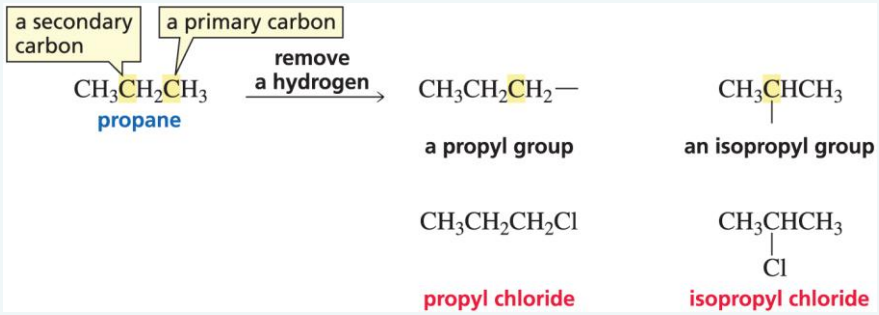
Replace "ane" of alkane with "yl."

Common Names

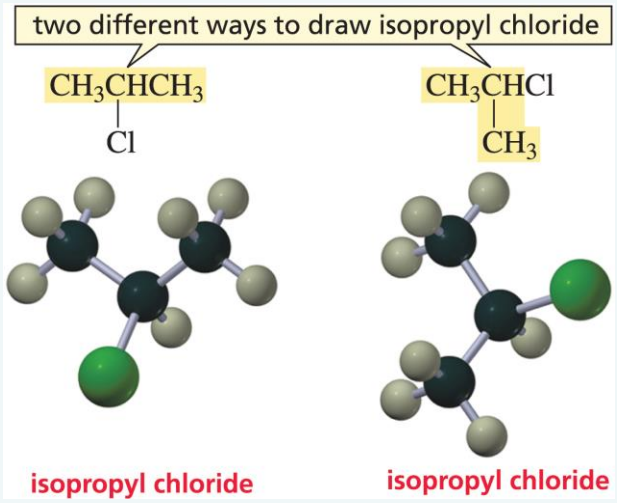
R—OH	R—NH_2	R—X	X = F, Cl, Br, or I	R—O—R
an alcohol	an amine	an alkyl halide		an ether

CH_3OH	$CH_3CH_2NH_2$	$CH_3CH_2CH_2Br$	$CH_3CH_2CH_2CH_2Cl$
methyl alcohol	ethylamine	propyl bromide	butyl chloride
CH_3I	CH_3CH_2OH	$CH_3CH_2CH_2NH_2$	$CH_3CH_2OCH_3$
methyl iodide	ethyl alcohol	propylamine	ethyl methyl ether

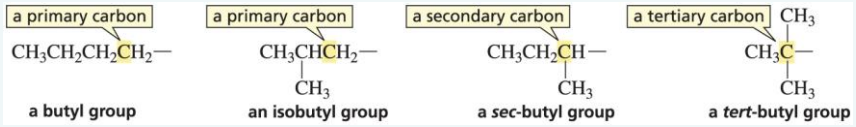
Propyl and Isopropyl



Two ways to draw Isopropyl Chloride



There are four Butyl Groups



n = An Unbranched Chain

$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2CH_2CH_2CH_2F$
butyl bromide	pentyl fluoride
or	or
n-butyl bromide	*n*-pentyl fluoride

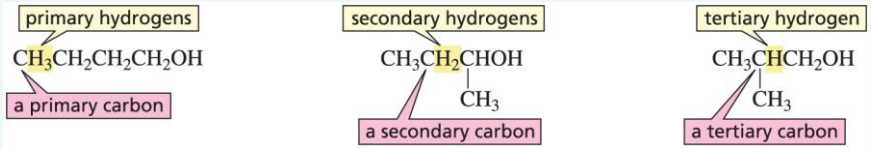
Common names sometimes use "*n*" to indicate a straight-chain alkane.

Primary, Secondary, and Tertiary Carbons

A primary carbon is bonded to one carbon.

A secondary carbon is bonded to two carbons.

A tertiary carbon is bonded to three carbons.



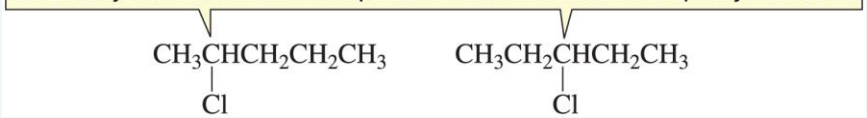
Primary hydrogens are attached to primary carbons.

Secondary hydrogens are attached to secondary carbons.

Tertiary hydrogens are attached to tertiary carbons.

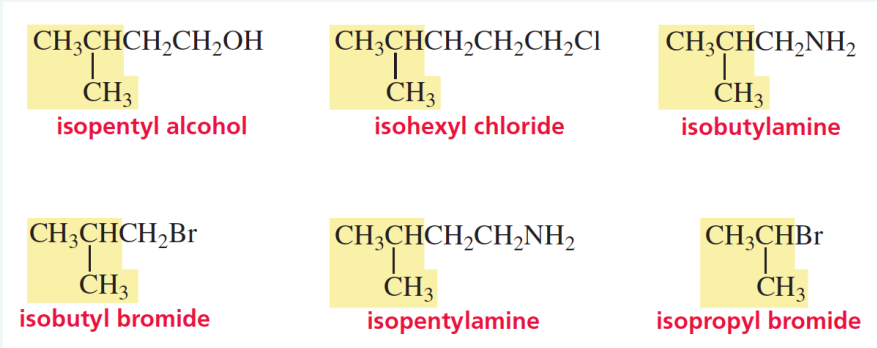
sec-Pentyl is not a good Name

Both alkyl halides have five carbon atoms with a chlorine attached to a secondary carbon, but two compounds cannot be named *sec*-pentyl chloride.



A name must specify only one compound.

"Iso"



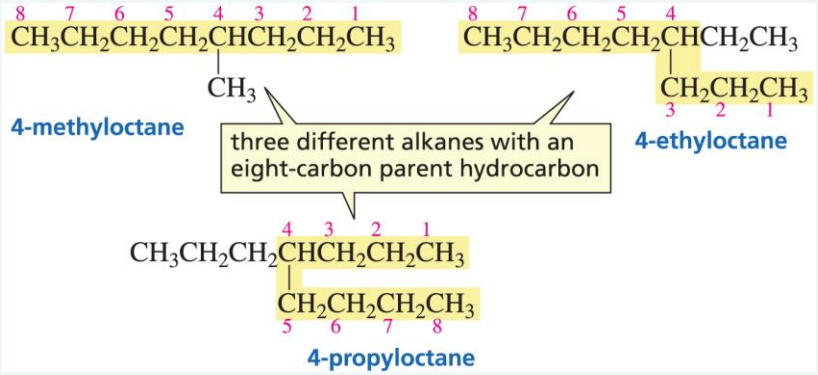
Iso is at one end, and the substituent is at the other end.

Alkyl Group Names

Table 3.2 Names of Some Common Alkyl Groups

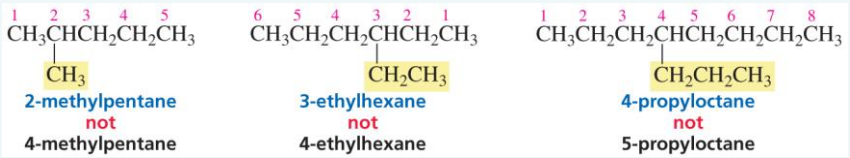
methyl	CH_3-	isobutyl	CH_3CHCH_2- (CH3 below)	pentyl	$CH_3CH_2CH_2CH_2CH_2-$
ethyl	CH_3CH_2-			isopentyl	$CH_3CHCH_2CH_2-$ (CH3 below)
propyl	$CH_3CH_2CH_2-$	*sec*-butyl	CH_3CH_2CH- (CH3 below)		
isopropyl	CH_3CH- (CH3 below)				
				hexyl	$CH_3CH_2CH_2CH_2CH_2CH_2-$
butyl	$CH_3CH_2CH_2CH_2-$	*tert*-butyl	CH_3C- (CH3 below)	isohexyl	$CH_3CHCH_2CH_2CH_2-$ (CH3 below)

Alkanes Systematic Nomenclature



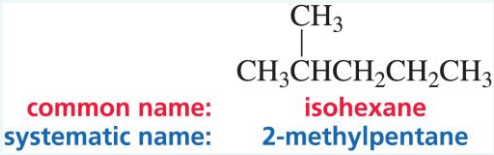
1- Identify the longest continuous chain
(this is called the parent hydrocarbon)

Add the Name of the Substituent



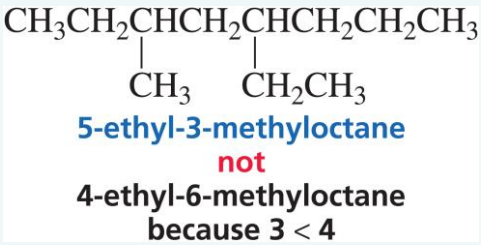
2- Number the chain in the direction that gives the substituent as low a number as possible.

Common *versus* Systematic Nomenclature



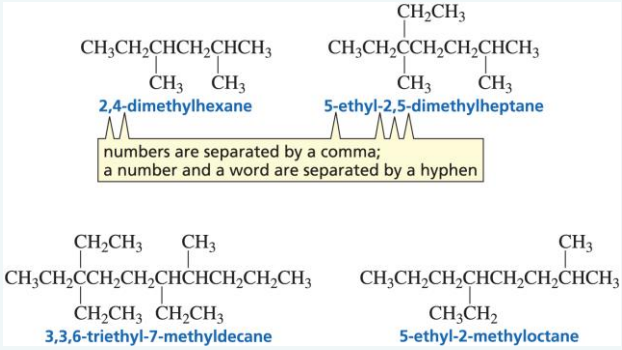
- Common names never have numbers.
- Only systematic names can have numbers.

List Substituents in Alphabetical Order



3-The correct name is the one that contains the lowest of the possible numbers.

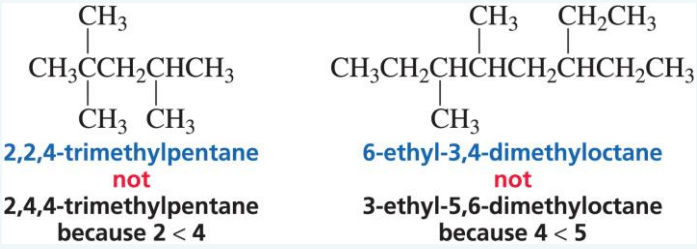
Multiple Substituents



Chain is numbered in the direction that puts the lowest number in the name.

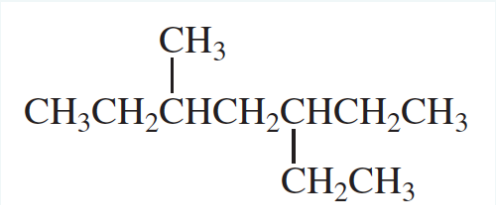
4- Substituents are listed in alphabetical order (di- and tri- are not alphabetized).

When both have the same Lowest Number



5- When both names have the same lowest number, go for the next lowest number.

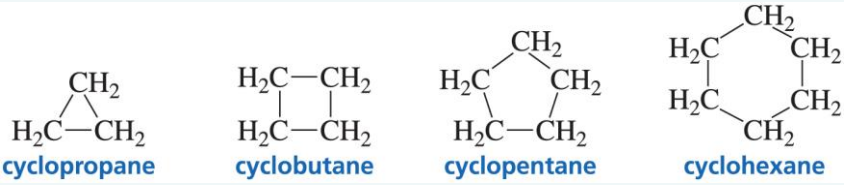
When both have the same Number



3-ethyl-5-methylheptane
not
5-ethyl-3-methylheptane

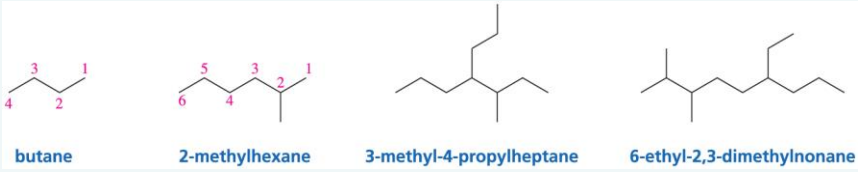
6- When the same numbers are obtained in both directions, the first group (alphabetical order) listed gets the lower number.

Cycloalkanes

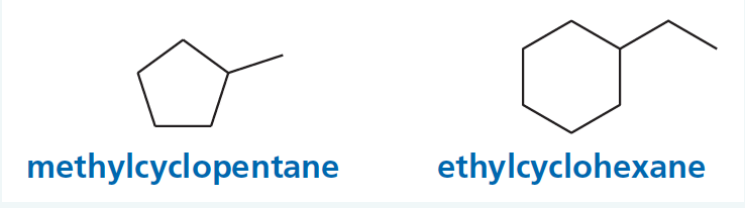


Skeletal structures do not show Cs and Hs bonded to Cs.

Skeletal Structures

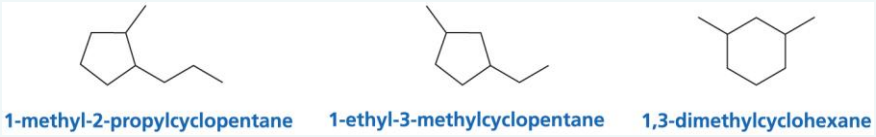


Mono-Substituted Cycloalkanes



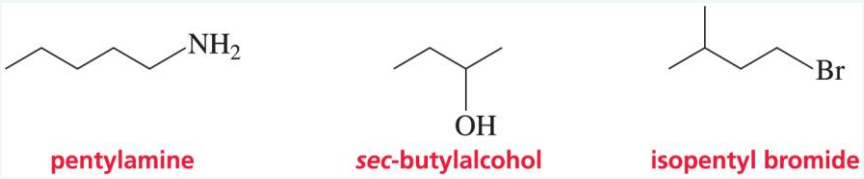
A number is not needed

Di-Substituted Cycloalkanes

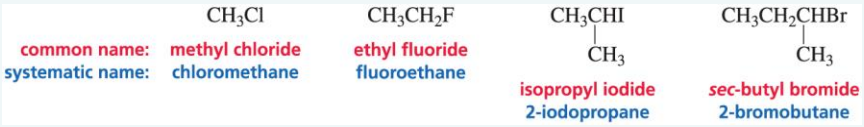


- Substituents are stated in alphabetical order.
- #1 goes to first-listed substituent.

Skeletal Structures

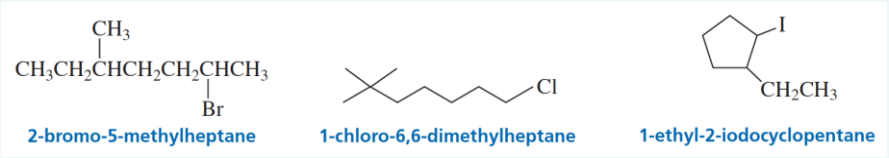


Nomenclature of Akyl Halides



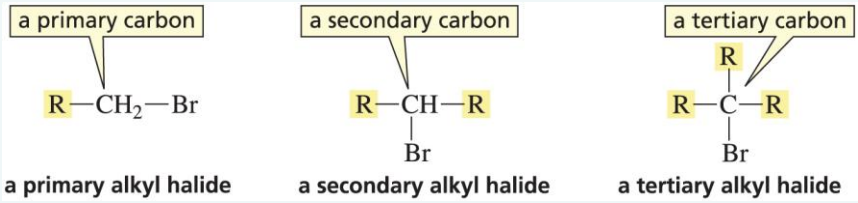
- Numbers are used only for systematic names.
- Common names never have numbers.

Nomenclature of Alkyl Halides



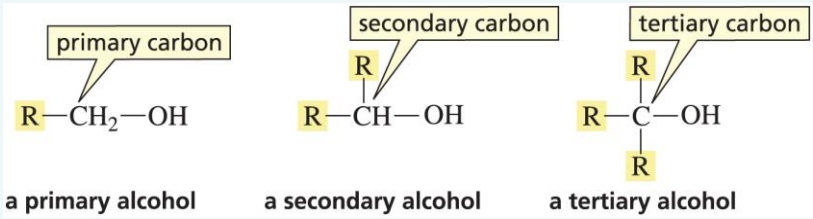
Rules:
The root name is based on the longest chain containing the halogen.
This root give the alkyl part of the name.
In cyclic compounds: list substituents in alphabetical order

Classification of Alkyl Halides



- Primary = Halogen is on a primary carbon.
- Secondary = Halogen is on a secondary carbon.
- Tertiary = Halogen is on a tertiary carbon.

Classification of Alcohols



- Primary alcohol = OH is on a primary carbon.
- Secondary alcohol = OH is on a secondary carbon.
- Tertiary alcohol = OH in on a tertiary carbon.

Classification of Amines

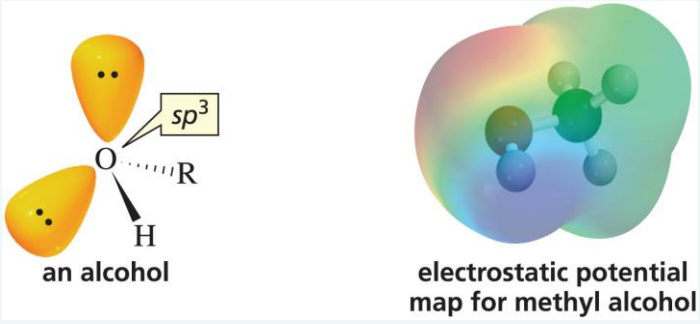
The classification depends on how many groups are bonded to N.

- Primary amine = one group bonded to N
- Secondary amine = two groups bonded N
- Tertiary amine = three groups bonded N

The Structure of an Alkyl Halide

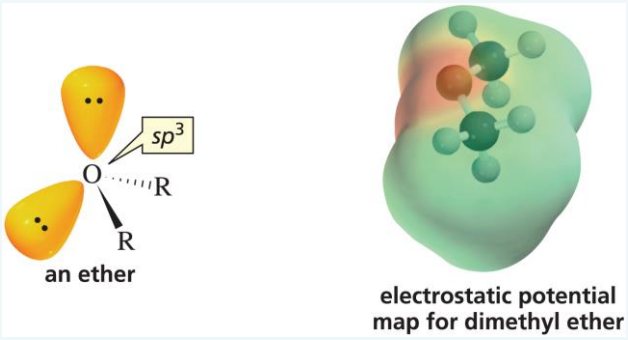
The C—X bond of an alkyl halide becomes longer and weaker as the size of the halogen increases.

The Structure of an Alcohol Resembles the Structure of Water



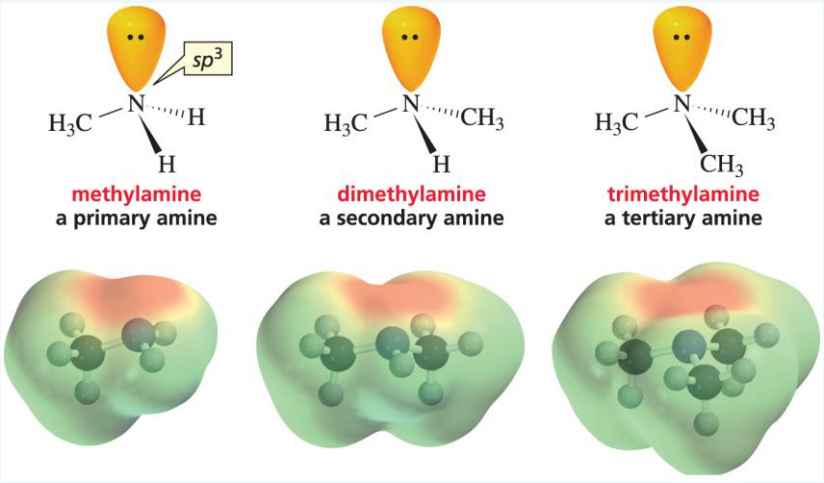
An alcohol is structurally like water with one H replaced by an R.

The Structure of an Ether Resembles the Structure of Water



An ether is structurally like water with both Hs replaced by Rs.

Structures of Amines



Boiling Points

The greater the attractive forces between molecules, the higher the boiling point.

Types of attractive forces

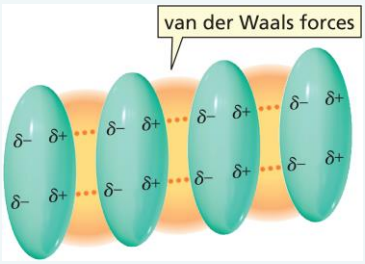
1- Van der Waals forces

2- dipole–dipole interactions

3- hydrogen bonds

Boiling Points

- Methane –167.7 ° C
- Ethane –88.6 ° C
- Propane –42.1 ° C
- Butane –0.5 ° C
- Pentane 36.1 ° C
- Hexane 68.7 ° C
- Heptane 98.4 ° C
- Octane 125.7 ° C

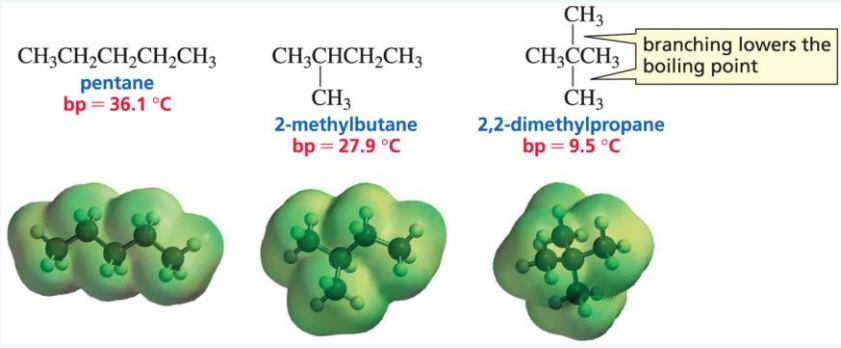


induced dipole-induced dipole interactions

van der Waals forces

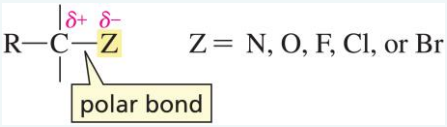
The greater the surface area of the molecule, the higher the boiling point

Branching Lowers the Boiling Point

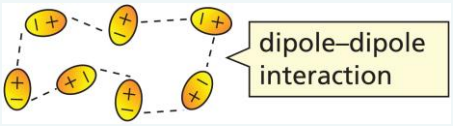


"cigar" "tennis ball"

Dipole–Dipole Interactions



Dipole–dipole interactions are stronger than van der Waals forces.



cyclopentane
bp = 49.3 °C

tetrahydrofuran
bp = 65 °C

Van der Waals

Van der Waals
dipole–dipole

Comparative Boiling Points

Table 3.3 Comparative Boiling Points (°C)

Alkanes	Ethers	Alcohols	Amines
$CH_3CH_2CH_3$	CH_3OCH_3	CH_3CH_2OH	$CH_3CH_2NH_2$
–42.1	–23.7	78	16.6
$CH_3CH_2CH_2CH_3$	$CH_3OCH_2CH_3$	$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2NH_2$
–0.5	10.8	97.4	47.8

Both have H-bonding

Why alcohols have Higher BPs?

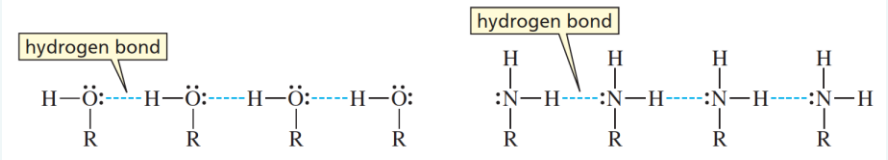
Comparative Boiling Points

Table 3.4 Comparative Boiling Points of Alkanes and Alkyl Halides (°C)

—Y	H	F	Cl	Br	I
CH_3—Y	–161.7	–78.4	–24.2	3.6	42.4
CH_3CH_2—Y	–88.6	–37.7	12.3	38.4	72.3
$CH_3CH_2CH_2$—Y	–42.1	–2.5	46.6	71.0	102.5
$CH_3CH_2CH_2CH_2$—Y	–0.5	32.5	78.4	101.6	130.5
$CH_3CH_2CH_2CH_2CH_2$—Y	36.1	62.8	107.8	129.6	157.0

The larger the halogen, the larger the electron cloud, the stronger are van der Walls forces, the more polarizable it is.

Hydrogen Bonds in H_2O and NH_3



CH_4 –167.7 ° C

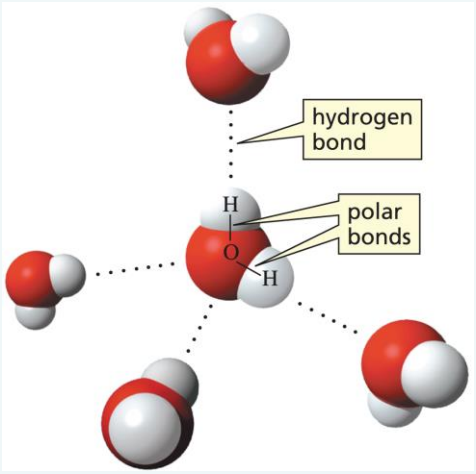
no hydrogen bonds

H_2O 100 ° C

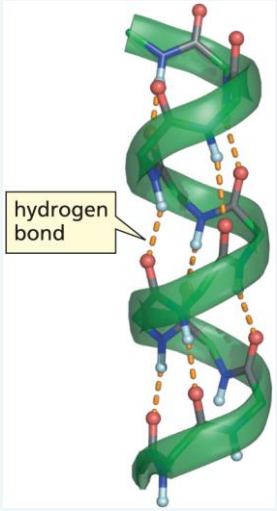
hydrogen bonds

Hydrogen bonds are stronger than other dipole–dipole interactions.

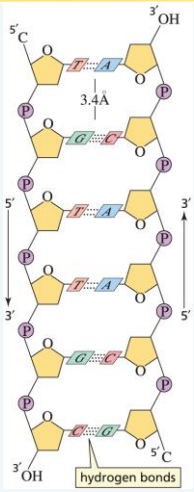
Hydrogen Bonds in Water



Hydrogen Bonds in Proteins

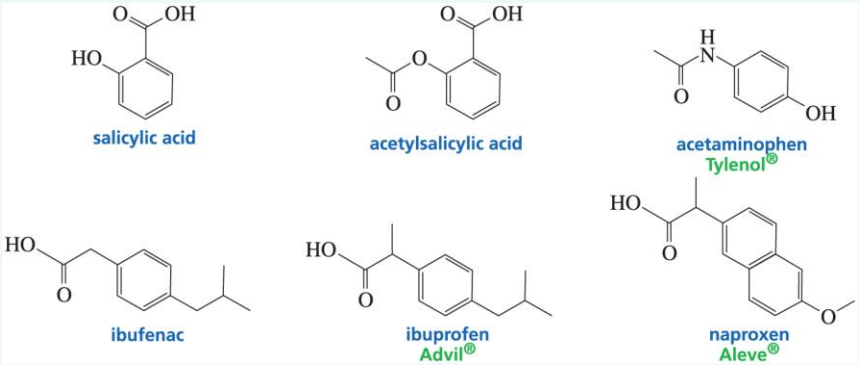


Hydrogen Bonds in DNA



Nitrogen bases: adenine (A), thymine (T), guanine (G) and cytosine (C)
All contain N-H bonds

Compounds with Similar Shapes and Properties often have Similar Physiological Activities



Drugs bind to their receptors by van der Waals interactions, dipole-dipole interactions, and hydrogen bonding.

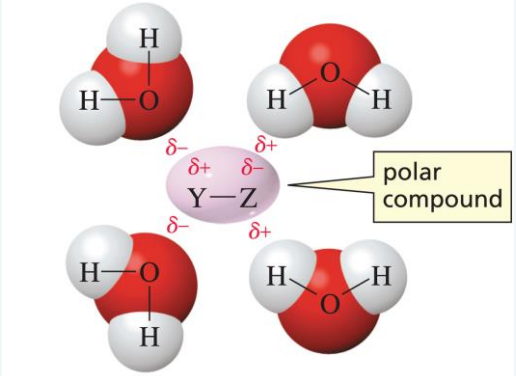
Solubility

like dissolves like

Polar compounds dissolve in polar solvents (H_2O).

Nonpolar compounds dissolve in nonpolar solvents (hexane).

Solvation



solvation of a polar compound by water

Solvation is the interaction between solute molecules and solvent molecules.

An Oxygen can Drag Three Carbons into Water

Table 3.5 Solubilities of Ethers in Water

2 Cs	CH_3OCH_3	soluble
3 Cs	$CH_3OCH_2CH_3$	soluble
4 Cs	$CH_3CH_2OCH_2CH_3$	slightly soluble (10 g/100 g H_2O)
5 Cs	$CH_3CH_2OCH_2CH_2CH_3$	minimally soluble (1.0 g/100 g H_2O)
6 Cs	$CH_3CH_2CH_2OCH_2CH_2CH_3$	insoluble (0.25 g/100 g H_2O)

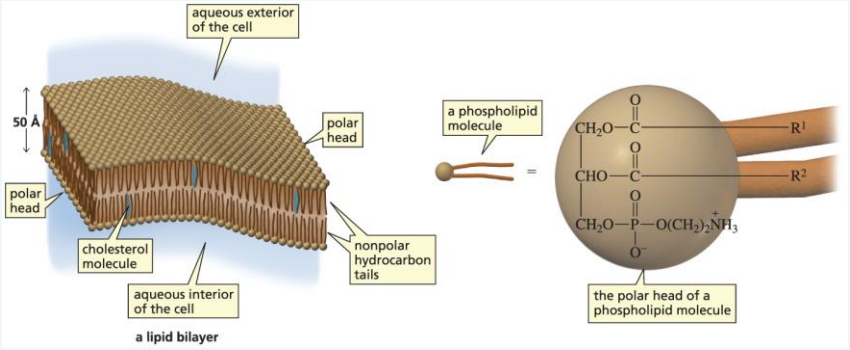
Solubilities of Alkyl Halides

Table 3.6 Solubilities of Alkyl Halides in Water

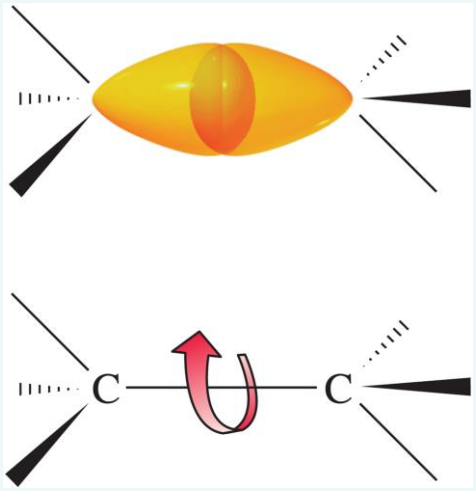
CH_3F	CH_3Cl	CH_3Br	CH_3I
very soluble	soluble	slightly soluble	slightly soluble
CH_3CH_2F	CH_3CH_2Cl	CH_3CH_2Br	CH_3CH_2I
soluble	slightly soluble	slightly soluble	slightly soluble
$CH_3CH_2CH_2F$	$CH_3CH_2CH_2Cl$	$CH_3CH_2CH_2Br$	$CH_3CH_2CH_2I$
slightly soluble	slightly soluble	slightly soluble	slightly soluble
$CH_3CH_2CH_2CH_2F$	$CH_3CH_2CH_2CH_2Cl$	$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2CH_2CH_2I$
insoluble	insoluble	insoluble	insoluble

Why?

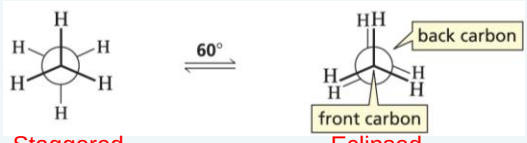
A Cell Membrane



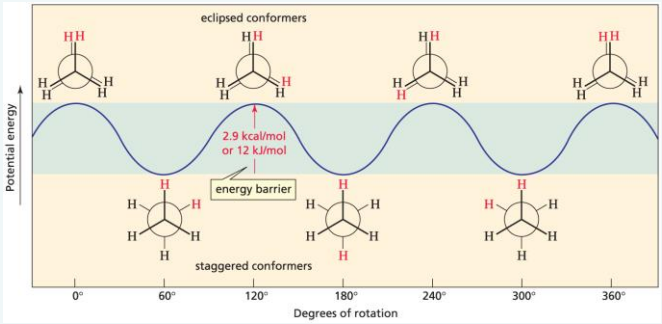
Structure of alkanes: Rotation Occurs About Single Bonds



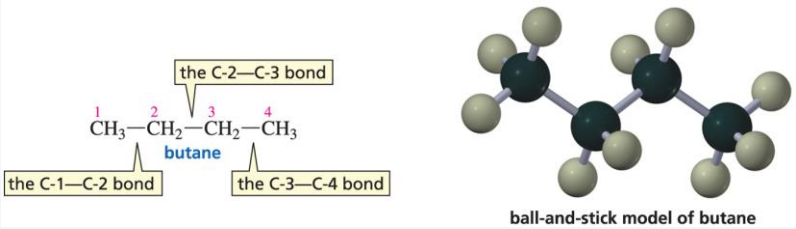
Staggered and Eclipsed Conformers of Ethane (Newman projection)



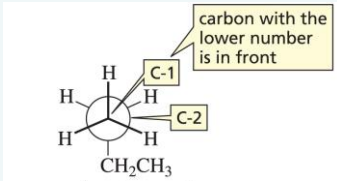
Staggered Eclipsed



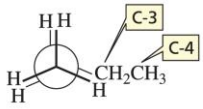
Rotation Can Occur About the Three Carbon—Carbon Bonds in Butane



ball-and-stick model of butane

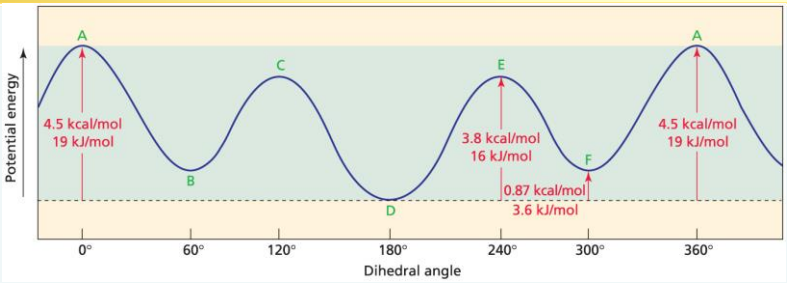


staggered conformer that results from rotation about the C-1—C-2 bond in butane

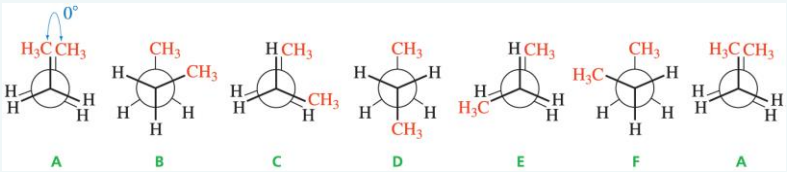


eclipsed conformer that results from rotation about the C-1—C-2 bond in butane

Rotation About C-2—C-3 in Butane

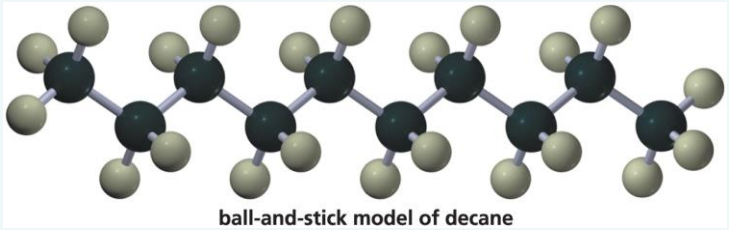


Steric strain is repulsion between the electron clouds of atoms or groups.



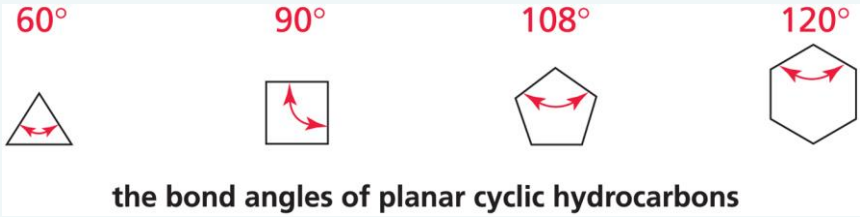
Gauche conformer | Anti conformer | Gauche conformer

Zigzag Arrangement



ball-and-stick model of decane

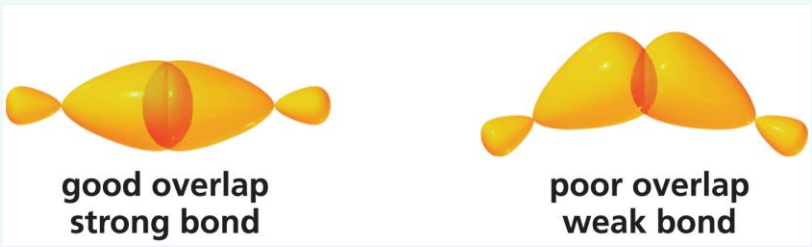
Bond Angles in Planar Cyclic Alkanes



the bond angles of planar cyclic hydrocarbons

The actual bond angle in cyclohexane is 111

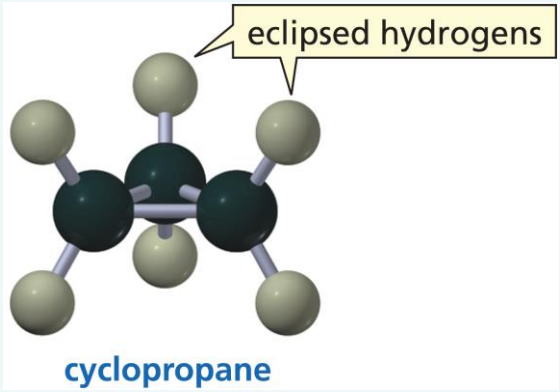
Angle Strain



tetrahedral bond angle = 109.5˚ bond angle < 109.5˚

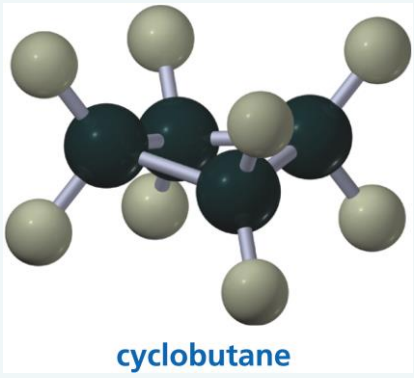
Angle strain results from poor orbital–orbital overlap because bonds have to deviate from the ideal (109.5˚) bond angle.

Cyclopropane



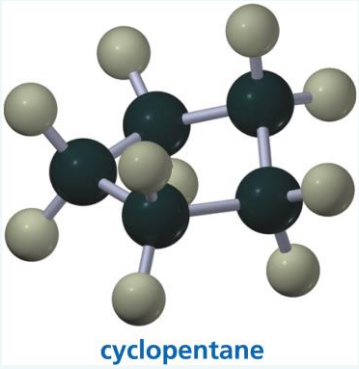
High angle strain and eclipsed hydrogens: unstable.

Cyclobutane



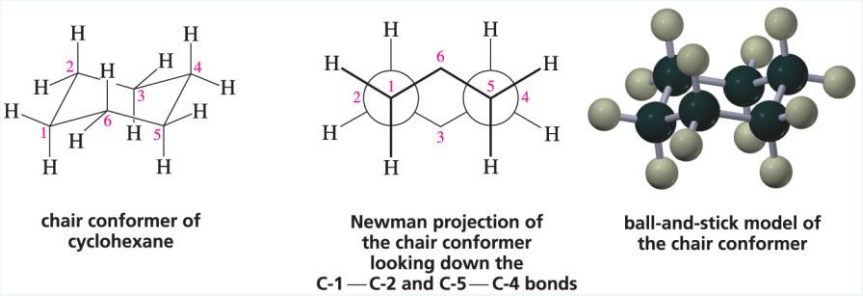
Molecules twist out of a planar arrangement to minimize angle strain and the number of eclipsed hydrogens.

Cyclopentane



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

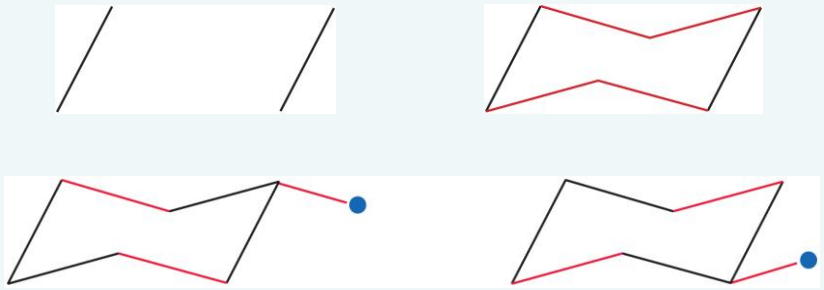
Chair Conformer of Cyclohexane



The chair conformer of cyclohexane is completely free of strain.

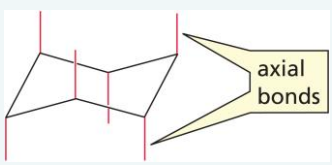
All bond angles are 111° and all adjacent bonds are staggered.

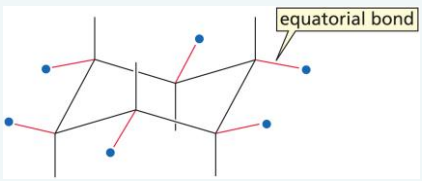
Drawing the Chair Conformer

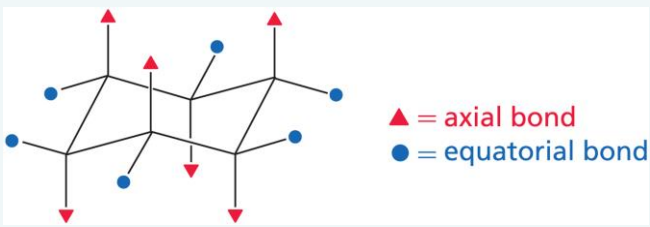


Notice that each equatorial bond is parallel to two ring bonds.

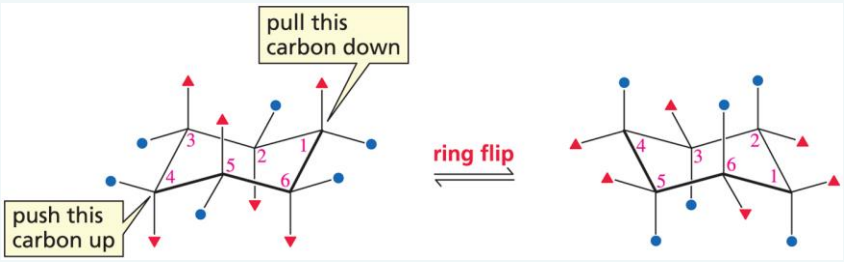
Axial and Equatorial Bonds





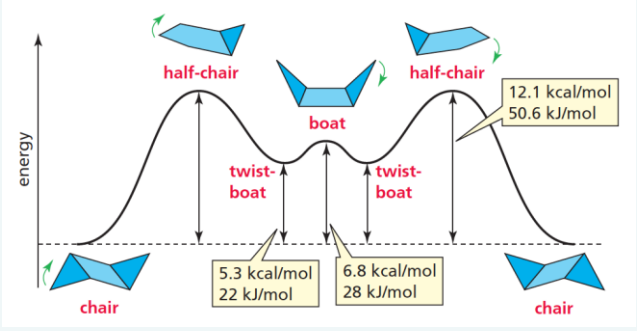


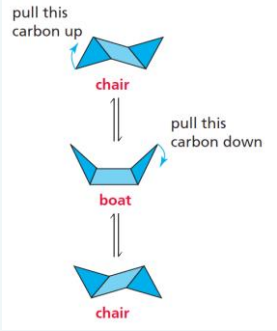
Ring Flip



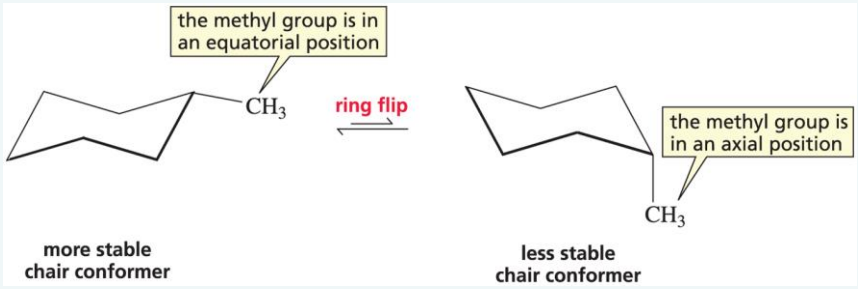
Cyclohexane interconverts between two stable chair conformers.

Conformers of Cyclohexane

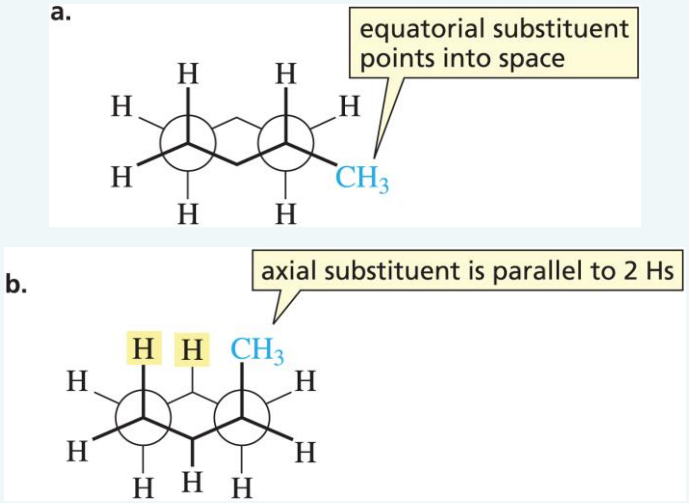




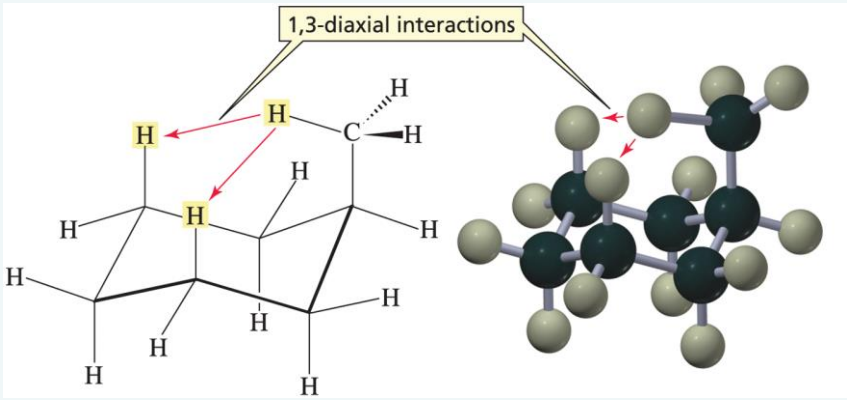
Conformers of Monosubstituted Cyclohexanes



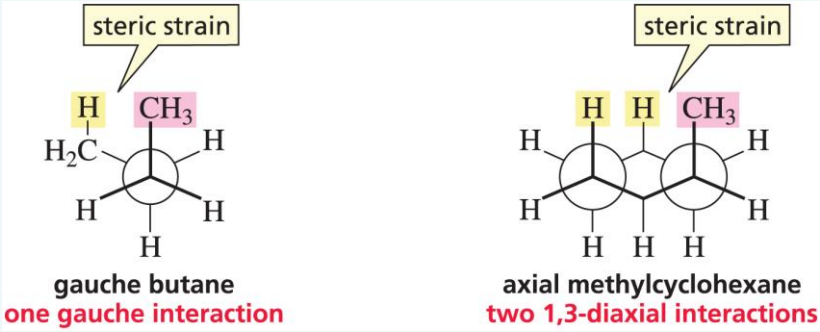
A Substituent is More Stable in an Equatorial Position



1,3-Diaxial Interactions



Comparing Gauche and 1,3-Diaxial Interactions



gauche butane
one gauche interaction

Gauche is 0.87 kcal/mole less sable than anti.

axial methylcyclohexane
two 1,3-diaxial interactions

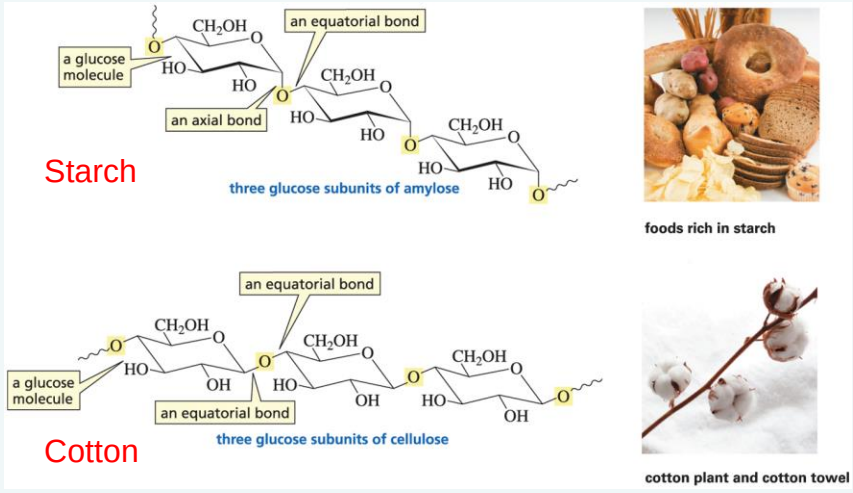
Axial is 1.74 (2 × 0.87) kcal/mol less sable than equatorial.

The larger the substituent, the more the equatorial-substituted conformer will be favored.

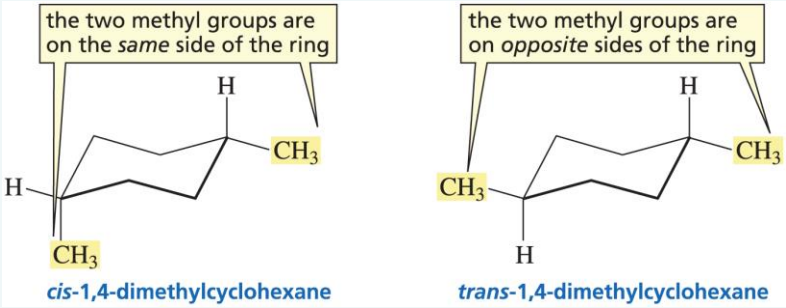
Table 3.7
Equilibrium Constants for Several Monosubstituted Cyclohexanes at 25 °C

Substituent	$K_{eq} = \frac{[\text{equatorial}]}{[\text{axial}]}$
H	1
CH_3	18
CH_3CH_2	21
$CH_3CH(CH_3)$	35
$CH_3C(CH_3)_2$	4800
CN	1.4
F	1.5
Cl	2.4
Br	2.2
I	2.2
HO	5.4

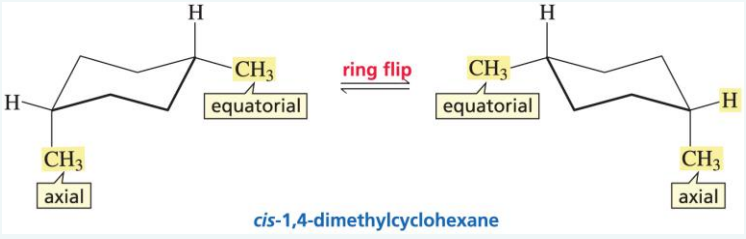
The Only Difference Between Starch and Cotton is an Equatorial Bond versus an Axial Bond

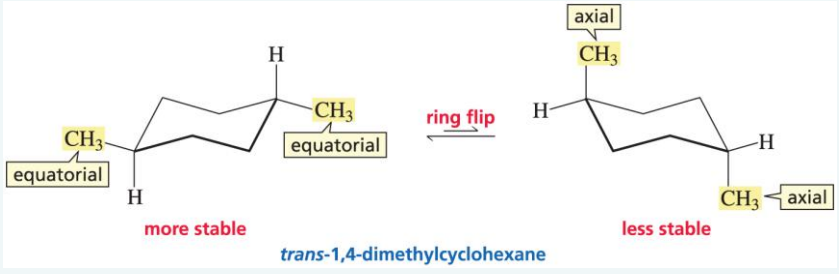


Cis and Trans Isomers of Cyclohexanes

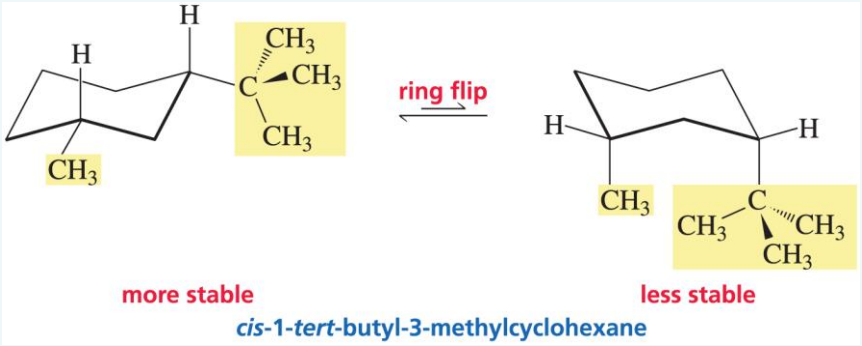


Each Isomer has Two Chair Conformers

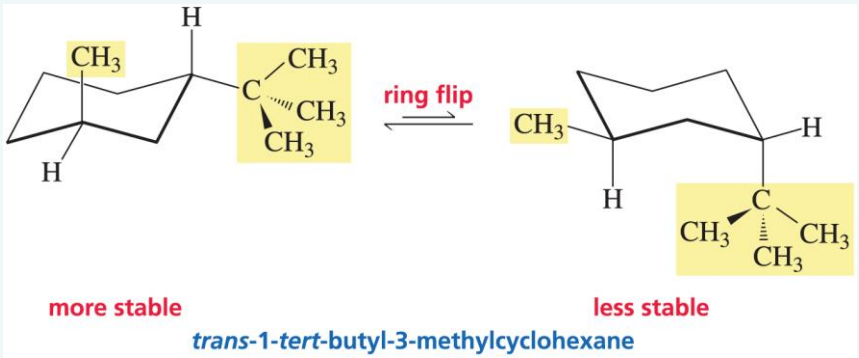




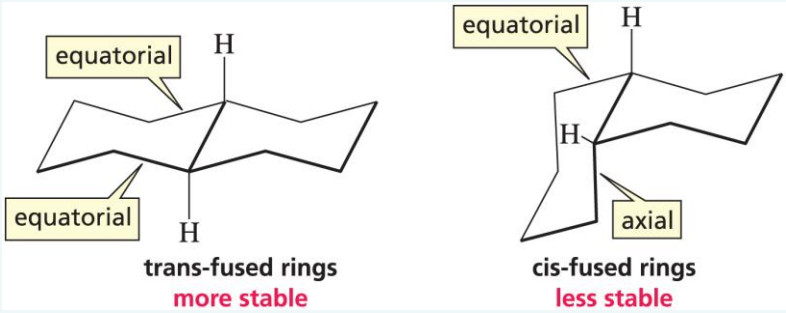
cis-1-*tert*-butyl-3-methylcyclohexane



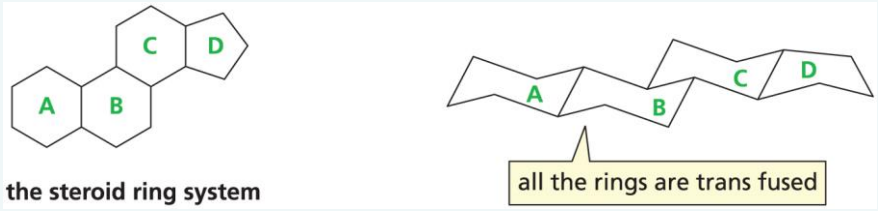
trans-1-*tert*-butyl-3-methylcyclohexane

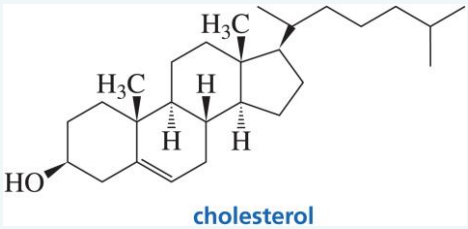


Rings can be Trans Fused or Cis Fused



The Steroid Ring System





Aspartame

Made of two amino acids:

phenylalanine (bitter)

aspartic acid (tasteless)