

## RECALL:

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

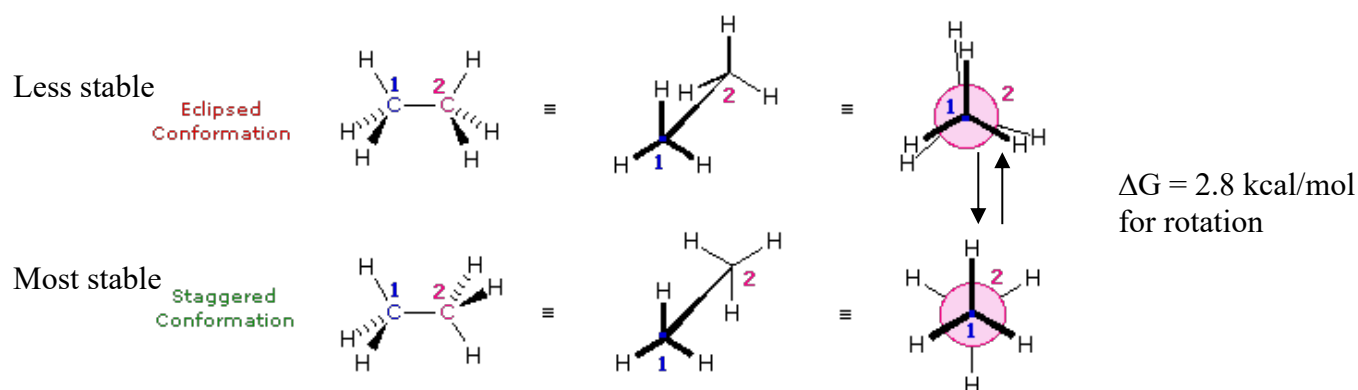
- Structural (Constitutional) Isomers
- Stereoisomers
  - Diastereomers
  - Enantiomers

## 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



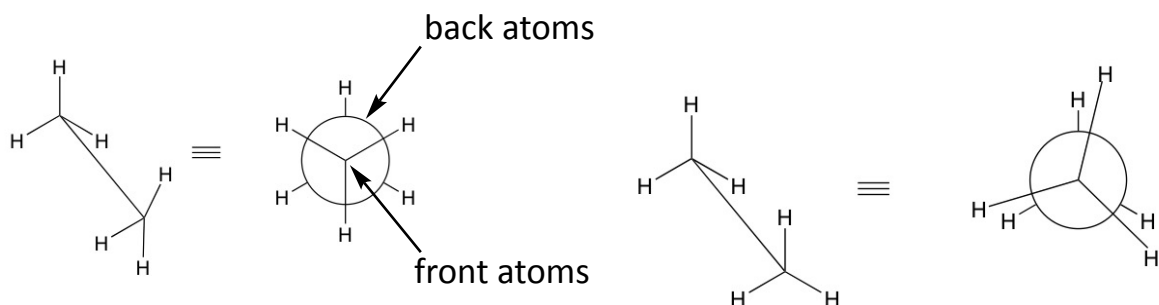
At room temperature (20 °C): 15-20 kcal/mol of energy available. This allows for rotation around C-C to occur rapidly at room temperature. – Important to know

There is a **Steric effect** between neighboring bonds to hydrogens: **Repulsion of filled shells of e<sup>-</sup>**

## 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

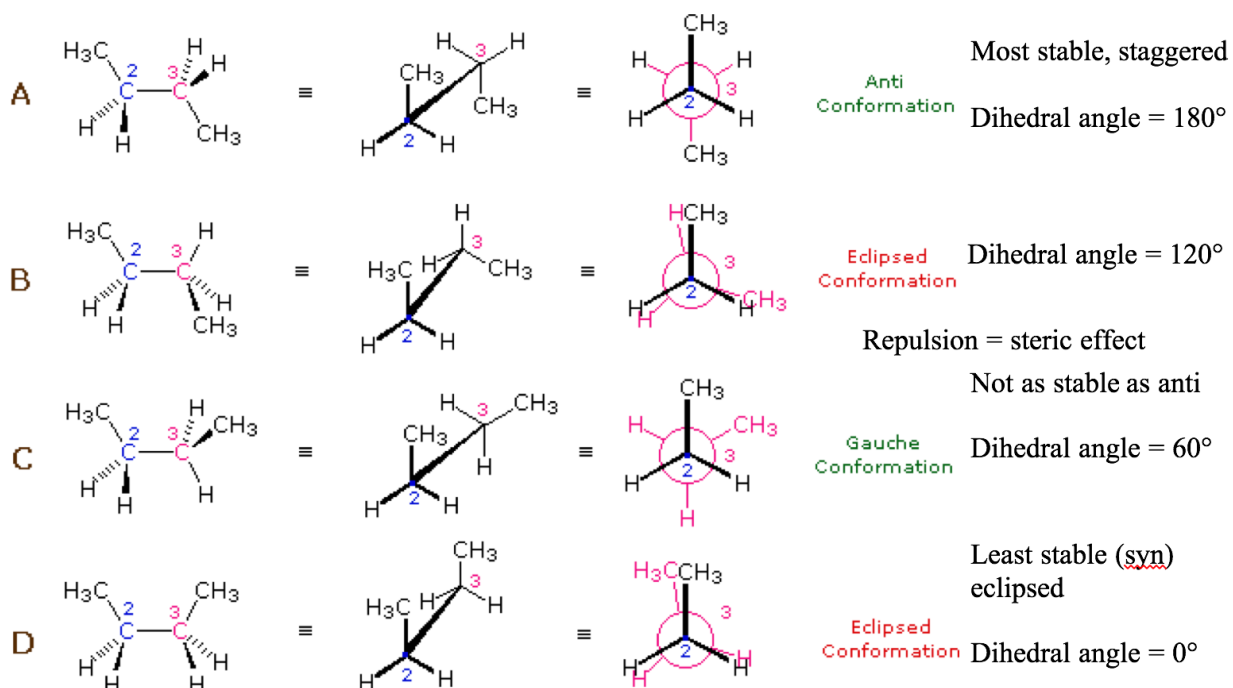
- Needs energy to go from one conformation to another
- Steric effect – repulsion between two filled shells of electrons
- Increased repulsion is observed as the H move closer in space. Staggered conformation has a lower energy than eclipsed conformation due to less steric repulsion between the H atoms.

**Example:** n-butane ( $C_4H_{10}$ )

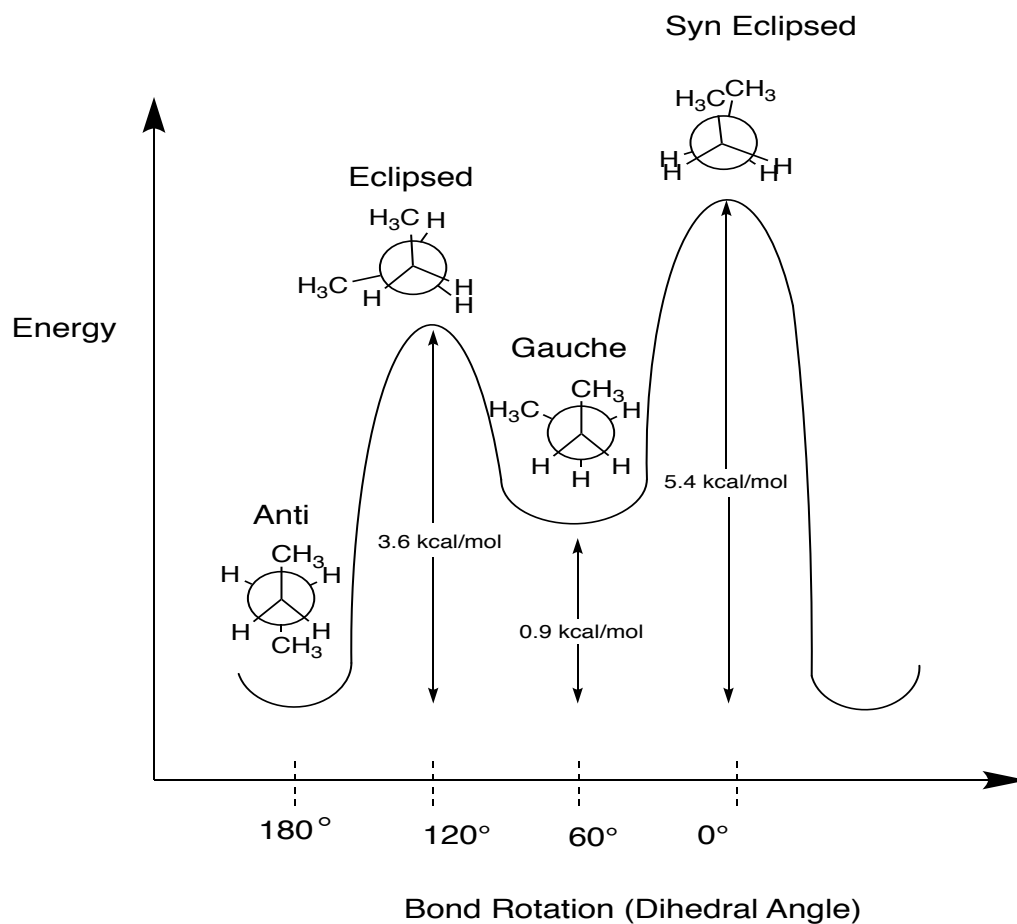
Rotation around all bonds still very rapid.

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

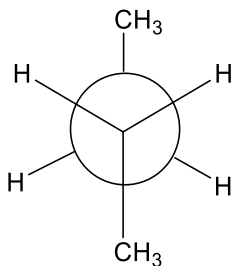


Butane Conformational Energy Diagram:

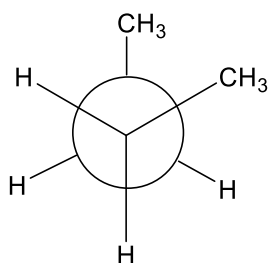


Notes:

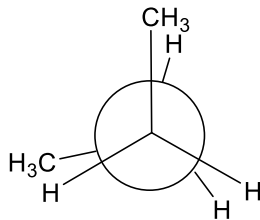
**Anti Staggered** – two large groups (i.e., CH<sub>3</sub>) are as far away from each other as possible (180°) (lowest energy, favourable)



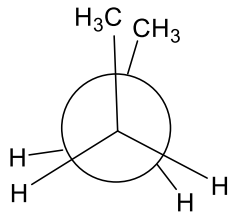
**Staggered Gauche** – two large groups are  $60^\circ$  relative to each other



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

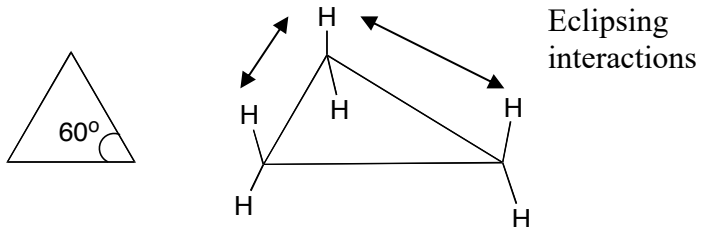


**Syn Eclipsed** – two large groups are as close together in space as possible. Two large groups are  $0^\circ$  relative to each other (**highest energy, unfavourable**)



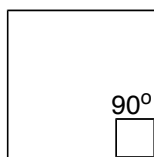
### **Cycloalkane Conformations:**

**Cyclopropane** – bond angle  $60^\circ$  – relatively rigid structure, very reactive

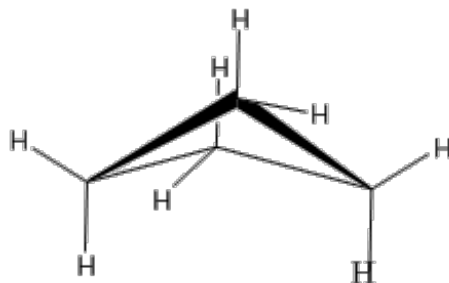


- High energy molecule due to the internal angle being  $60^\circ$  and the eclipsing interactions between the H.

**Cyclobutane** – bond angle close to  $90^\circ$  – does have some flexibility

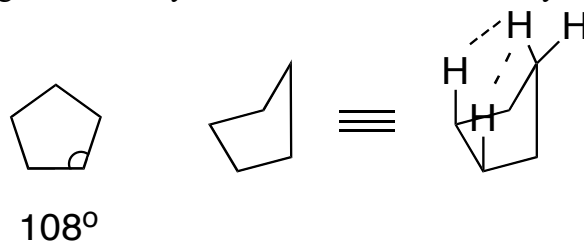


3D structure of cyclobutane:

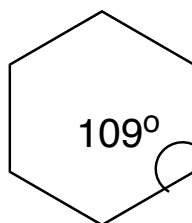


- Not completely flat and adopts a bent shape

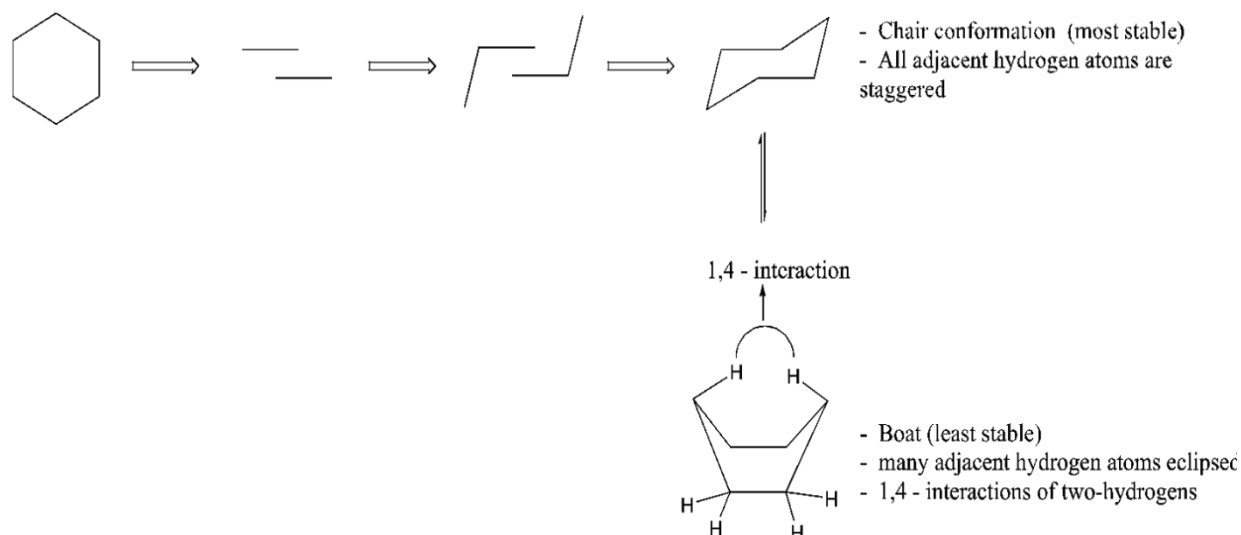
**Cyclopentane** – bond angles nominally  $108^\circ$  – more flexible than cyclobutane



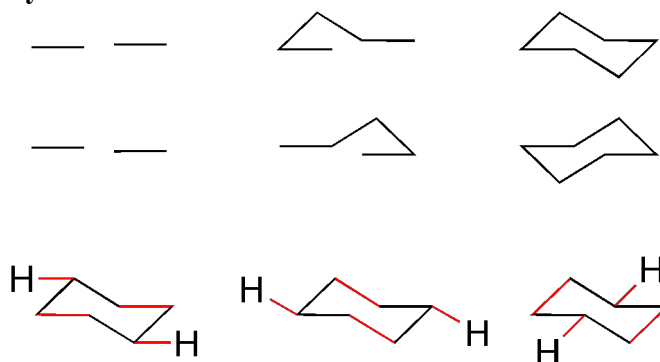
**Cyclohexane** – bond angles actually  $109^\circ$ , not  $120^\circ$  as in flat hexagon, due to the C being  $sp^3$  hybridized



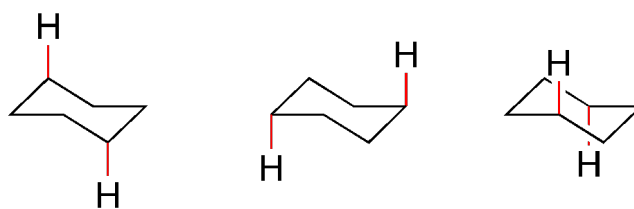
## Cyclohexane Conformations – How to draw:



## Another way to draw cyclohexane:

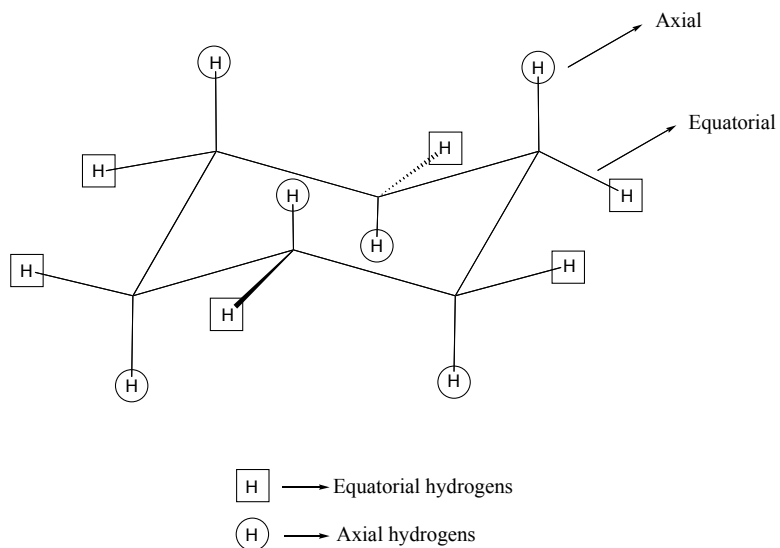


Parallel Lines in Equatorial Position

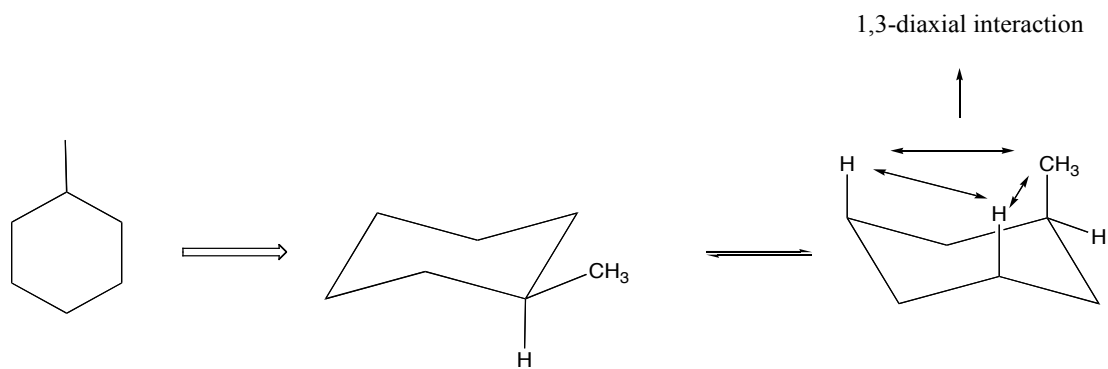


Vertical Lines in Axial Position

## Cyclohexane Conformations Axial vs Equatorial Positions

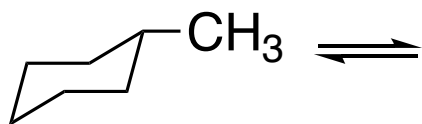


## Substituted Cyclohexanes – Draw the most stable conformation

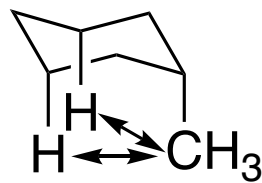


- Largest (bulkiest group close to ring) group placed equatorial – otherwise get unfavorable 1,3-diaxial interactions

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



Equatorial methyl  
interaction  
More stable

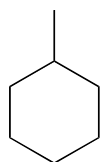
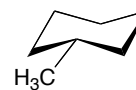


Axial methyl interaction  
Less stable

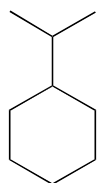
### Examples of Most Stable Conformation of Substituted Cyclohexanes :

#### 1. Methylcyclohexane

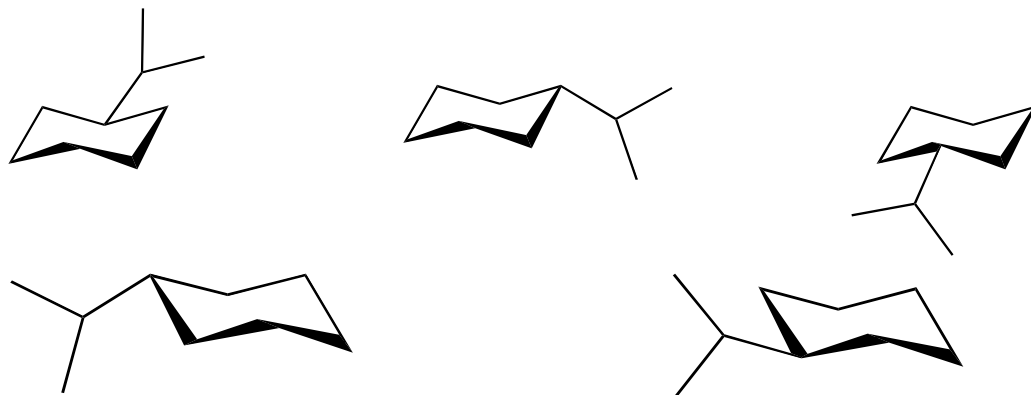
– 6 drawings of same molecule



#### 2. Isopropylcyclohexane





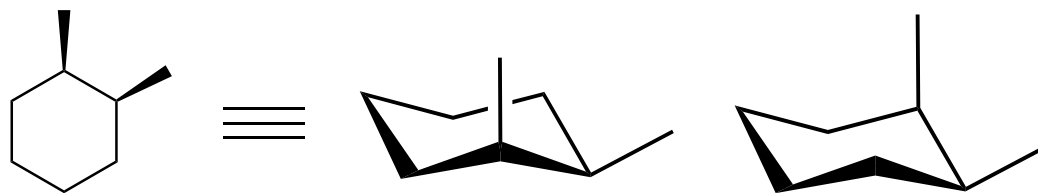


NB: For most stable conformation, largest group at equatorial position

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

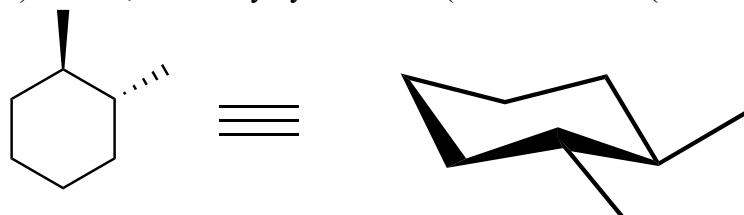
#### Examples:

1) cis-1,2-dimethylcyclohexane



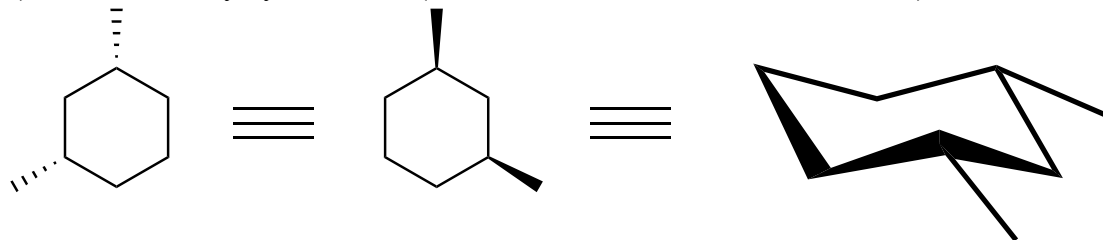
- One methyl group axial and one methyl group equatorial

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



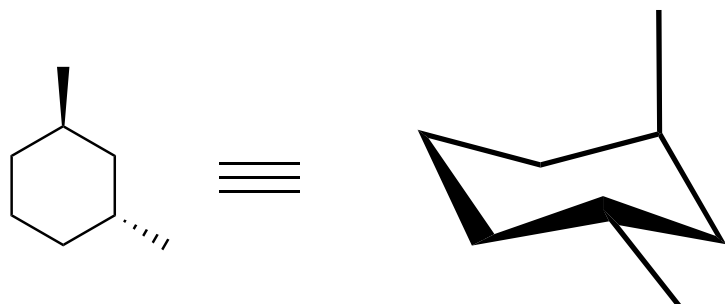
- Both methyl groups equatorial

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



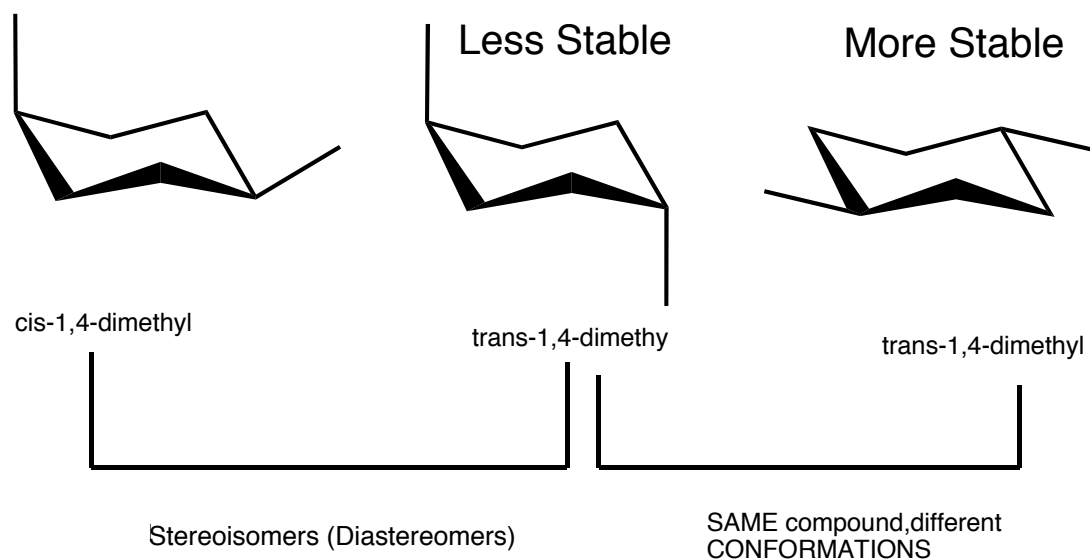
- Both methyl groups equatorial

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

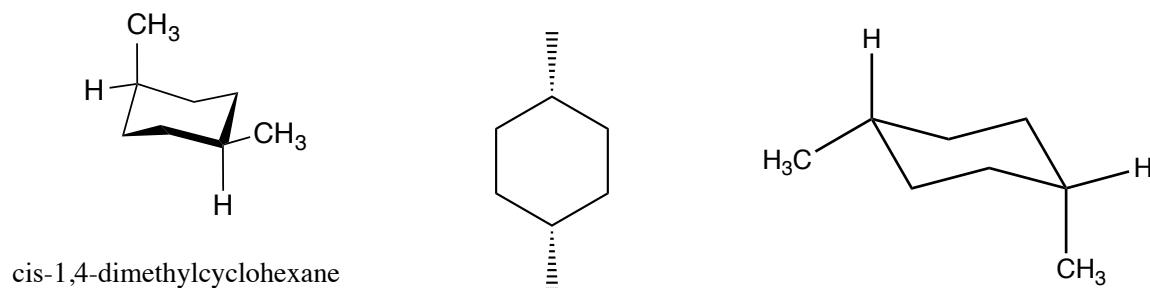


- One methyl group axial and one methyl group equatorial

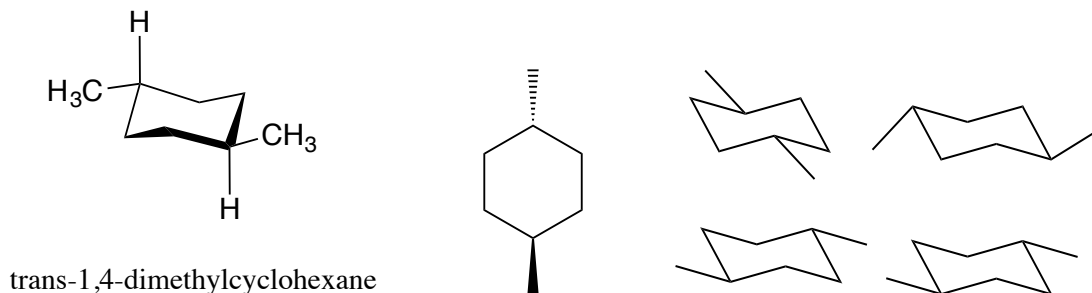
5) cis-1,4-dimethylcyclohexane and trans-1,4-dimethylcyclohexane:



6) cis-1,4-dimethylcyclohexane:

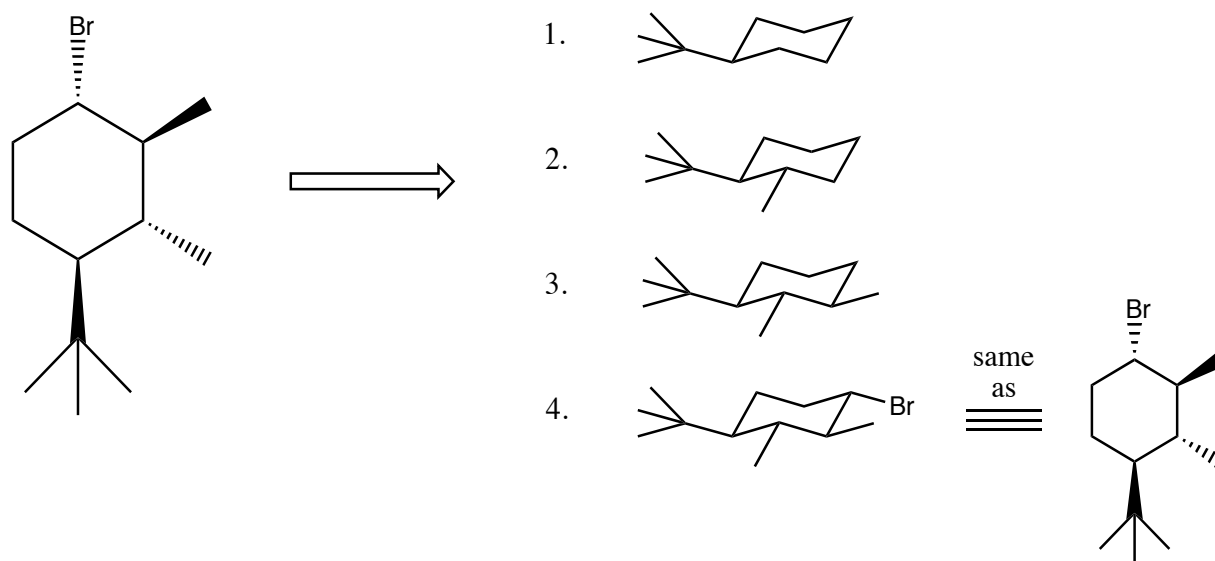


7) trans-1,4-dimethylcyclohexane:



**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:

