

RECALL:

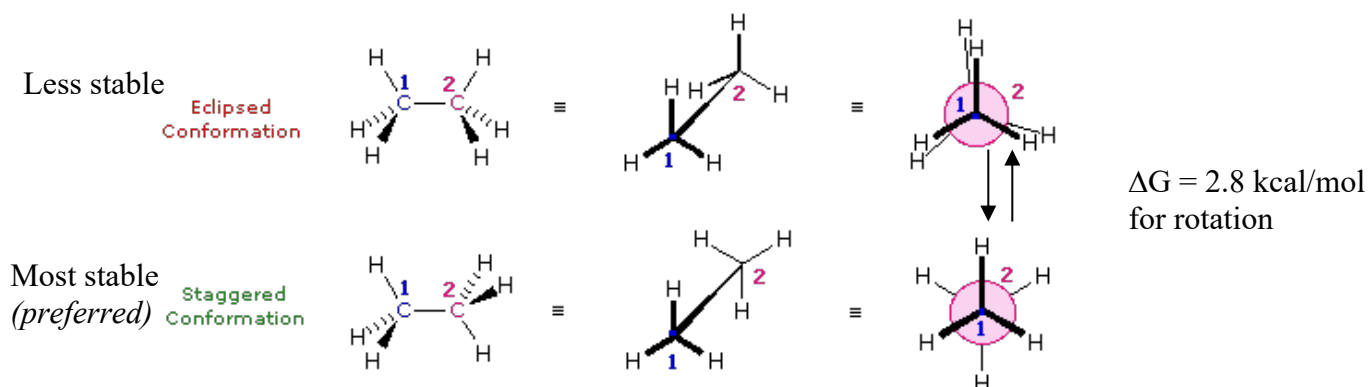
Isomers are compounds with the same molecular formula & a different arrangement of atoms in the molecule

- Structural (Constitutional) Isomers
- Stereoisomers
 - Diastereomers
 - Enantiomers

Odd Hassel – proposed conformations of tetrahedral carbon-carbon bond; won the 1969 Nobel Prize with Derek Barton

Conformation

Different 3D shapes of a single (the same) molecule obtained by rotation about single bonds
A molecular conformation is any spatial arrangement of atoms that can be interconverted by rotation about single bonds of the molecule

Example: Ethane

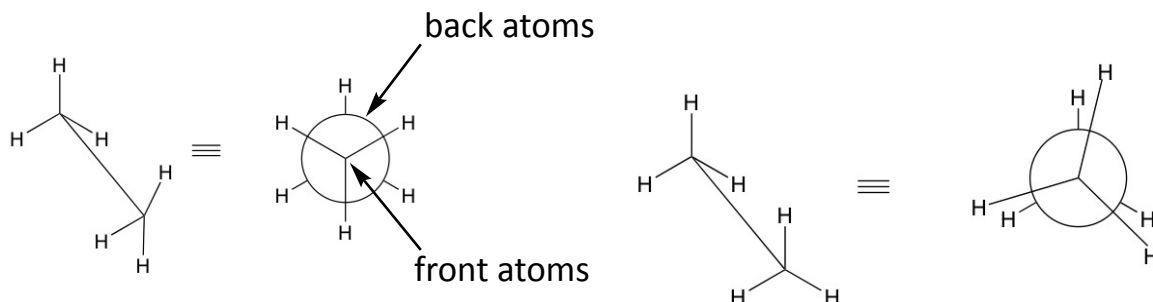
At room temperature (20 °C): 15-20 kcal/mol of energy available. This allows for rotation around C-C to occur rapidly at room temperature. – Important to know

There is a **Steric effect** between neighboring bonds to hydrogens: **Repulsion of filled shells of e⁻**

Newman Projections

This is a tool to examine the conformation (rotational 3D geometry) about one specific bond

- Look at one bond at a time
- Back C is a large circle and the front C is a dot



Staggered conformation (hydrogens are **anti**)
Anti means opposite side

Eclipsed conformation (hydrogens are **syn**)
Syn means same side

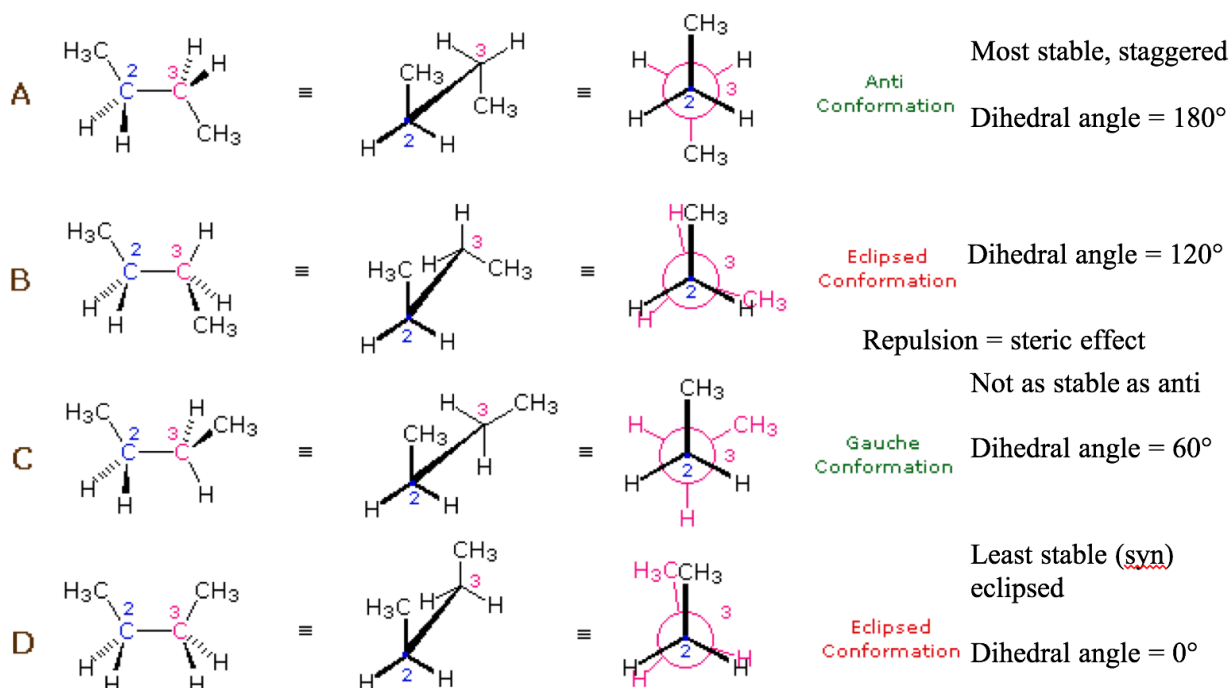
- Needs energy to go from one conformation to another
- Steric effect – repulsion between two filled shells of electrons
- Increased repulsion is observed as the H move closer in space. Staggered conformation has a lower energy than eclipsed conformation due to less steric repulsion between the H atoms.

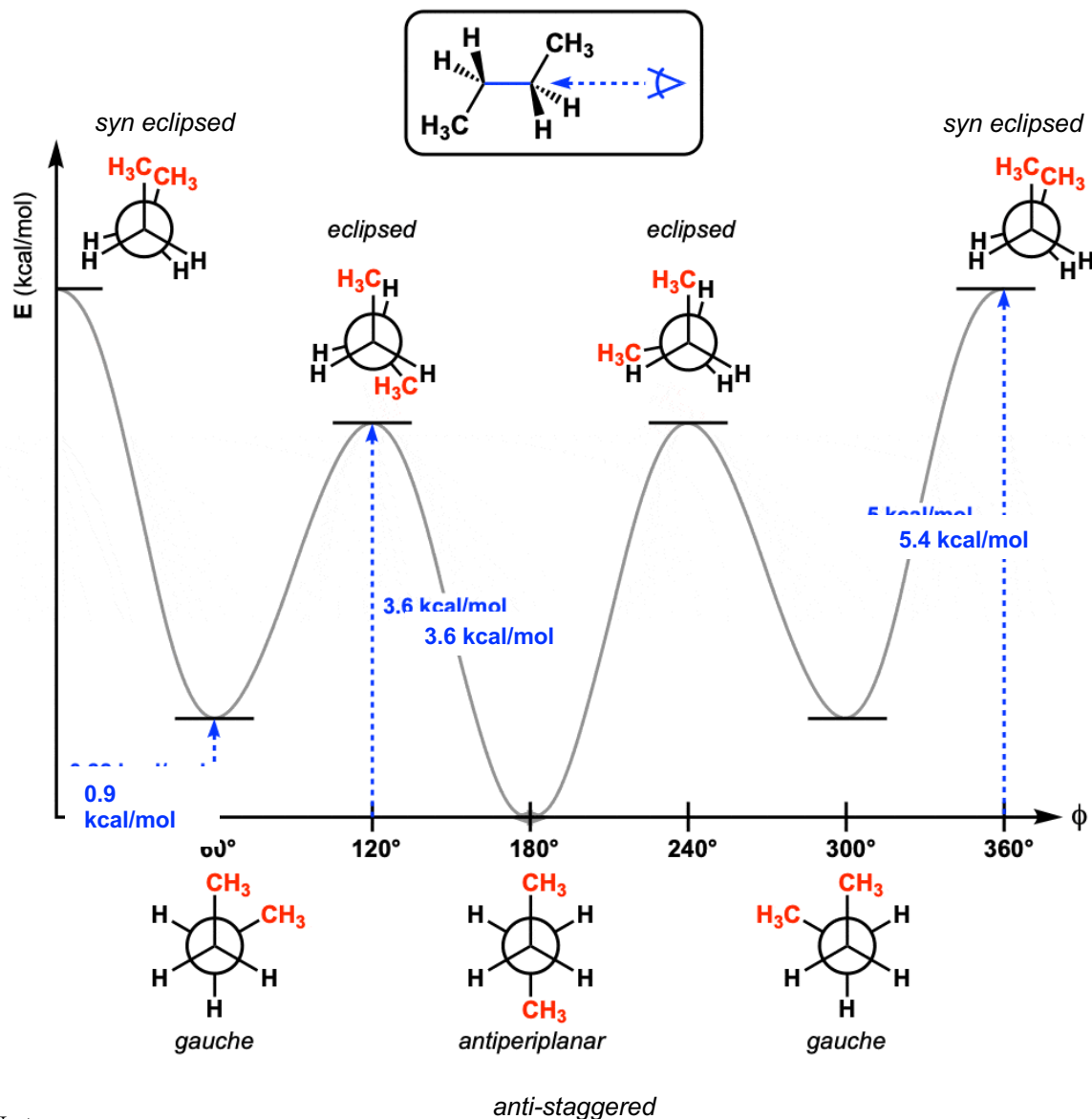
Example: n-butane (C_4H_{10})

Rotation around all bonds still very rapid.

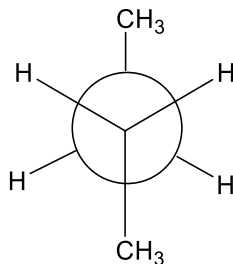
Most stable (most populated conformation) is called anti and has groups as far away as possible.

Note: Newman Projection allows you to look at only one bond at a time. In the case of n-butane, we are looking through the central bond

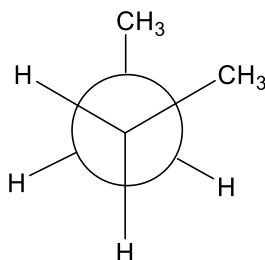


Butane Conformational Energy Diagram:Notes:

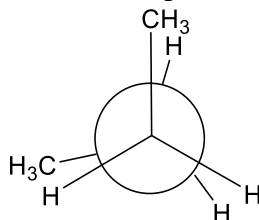
Anti Staggered – two large groups (i.e., CH₃) are as far away from each other as possible (180°) (lowest energy, favourable)



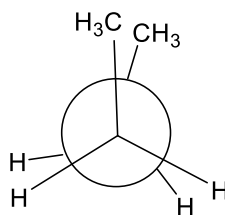
Staggered Gauche – two large groups are 60° relative to each other



Eclipsed – the groups are as close to each other as possible.

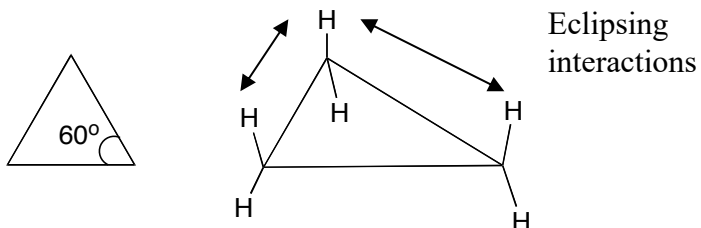


Syn Eclipsed – two large groups are as close together in space as possible. Two large groups are 0° relative to each other (**highest energy, unfavourable**)



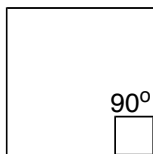
Cycloalkane Conformations:

Cyclopropane – bond angle 60° – relatively rigid structure, very reactive

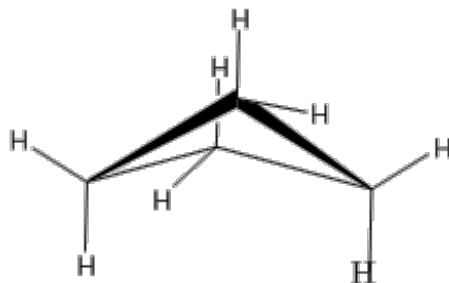


- High energy molecule due to the internal angle being 60° and the eclipsing interactions between the H.

Cyclobutane – bond angle close to 90° – does have some flexibility

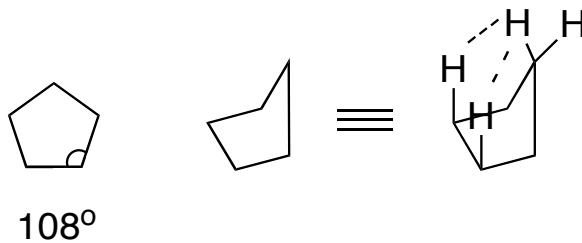


3D structure of cyclobutane:

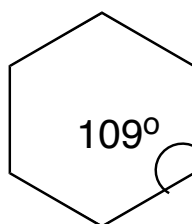


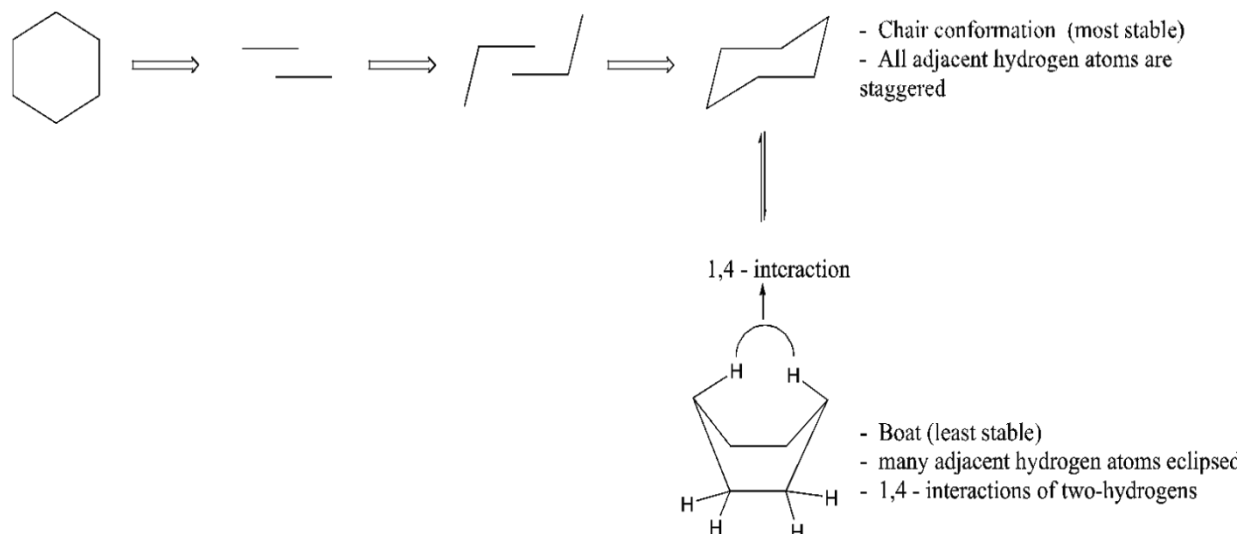
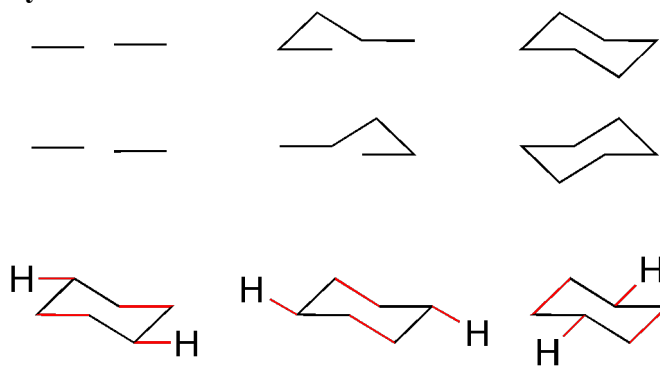
- Not completely flat and adopts an envelope / bent shape

Cyclopentane – bond angles nominally 108° – more flexible than cyclobutane; close to 109° but geometry is still constrained

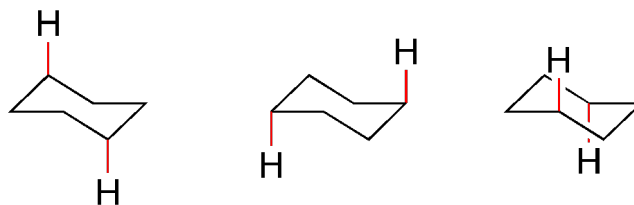


Cyclohexane – bond angles actually 109° , not 120° as in flat hexagon, due to the C being sp^3 hybridized



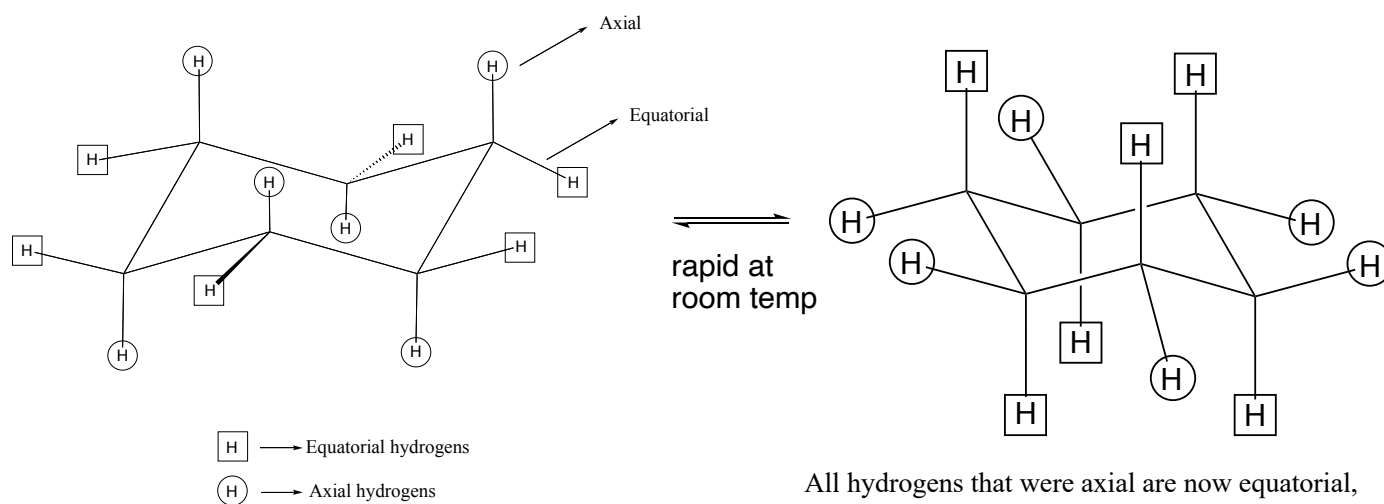
Cyclohexane Conformations – How to draw:**Another way to draw cyclohexane:**

Parallel Lines in Equatorial Position

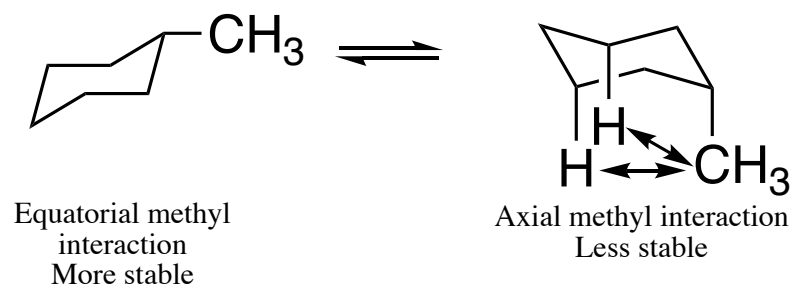
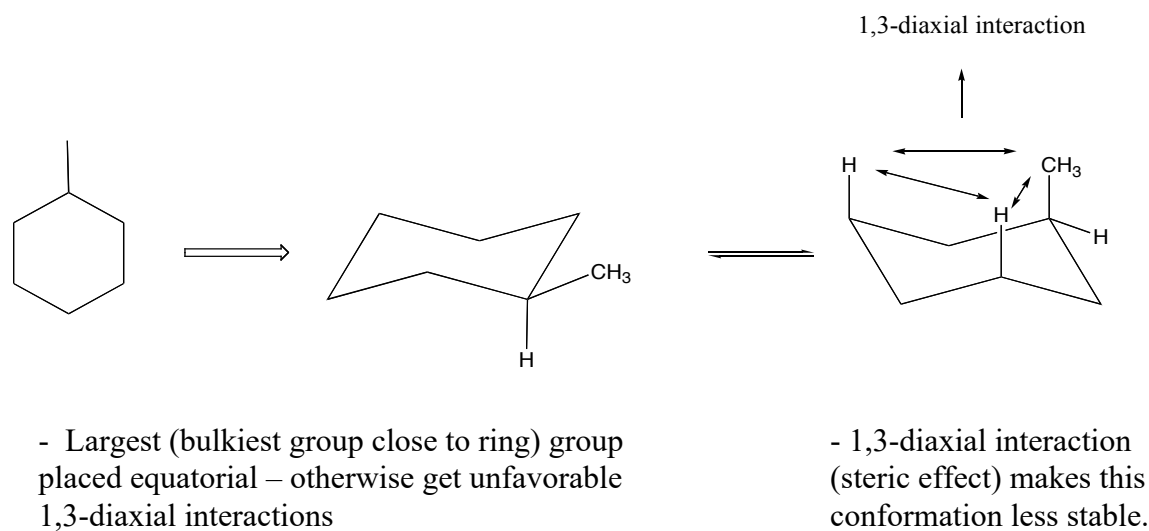


Vertical Lines in Axial Position

Cyclohexane Conformations Axial vs Equatorial Positions and Ring Flip

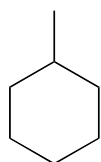
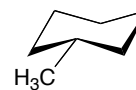
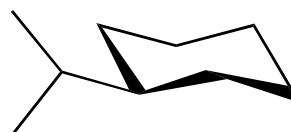
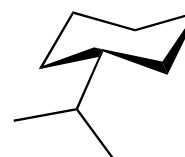
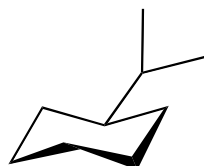
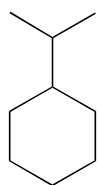


Substituted Cyclohexanes – Draw the most stable conformation



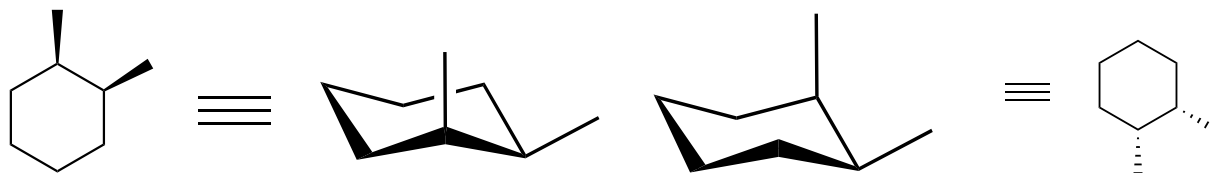
Examples of Most Stable Conformation of Substituted Cyclohexanes :**1. Methylcyclohexane**

– 6 drawings of same molecule

**2. Isopropylcyclohexane****For most stable conformation, largest group at equatorial position**

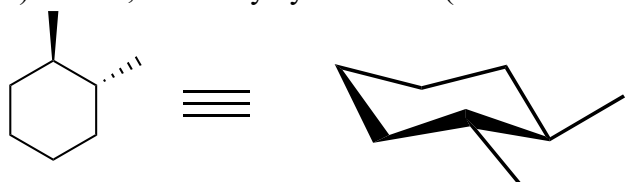
Examples of Most Stable Conformation of Polysubstituted cyclohexanes:**Examples:**

1) cis-1,2-dimethylcyclohexane



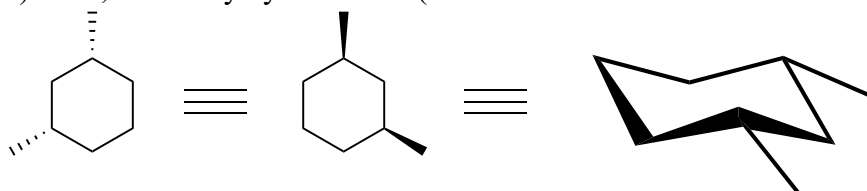
- One methyl group axial and one methyl group equatorial

2) trans-1,2-dimethylcyclohexane (a stereoisomer (diastereomer) of above structures)



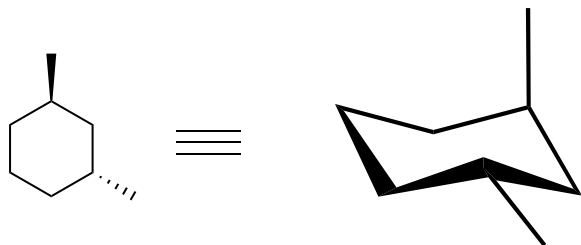
- Both methyl groups equatorial

3) cis-1,3-dimethylcyclohexane (a structural isomer of above structures)



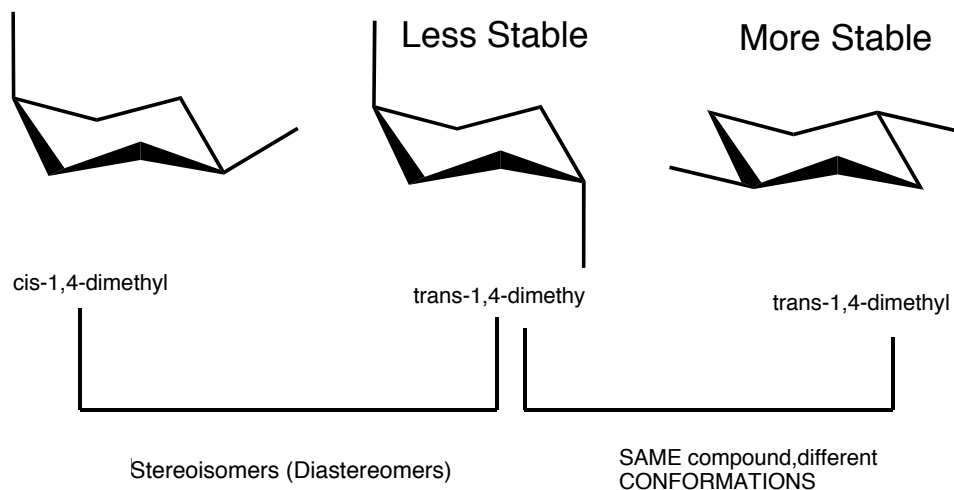
- Both methyl groups equatorial

4) trans-1,3-dimethylcyclohexane : a stereoisomer of above cis-1,3- dimethylcyclohexane

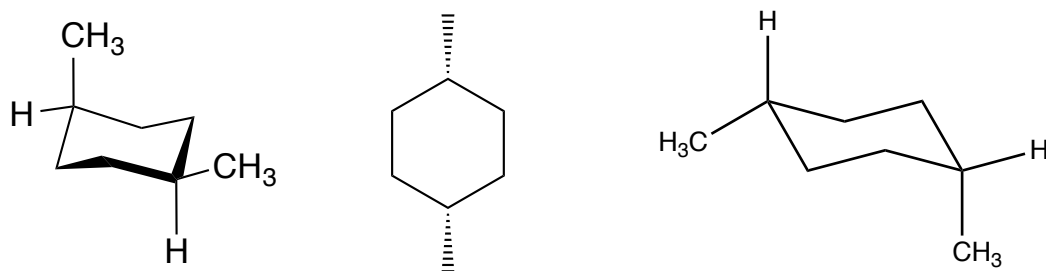


- One methyl group axial and one methyl group equatorial

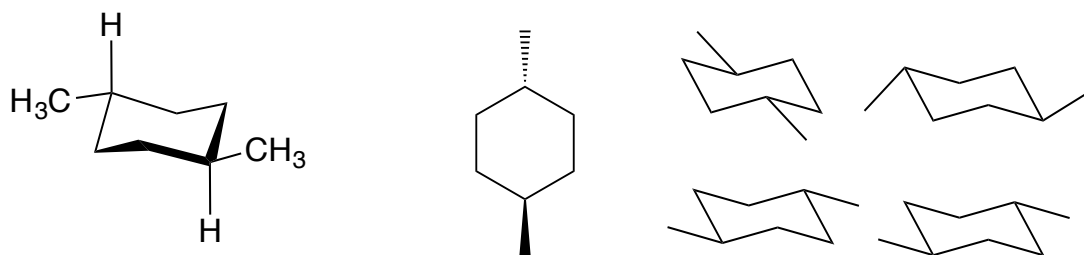
5) cis-1,4-dimethylcyclohexane and trans-1,4-dimethylcyclohexane:



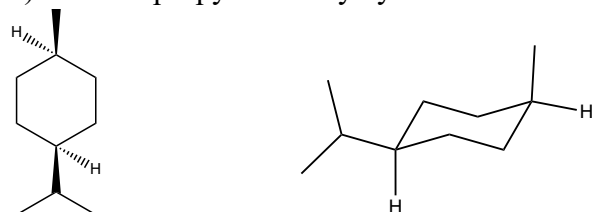
6) cis-1,4-dimethylcyclohexane:



7) trans-1,4-dimethylcyclohexane:



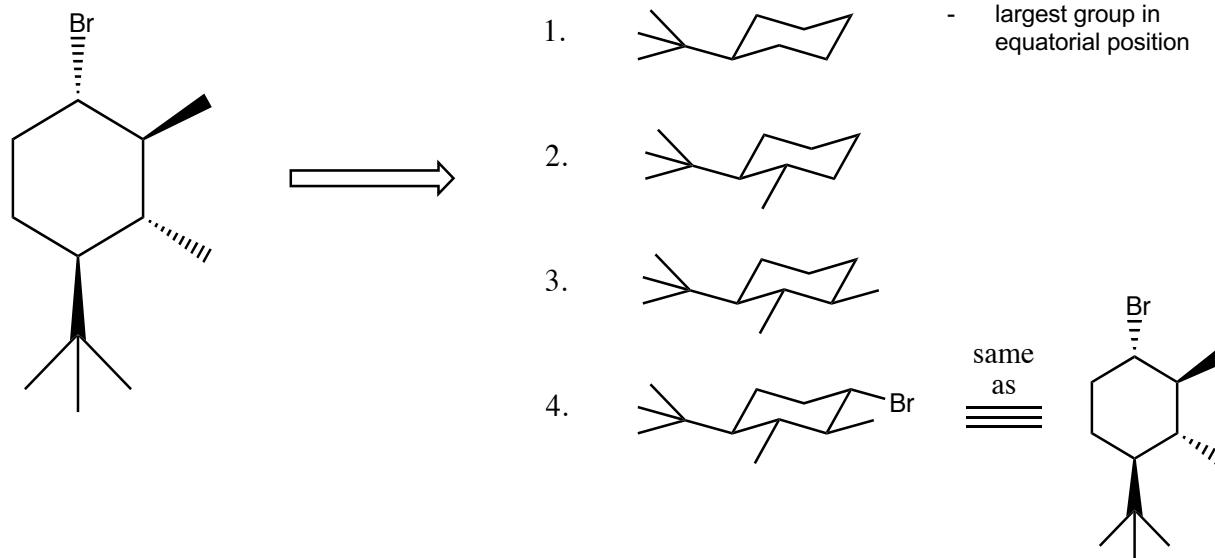
8) cis-1-isopropyl-4-methylcyclohexane



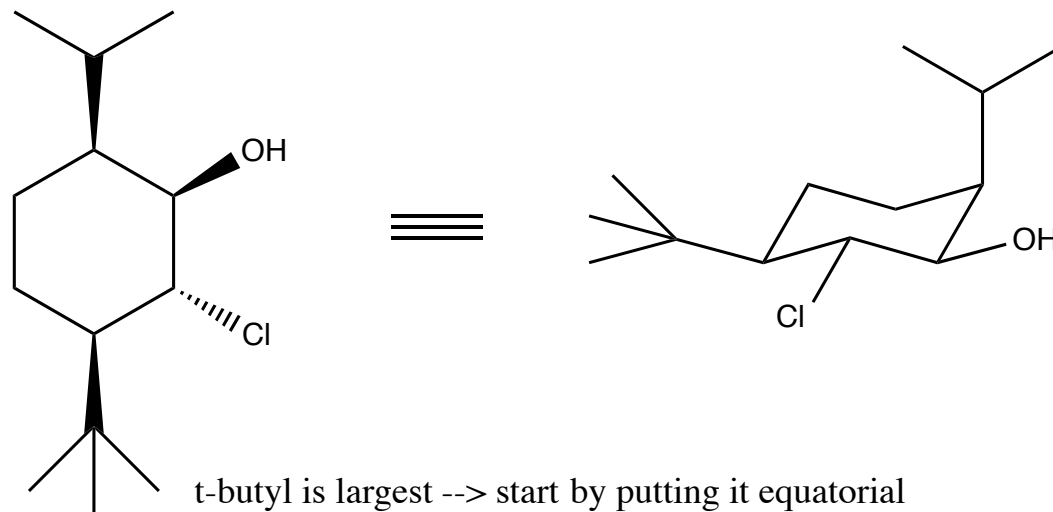
most stable conformation (bulky isopropyl group is in the equatorial position)

How to draw the most stable conformation of substituted cyclohexanes:

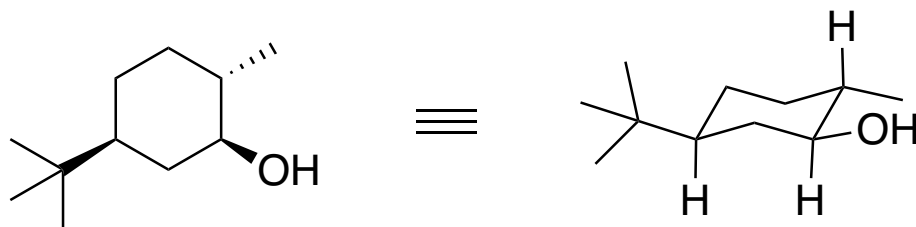
1. Start by drawing the chair conformation of cyclohexane
Put the largest group in an equatorial position
2. Draw the next group(s) on the correct atom(s) with respect to the largest group in correct geometry



Note that the largest substituent (tertiary butyl) is placed in the equatorial position to avoid destabilizing 1,3-diaxial interactions

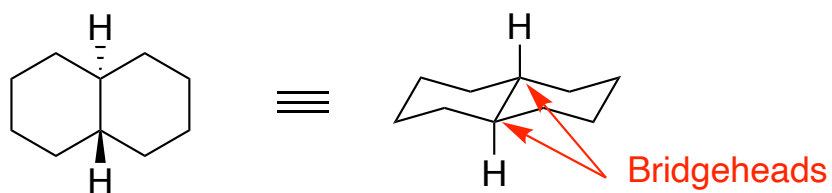
Another example:

More example:

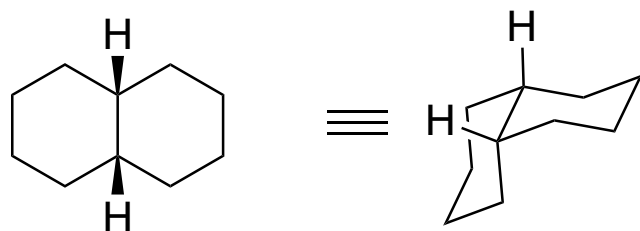


Bicyclic structures

Trans-decalin (4.4.0 bicyclodecane)



Cis-decalin (4.4.0 bicyclodecane)



Norbornane (2.2.1 bicycloheptane)

