Chapter 2. The Nature of Organic Molecules

There are more than 27 million known organic molecules.

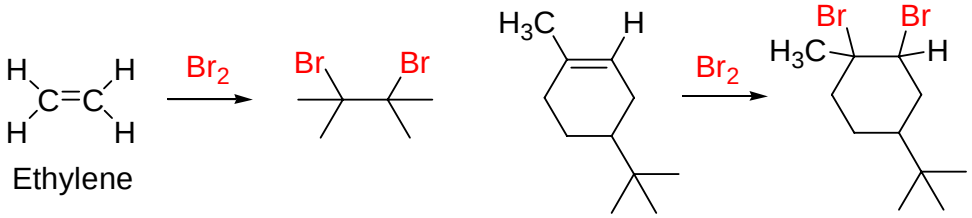
There are a few dozen families of compounds (functional groups) whose chemistry is reasonably predictable.

2.1 Functional Groups

The structural features that make it possible to classify compounds **by reactivity** are called **functional group**.

A functional group is a group of atoms within a larger molecule that has a characteristic chemical behavior.

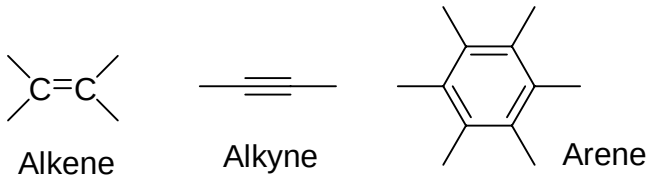
The chemistry of every organic molecule, regardless of size and complexity, is determined by the functional groups it contains.



Ethylene

Menthene

A. Functional Groups with Carbon-Carbon Multiple Bonds



Alkene

Alkyne

Arene

B. Functional Groups with Carbon Singly Bonded to an Electronegative Atom

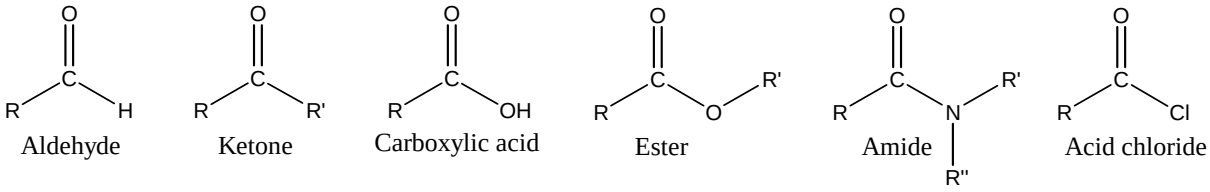
Alkyl halides **R-X**, alcohols **R-OH**, ethers **R-O-R'**, amines **R-NR$_2$**, thiols **R-SH**, and sulfides **R-S-R**

Electronegative atom: halogen (X), oxygen (O), nitrogen (N), or sulfur (S)

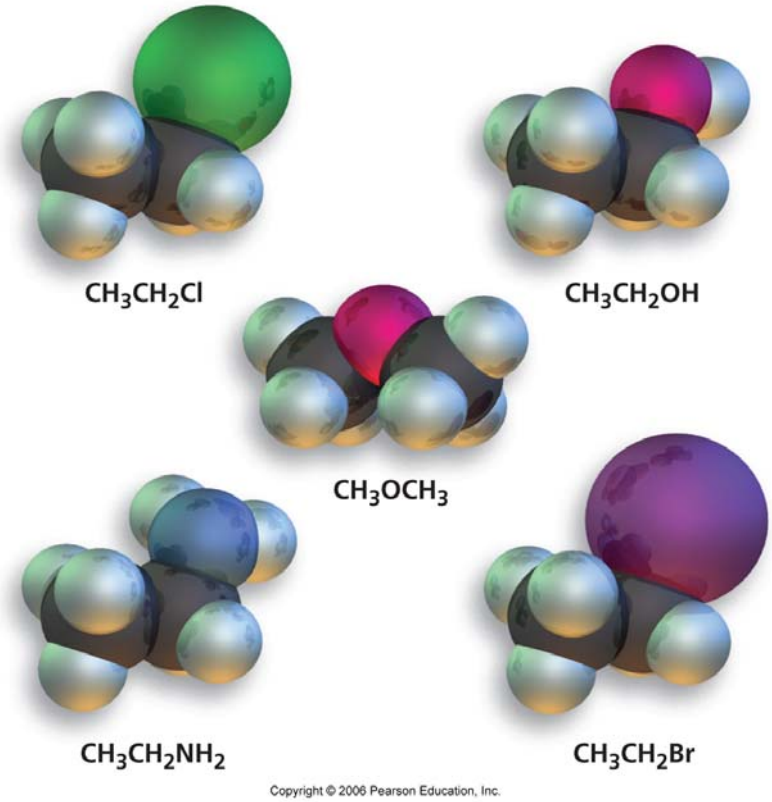
Bonds are polar, with the carbon atom bearing a partial positive charge (δ+) and the electronegative atom bearing a partial negative charge (δ-).

C. Functional Groups with a Carbon-Oxygen Double Bond (Carbonyl Groups) C=O

The chemistry of these compounds depends greatly on the identity of the atoms bonded to the carbonyl-group carbon



Aldehyde Ketone Carboxylic acid Ester Amide Acid chloride



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2.2 Alkanes and Alkyl Groups: Isomers

Alkanes: Saturated hydrocarbons

***Saturated*:** they have only C-C and C-H single bonds and thus contain maximum possible number of hydrogens per carbon.

***Hydrocarbons*:** they contain only carbon and hydrogen atoms

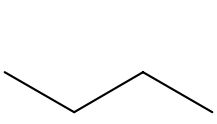
General formula: C_nH_{2n+2}

Isomers: Compounds which have the same formula but different structures

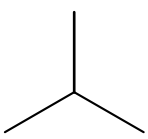
Isomers have the same numbers and kinds of atoms but differ in the way the atoms are arranged.

Constitutional isomers: Compounds whose atoms are connected differently

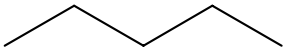
Straight-chain alkanes branched-chain alkanes



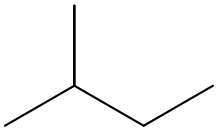
Butane
(normal butane)



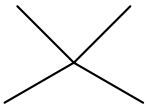
Isobutane
(2-methylpropane)



Pentane



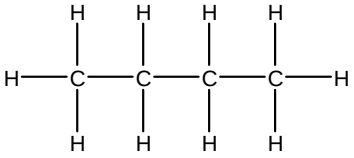
Isopentane
(2-methylbutane)

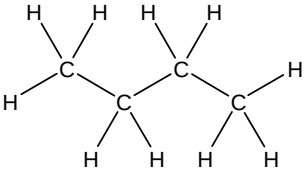


Neopentane
(2,2-dimethylpropane)

Representation of alkanes:

e.g. Butane





$CH_3CH_2CH_2CH_3$ n-C_4H_{10}

$CH_3(CH_2)_2CH_3$

Naming the straight-chain alkanes:

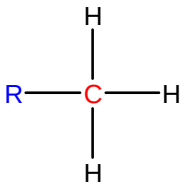
Name according to the number of carbon atoms they contain based on Greek number with the exception of the first four compounds (metha-, etha-, propa-, buta-).

Add –**ane** to the end of each name.

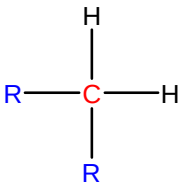
Alkyl group (R): The functional group in which a hydrogen atom is removed from an alkane.

Naming: replace the –**ane** ending with –**yl** ending.

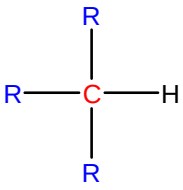
The prefixes – **primary (1°), sec (secondary, 2°), tert (tertiary, 3°), and quat (quaternary, 4°)** – refer to the number of other carbon atoms attached to the branched carbon atom.



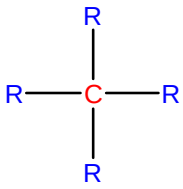
primary



secondary



tertiary



quaternary

2.3 Naming Branched-Chain Alkanes

IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature

Prefix——**Parent**——**Suffix**

Where are the substituents?
(location of substituents)

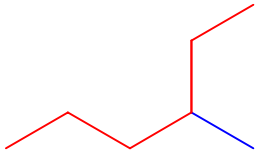
How many carbons?

What family? (functional group)

Four steps in naming branched-chain alkanes

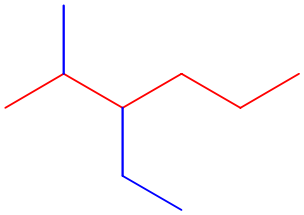
Step 1. Find the parent hydrocarbon.

(a) Find **the longest continuous carbon chain** in the molecule and use the name of that chain as the parent name.

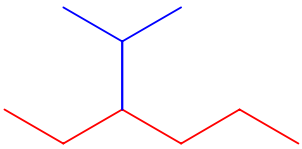


3-Methylhexane

(b) If two chains of equal length are present, choose the one with the larger number of branch points as the parent.



3-Ethyl-2-methylhexane



3-Isopropylhexane

Step 2. Number the atoms in the main chain.

Beginning at the end nearer the **first branch point**, number each carbon atom in the parent chain

Step 3. Identify and number the substituents.

Assign a number to each substituent according to its point of attachment on the parent chain.

Step 4. Write the name as a single word.

Use hyphens to separate the various prefixes and **commas** to separate numbers.

If two or more different side chains are present, cite them **in alphabetical order**.

If two or more identical side chains are present, use one of the prefixes di-, tri-, tetra-, and so on (don't use these prefixes for alphabetizing).

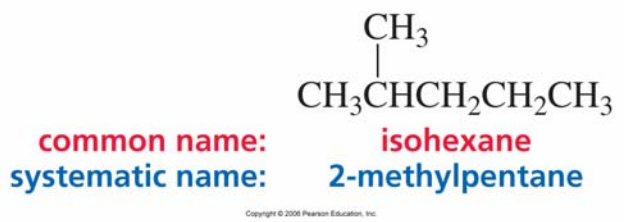


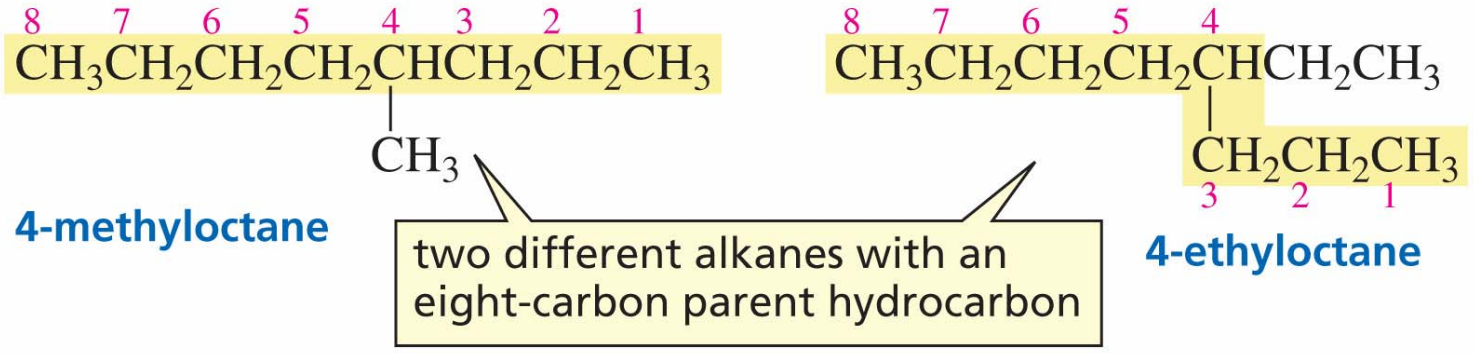
Table 3.1 Nomenclature and Physical Properties of Some Straight-Chain Alkanes

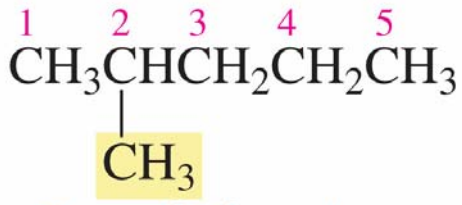
Number of carbons	Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Density[a] (g/mL)
1	CH_4	methane	CH_4	−167.7	−182.5	
2	C_2H_6	ethane	CH_3CH_3	−88.6	−183.3	
3	C_3H_8	propane	$CH_3CH_2CH_3$	−42.1	−187.7	0.5005
4	C_4H_{10}	butane	$CH_3CH_2CH_2H_3$	−0.5	−138.3	0.5787
5	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.

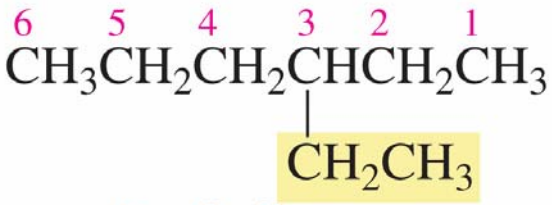
Table 3.2 Names of Some Alkyl Groups

methyl	CH_3-	*sec*-butyl	$CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$	hexyl	$CH_3CH_2CH_2CH_2CH_2CH_2-$
ethyl	CH_3CH_2-			isohexyl	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{CH}}CH_2CH_2CH_2-$
propyl	$CH_3CH_2CH_2-$		$\begin{matrix}CH_3\\ \vert\\ CH_3C-\\ \vert\\ CH_3\end{matrix}$		
isopropyl	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$	*tert*-butyl			
butyl	$CH_3CH_2CH_2CH_2-$	pentyl	$CH_3CH_2CH_2CH_2CH_2-$		
isobutyl	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{CH}}CH_2-$	isopentyl	$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{CH}}CH_2CH_2-$		

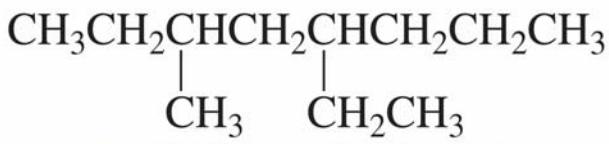




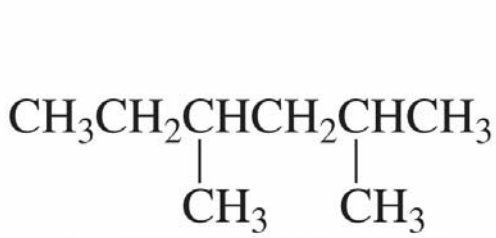
2-methylpentane



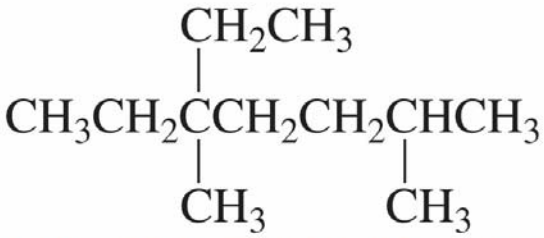
3-ethylhexane



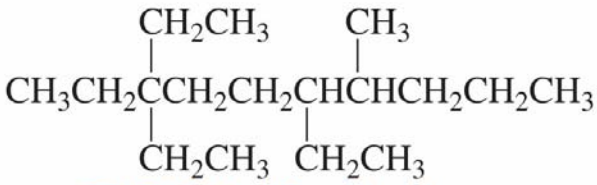
5-ethyl-3-methyloctane
not
4-ethyl-6-methyloctane
because 3 < 4



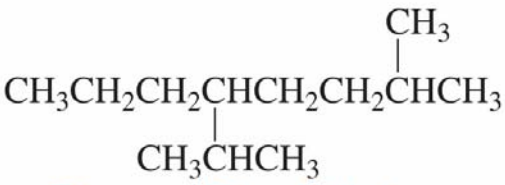
2,4-dimethylhexane



5-ethyl-2,5-dimethylheptane



3,3,6-triethyl-7-methyldecane



5-isopropyl-2-methyloctane

2.4 Properties of Alkanes

Regardless of the molecule, the average **C-C bond parameters** are nearly the same in all alkanes, with bond lengths of 154±1 pm and bond strengths of 355±20 kJ/mol (85±5 kcal/mol).

C-H bond parameters are also nearly constant at 109±1 pm and 400±20 kJ/mol (95±5 kcal/mol).

Alkanes show regular increases in both boiling point and melting point as molecular weight increases. They can be separated by fractional distillation.

Combustion

The reaction of an alkane with O_2 to produce CO_2, H_2O, and a large amount of heat.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 890\ \text{kJ/mol (213 kcal/mol)}$$

Halogenation

The reaction of an alkane with Cl_2 occurs when a mixture of the two is irradiated with ultraviolet light

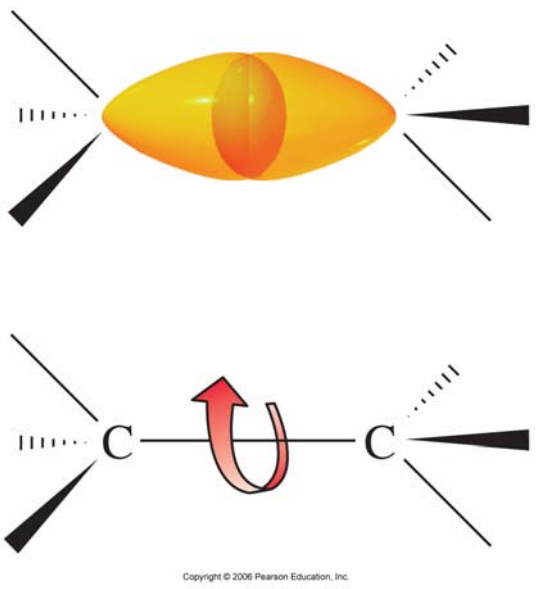
$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$CH_3Cl \xrightarrow{h\nu} CH_2Cl_2 + HCl \quad \text{etc.}$$

2.5 Conformations of Ethanes

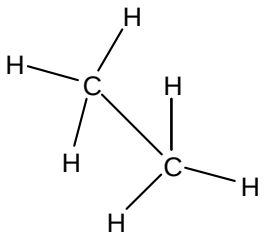
C-C bonds in alkanes result from σ overlap of two tetrahedrally oriented sp^3 orbitals.

The different arrangements of atoms that result from rotation around a single bond are called **conformations** - the spatial relationship between the hydrogens on one carbon and the hydrogens on the other.

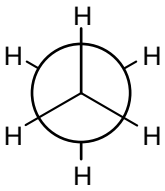


Representation of different conformations

1. **Sawhorse** representations



2. **Newman** projection



C-C bond rotation in ethane

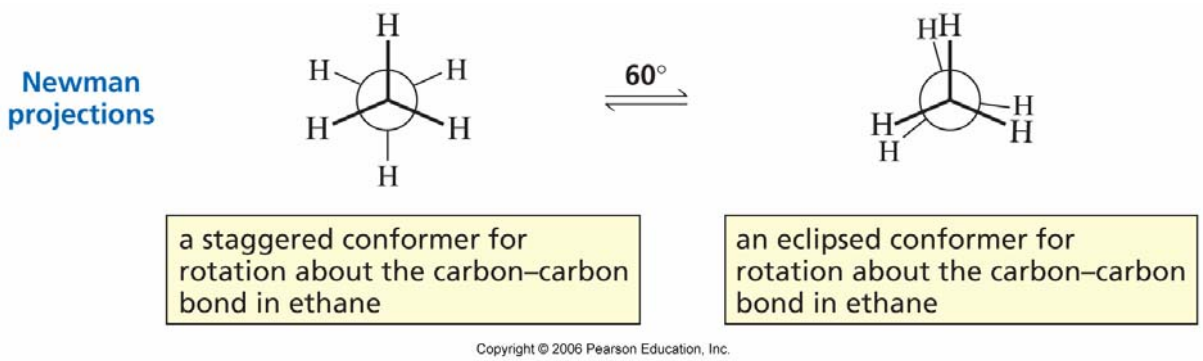
There is a slight (12 kJ/mol; 2.9 kcal/mol) energy barrier to rotation and some conformations are more stable than others

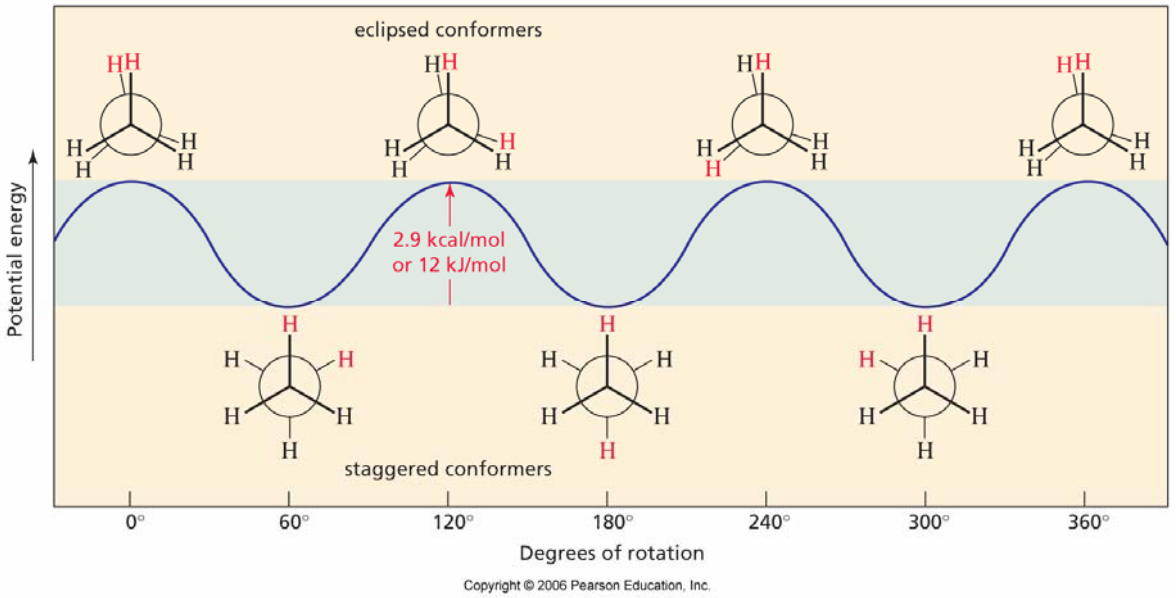
The lowest-energy, most stable conformation is the one in which all six C-H bonds are as far away from one another as possible – **Staggered conformation.**

The highest-energy, least stable conformation is the one in which the six C-H bonds are as close as possible – **Eclipsed conformation.**

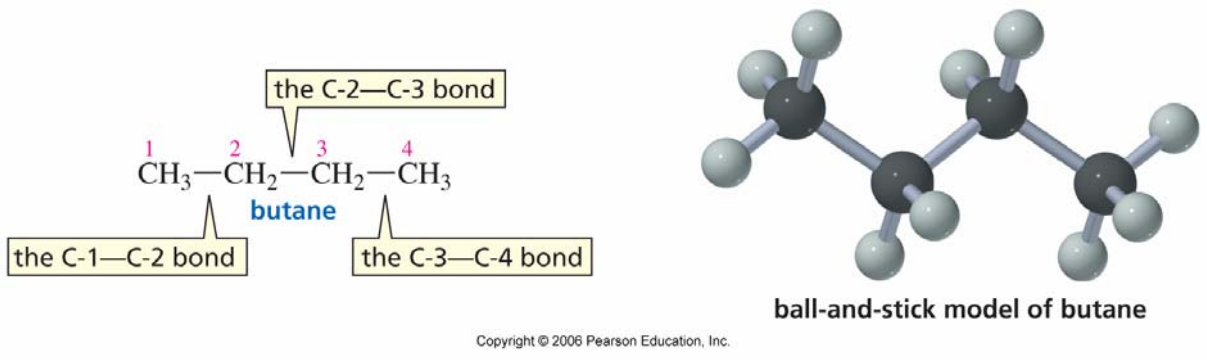
99% of ethane molecules have staggered conformation, and 1% eclipsed conformation.

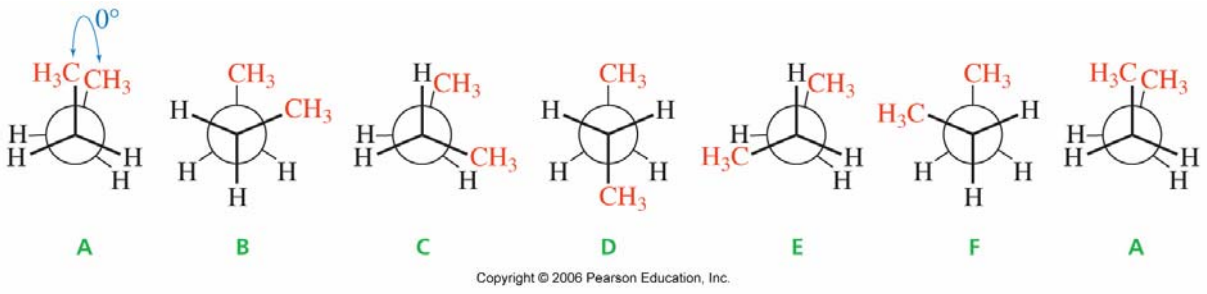
Staggered Conformation **Eclipsed Conformation**



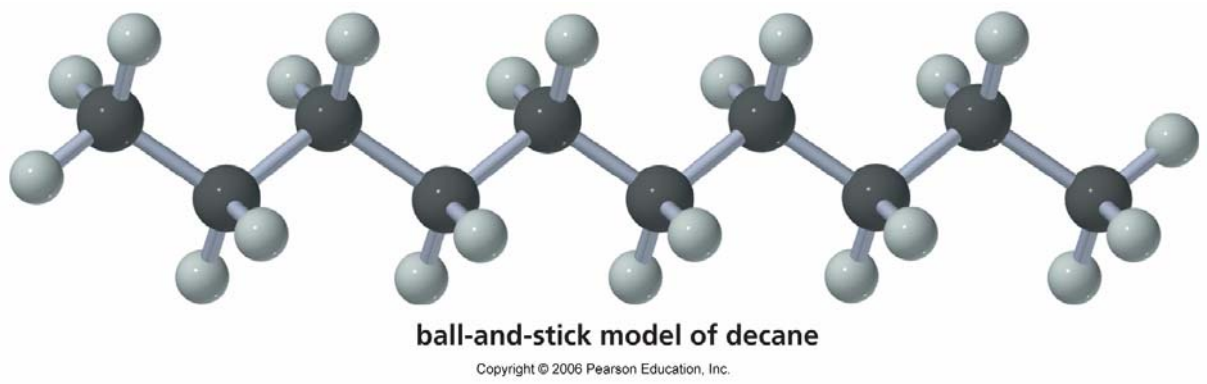


Butane





Decane



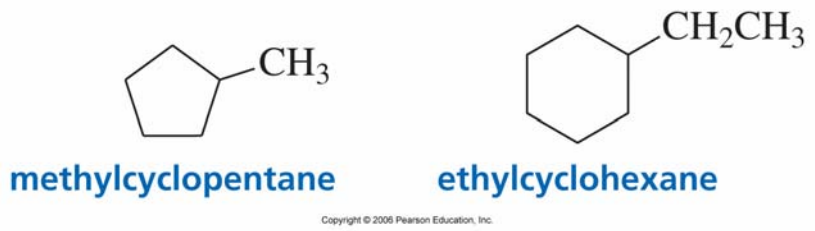
2.6 Cycloalkanes

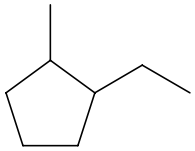
General Formula: $(CH_2)_n$ or C_nH_{2n}

Naming cycloalkanes

Step 1: Count the number of carbon atoms in the ring, and add the prefix **cyclo** to the name of the corresponding alkane

Step 2: For substituted cycloalkanes, start at a point of attachment and number around the ring following the alphabetical priority rule.

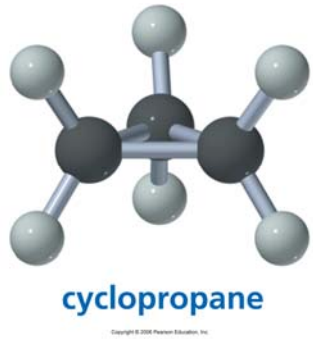




1-Ethyl-2-methylcyclopentane

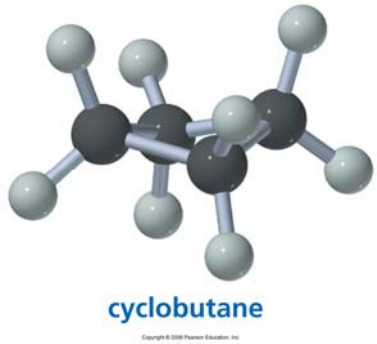
2.7 Conformations of Some Cycloalkanes

Cyclopropane

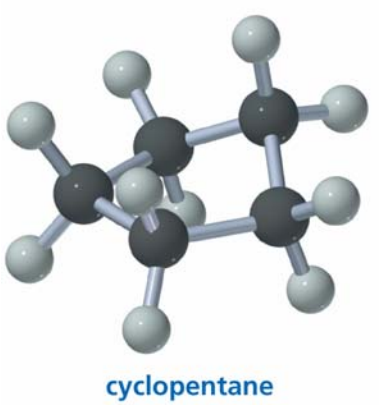


Cyclopropane is geometrically constrained to be rigid, planar, and Symmetrical molecule with C-C-C bond angles of 60^{o}. The deviation from the normal 109.5^{o} tetrahedral angle causes an **angle strain** in the molecule that raises its energy and makes it more reactive than unstrained alkanes.

Cyclobutane

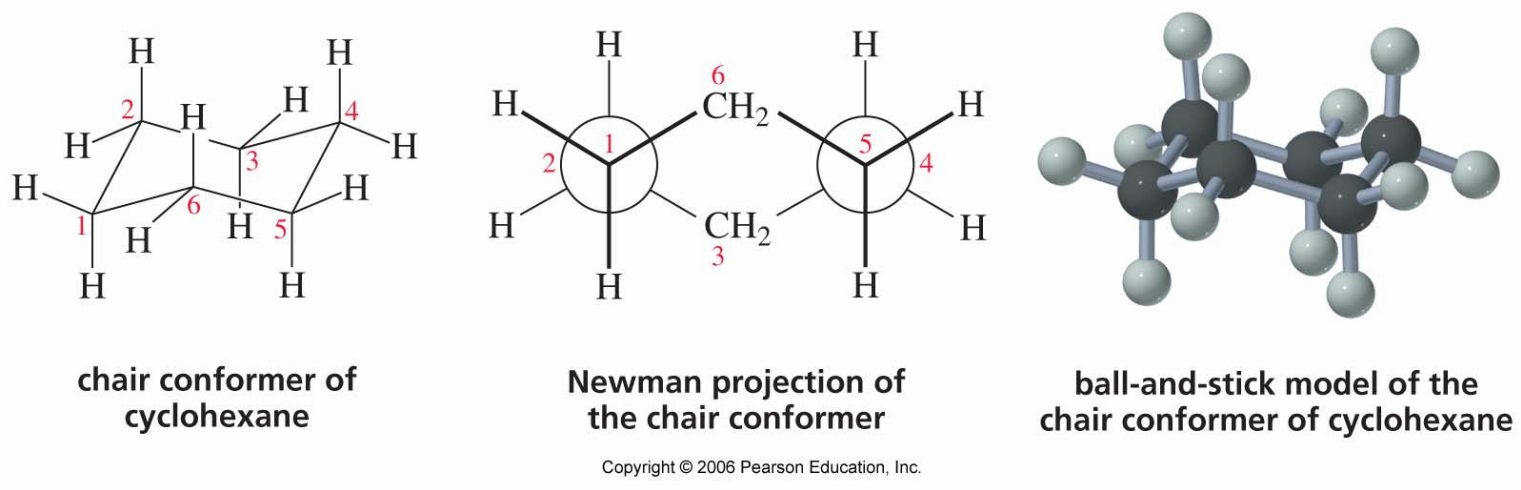


Cyclopentane

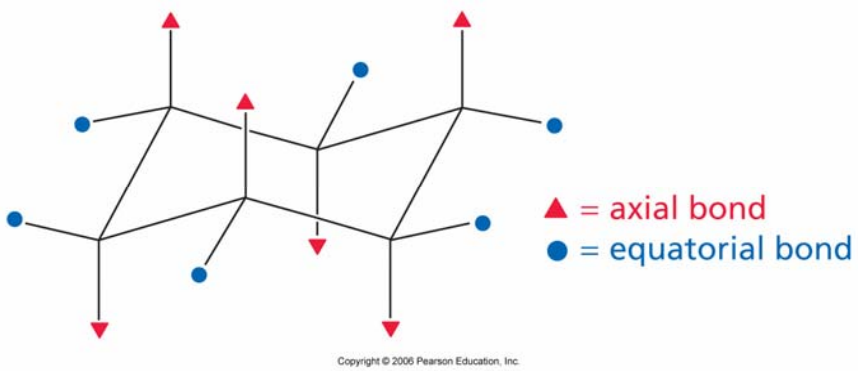


Cyclobutane and cyclopentane are slightly **puckered** rather than flat, which makes the C-C-C bond angles a bit smaller than they would otherwise be and **increases the angle strain**. The puckering relieves the eclipsing interactions of adjacent C-H bonds that would occur if the rings were flat.

2.8 Cyclohexane

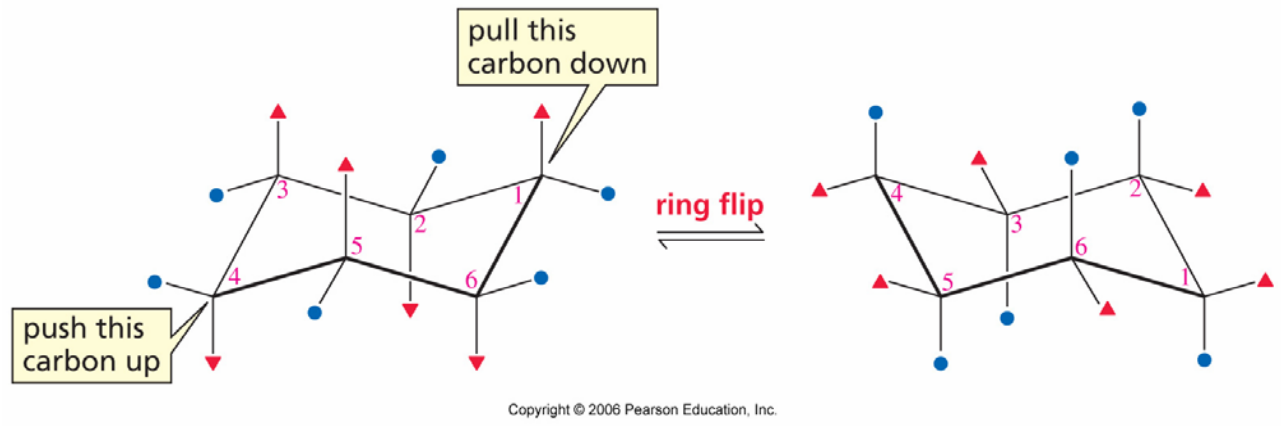


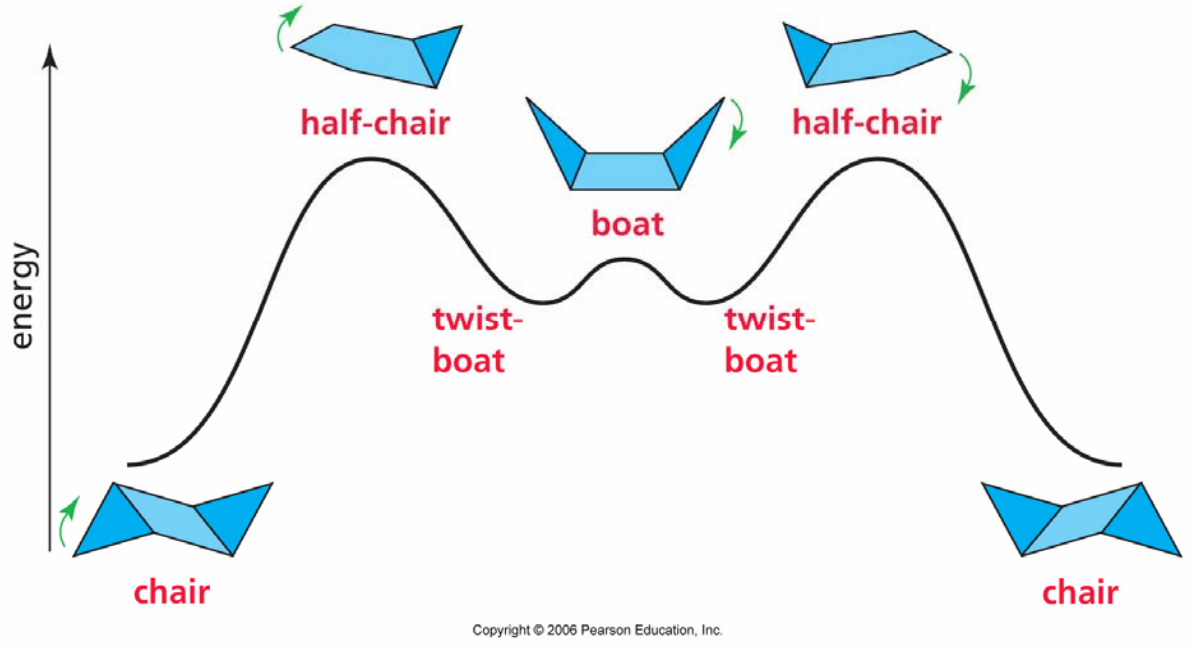
Cyclohexane is not flat. It is **puckered** into **a strain-free**, three-dimensional shape called a **chair conformation**, in which the C-C-C bond angles are close to the ideal 109.5^{o} tetrahedral value. In addition to being free of angle strain, chair cyclohexane is also **free of all C-H eclipsing interactions**.



The six **axial** C-H bonds are parallel to the ring axis, and the six **equatorial** C-H bonds are in a band around the ring equator.

Conformational Mobility of Cyclohexene





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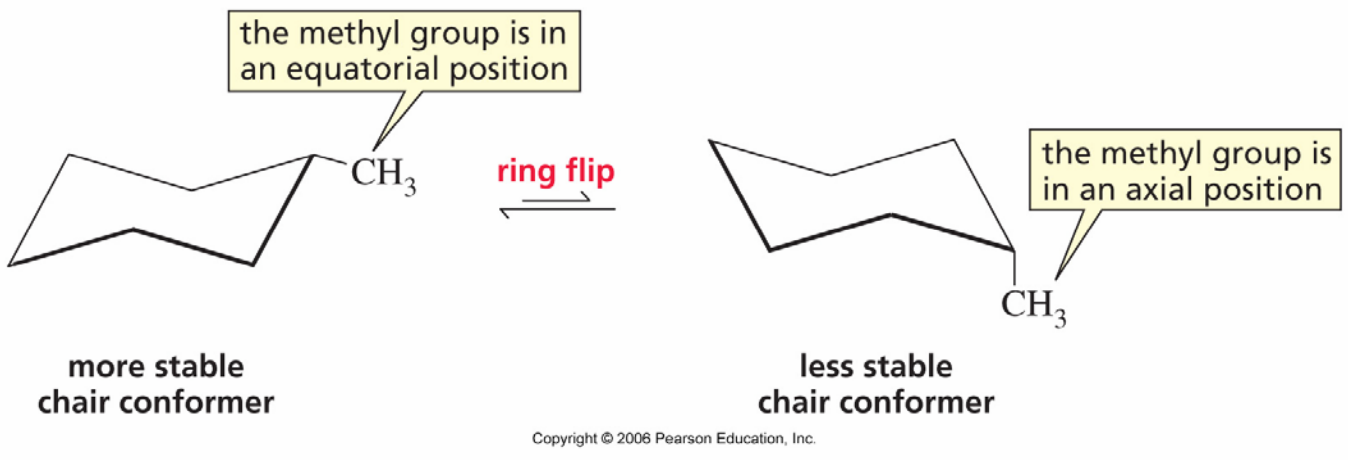
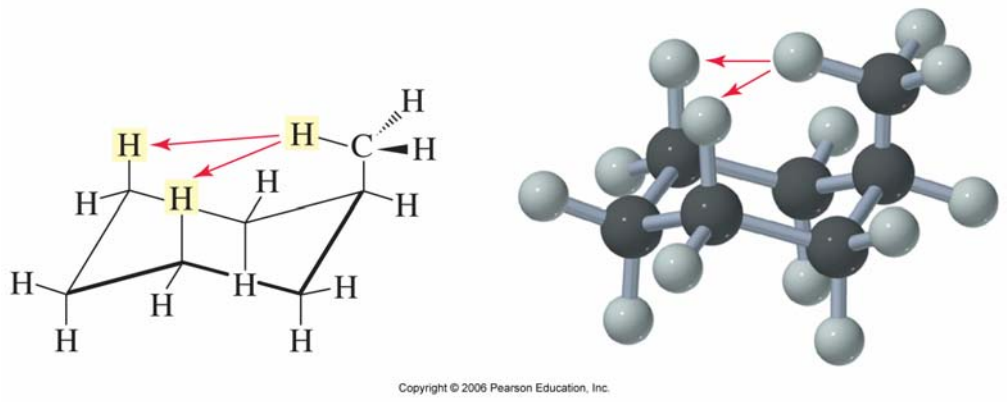
Ring-flip: Interconversion of chair conformations

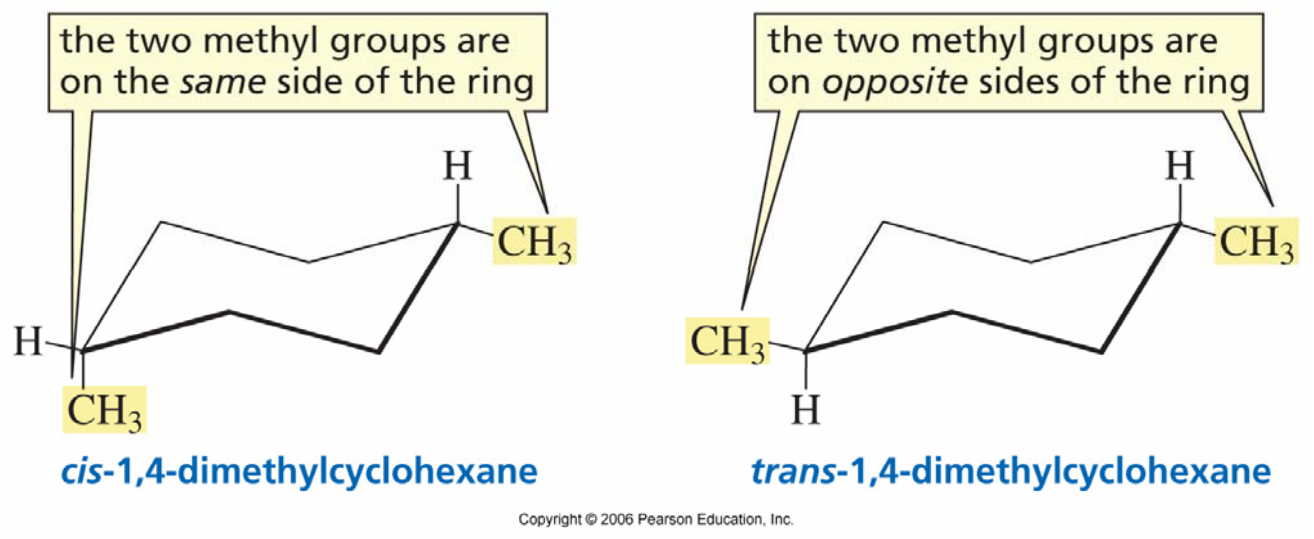


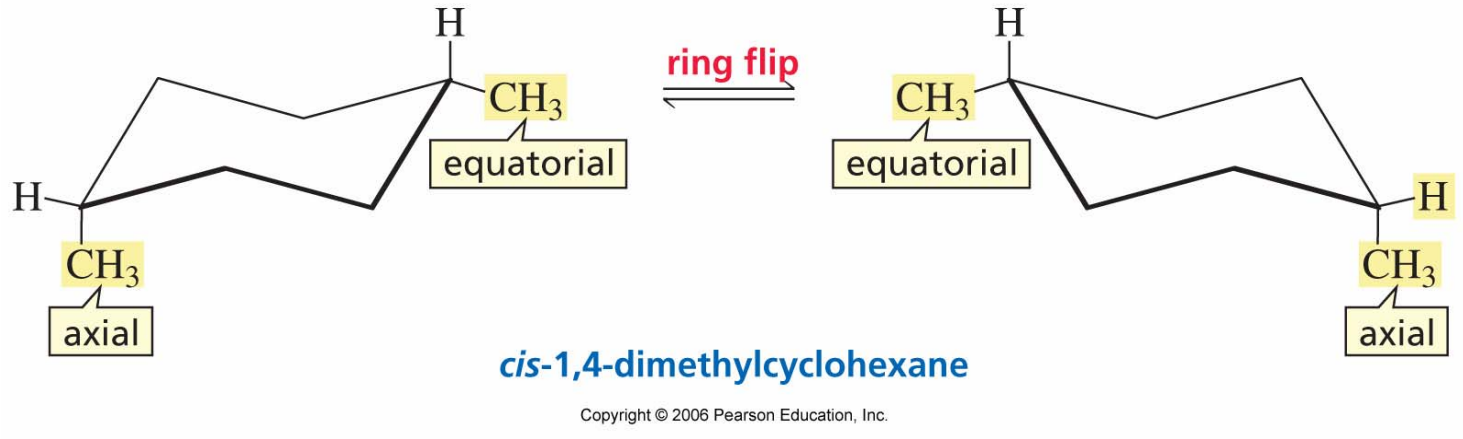
The conformation of the equatorial methyl is more stable than that of the axial methyl by **7.6 kJ/mol (1.8 kcal/mol)**, meaning that about 95% of methylcyclohexane molecules have their methyl group equatorial at any given instant. This is because of the unfavorable **steric interaction** that occurs in the axial conformation between the methyl group and the two axial hydrogen atoms (**1,3-diaxial interaction**).

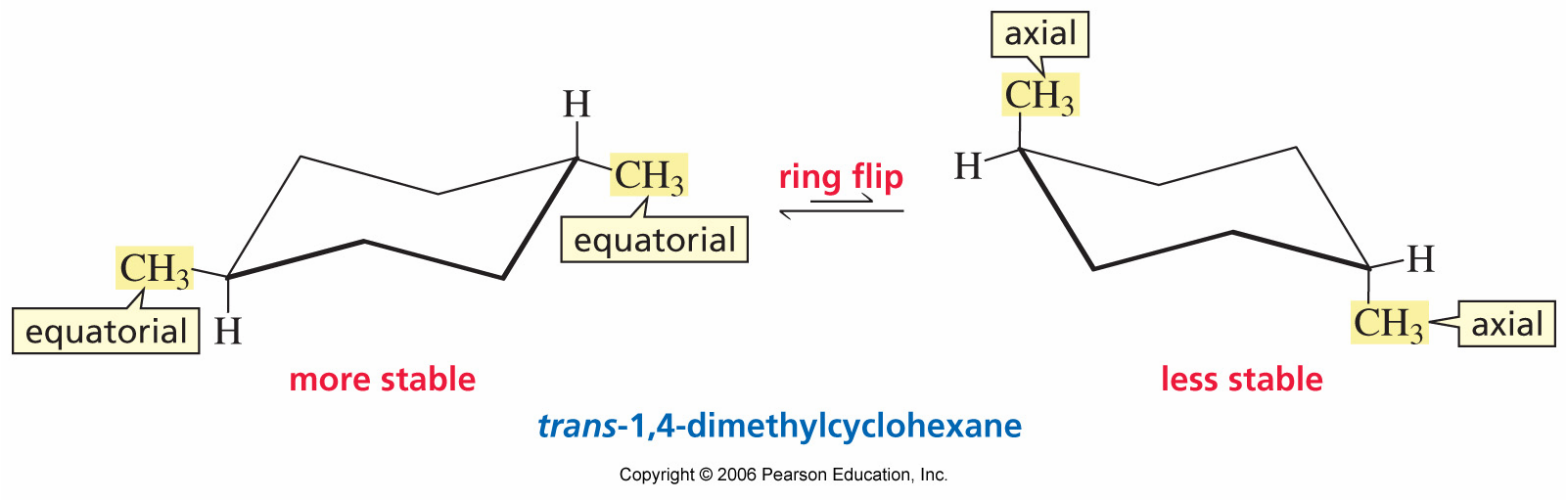


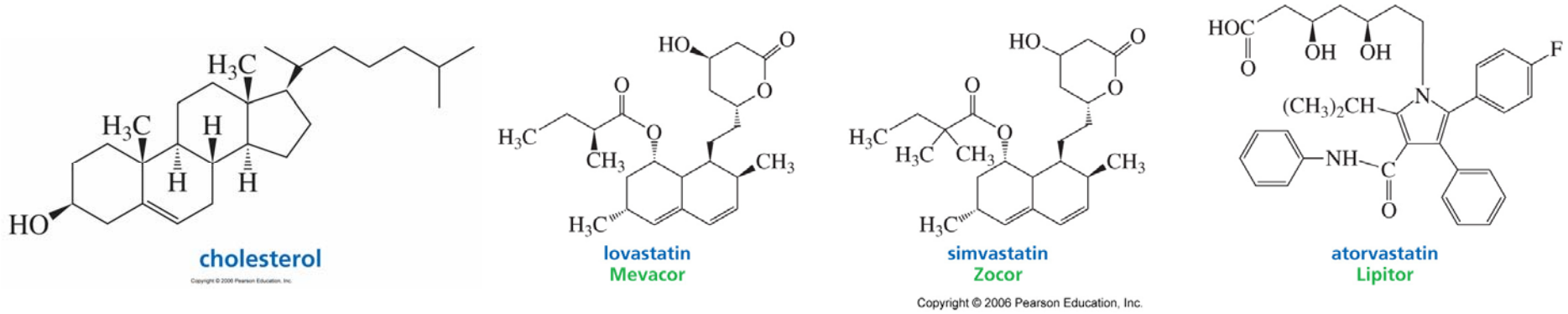
A substituent is always more stable in an equatorial position than in an axial position. Chapter_02_03.ppt

“Cis” and “Trans” Nomenclature in Cycloalkanes









Title: Structures of Cholesterol Reducing Drugs

Caption: Structures of lovastatin, simvastatin, atorvastatin.

Notes: These drugs are used to lower the amount of cholesterol in the body.