

RECALL:

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

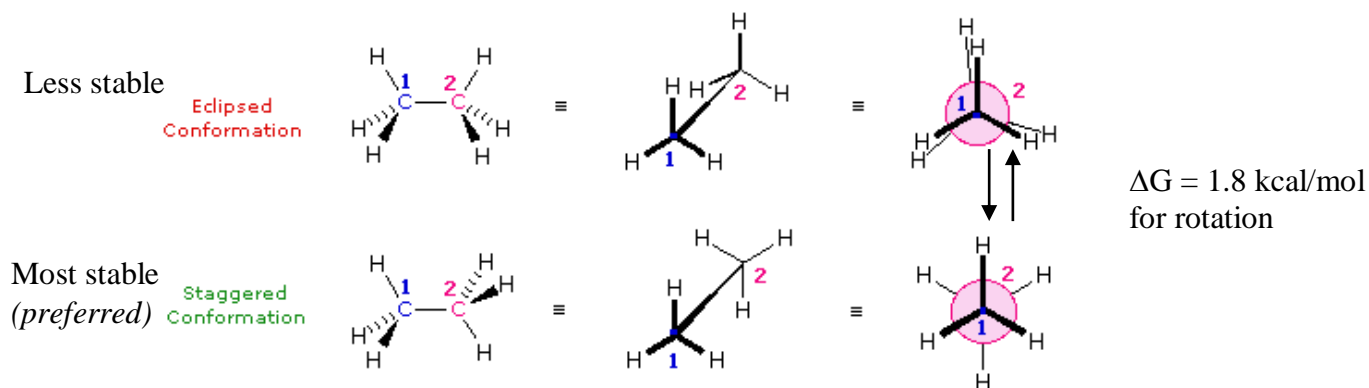
- Structural (Constitutional) Isomers
- Stereoisomers
 - Diastereomers
 - Enantiomers

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 (facile rotation), not observed with double or triple bonds.

A molecular conformation is any spatial arrangement of atoms that can be interconverted by rotation about single bonds of the molecule

Example: Ethane

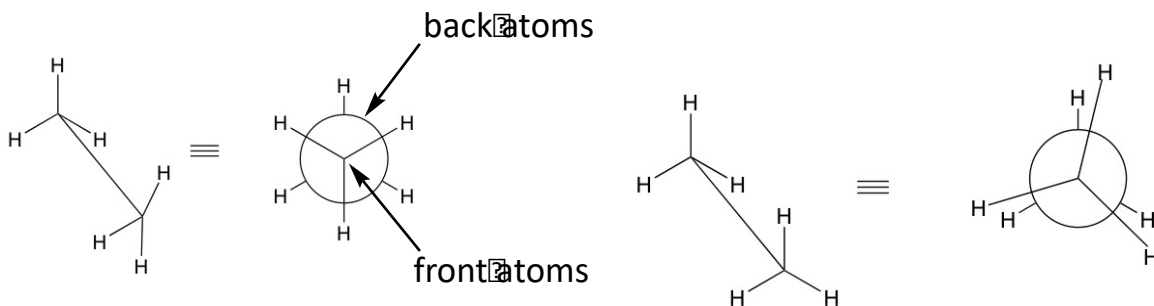
At room temperature (20 °C): 15-20 kcal/mol of energy available. This allows for rotation around C-C to occur rapidly at room temperature. – Important to know

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

Newman Projections

This is a conventional 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

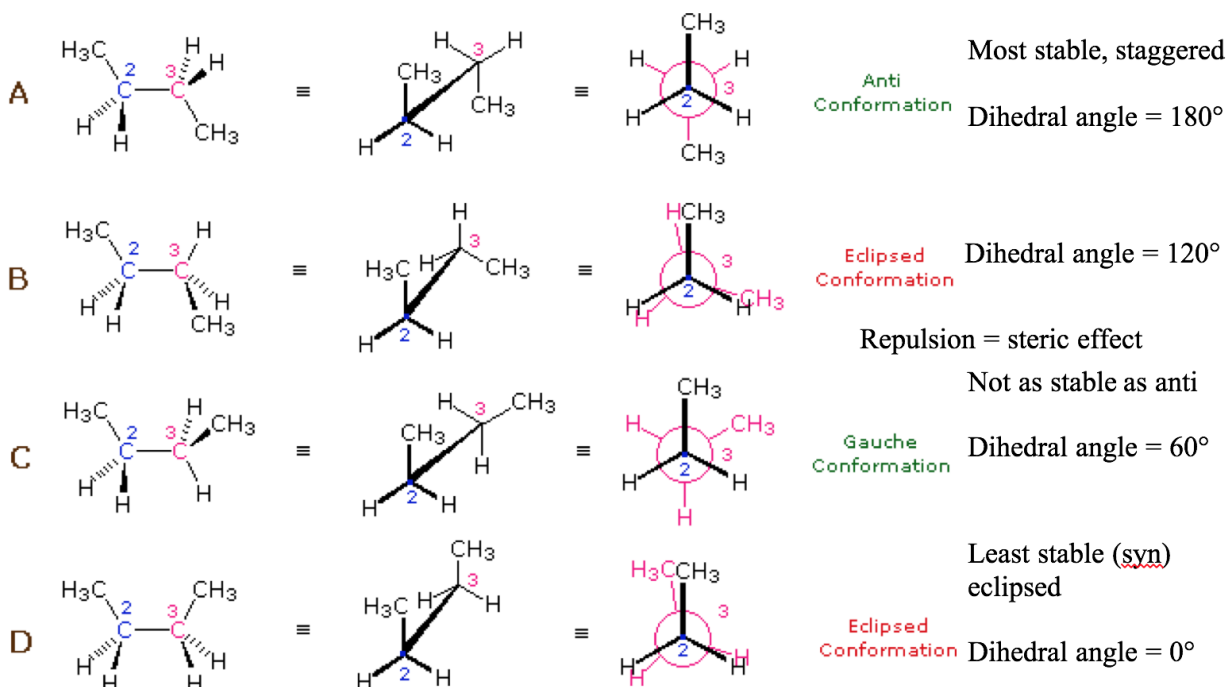
- Needs energy to go from one conformation to another
- Steric effect – repulsion between two filled shells of electrons
- Increased repulsion is observed as the H move closer in space. Staggered conformation has a lower energy than eclipsed conformation due to less steric repulsion between the H atoms.

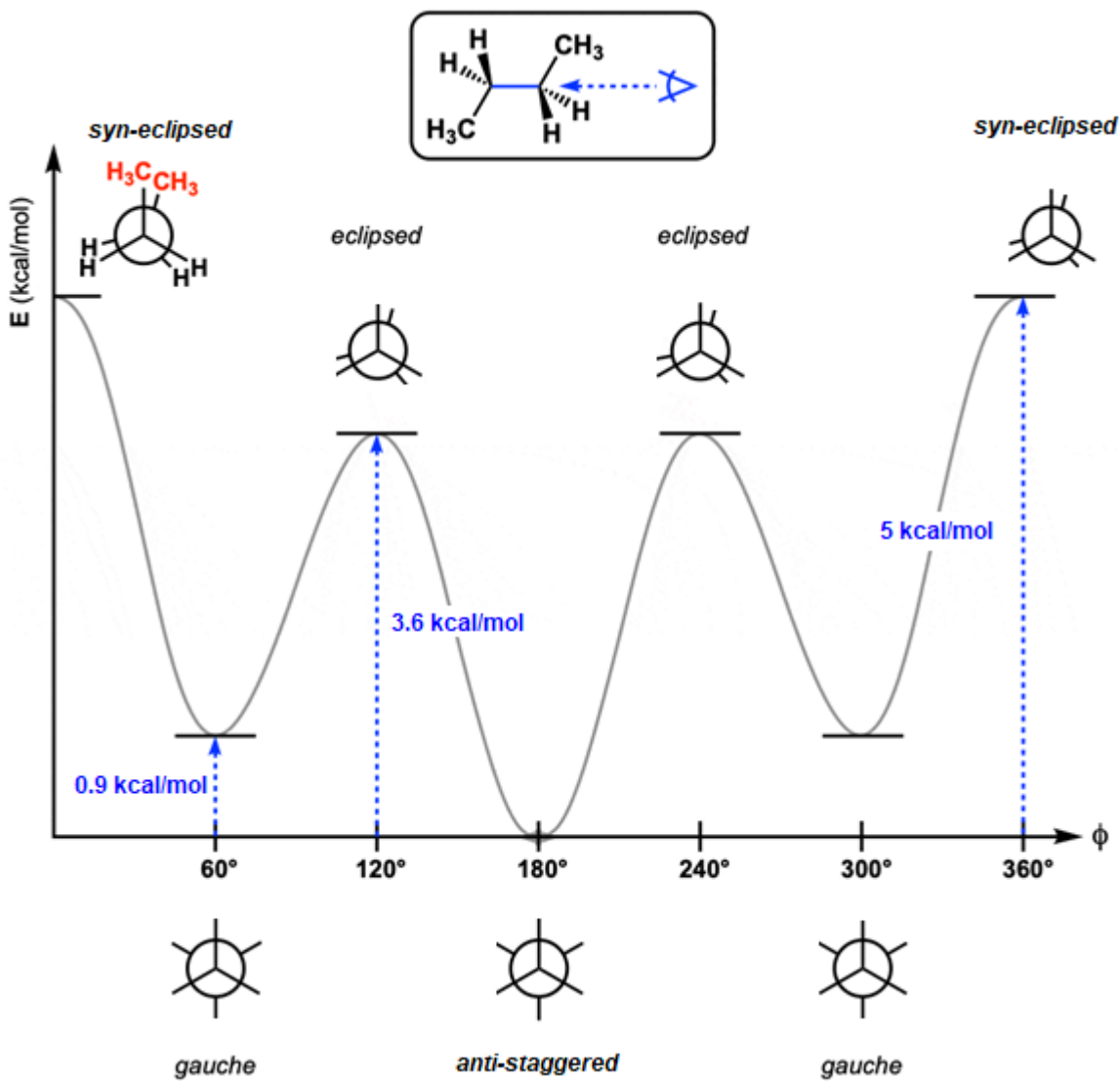
Example: n-butane (C_4H_{10})

Rotation around all bonds still very rapid.

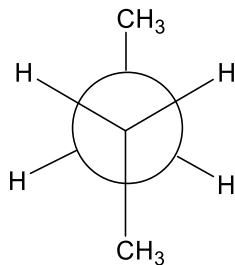
Most stable (most populated conformation) is called anti and has groups as far away as possible.

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

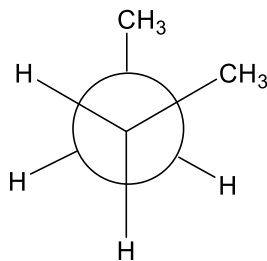


Butane Conformational Energy Diagram:Notes:

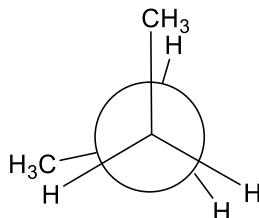
Anti Staggered – two large groups (i.e., CH_3) are as far away from each other as possible (180°) (lowest energy, favourable)



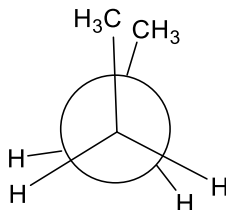
Staggered Gauche – two large groups are 60° relative to each other



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

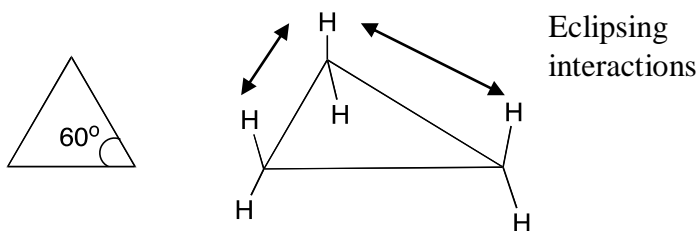


Syn Eclipsed – two large groups are as close together in space as possible. Two large groups are 0° relative to each other (**highest energy, unfavorable**). Significant steric repulsion.



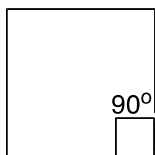
Cycloalkane Conformations:

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

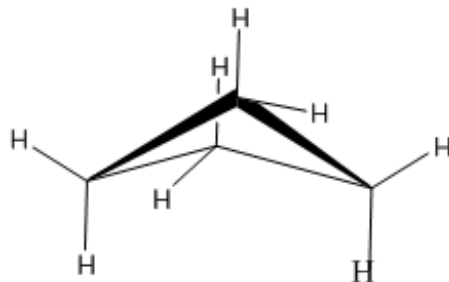


- High energy molecule due to the internal angle being 60° and the eclipsing interactions between the H.

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

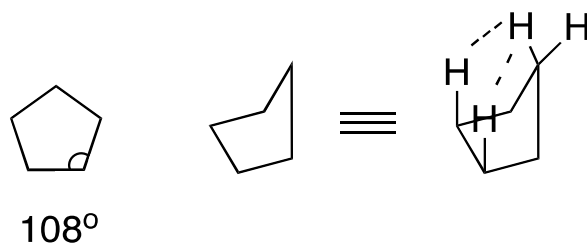


3D structure of cyclobutane:

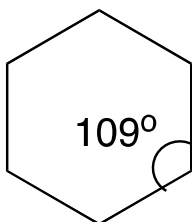


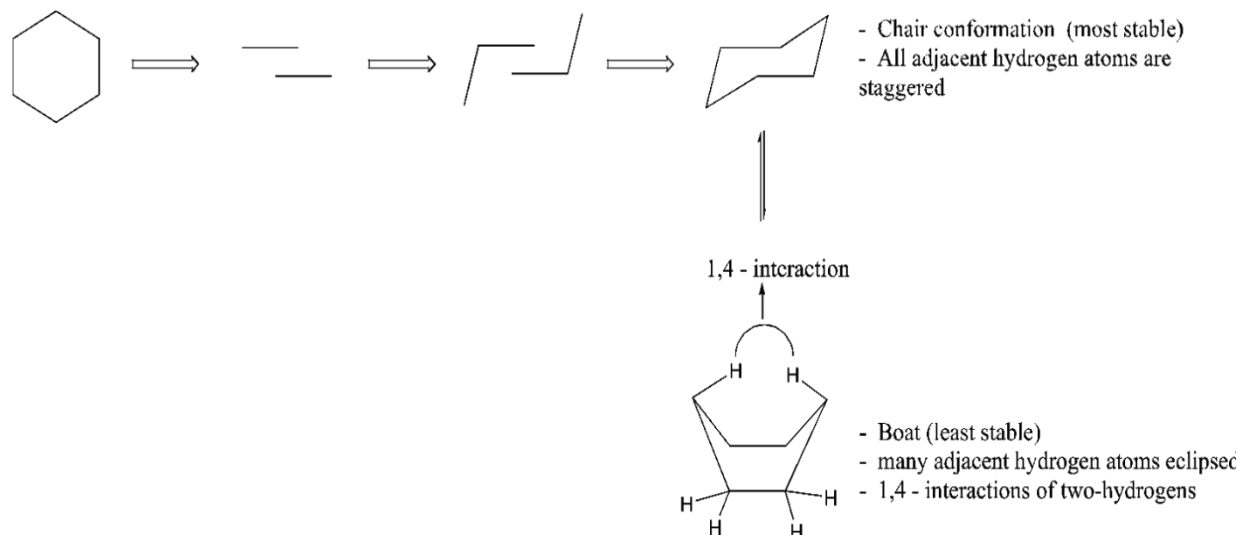
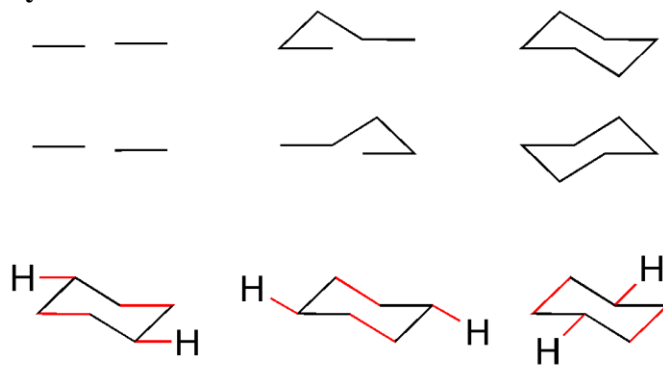
- Not completely flat and adopts an envelope / bent shape

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

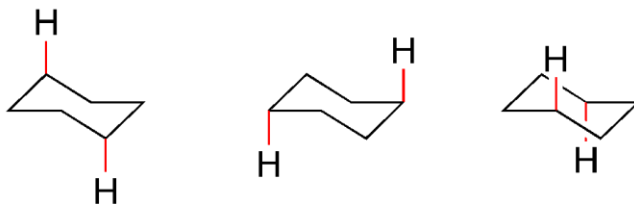


Cyclohexane – bond angles actually 109° , not 120° as in flat hexagon, due to the C being sp^3 hybridized



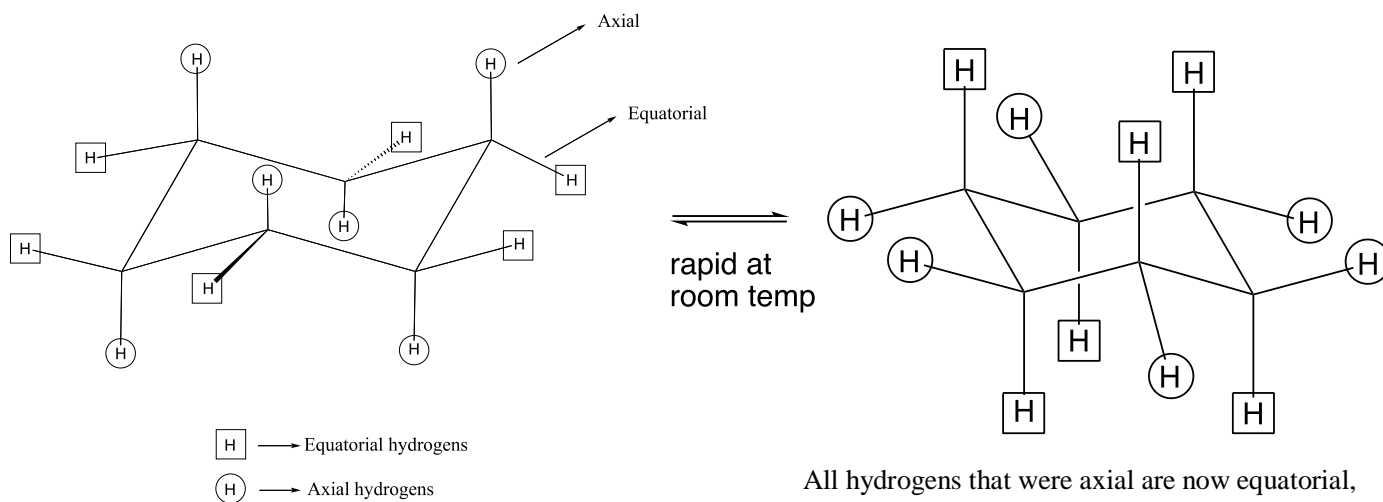
Cyclohexane Conformations – How to draw:**Another way to draw cyclohexane:**

Parallel Lines in Equatorial Position

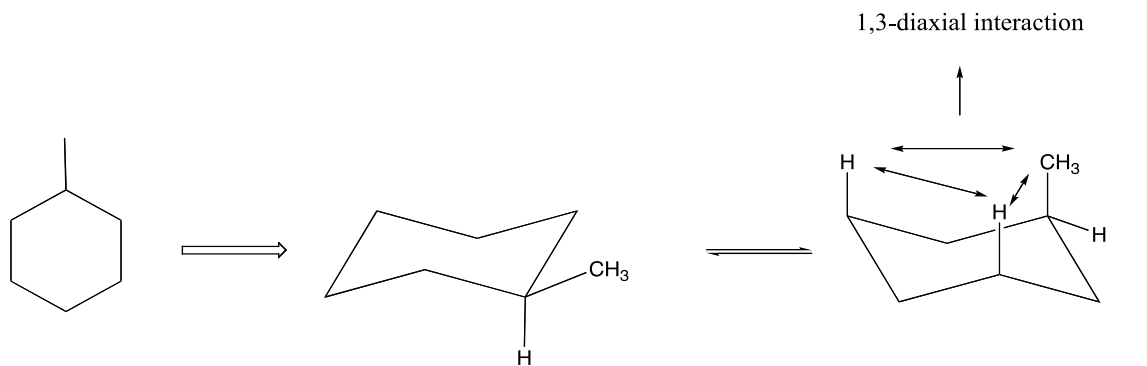


Vertical Lines in Axial Position

Cyclohexane Conformations Axial vs Equatorial Positions and Ring Flip

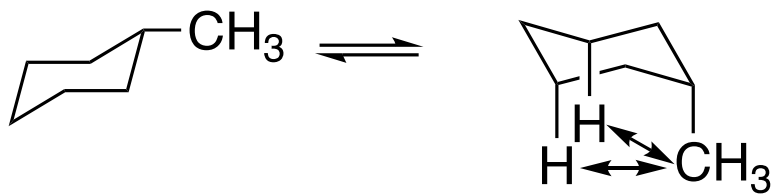


Substituted Cyclohexanes – Draw the most stable conformation



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

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



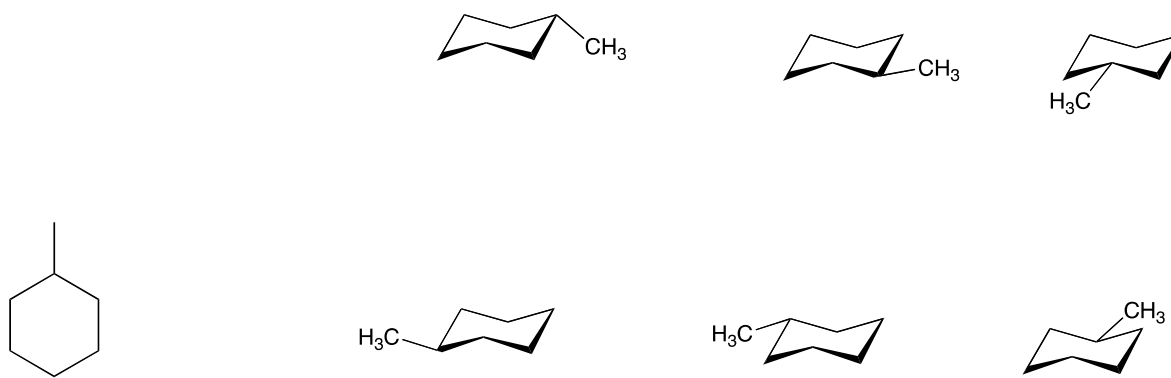
Equatorial methyl
interaction
More stable

Axial methyl interaction
Less stable

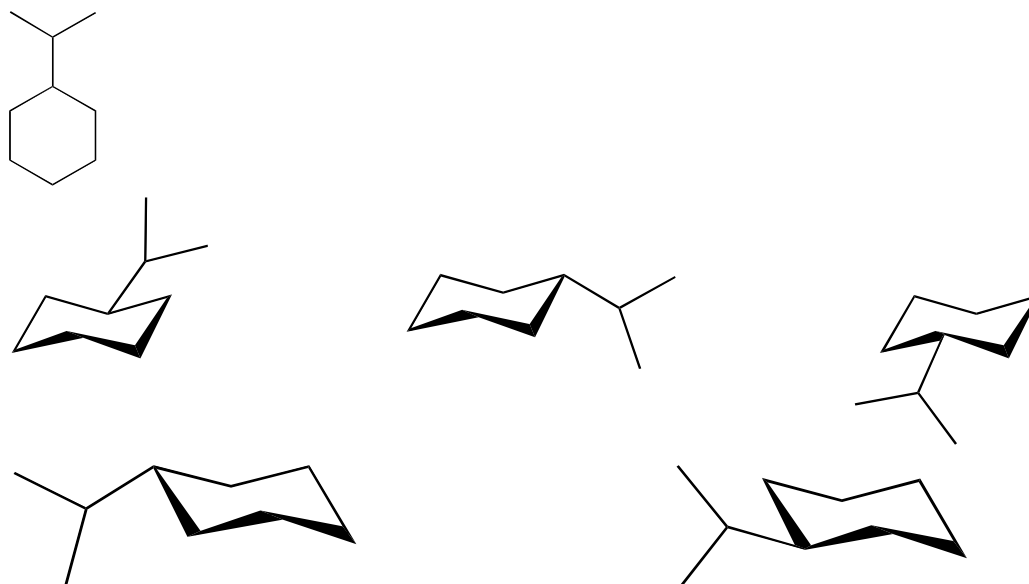
Examples of Most Stable Conformation of Substituted Cyclohexanes :

1. Methylcyclohexane

– 6 drawings of same molecule



2. Isopropylcyclohexane



For **most stable conformation**, **largest group** at **equatorial** position