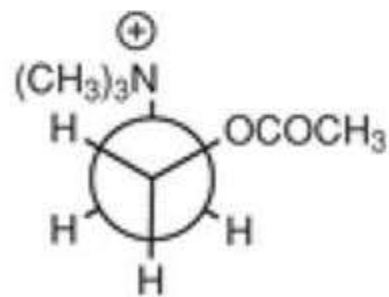
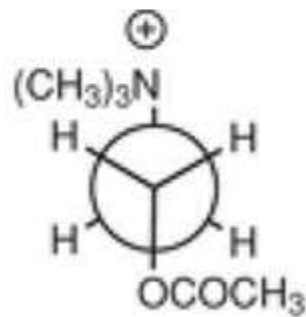


# CONFORMATIONAL ISOMERS



Synclinal



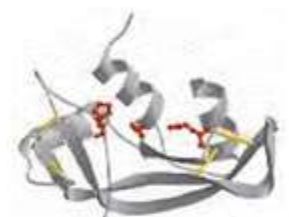
Antiperiplanar



Cytochrome c



Lysozyme



Ribonuclease

Amit Chaudhari

# CONFORMATION

## CONFORMATIONAL ISOMERS

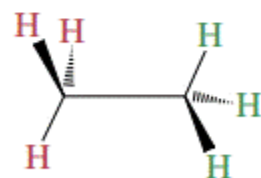
↷ Conformations are different spatial arrangements of a molecule that are generated by rotation about single bonds.

[sun14, sun12, sun 10] [win14]

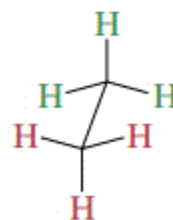
- Different conformations of the same molecule are sometimes called *conformers* or *rotamers* or *conformational isomers*.



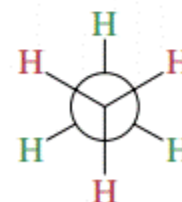
Ethane



Wedge-and-dash



Sawhorse



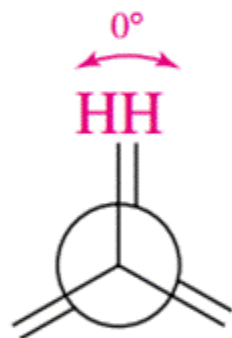
Newman  
projection

representations  
of conformation

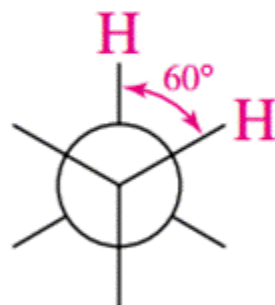
# CONFORMATION

## TORSION ANGLE OR DIHEDRAL ANGLE

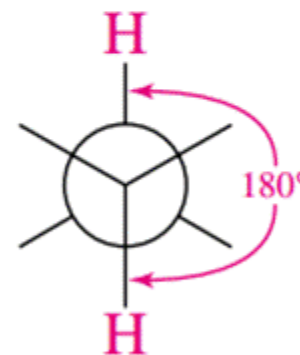
- angle between the H-C-C *plane* and the C-C-H *plane*. The torsion angle is easily seen in a Newman projection of ethane



Torsion angle = 0°  
Eclipsed



Torsion angle = 60°  
Gauche

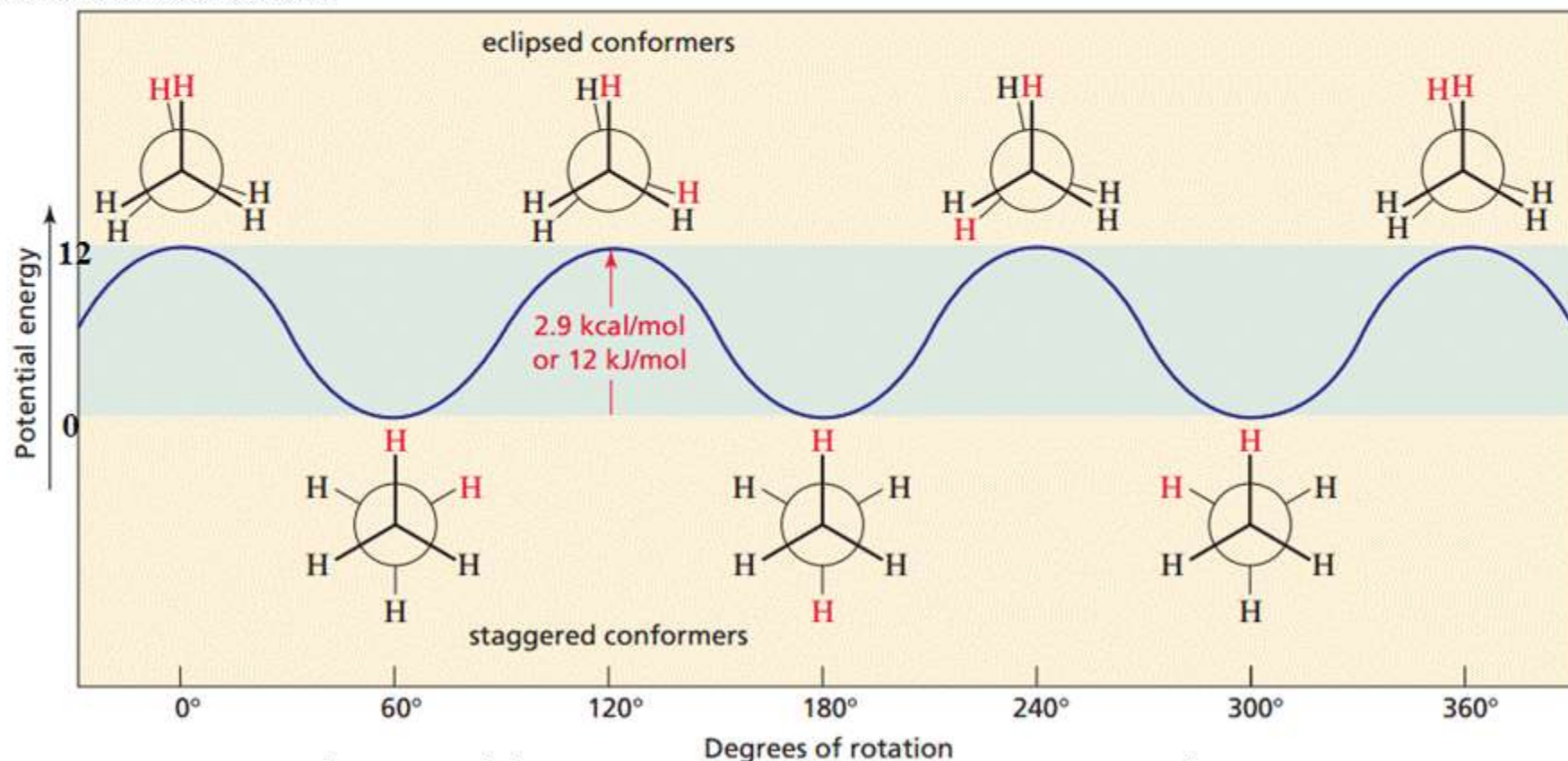


Torsion angle = 180°  
Anti

# CONFORMATION

## CONFORMATIONS OF ETHANE

-Ethane has two conformations called the staggered and eclipsed conformations.



# CONFORMATION

## CONFORMATIONS OF ETHANE

**why is the eclipsed conformation higher in energy than the staggered conformation?**

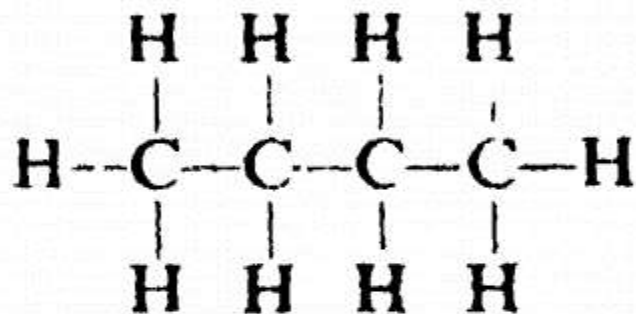
[sum15] [win13, win11]

- there is some steric repulsion between the hydrogen atoms in the eclipsed conformation that is reduced in the staggered conformation.
- in eclipsed conformation the electron cloud of C-H bonds are most nearer and thus their repulsion increases.
- These repulsive forces creates torsional strain in molecule
- the more strain, the more will be internal energy of conformer

# CONFORMATION

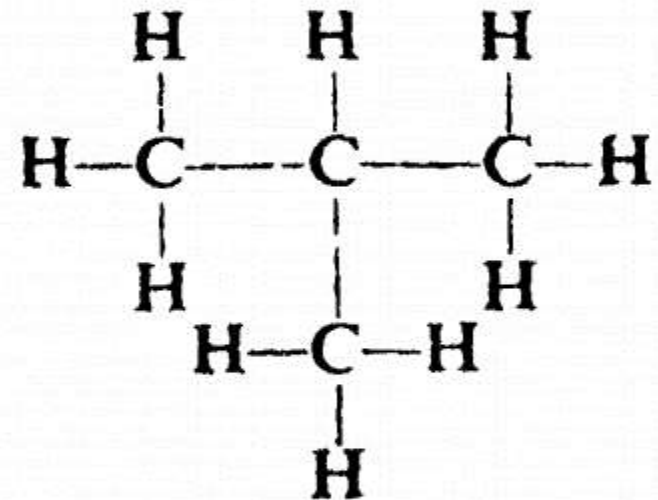
## CONFORMATIONAL ANALYSIS OF *n*-BUTANE

[sun14, sun 10] [win14]



II

*n*-Butane



III

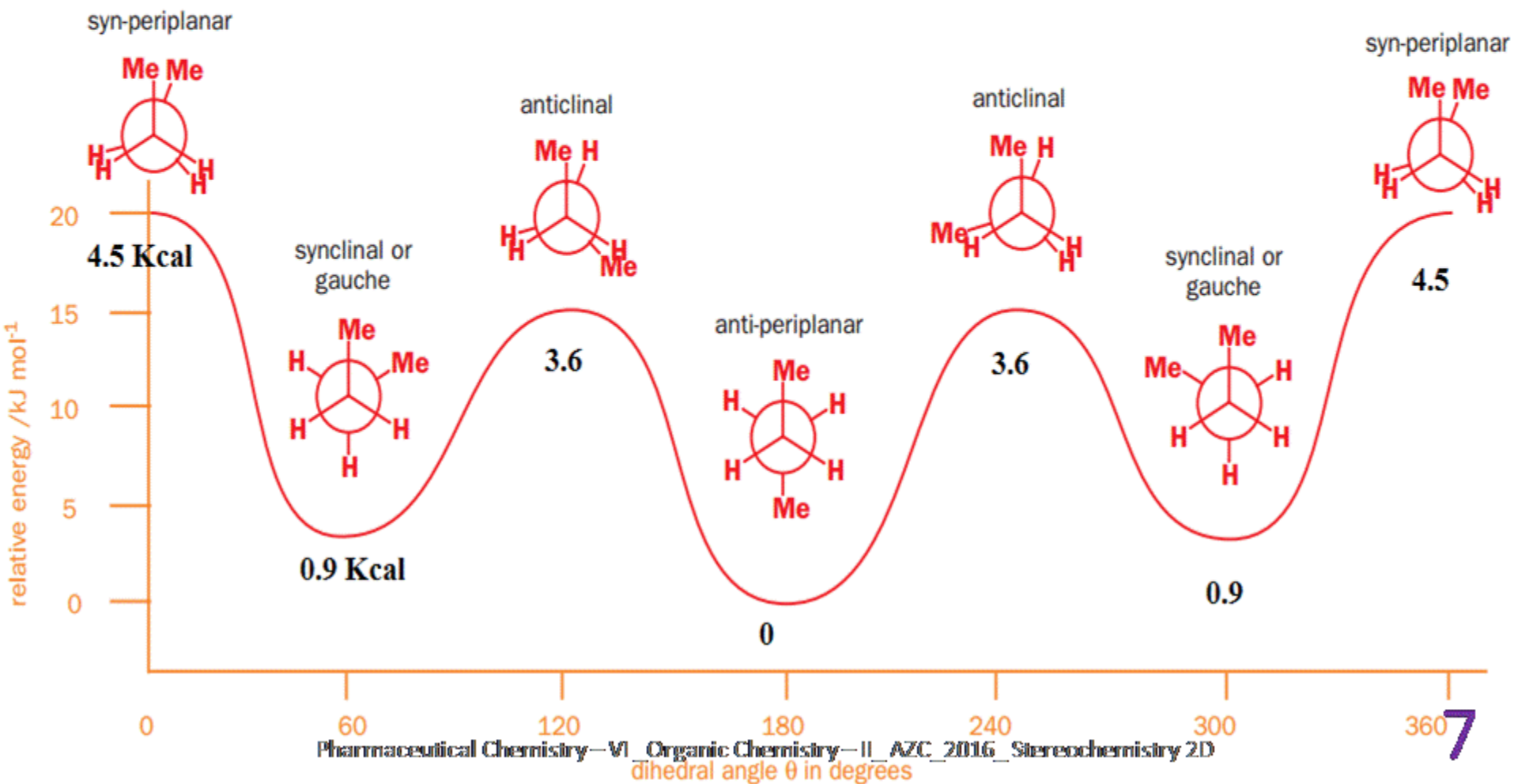
Isobutane



# CONFORMATION

## CONFORMATIONAL ANALYSIS OF n-BUTANE

- Various conformational isomers with their internal energy are shown as bellow



# CONFORMATION

## CONFORMATIONAL ANALYSIS OF n-BUTANE

### *Eclipsed conformation*

- syn-periplanar conformer - dihedral angle is  $0^\circ$  and  $360^\circ$ 
  - max. energy
- Anticlinal conformer - dihedral angle is  $120^\circ$  and  $240^\circ$ 
  - energy is lower but not least

### *Staggered conformation*

- synclinal (gauche) conformer - dihedral angle is  $60^\circ$  and  $300^\circ$ 
  - Energy is 0.9 Kcal
- anti- periplanar conformer - dihedral angle is  $180^\circ$ 
  - have least internal energy than others



# CONFORMATION

## CONFORMATIONAL ANALYSIS OF n-BUTANE

Energy difference (stability and potential energy changes) in conformers is due to ,

- Steric repulsion observed in diff. conformers

E.g.

- In syn-periplanar conformer on n-butane -- methyl groups are most nearer to each other, cause steric repulsion and reach to most highest energy state of 4.5 Kcal

- In anticlinal conformer – cause steric repulsion btwn methyl group and H atom

- In **anti-periplanar** conformer all atoms are far apart especially methyl groups, cause least steric repulsion and reach to most lowest energy state i.e. *most stable conformer of n-butane*

# CONFORMATION

## CONFORMATIONAL ANALYSIS OF n-BUTANE

GTU Q- What are the different possible conformations of 1,2-dibromoethane? Which one is more stable? Why? [sum12]

Answer ?

# CONFORMATION

## CONFORMATIONAL ANALYSIS OF n-BUTANE

GTU Q- What are the different possible conformations of 1,2-dibromoethane? Which one is more stable? Why? [sum12]

- In n-butane conformers remove  $-CH_3$  and put  $-Br$
- Forgot the exact value of energy
- The relative energy of conformers remains same

# CONFORMATION

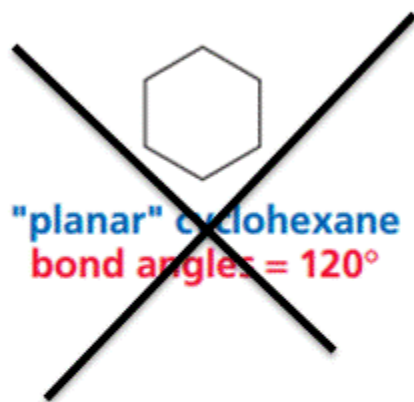
## CYCLOHEXANE

[sun15, sun15, sun13]

- Draw a structure of cyclohexane .....

# CONFORMATION

## CYCLOHEXANE

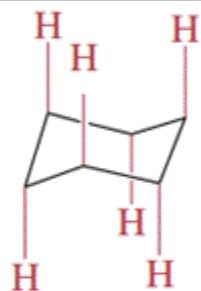
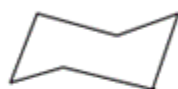


- All C are  $sp^3$  hybridized thus all bonds must create 109° bond angles.
- This leads to 2 types of conformation in 3D – Boat shape and chair shape

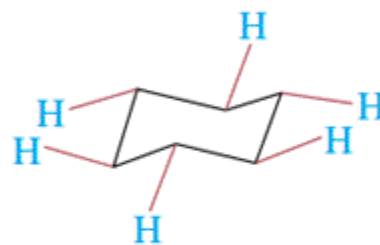
# CONFORMATION

## CYCLOHEXANE

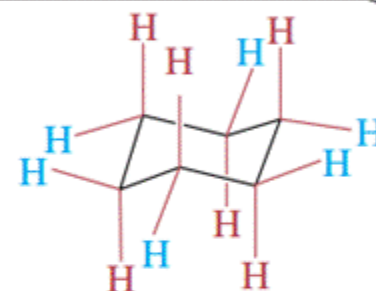
### ❖ Chair conformation



Axial C—H bonds



Equatorial C—H bonds



Axial and equatorial bonds together

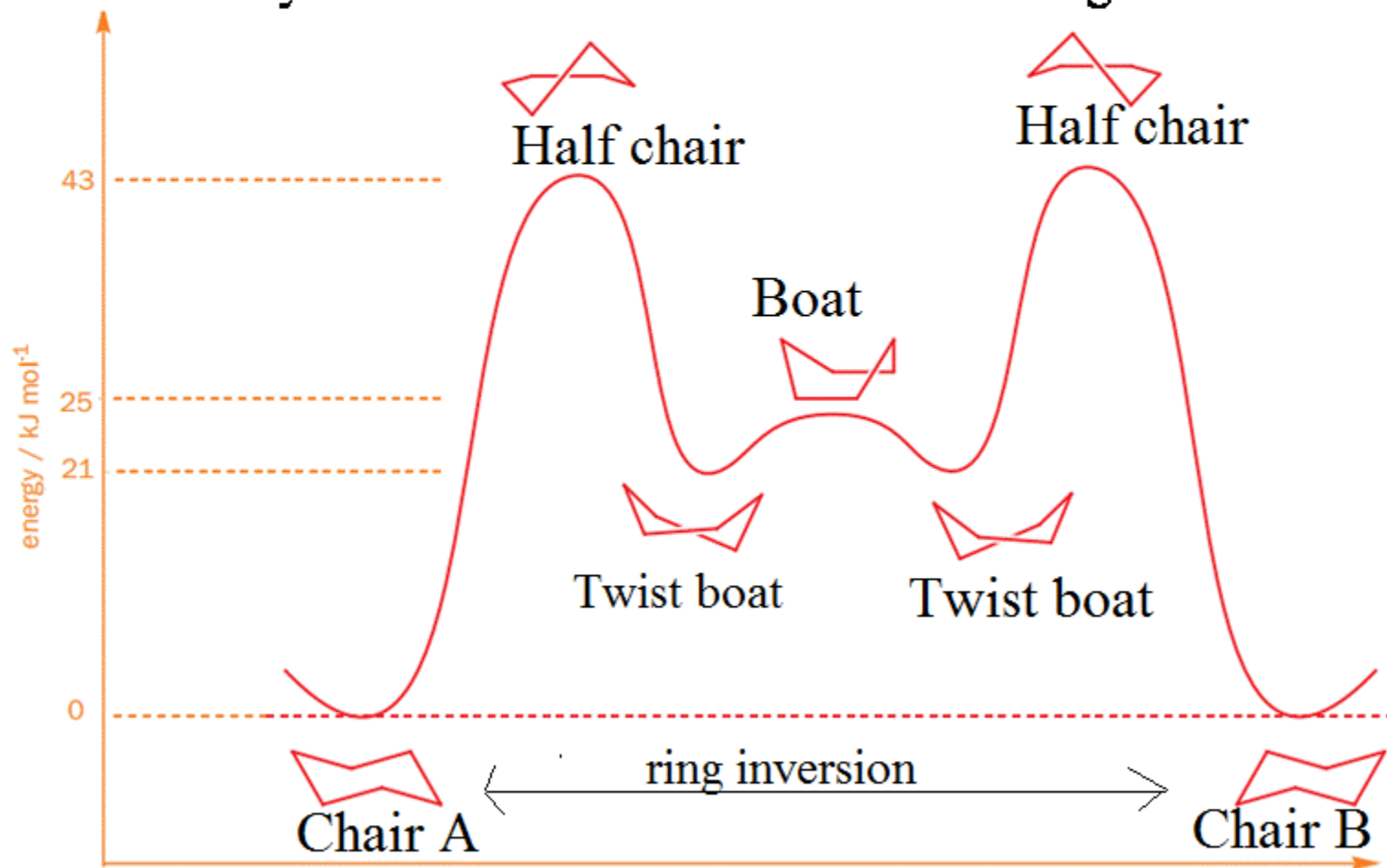
Axial And Equatorial Bonds In Cyclohexane

# CONFORMATION

## CONFORMATIONAL ANALYSIS OF CYCLOHEXANE

[sun15, sun15, sun13]

- Relative stability of conformers is as shown in diagram





# CONFORMATION

## CONFORMATIONAL ANALYSIS OF CYCLOHEXANE

### Conformers and their internal energy

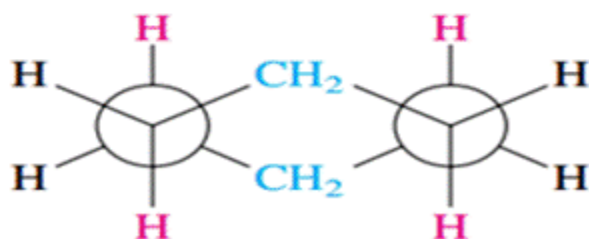
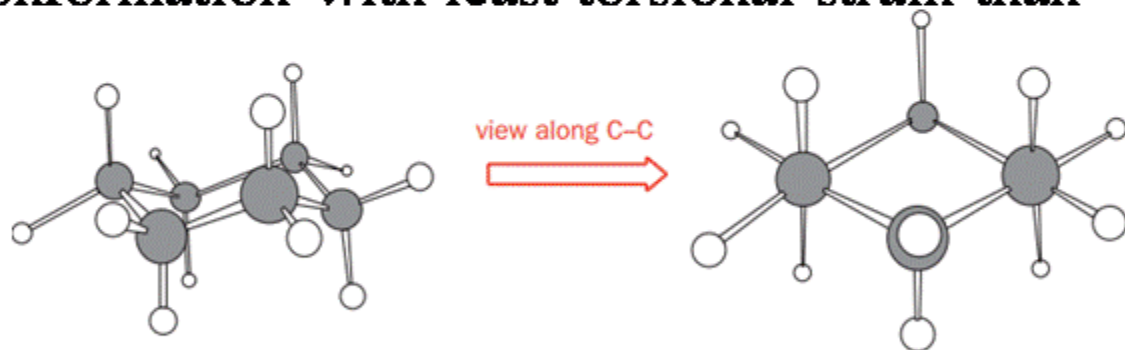
- Chair - nearly zero , most stable
  - Boat - 25KJ/mol
  - Half chair - 43 KJ/mol
  - Twist boat - 21 KJ/mol
- Boat form can be obtained from chair conformer by bending the bonds.
- During transformation two other forms arise i.e. half chair and twist boat.
- Chair A to Chair B conversion is called as ring inversion or ring flipping

# CONFORMATION

## CONFORMATIONAL ANALYSIS OF CYCLOHEXANE

Chair form is most stable form

- Bc all bonds forms tetrahedron bond angle of  $109^\circ$
- It adopts staggered arrangement
- All this makes chair conformation with least torsional strain than other isomers



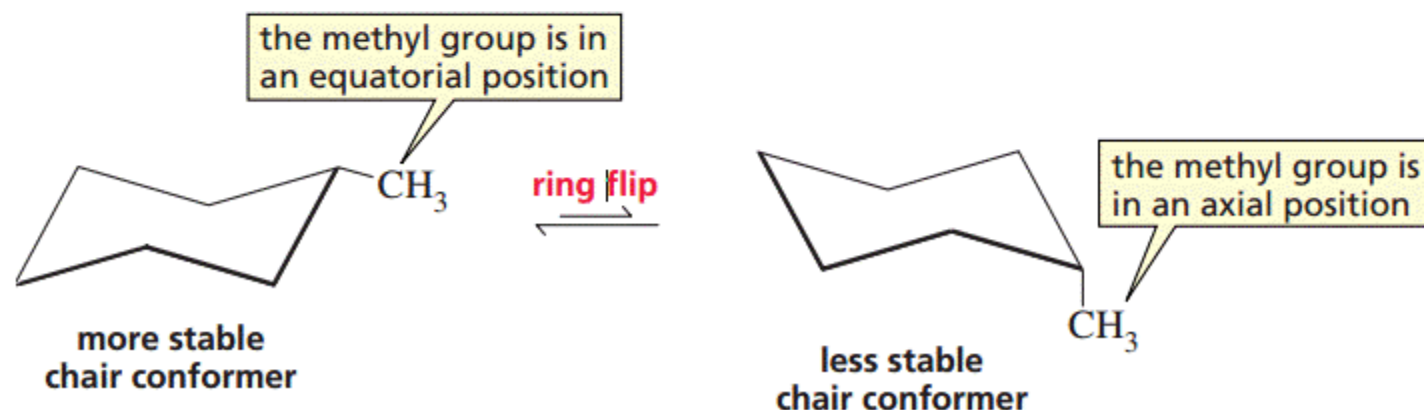
Staggered arrangement of bonds in chair conformer

# CONFORMATION

## CONFORMATIONAL ANALYSIS OF METHYL CYCLOHEXANE

[Sum 11]

- It is monosubstituted cyclohexane
- Cyclohexane has two equivalent chair conformers (Chair A and Chair B)
- the two chair conformers of a monosubstituted cyclohexane such as methylcyclohexane are not equivalent.
- The methyl substituent is in an equatorial position in one conformer and in an axial position in the other.



# CONFORMATION

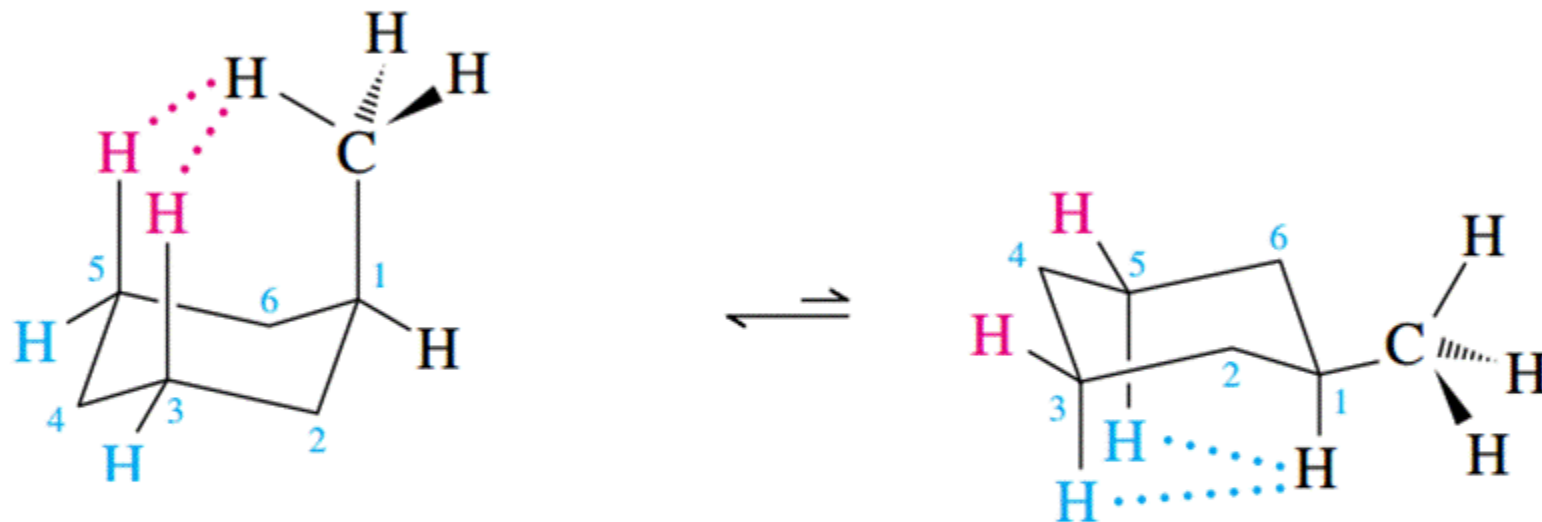
## CONFORMATIONAL ANALYSIS OF METHYL CYCLOHEXANE

The chair conformer with the methyl substituent in an equatorial position is the more stable conformer

- because a substituent has more space (are less hindered) and, therefore, fewer steric interactions when it is in an **equatorial position**.
- In contrast, when the methyl group is in an **axial position**, there are unfavorable steric interactions between the axial methyl group and both the axial substituent on C-3 and the axial substituent on C-5 (in this case, hydrogens).

# CONFORMATION

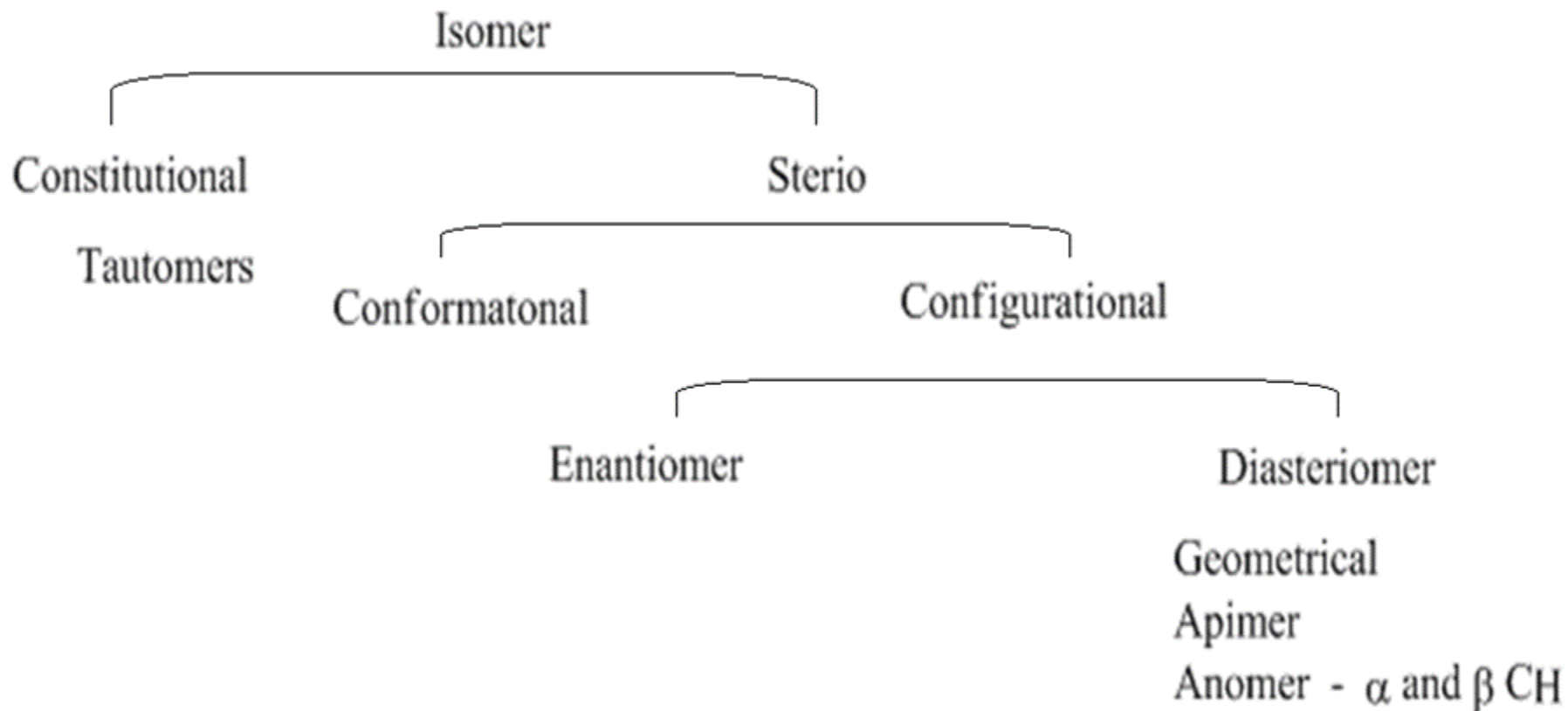
## CONFORMATIONAL ANALYSIS OF METHYL CYCLOHEXANE



1,3-diaxial interactions

- Because the interacting substituents are on 1,3-positions relative to each other, these unfavorable steric interactions are called 1,3-diaxial interactions.

# Class of isomers



# End of topic

## Reference:

Organic Chemistry– Morrison & boyd

Organic Chemistry – P.L. Sony

Organic Chemistry – Bahl & Bahl

Organic Chemistry - Clayden

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