Chapter 4 Alkanes

I. Alkanes – An Introduction

Alkanes are aliphatic hydrocarbons having only C–H and C–C σ-bonds. They can be cyclic or acyclic.

- Acyclic alkanes have the molecular formula C_nH_{2n+2} (where n = an integer.) They are also called saturated hydrocarbons because they have the maximum number of hydrogen atoms per carbon.
- Cyclic alkanes contain carbon atoms joined into a ring. They have molecular formula C_nH_{2n}. (Notice: 2 less hydrogens than saturated alkanes – Why?

A. Unbranched Alkanes

Alkanes with unbranched carbon chains are also known as normal alkanes or *n*-alkanes.

The first four *n*-alkanes:
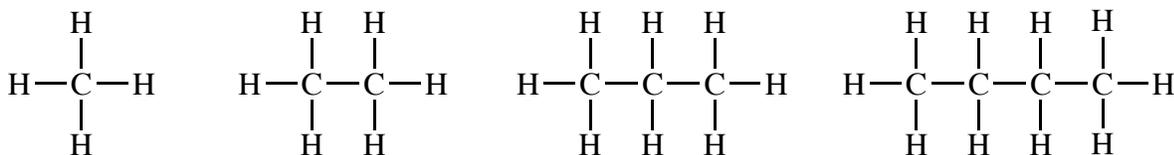
- This is an example of a family of compounds known as **homologous series** (each member differs from the next by the addition of one **methylene group** (CH_2).

The first 12 *n*-alkanes are listed in the handout Essential Nomenclature.

Look at the various representations of propane:
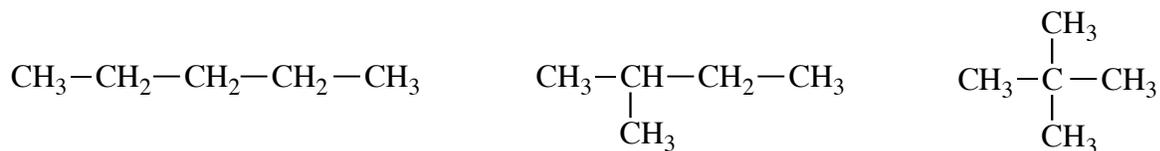
C_3H_8 $CH_3CH_2CH_3$
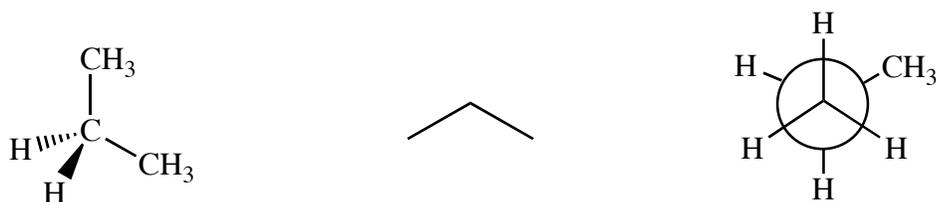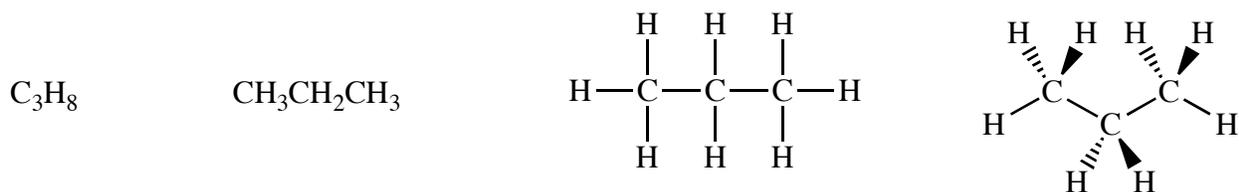
B. Branched Alkanes

As the number of carbons of an alkane increase beyond three, the number of possible structures increases. An alkane with molecular formula C_4H_{10}, for example has two different ways to connect atoms together:

$CH_3-CH_2-CH_2-CH_3$

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$
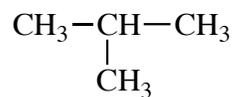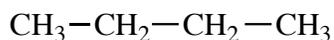
These are examples of ***constitutional isomers***: Compounds that have the same molecular formula but different connectivity.

There are *three* constitutional isomers with molecular formula C_5H_{12}:

$CH_3-CH_2-CH_2-CH_2-CH_3$ $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$ $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

- The # constitutional isomers increases dramatically as the number of carbons increases!

C_6H_{14}: $C_{10}H_{22}$: $C_{15}H_{32}$:

Carbons in alkanes or other organic compounds can be classified as primary (1°), secondary (2°), tertiary (3°), and quaternary:

- a primary carbon is bound to one other carbon
- a secondary carbon is bound to two other carbons
- a tertiary carbon is bound to three other carbons
- a quaternary carbon is bound to four other carbons

Hydrogens can also be classified as 1°, 2°, 3°:

- primary H's are attached to primary carbons
- secondary H's are attached to secondary carbons
- tertiary H's are attached to tertiary carbons

Example:

$$
\begin{array}{ccccc}
 & & CH_3 & CH_3 & \\
 & & | & | & \\
CH_3CH_2 & - & C & - C & - CH_3 \\
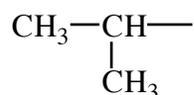 & & | & | & \\
 & & H & CH_3 &
\end{array}
$$
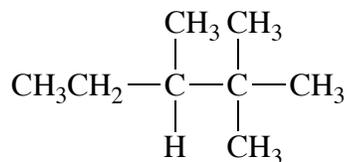
C. Alkyl Groups

Removing a H from an alkane gives an alkyl group or alkyl substituent. Alkyl groups are named by changing the *–ane* ending of an alkane with *–yl*.

CH_3- CH_3CH_2-
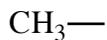
There are two possible alkyl groups that can be made from 3 C's:

$CH_3CH_2CH_2-$

$$
\begin{array}{c}
CH_3-CH- \\
| \\
CH_3
\end{array}
$$

There are four possible alkyl groups that can be made from 4 C's (see *Essential Nomenclature* handout.

II. Systematic (IUPAC) Nomenclature of Alkanes

The systematic name of an alkane is obtained using the following rules:

1. The unbranched alkanes are named according to the # carbon atoms as shown in the *Essential Nomenclature* handout. (know 1-10).

2. For alkanes containing branched carbon chains, find the longest continuous chain (if two or more chains within a structure have the same length, choose the one with the greatest # branches). This is your ***parent chain.***

$$CH_3-CH-CH-CH-CH_2$$

with substituents CH_2CH_3 and CH_3 above, and CH_3 and CH_3 below.
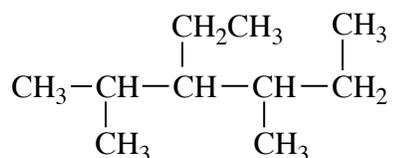
3. Number the carbons of the parent chain from one end to the other in the direction that gives the *first branch the lower #*.

$$CH_3-CH-CH-CH-CH_2$$

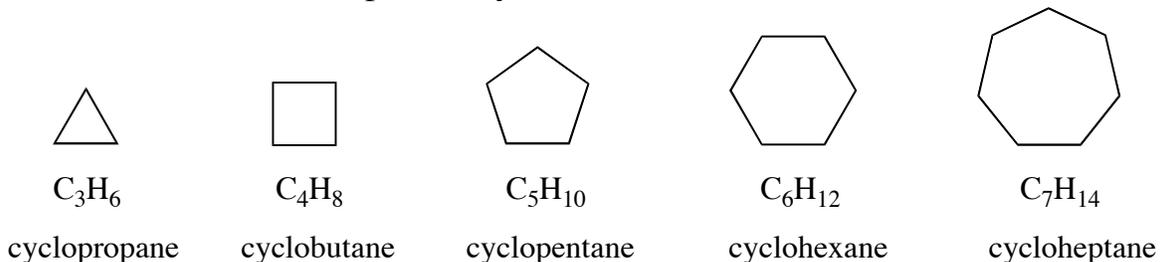with substituents CH_2CH_3 and CH_3 above, and CH_3 and CH_3 below.
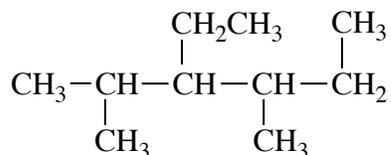
4. Name each branch (***substituent***) and identify the carbon # of the parent chain at which it occurs. If two substituents are on the same carbon atom, use that number twice. When two or more substituents are identical, use a prefix di-, tri-, tetra, etc. to indicate how many. Alkyl substituents are named by changing the *ane* ending to *yl*.

5. Construct the name by writing substituents first, followed by the name of the alkane corresponding to the parent chain. The substituent groups are listed in alphabetical order (the numerical prefixes di-, tri-, etc. as well as the prefixes tert- and sec- are *ignored* in alphabetizing, but the prefixes iso, neo, and cyclo *are considered* in alphabetizing substituent groups).

III. Nomenclature of Cycloalkanes:

General formula: C_nH_{2n}
Nomenclature: Add prefix "**cyclo**" to alkane name

|				
C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_7H_{14}
cyclopropane	cyclobutane	cyclopentane	cyclohexane	cycloheptane

- Substituents are named similar to the way they are in straight-chain alkanes.
- If the ring has two different substituents, they are cited in alphabetical order, and the number one position is given to the substituent cited first.
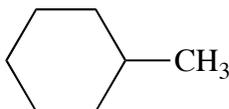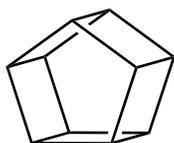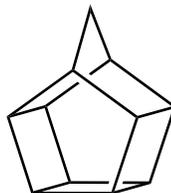
IV. Common Names

Some organic compounds are identified using common names that do not follow the IUPAC system of nomenclature. Acetic acid and ethyl alcohol are common names, as are the names for many biological compounds like estrogen and testosterone. The following alkanes are named for their interesting shapes:
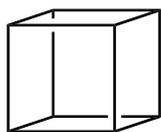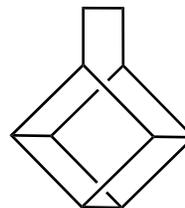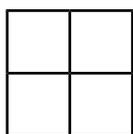
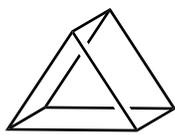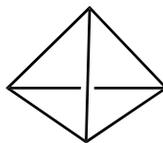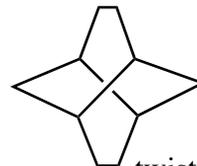cubane   housane   churchane   basketane

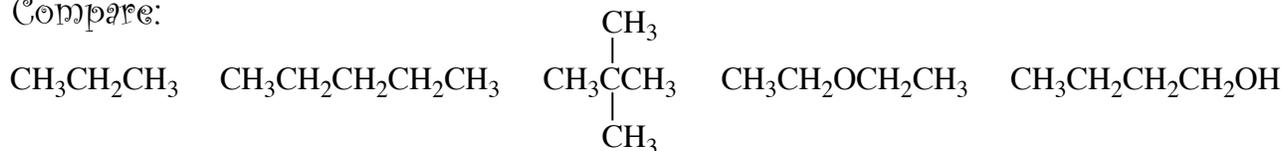windowpane   prismane   tetrahedrane   twistane

V. Physical Properties of Alkanes

Alkanes contain only nonpolar C–H and C–C bonds, and as a result they exhibit only weak van Der Waals forces.

Compare:

$CH_3CH_2CH_3$ $CH_3CH_2CH_2CH_2CH_3$ $CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_3$ $CH_3CH_2OCH_2CH_3$ $CH_3CH_2CH_2CH_2OH$

- Alkanes have low bp's and mp's compared to more polar compounds of comparable size.
- Bp and mp increases as the number of carbons increases because of increased surface area.
- Bp decreases with increased branching because of decreased surface area.
- Mp increases with increased symmetry.

VI. Conformations of Alkanes

A. Conformations of Ethane
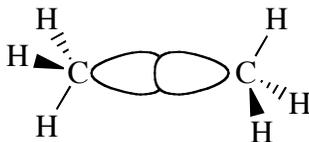

- The two methyl groups are not fixed in a single position but are free to rotate about the σ -bond connecting the two carbons.

The different spatial arrangements of the atoms that result from rotation about a single bond are called ***conformations***.

## Names are given for two different conformations:

- In the staggered conformation, the C–H bonds on one carbon bisect the H–C–H bond angle on the adjacent carbon.
- In the eclipsed conformation, the C–H bonds on one carbon are directly aligned with the C–H bonds on the adjacent carbon.
- *Newman projections* are used to show these conformations clearly:
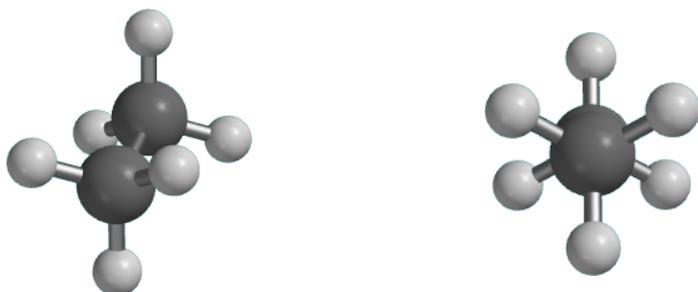
Why is the eclipsed conformation higher in energy? Electron-electron repulsion between the bonds in the eclipsed conformation increases its energy. This is called **torsional strain**.

- ☛ Ethane goes from a staggered to eclipsed conformation *via* an internal rotation.

  - The difference in energy between the two conformations in ethane is 2.9 kcal/mole.
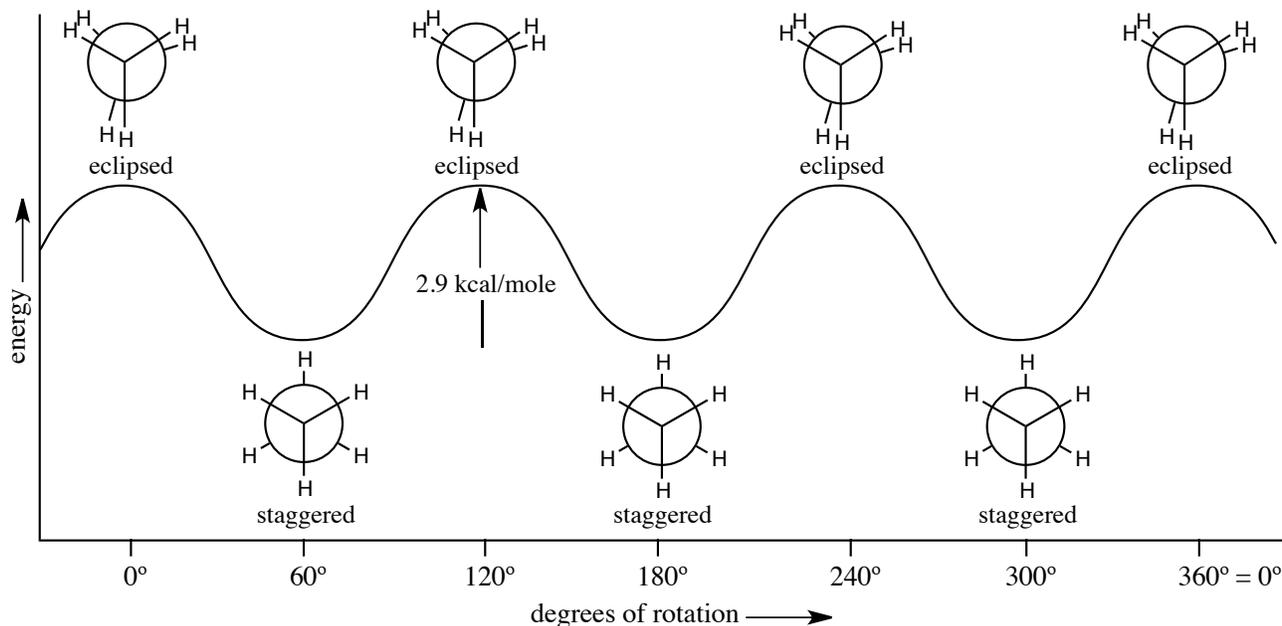
- @ room temperature, molecules have enough kinetic energy to overcome energy barriers of ≈ 20 kcal/mole, ∴ rotation about the C-C bond in ethane is constant, yet the molecules spend most of their time in the energy valleys represented by the staggered conformation.
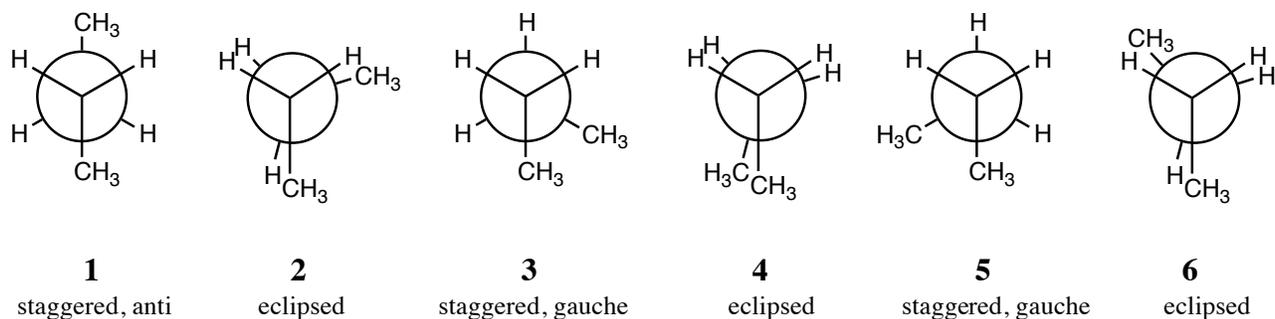
B.   Conformations of Butane

Butane and higher MW alkanes have more than one C–C bond that can rotate:
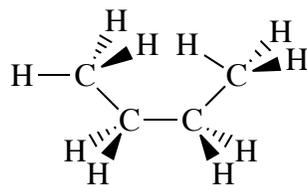
78
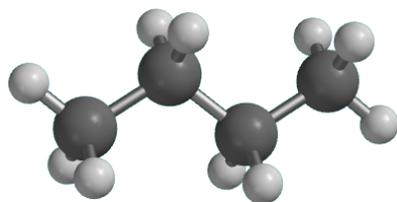
Rotation about the C–1 — C–2 bond:

- All staggered conformations are equal in energy.

Rotation about the C–2 — C–3 bond:

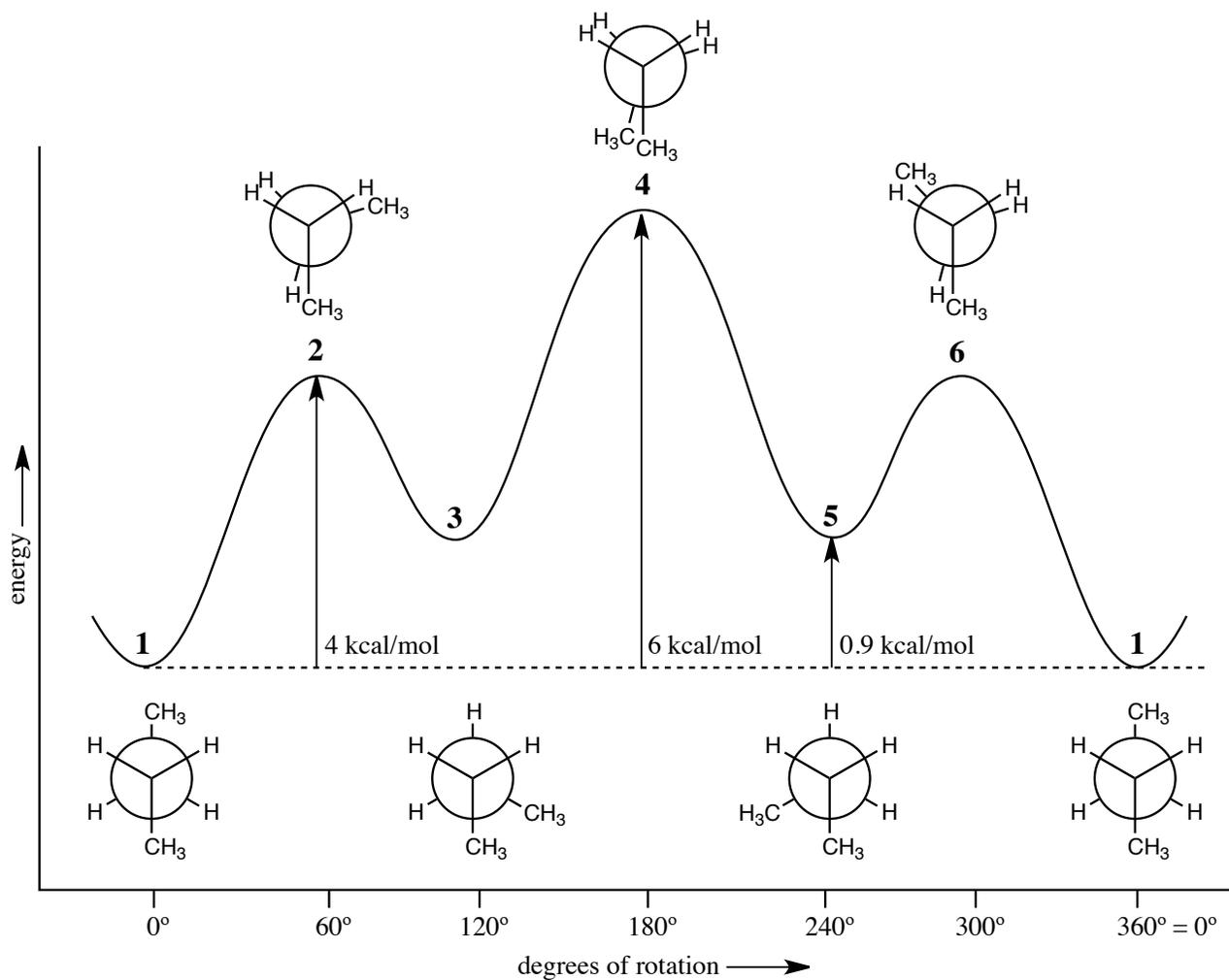| 1	2	3	4	5	6
staggered, anti	eclipsed	staggered, gauche	eclipsed	staggered, gauche	eclipsed

- All staggered conformations are **not** equal in energy
- A staggered conformation with two larger groups 180° from each other is called **anti**.
- A staggered conformation with two larger groups 60° from each other is called **gauche**.
- The anti conformation is 0.9 kcal lower in energy than the gauche conformation because of **steric strain**. Steric strain (*steric hindrance*) is an increase in energy resulting when atoms are forced too close to one another.

Another view of the steric strain in conformation 4:

The energies can be plotted:

energy ⟶

4 kcal/mol

6 kcal/mol

0.9 kcal/mol

0°   60°   120°   180°   240°   300°   360° = 0°

degrees of rotation ⟶

Notice:
- Staggered conformations **1**, **3**, and **5** are at energy minima.
- Anti conformation **1** is lower in energy than gauche conformations **3** and **5**, which possess steric strain.
- Eclipsed conformations **2**, **4**, and **6** are at energy maxima.

80

- Eclipsed conformation **4**, which has additional steric strain due to two eclipsed CH_3 groups, is highest in energy.
- The values in this energy diagram can be used to estimate the destabilization caused by other eclipsed groups:

H, H eclipsing: 1
H, CH_3 eclipsing: 1.5
CH_3, CH_3 eclipsing: 4
Gauche CH_3 groups: 0.9
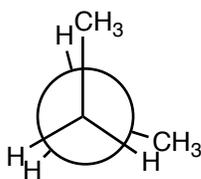
- The energy difference between the lowest and highest energy conformations is called the barrier to rotation.

- The conformations of butane are at equilibrium, and interconvert rapidly at room temperature

VII. Conformations of Cycloalkanes

C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}
cyclopropane	cyclobutane	cyclopentane	cyclohexane

Ring strain: 27.6   26.2   6.3   0
(kcal/mole)

C_7H_{14}	C_8H_{16}	C_9H_{18}
cycloheptane	cyclooctane	cyclononane

Ring strain: 6.4   9.9   12.8
(kcal/mole)

Q. How do we determine ring strain?
A. By comparing heats of combustion of cycloalkanes with unbranched alkanes.

Three factors contribute to ring strain:

1. *angle strain:* When the angles between carbon-carbon bonds are constrained by the size of the ring to be much smaller than the ideal tetrahedral angle of 109.5°, there will be significant angle strain.
2. *eclipsed interactions (AKA: torsional strain):* When the hydrogens are eclipsed due to the constraints of the ring, this contributes to ring strain. The larger the number of eclipsed interactions, the larger the ring strain.
3. *steric strain:* caused by atoms or groups of atoms approaching each other too closely

A. Cyclopropane:

Because the three carbons define a plane, cyclopropane is planar and has severe angle strain and torsional strain.
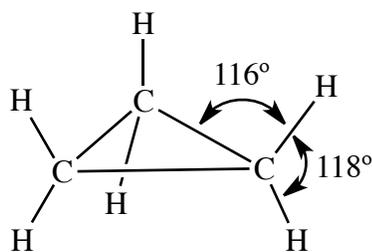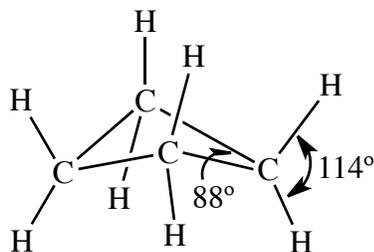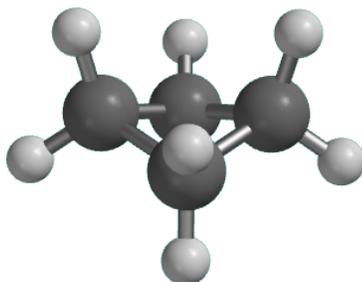

bonding in cyclopropane:
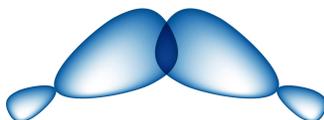
B. Cyclobutane

Cyclobutane suffers from severe angle strain.

- Cyclobutane also suffers from van der Waals repulsions due to the eclipsed H's. This is relieved somewhat by 1 atom in the ring bending out of the plane by 20°. Cyclobutane consists of two puckered conformations in rapid equilibrium.

C. Cyclopentane: A regular pentagon has bond angles of 108°, close to the ideal 109.5° for sp³ C's.

Cyclopentane is not a regular pentagon, however. **Why?**
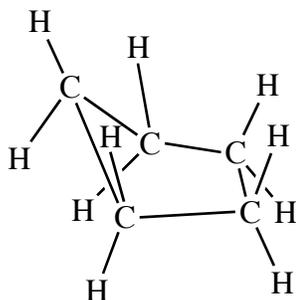

- The carbon atom that is out of the plane moves around the ring in a phenomenon known as **pseudorotation** so that eclipsing of the hydrogen atoms at various points in the ring is relieved at least part of the time.

D. Cyclohexane

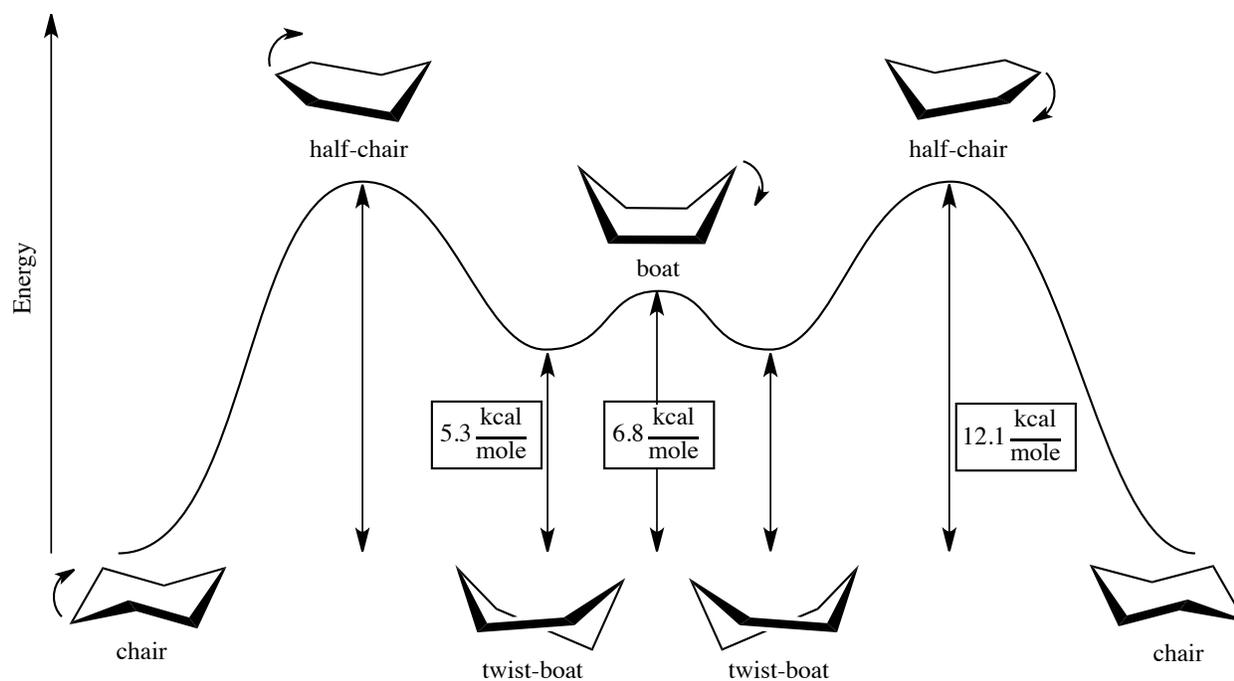The most stable conformation of hexane is the chair conformation.

chair conformation

convert to
Newman projection

Newman projection
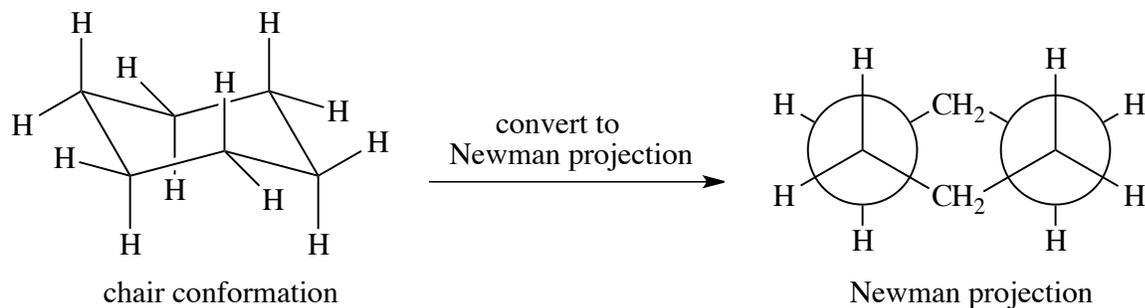
There are two kinds of H's:
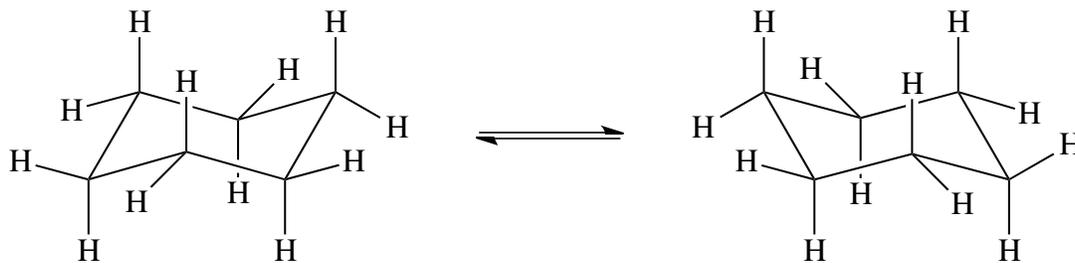
- For cyclohexane, both chair conformations have equal energy.
- The energy barrier between the two chair conformations is 10.8 kcal/mole, low enough that at room temperature, chair flip is very rapid (about 10^5 chair flips per second.)

In order to go from one chair conformation to another, cyclohexane must go through a half-chair, a boat and a twist boat conformation.

half-chair

half-chair

Energy

boat

$5.3 \dfrac{\text{kcal}}{\text{mole}}$

$6.8 \dfrac{\text{kcal}}{\text{mole}}$

$12.1 \dfrac{\text{kcal}}{\text{mole}}$
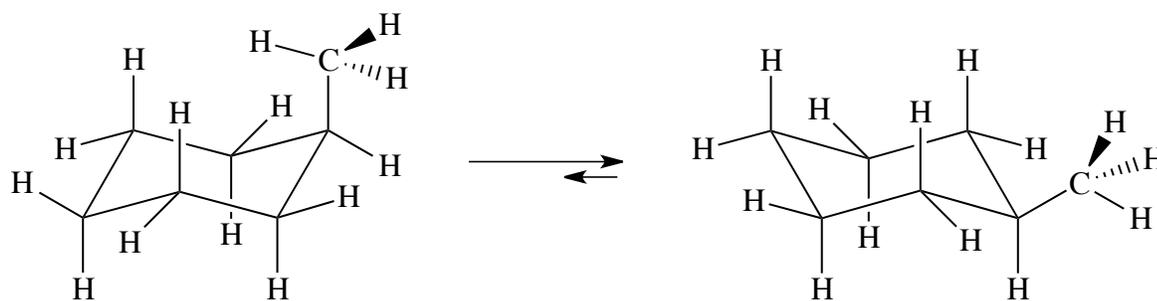
chair

twist-boat

twist-boat

chair

E. Monosubstituted Cyclohexane

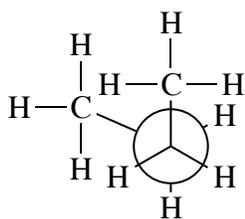If a substituent replaces a hydrogen atom in cyclohexane, the two chair conformations are no longer equivalent!

Look @ methylcyclohexane:

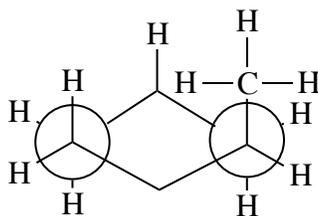*methyl in the **axia**l position:*   *methyl in the **equatoria**l position:*
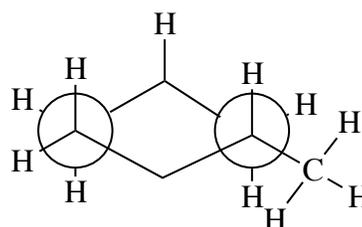
1,3-diaxial interaction shown in Newman Projection:

gauche-butane   axial methylcyclohexane   equatorial methylcyclohexane

The larger the substituent, the greater the repulsive interactions when it occupies an axial position.

☞ Look at the following table, which shows equilibrium constants for several monosubstituted cyclohexanes:

$$\text{Axial} \quad \underset{\xrightarrow{\hspace{1cm}}}{\overset{K_{eq}}{\rightleftharpoons}} \quad \text{Equatorial}$$

Substituent	strain energy for each 1,3-diaxial interaction (kJ/mole)	total strain energy "A value"	K_{eq} (eq/axial)
-F	.54	1.1	1.7
-Cl	1.0	2.0	2.5
-Br	0.9	1.8	2.3
-I	0.9	1.8	2.3
-OH	1.95	3.9	6.1
$-NH_2$	2.7	5.4	12.2
$-N(CH_3)_2$	4.4	8.8	60
$-CH_3$	3.55	7.1	27
$-CH_2CH_3$	3.65	7.3	30
$-CH(CH_3)_2$	4.5	9	65
$-C(CH_3)_3$	>9	>18	>4300
$-CH_2C(CH_3)_3$	4.2	8.4	50
$-C_6H_5$	6.3	12.6	348
$-CO_2H$	2.9	5.8	14.8
-CN	0.4	0.8	1.5

F. Disubstituted Cyclohexanes: *Cis* and *Trans* **Isomers**

We know that for cyclohexane with a single substituent in the ring, the preferred conformation is the chair form in which the substituent is in the equatorial position.

What about disubstituted cycloalkanes?

Look at 1-chloro-2-methylcyclohexane:
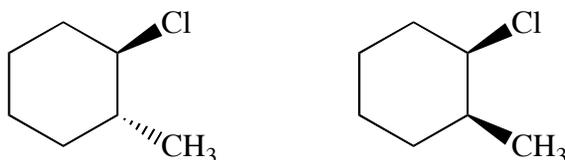
Notice: Restricted rotation around the C-C bonds of the ring does not allow these two isomers to interconvert!
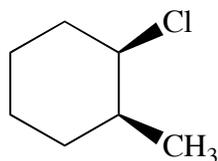
Convert to chair conformations:

Remember:

- axial bonds point in the same direction as the point of the chair to which they are attached.
- equatorial bonds point slightly up @ the carbons that have axial bonds pointing down, and slightly down at carbons that have axial bonds pointing up.

If we convert *trans*-1-chloro-2-methylcyclohexane to a chair conformation:
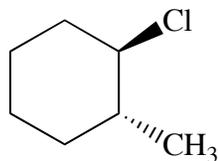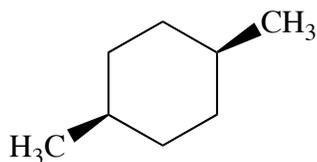

Look at the *cis* isomer and convert to the chair conformation:

The same definition of *cis* and *trans* substitution can be applied to substituent groups in other positions on a cyclohexane ring:

**Example:** Draw the structures of the two chair conformations of *cis*-1,4-dimethylcyclohexane.

- These two conformers have equal energy and are present in equal amounts.

G. Disubstituted Cyclopentanes

Rotation around the C–C bonds in a cyclopentane ring are also restricted, so there are cis and trans isomers. There are two ways to draw 5-membered ring cis and trans isomers:

Look @ 1,2-dimethylcyclopentane:
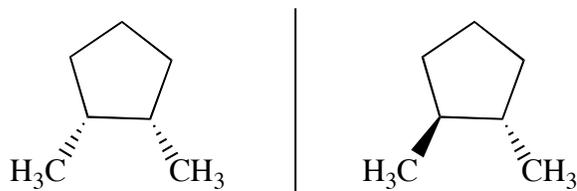
VIII. Oxidation of Alkanes

Alkanes are extremely unreactive, stable, low energy species derived from petroleum and petroleum by-products. Petroleum: complex mixture of alkanes, cycloalkanes, and aromatic hydrocarbons formed by the decomposition of plant and animal material under the earth's crust. The components are separated into fractions by distillation.
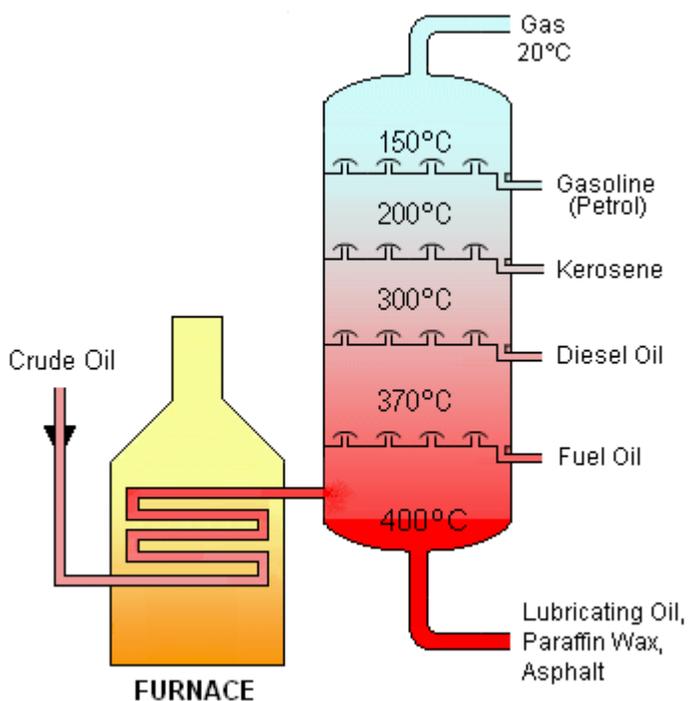
There are only two reactions that alkanes will undergo, both of which are **free-radical** reactions (*reactions involving highly reactive species with unpaired e-s*):

Reaction 1: Combustion

Alkanes are important constituents of fuel – *that is* they burn in the presence of oxygen.

$$CH_4 \quad + \quad 2O_2 \quad \longrightarrow$$

Reaction 2: Halogenation

Alkanes react with chlorine or bromine at high temperatures or in the presence of light (hv) to give alkyl chlorides or alkyl bromides. This reaction is used industrially to prepare alkyl halides (*more in chapter 15.*)

$$CH_4 \ + \ Cl_2 \quad \longrightarrow \quad CH_3Cl \ + \ CH_2Cl_2 \ + \ CHCl_3 \ + \ CCl_4 \ + \ Cl_3CCCl_3$$
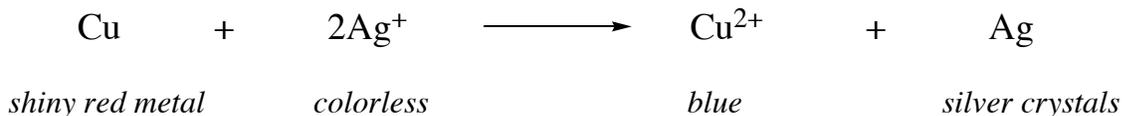
Both of these reactions are oxidation/reduction reactions.

Oxidation-reduction reactions involve the gain and loss of electrons, and a change in the oxidation state of the molecules involved:

> **Oxidation:** *loss* of electrons
> **Reduction:** *gain* of electrons

$$Cu \quad + \quad 2Ag^+ \quad \longrightarrow \quad Cu^{2+} \quad + \quad Ag$$

| *shiny red metal* | *colorless* | *blue* | *silver crystals* |

✳ If one molecule is oxidized, another is reduced.
✳ Electrons are *TRANSFERRED COMPLETELY* from one molecule to another.

For organic compounds, oxidation-reduction reactions result in a *CHANGE IN ELECTRON DENSITY* around the carbon atom rather than a complete transfer of electrons.

Oxidation: *loss* of "**electron density**"
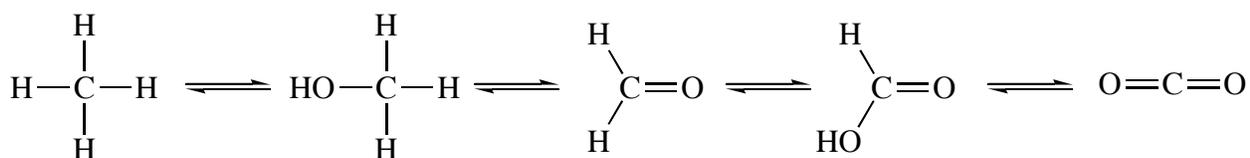Carbon "**loses**" electrons by forming bonds with elements that are more electronegative than it is.

> *loss* of:
> *gain* of:

Reduction: *gain* of "**electron density**"
Carbon "**gains**" electrons by giving up bonds to more electronegative elements and forming bonds with hydrogen atoms instead.
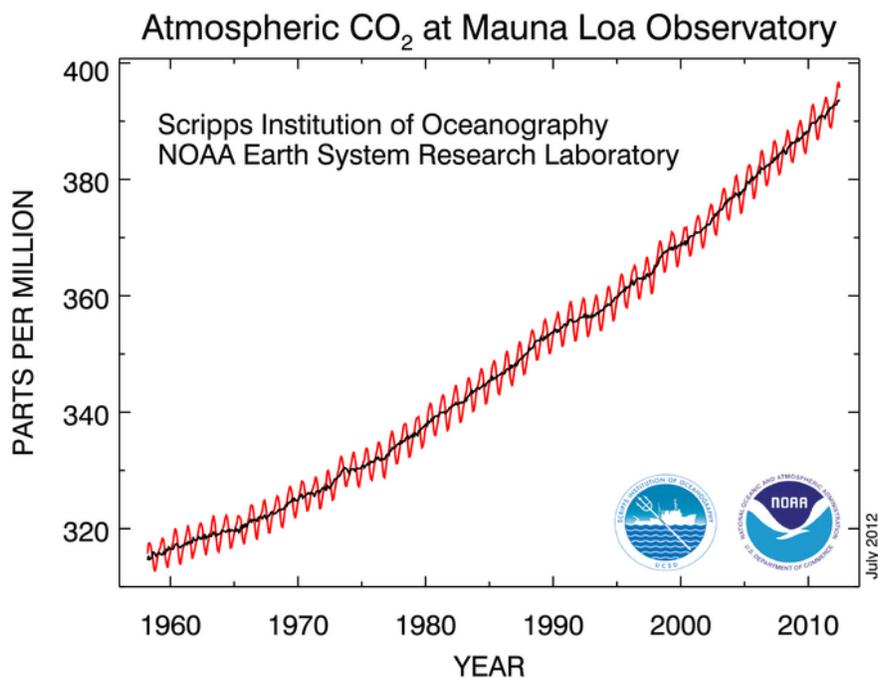
loss of:

gain of:

The following shows stepwise oxidation of methane (the most reduced form of carbon) all the way up to carbon dioxide (the most oxidized form of carbon):

$$
H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \;\rightleftharpoons\; HO-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \;\rightleftharpoons\; \overset{\displaystyle H}{\underset{\displaystyle H}{}}C{=}O \;\rightleftharpoons\; \overset{\displaystyle H}{\underset{\displaystyle HO}{}}C{=}O \;\rightleftharpoons\; O{=}C{=}O
$$

Combustion of Alkanes and other hydrocarbons adds a tremendous amount of CO_2 to the atmosphere each year.

Look at the following graph showing the changing concentration of CO_2 in the atmosphere since 1960:

Atmospheric CO_2 at Mauna Loa Observatory

Scripps Institution of Oceanography
NOAA Earth System Research Laboratory

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IX. Lipids – Part 1

Lipids are biomolecules whose properties resemble those of alkanes and other hydrocarbons. They are unlike any other class of biomolecules, though, because they are defined by a physical property, not by the presence of any functional group.

- Lipids are biomolecules that are soluble in organic solvents and insoluble in water.
- They are composed of many nonpolar C–H and C–C bonds, and have few polar functional groups.

Examples:

$$CH_3(CH_2)_{14}-C(=O)-O(CH_2)_{29}CH_3$$
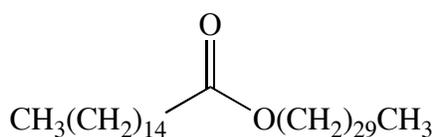
a component of beeswax

$PGF_{2\alpha}$

cholesterol
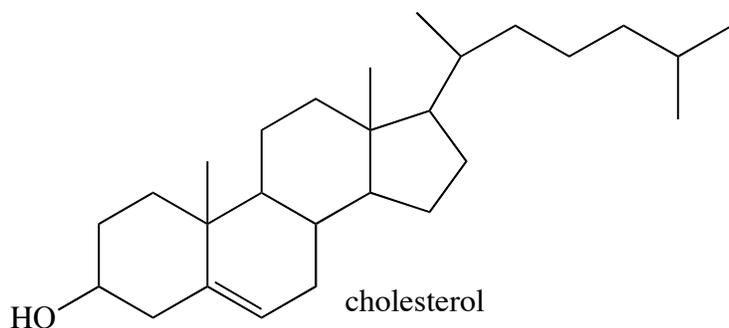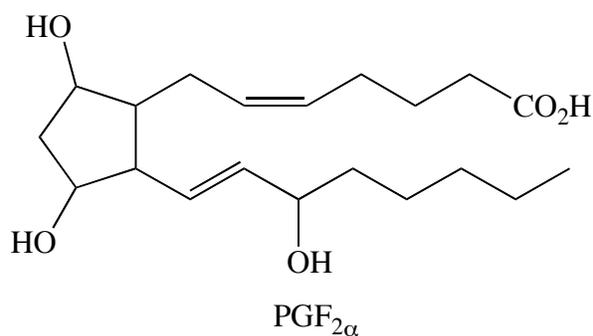
- Lipids have high energy content. Because they are composed mainly of C–C and C–H bonds, they are oxidized with the release of energy, just like alkanes.

Attributions

Page 90: Distillation of crude oil picture

Page 92: Atmospheric CO_2 Chart