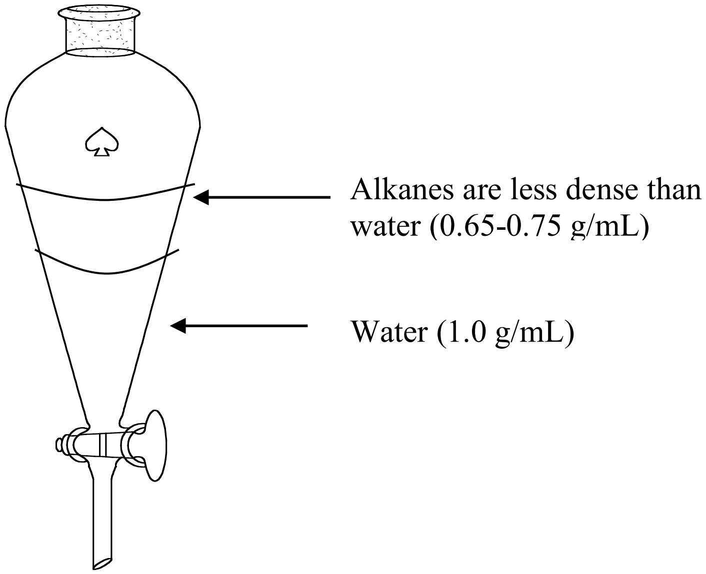
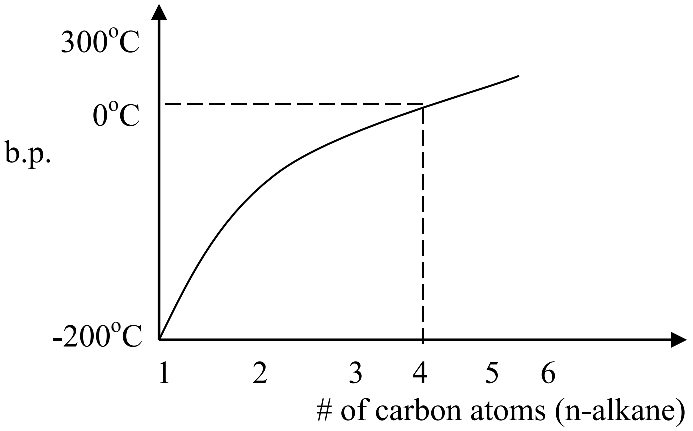
Physical Properties of Alkanes:

- Intermolecular forces are dominated by London forces
- Alkanes are non-polar because H and C have similar electronegativity
- Soluble in other organic solvents (like dissolves like)
- Not miscible with water → floats due to lower density
- Low density (ρ = rho = g/cm^3)
    - ρ water ~ 1 g/cm^3
    - ρ alkanes ~ 0.7 g/cm^3
- Low m.p., b.p.

Separatory Funnel *(density separation)*

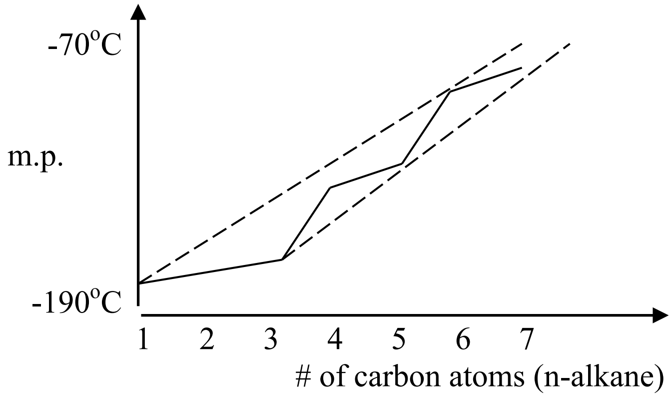


Boiling point trend



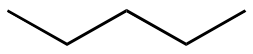
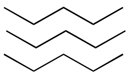
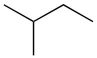
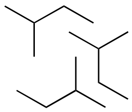
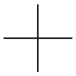
- As the straight chain length increases, so does the bp. This is due to London forces (hydrophobic forces) between the adjacent molecules.
- As the boiling point increases, the graph reaches a plateau where alkane starts to decompose (a process called "fracking", e.g. fracking in oil sands facilities)

Melting point trend:



- Melting points are related to the crystal structure packing efficiency
- The predicted line (dotted line) is not what we observe, but a zig zag line (continuous) resulting from crystal structure packing.

e.g. Pentane

	mp (°C)	bp (°C)	
 n-Pentane	-129	36	well packed 
 Isopentane 2-methylbutane	-160	28	 less well packed
 Neopentane 2,2-dimethylpropane	-13	9	"ball-like" shape, so B.P. comes down

- n-pentane has high bp due to multiple contacts of straight chains (London Forces)
- mp of neopentane determined by good crystal packing of spherical shape

Conformations

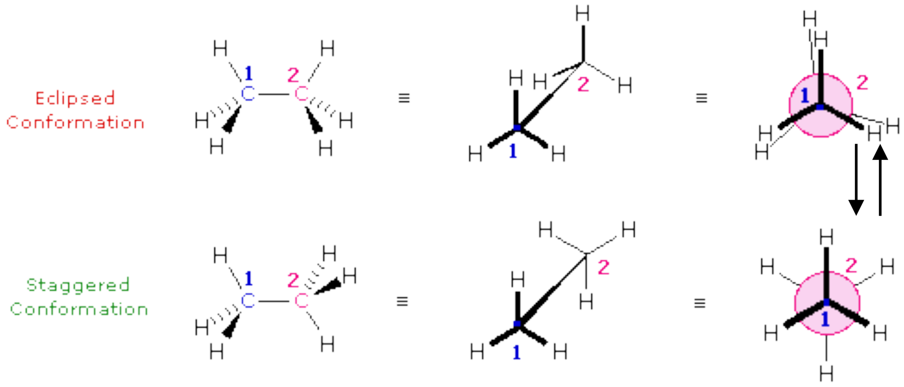
- Different 3-D shapes a molecule can assume by rotation around single bonds
- Room temperature (20 °C): 15-20 kcal/mol of energy available
- Rotation around C-C occurs rapidly at room temperature
- **Steric effect**: Repulsion of filled shells of e^-

Ethane (C_2H_6) (recall C_nH_{2n+2})

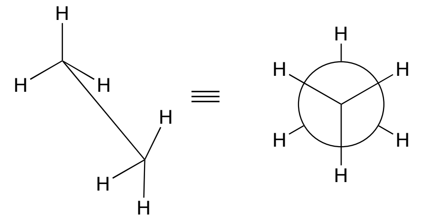
Newman Projection

Less stable

Most stable

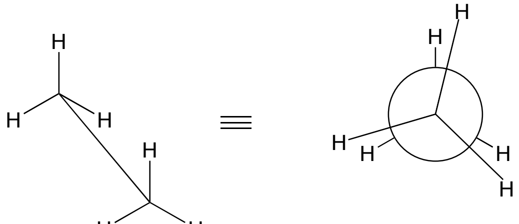


ΔG = 2.8 kcal/mol for rotation



STAGGERED

NEWMAN PROJECTION

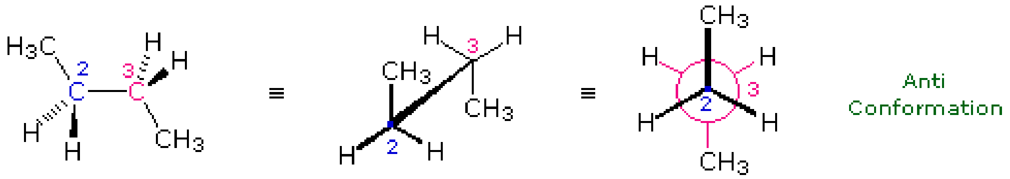


ECLIPSED

n-butane (C_4H_{10}) – Rotation around all bonds still very rapid

- Most stable (most populated conformation) is called anti and has groups as far away as possible

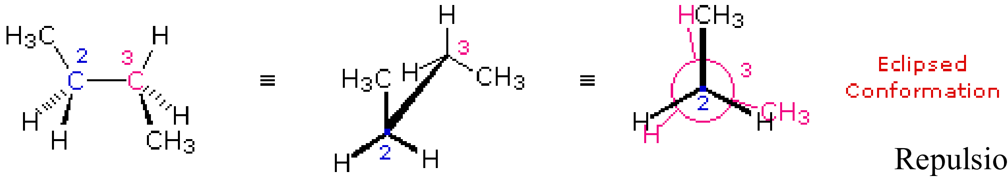
A



Most stable, staggered

Dihedral angle = 180°

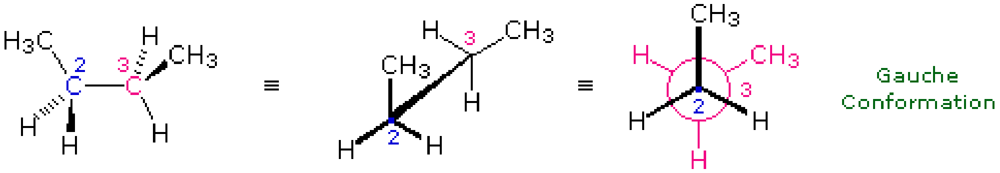
B



Dihedral angle = 120°

Repulsion = steric effect

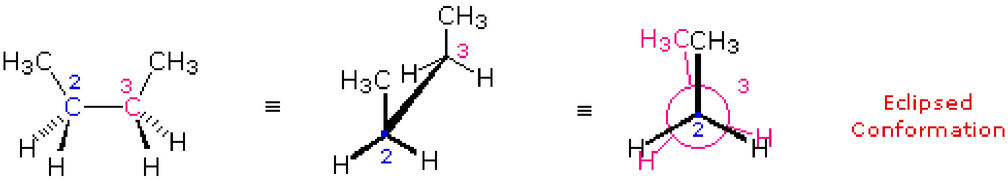
C



Not as stable as anti

Dihedral angle = 60°

D

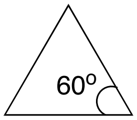


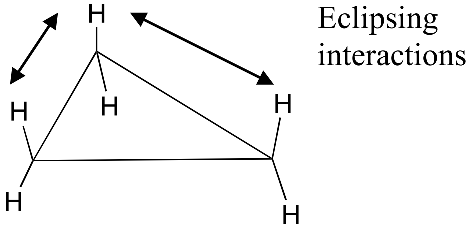
Least stable (syn) eclipsed

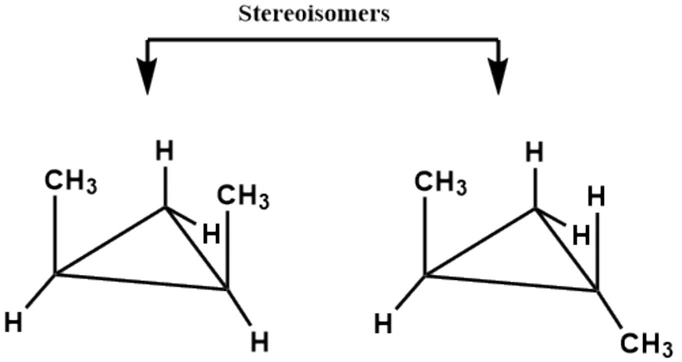
Dihedral angle = 0°

Cycloalkane Conformations

Cyclopropane –bond angle 60^o – relatively rigid structure, very reactive

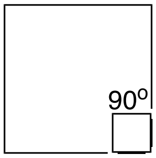




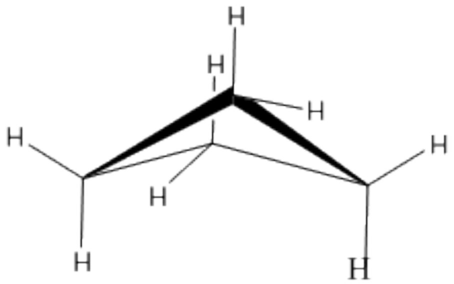


Cis-1,2-Dimethylcyclopropane **Trans-1,2-Dimethylcyclopropane**

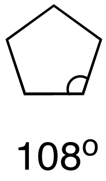
Cyclobutane – bond angle close to 90^o – does have some flexibility

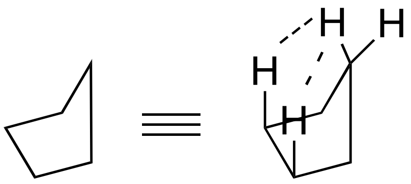


3D structure of cyclobutane

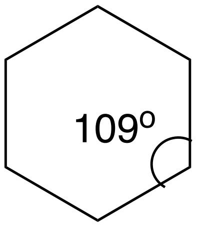


Cyclopentane – bond angles nominally 108^o – more flexible than cyclobutane

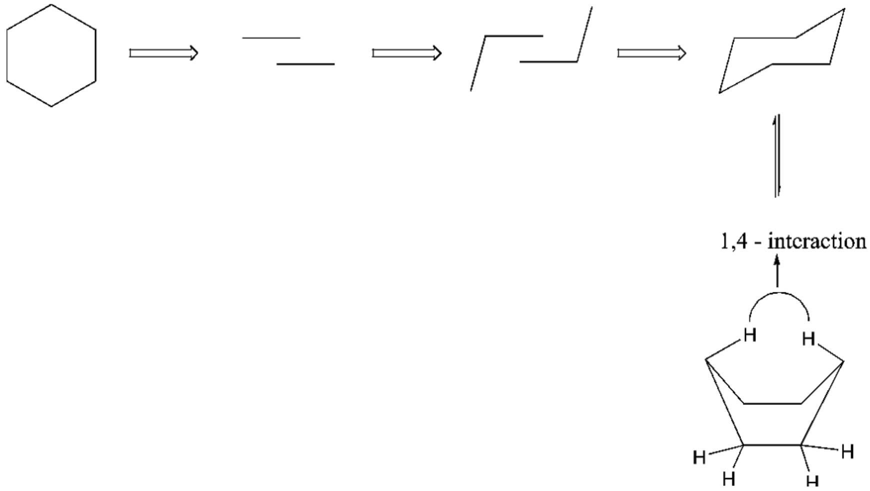




Cyclohexane – bond angles actually 109°, not 120° as in flat hexagon



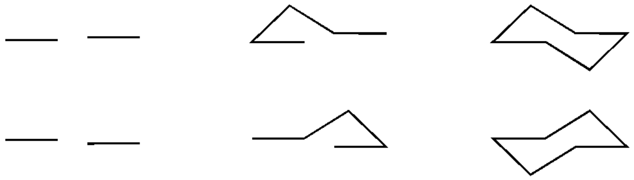
Cyclohexane Conformations – How to draw:

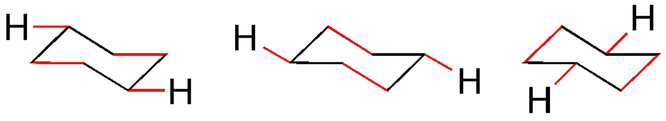


- Chair conformation (most stable)
- All adjacent hydrogen atoms are staggered

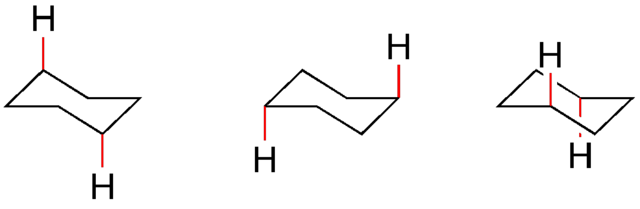
- Boat (least stable)
- many adjacent hydrogen atoms eclipse
- 1,4 - interactions of two-hydrogens

Another way to draw cyclohexane:



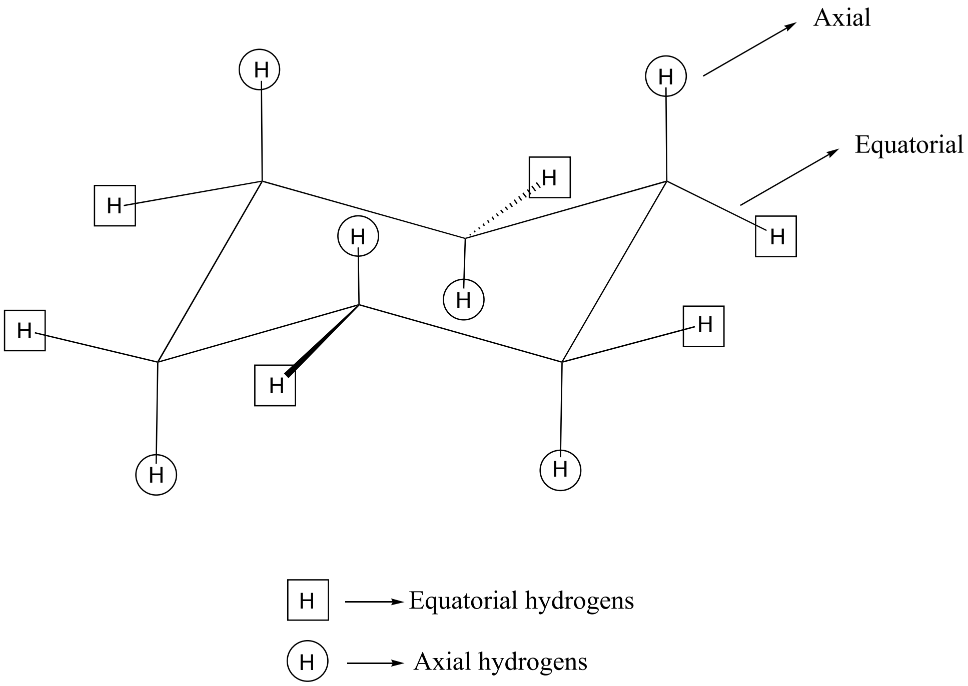


Parallel Lines in Equatorial Position

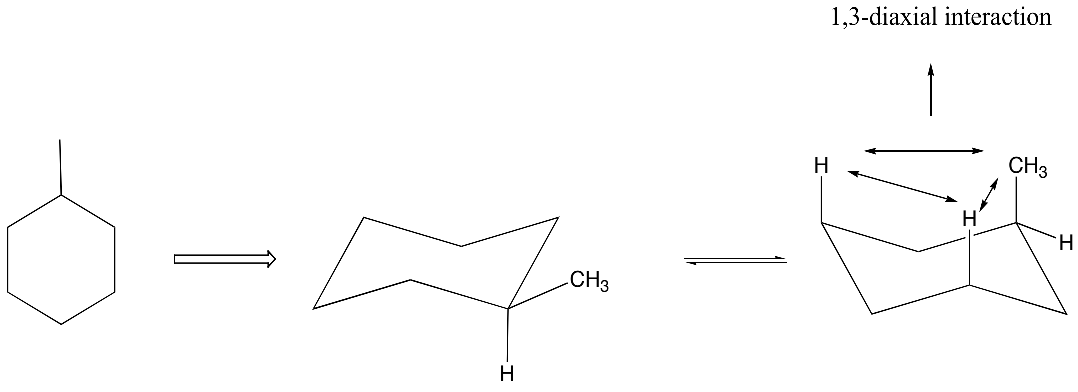


Vertical Lines in Axial Position

Cyclohexane Conformations Axial vs Equatorial positions

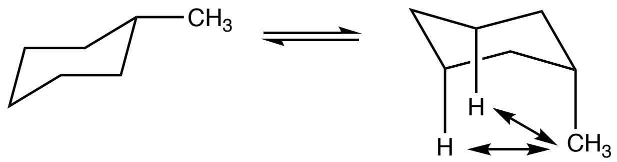


Substituted Cyclohexanes – Draw the most stable conformation



- Largest (bulkiest group close to ring) group generally placed equatorial – otherwise get unfavorable 1,3-diaxial interactions

- 1,3-diaxial interaction (steric effect) makes this conformation less stable.

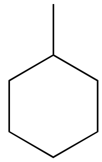


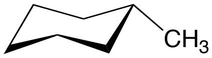
Equatorial methyln
interaction
More stable

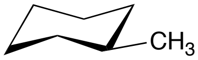
Axial methyl interaction
Less stable

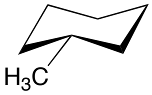
Most Stable Conformation of Methylcyclohexane – 6 drawings of same molecule below

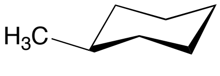
1. Methylcyclohexane

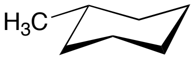


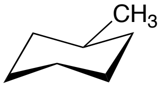




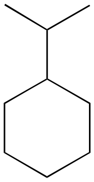


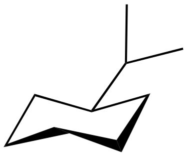


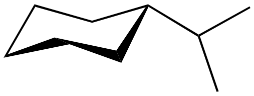


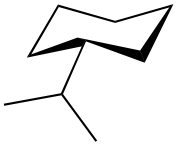


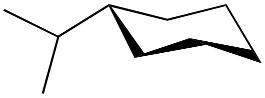
2. Isopropylcyclohexane

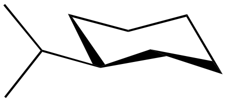












NB: For most stable conformation, largest group at equatorial position