Conformations

Course Name: General Chemistry
Course Code: CHEM F111
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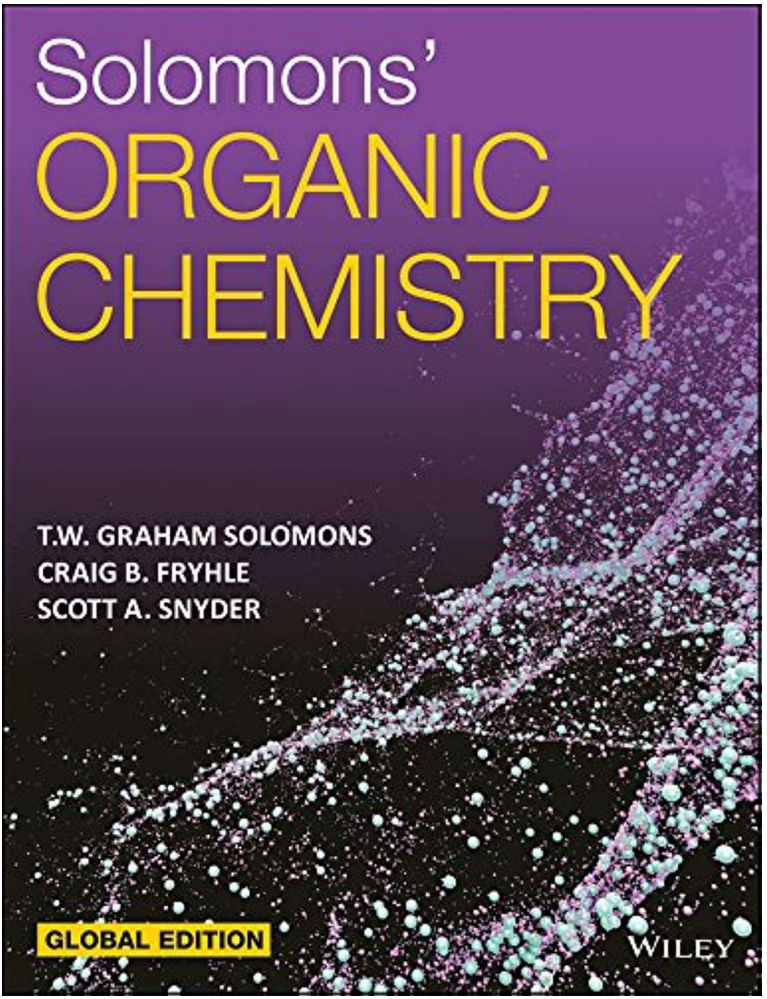
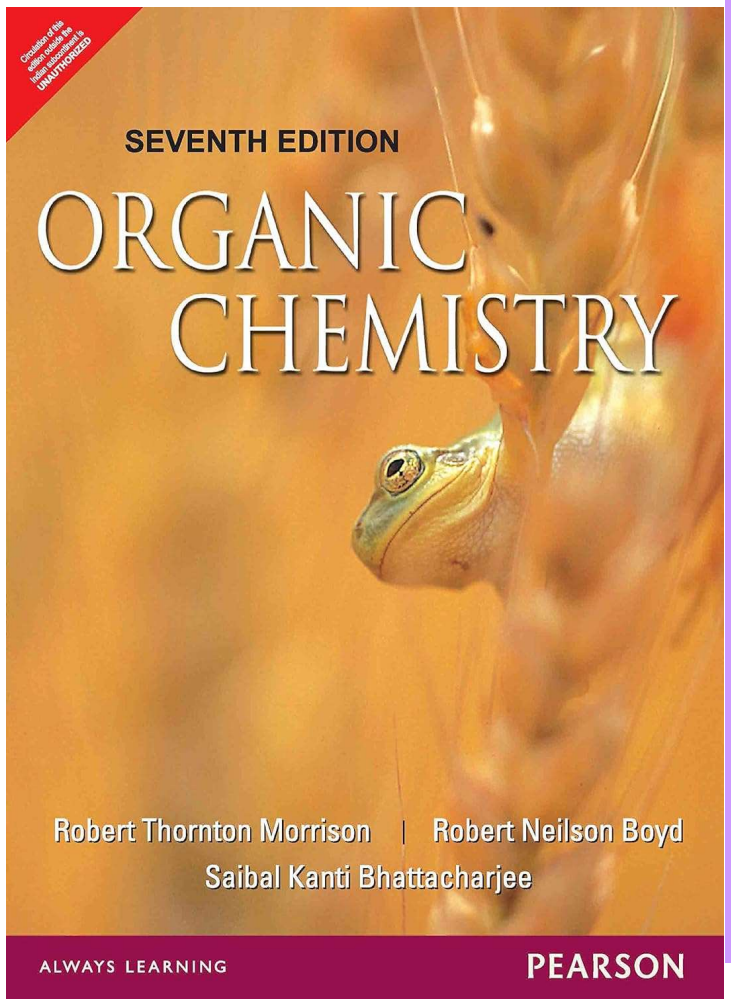
Chamber No: C 223
Chamber Consultation Hours: Thursday 4:00 PM to 4:50 PM

Text and Reference Books

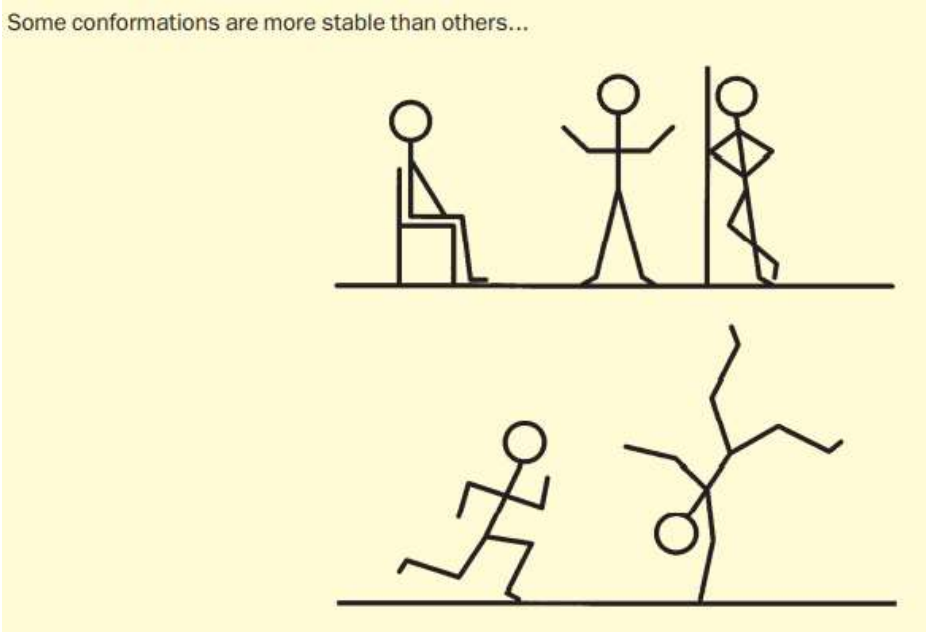




<u>Acknowledgement</u>: Most of the Lecture Slides are made from the text book. I am gratefully acknowledging Solomon's Organic Chemistry Book and many other Organic Chemistry Books.

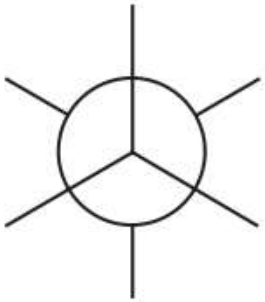
Conformations

Contents



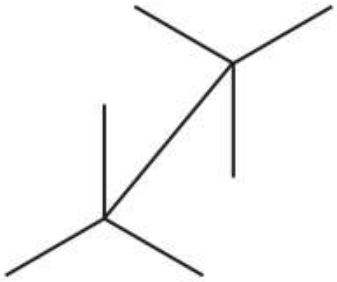
4.8 Sigma Bonds and Bond Rotation

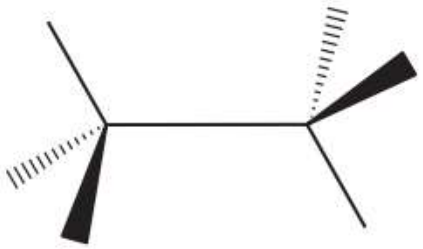
- Two groups bonded by only a single bond can undergo rotation about that bond with respect to each other.
- The *temporary molecular shapes* that result from such a rotation are called **conformations** of the molecule.
- Each possible structure is called a **conformer**.
- An analysis of the energy changes that occur as a molecule undergoes rotations about single bonds is called a **conformational analysis**.



American chemist Melvin Spencer Newman

Newman projection formula

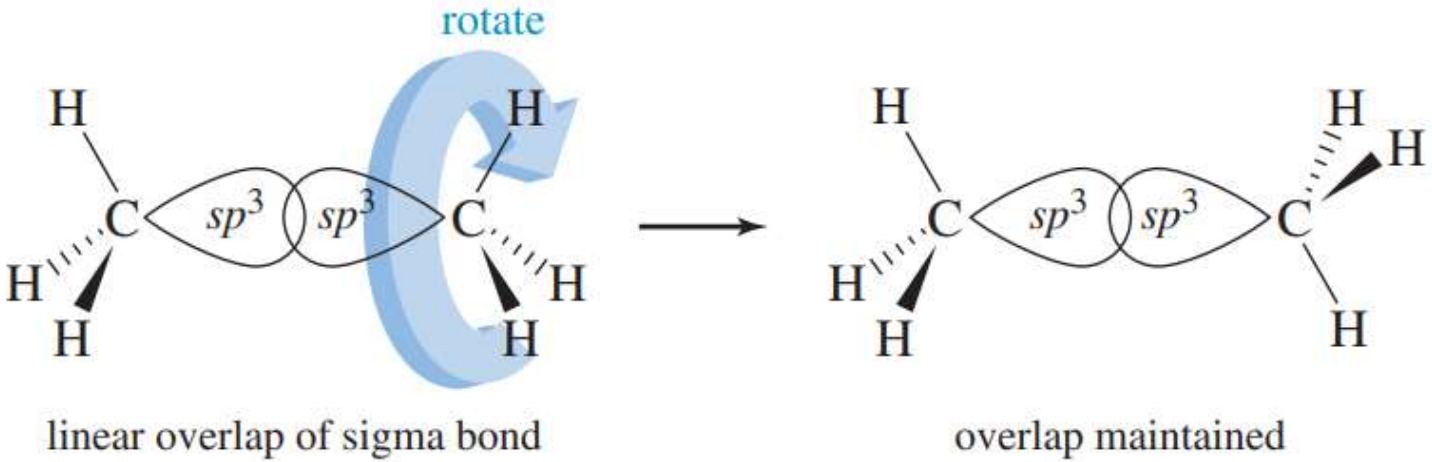




Sawhorse formula

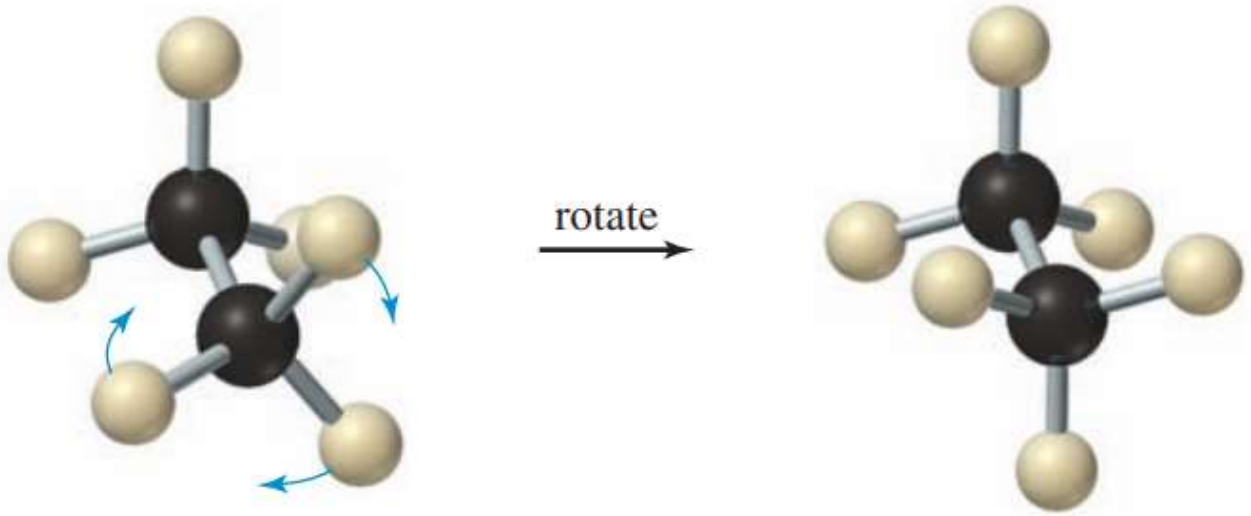
Sawhorse meaning a rack supporting wood for sawing

4.8 Sigma Bonds and Bond Rotation

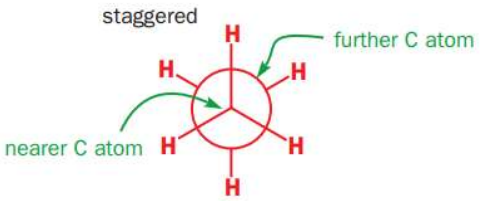


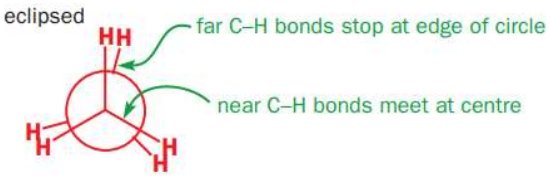
linear overlap of sigma bond

overlap maintained

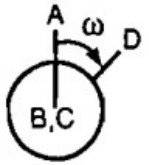


4.8 Sigma Bonds and Bond Rotation

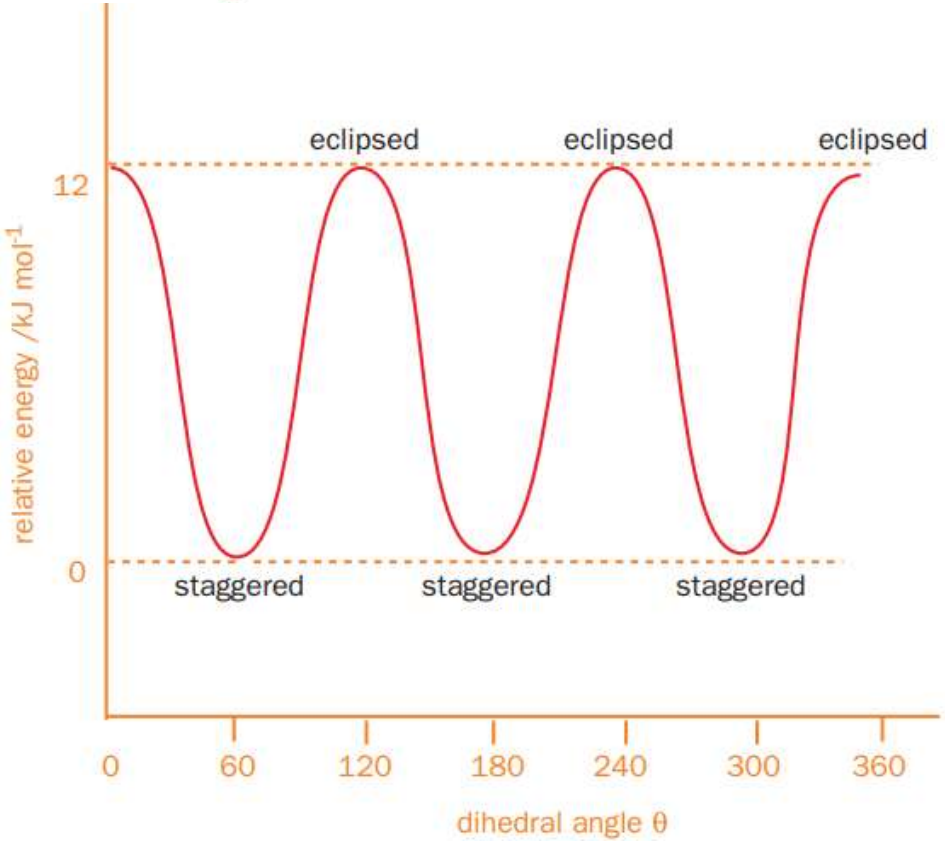


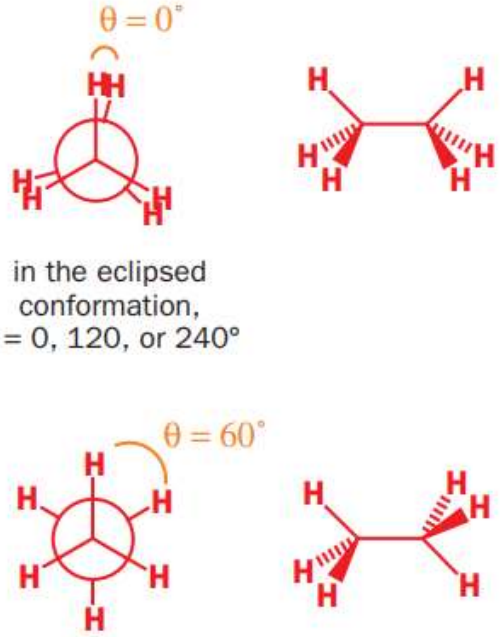


Conformations of A–B–C–D.



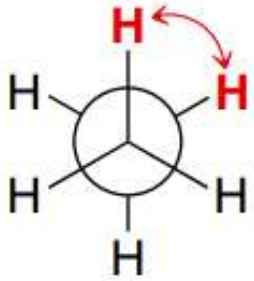
$180° > \omega > -180°$





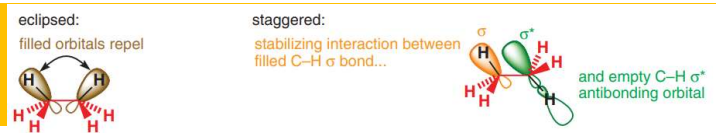
in the eclipsed conformation, θ = 0, 120, or 240°

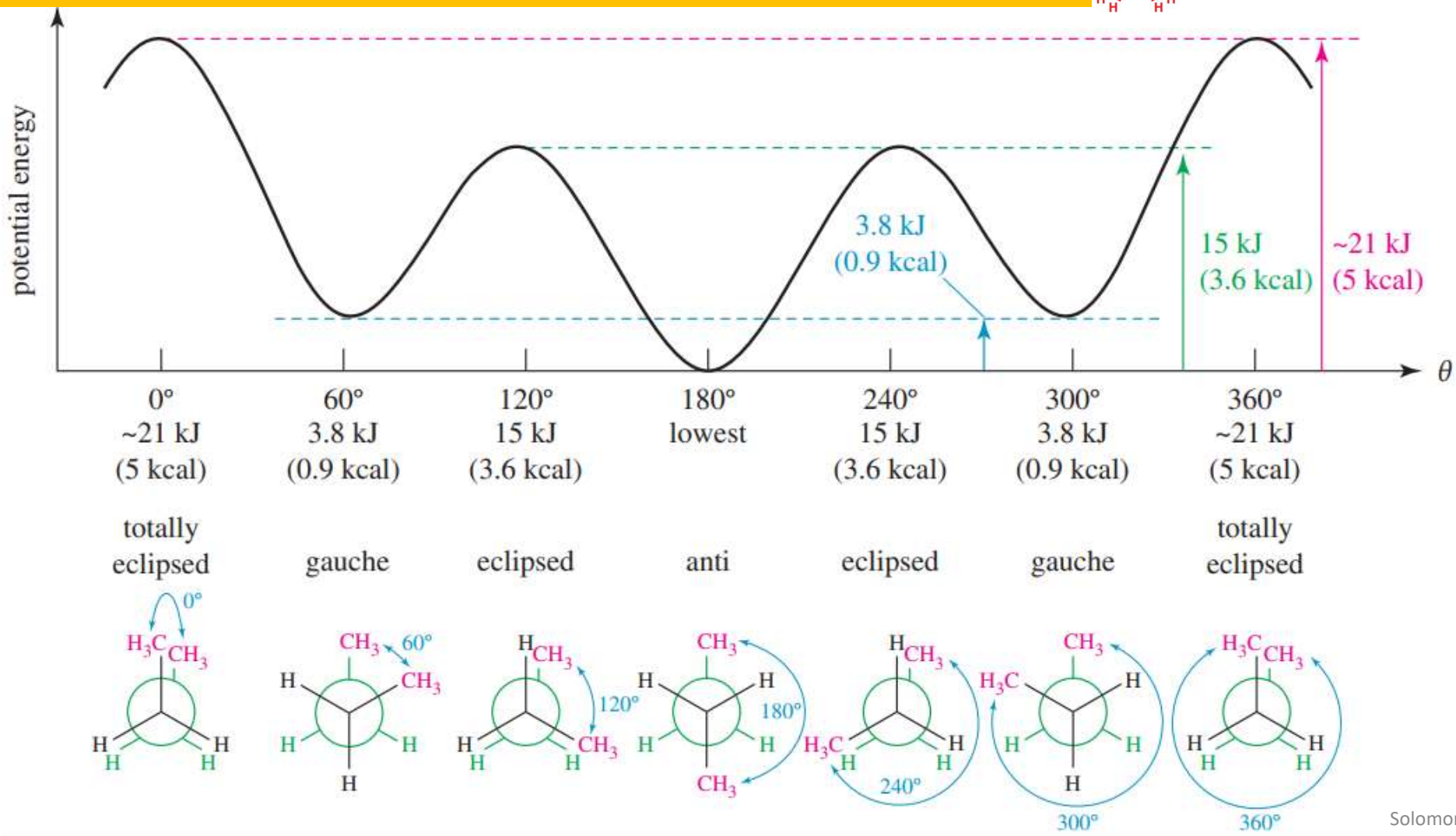
in the staggered conformation, θ = 60, 180, or 300°



Dihedral angle=60°

4.9 Conformational Analysis of Butane





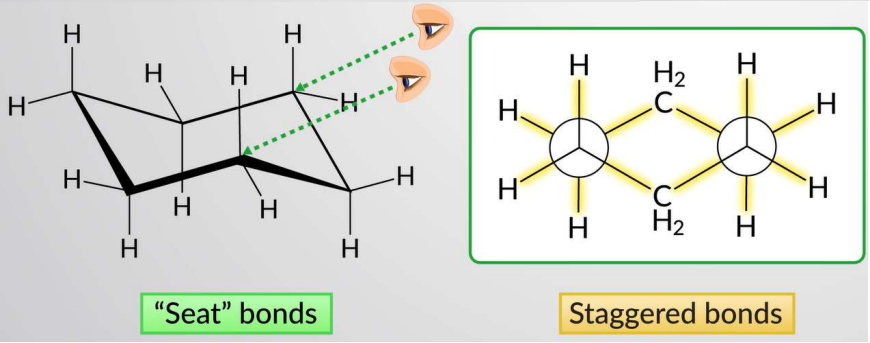
4.9A Stereoisomers and Conformational Stereoisomers

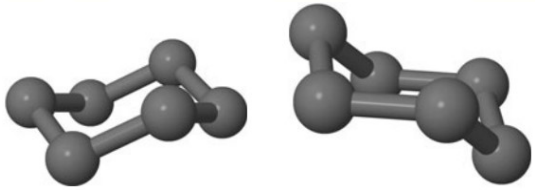
- Gauche conformers ***III*** and ***V*** of butane are examples of stereoisomers (check previous slide).
- Stereoisomers have the same molecular formula and connectivity but different arrangements of atoms in three-dimensional space.
- Conformational stereoisomers are related to one another by bond rotations.
- Conformational analysis is but one of the ways in which we will consider the three-dimensional shapes and stereochemistry of molecules.
- We shall see that there are other types of stereoisomers that cannot be interconverted simply by rotations about single bonds. Among these are cis–trans cycloalkane isomers that we shall consider.

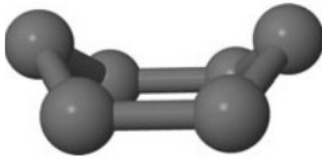
Energy Costs for Interactions in Alkane Conformers Energy Costs

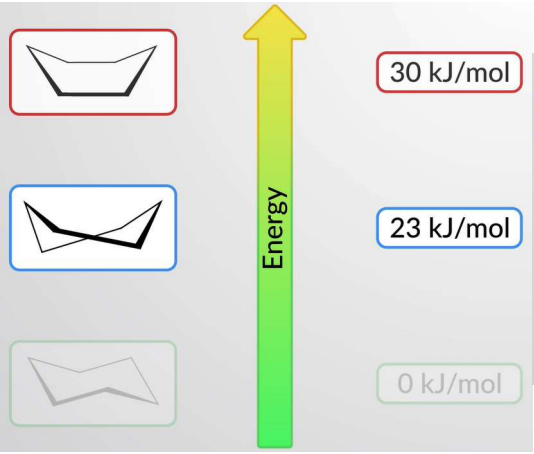
Interaction	Cause	Energy cost (kJ/mol)	Energy cost (kcal/mol)
H⟷H eclipsed	Torsional strain	4.0	1.0
H⟷CH_3 eclipsed	Mostly torsional strain	6.0	1.4
CH_3⟷CH_3 eclipsed	Torsional and steric strain	11.0	2.6
CH_3⟷CH_3 gauche	Steric strain	3.8	0.9

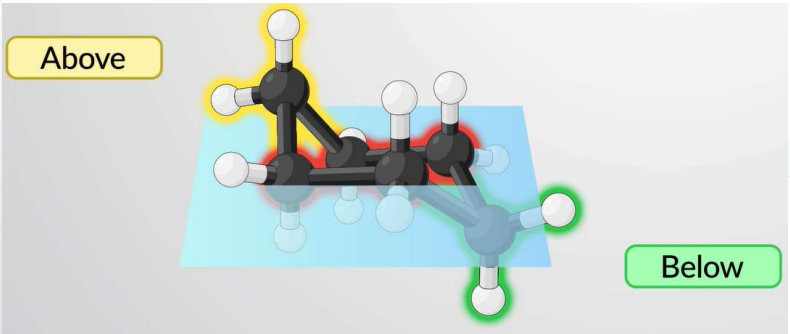
4.11 Conformations of Cyclohexane: The Chair, the Boat & Twist-Boat

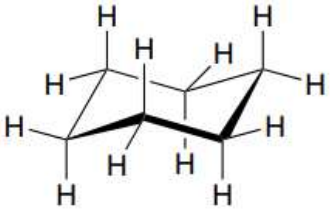


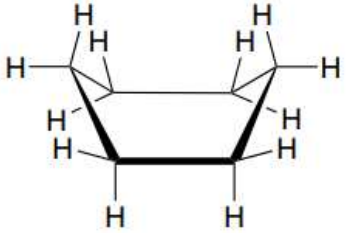




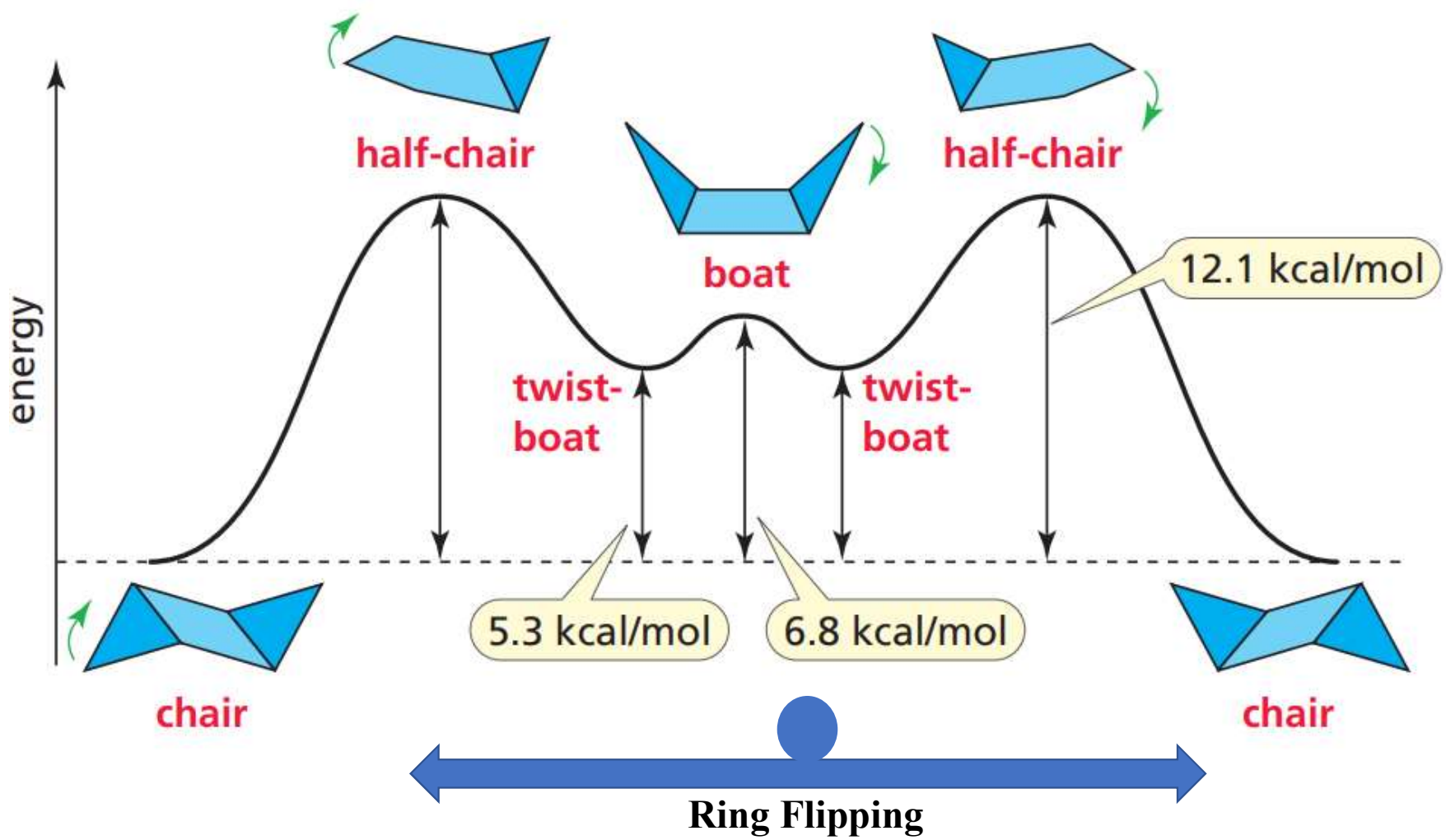




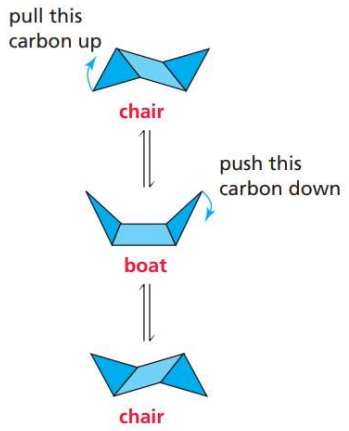

Chair


Boat

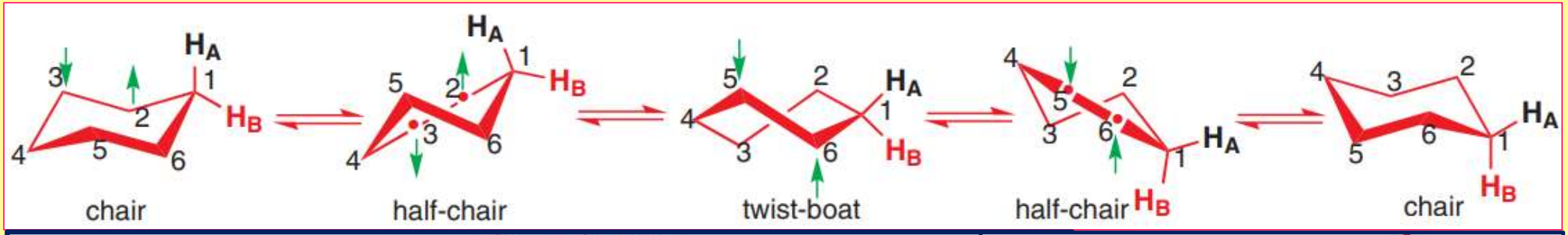
4.11 Conformations of Cyclohexane: The Chair and the Boat



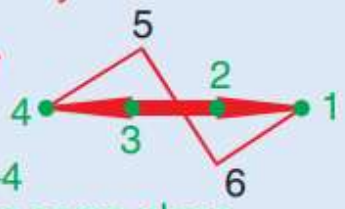
Ring Flipping



4.11 The whole inversion process: Ring Flipping



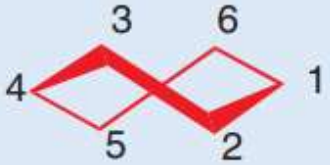
the easiest way to draw a half-chair

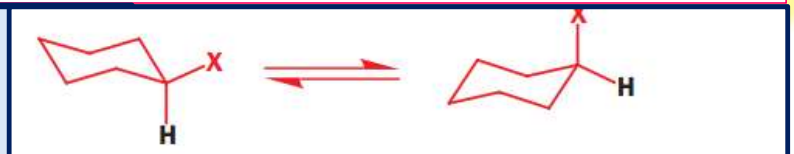


carbons 1–4 are all in the same plane

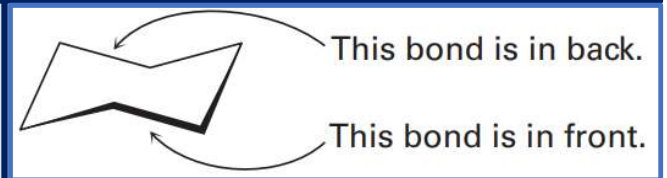
There are also a number of ways of drawing a twist-boat conformer but the easiest is this:

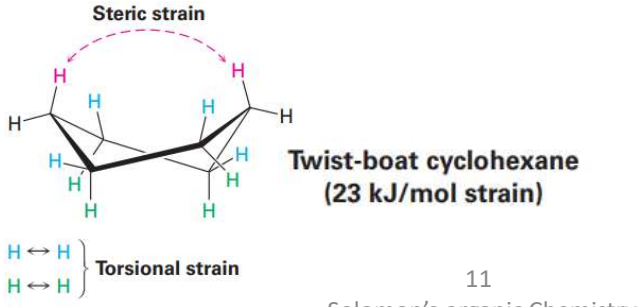
the easiest way to draw the twist-boat conformation



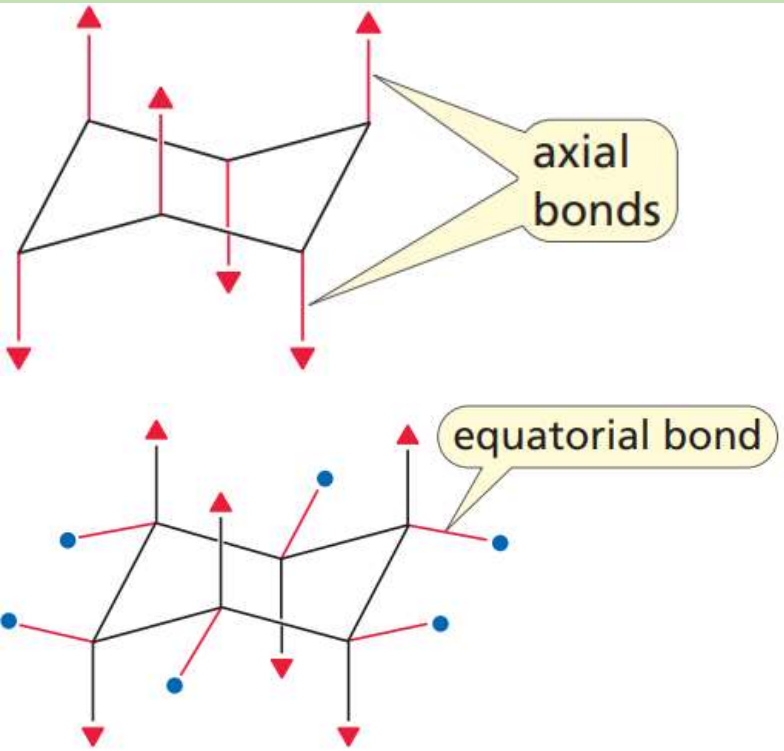


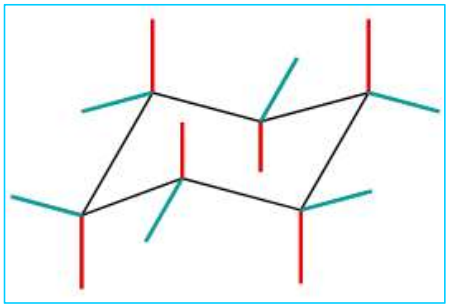
ring inversion of a monosubstituted cyclohexane
notice that the hydrogen atom shown changes from axial to equatorial

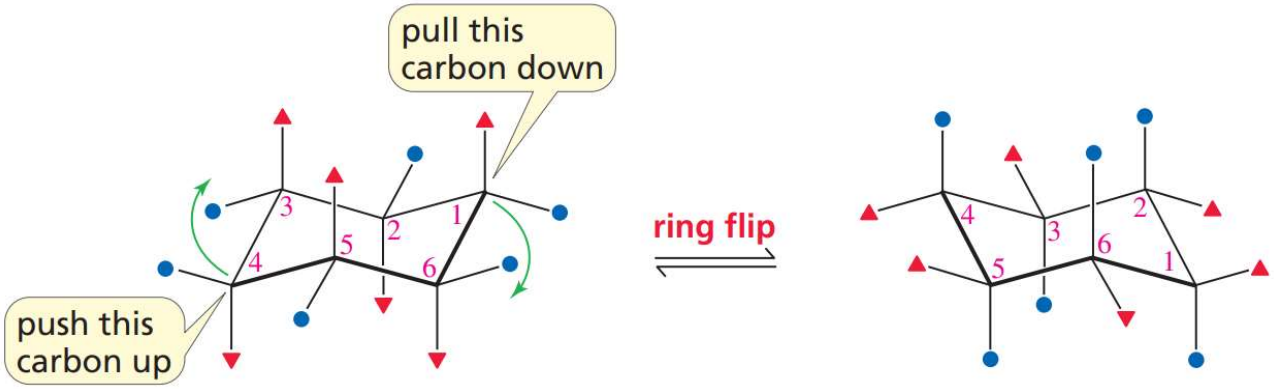




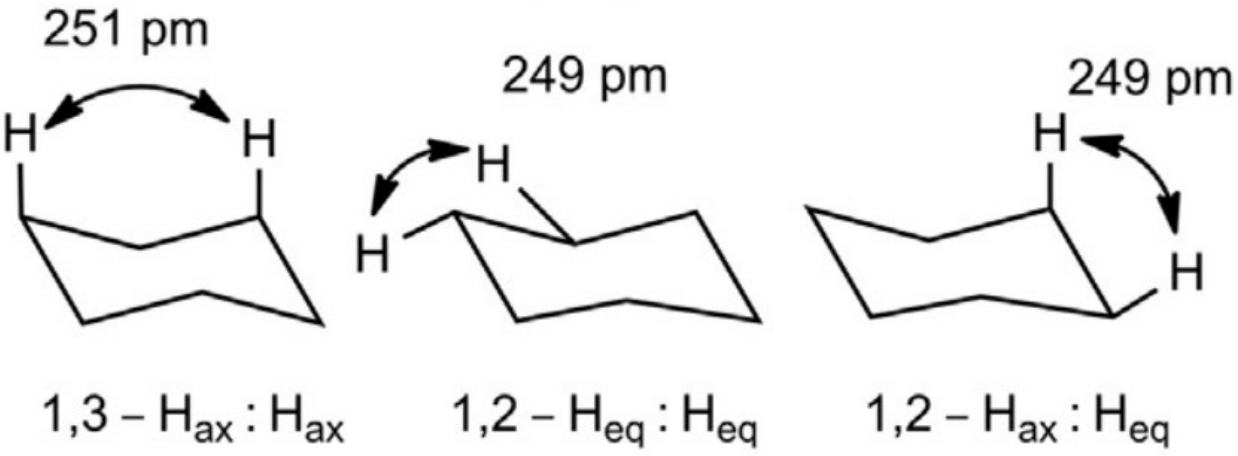
4.11 Conformations of Cyclohexane: The Chair



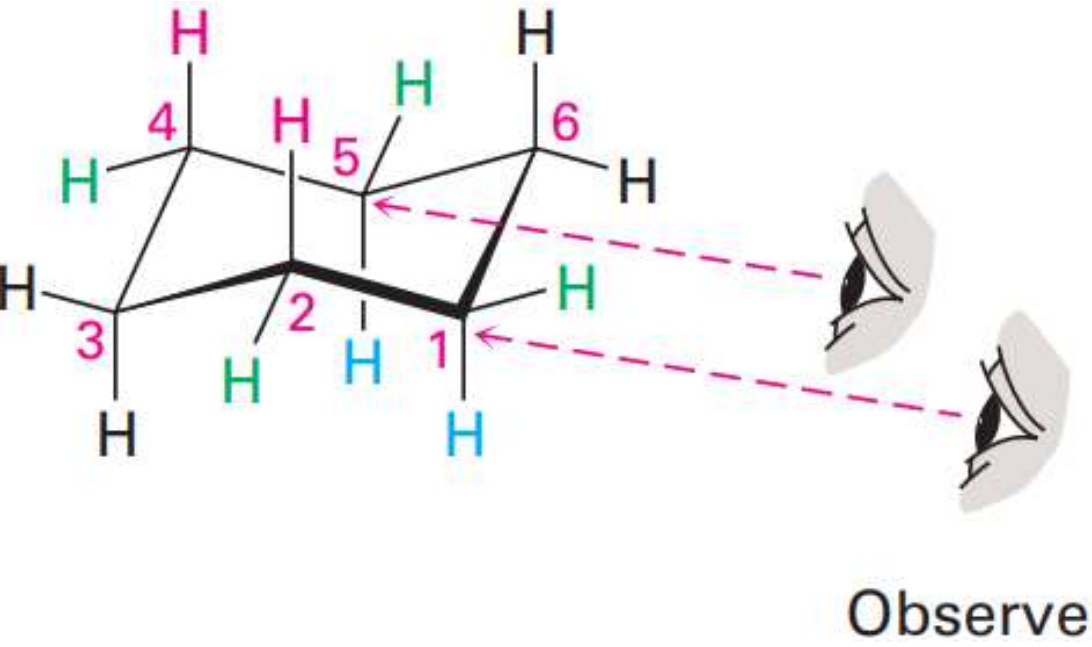




H – H distances



4.11 Conformations of Cyclohexane: Chair in (Double) Newman Projection



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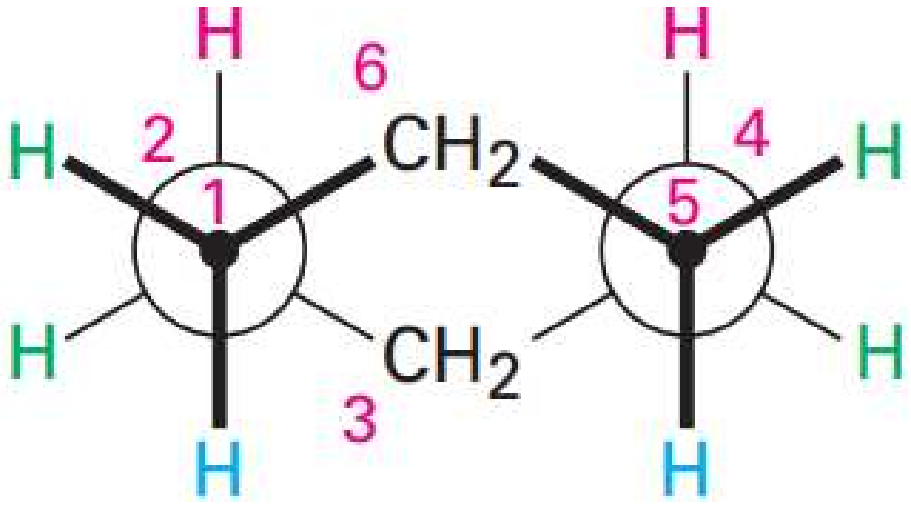
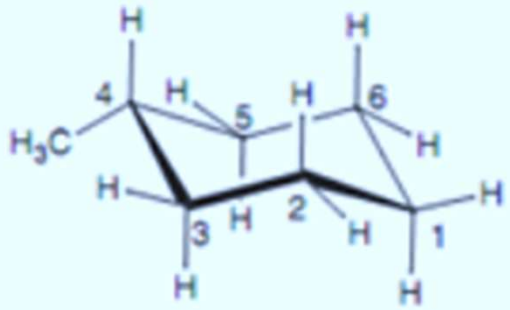
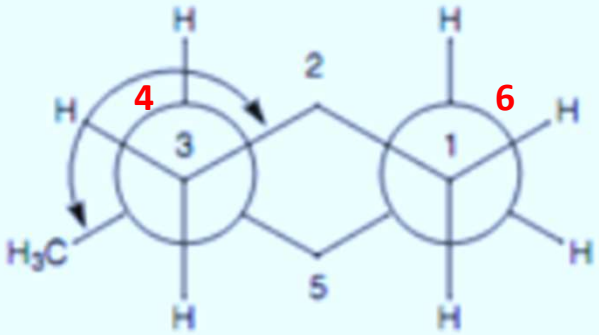
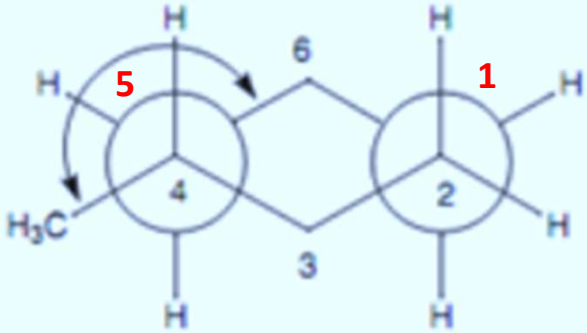


4.11 Conformations of Cyclohexane: Chair in Newman Projection

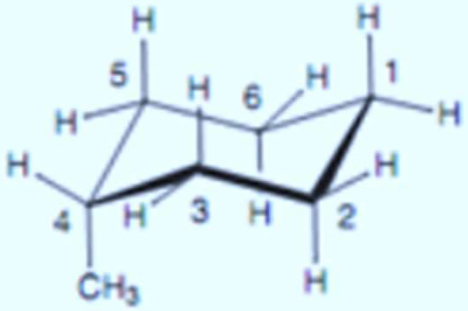
Equatorial methyl

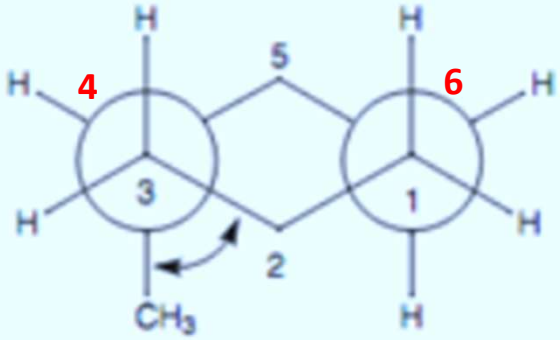


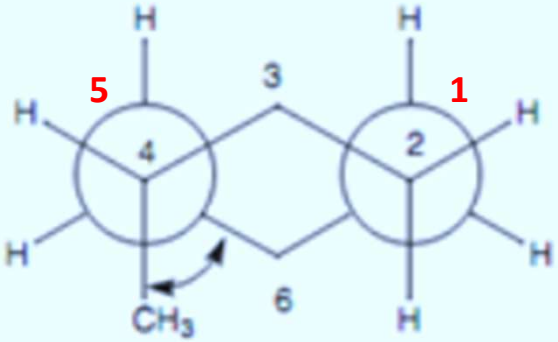




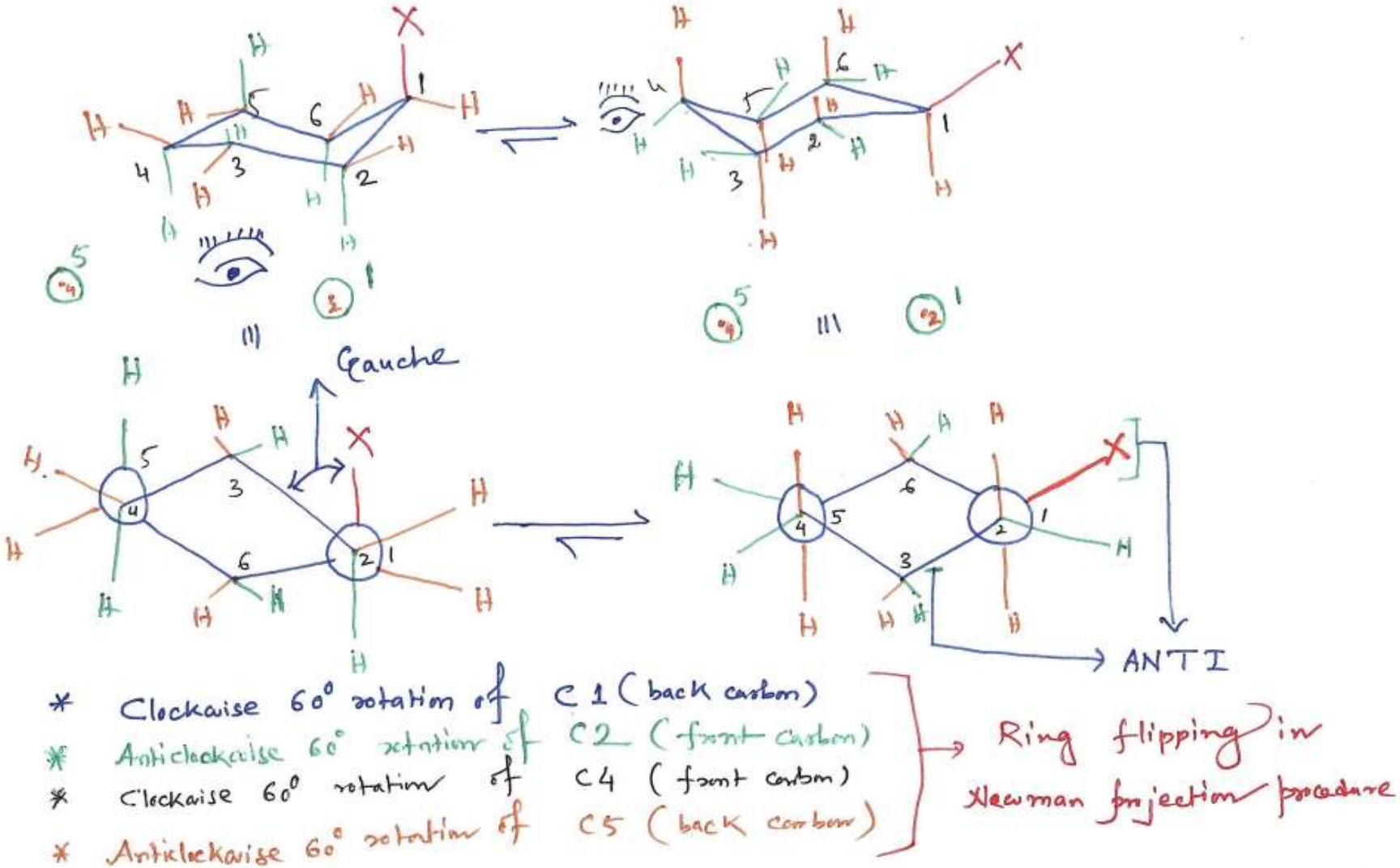
Axial methyl



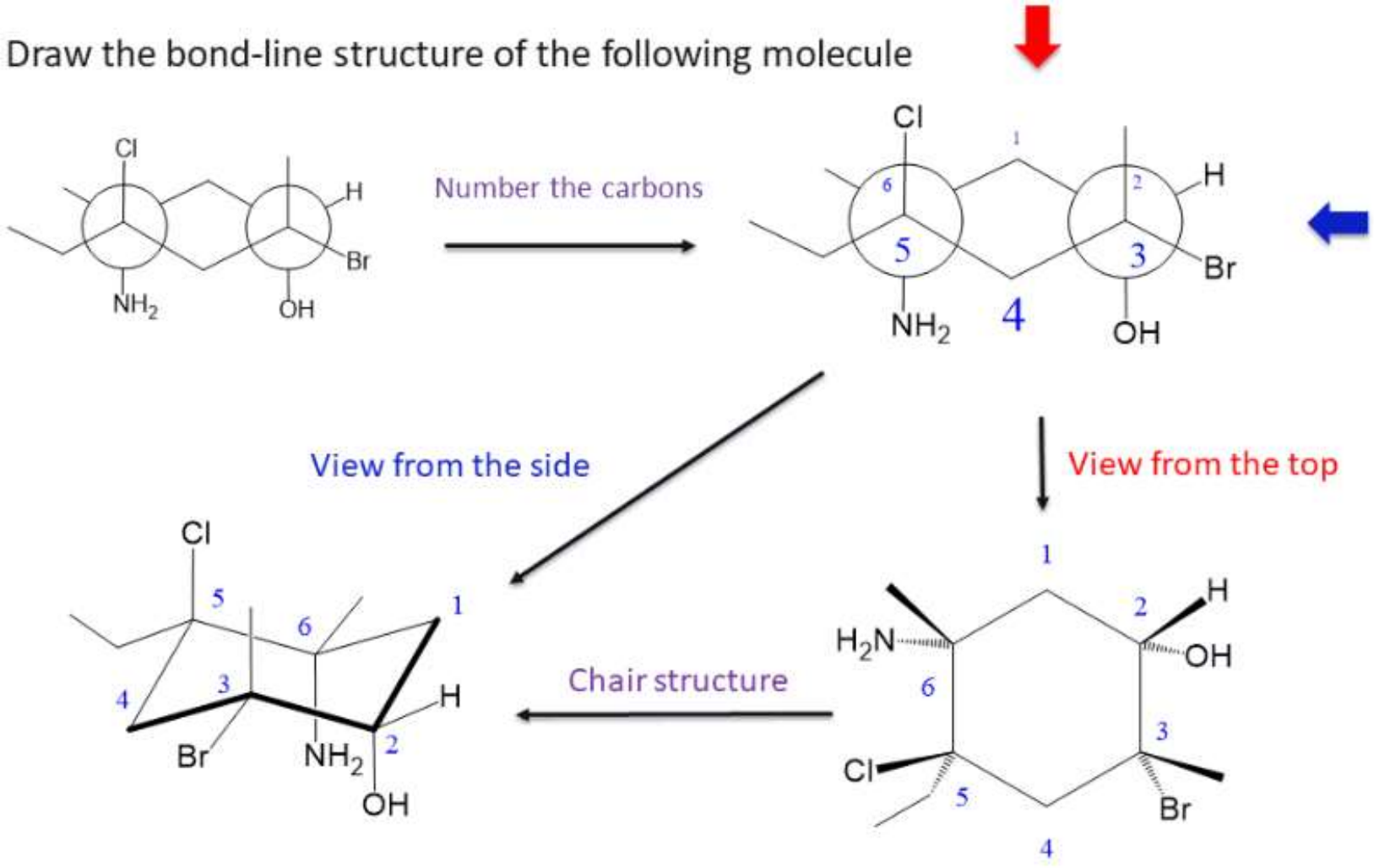




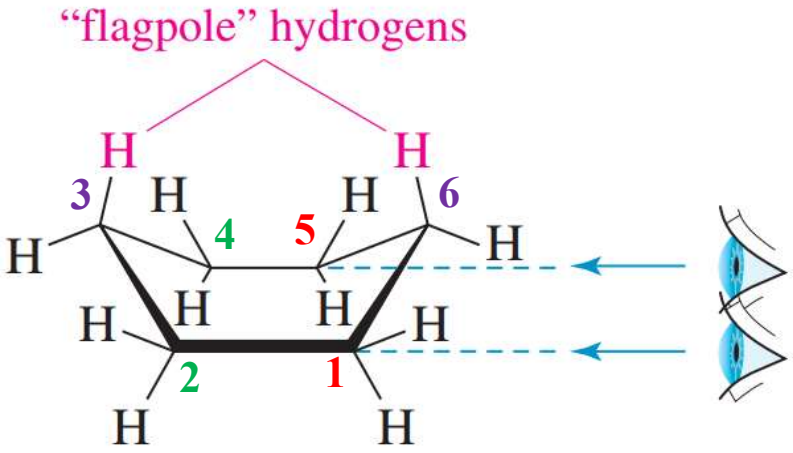
4.11 Ring Flipping in Newman Projection



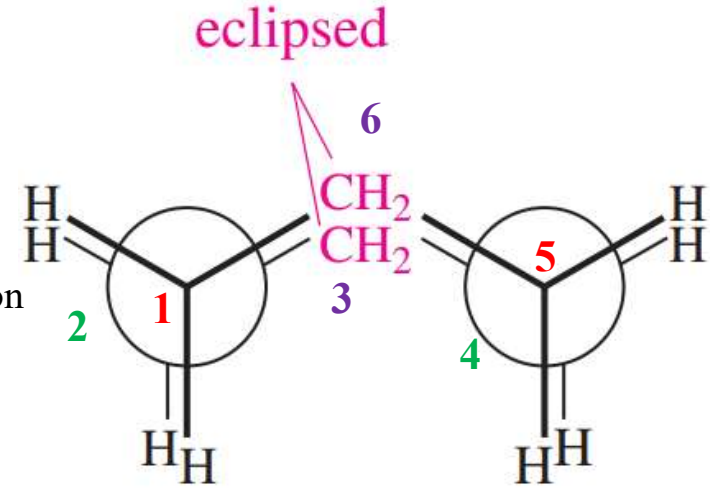
4.11 Chair in Newman Projection to Bond-line Structure



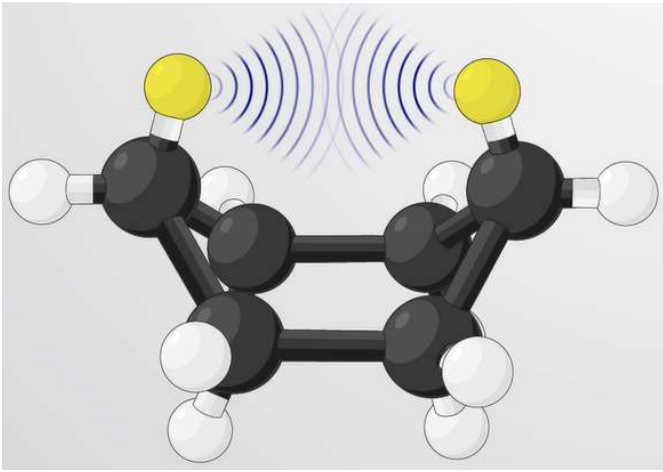
4.11 Conformations of Cyclohexane: The Boat in (Double) Newman Projections

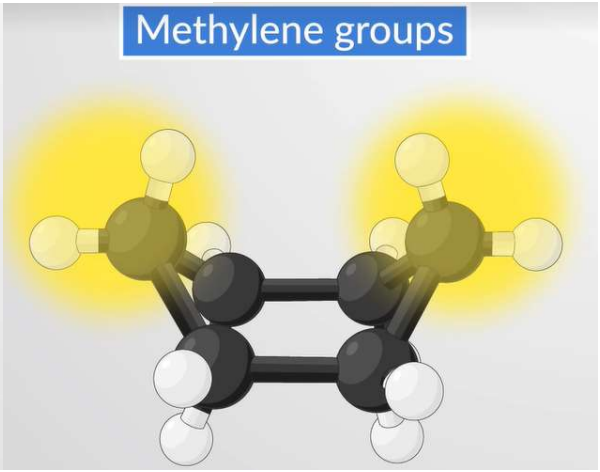


(Double) Newman Projection

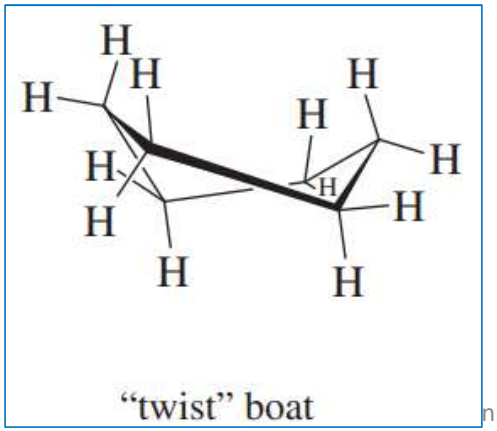


symmetrical boat

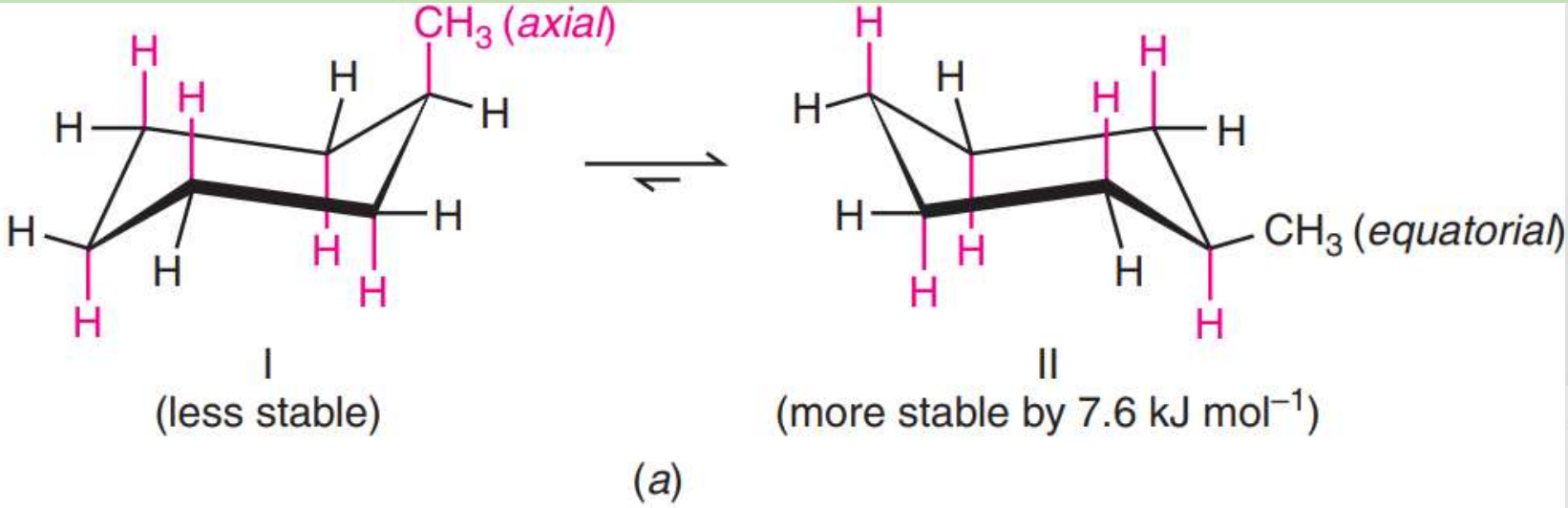




Newman projection



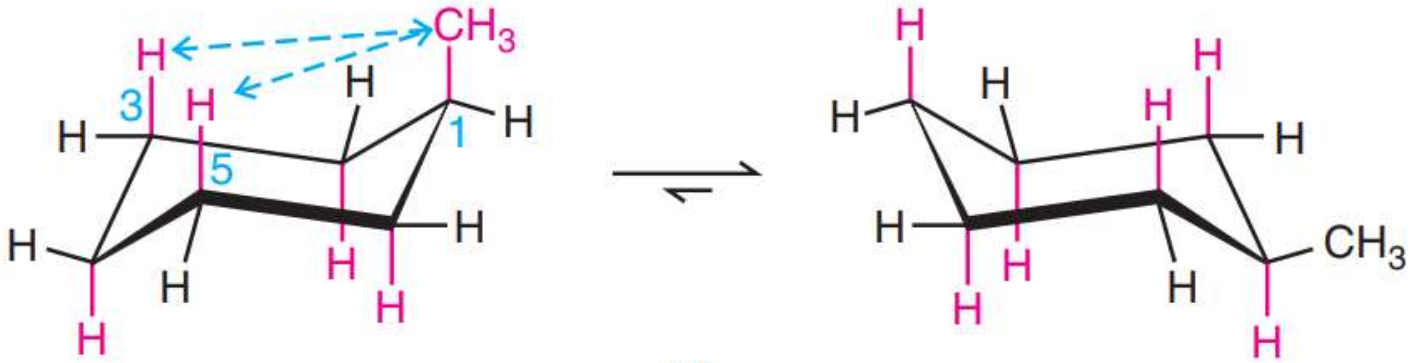
4.12 Mono-Substituted Cyclohexanes: A Conformational Analysis of Methylcyclohexane



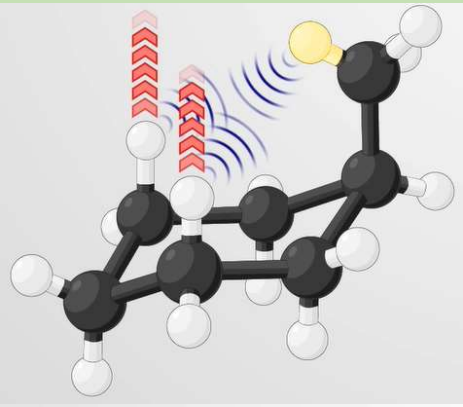
I
(less stable)

II
(more stable by 7.6 kJ mol^{-1})

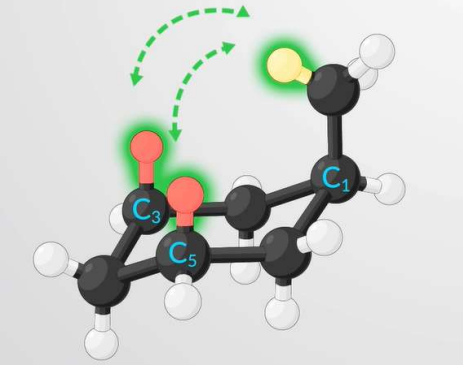
(*a*)



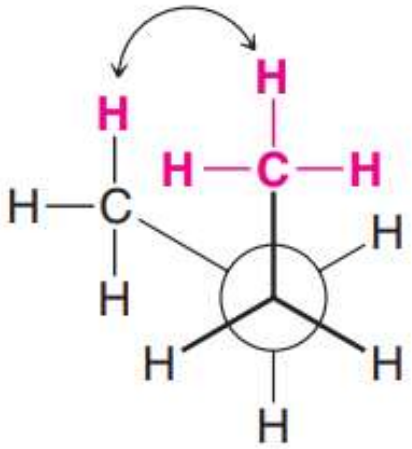
(*b*)



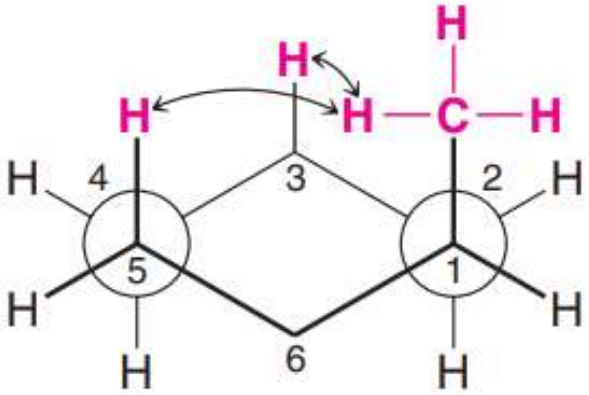
1,3-Diaxial Interaction



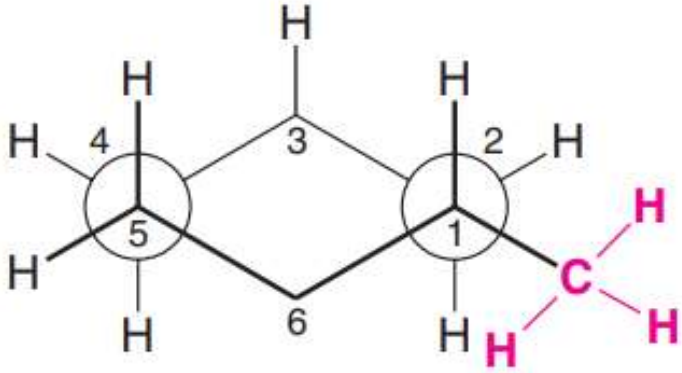
4.12 Mono-Substituted Cyclohexanes: A Conformational Analysis of Methylcyclohexane



gauche-Butane
(3.8 kJ mol^{-1} steric strain)



Axial methylcyclohexane
(two gauche interactions =
7.6 kJ mol^{-1} steric strain)



Equatorial methylcyclohexane
(more stable by 7.6 kJ mol^{-1})

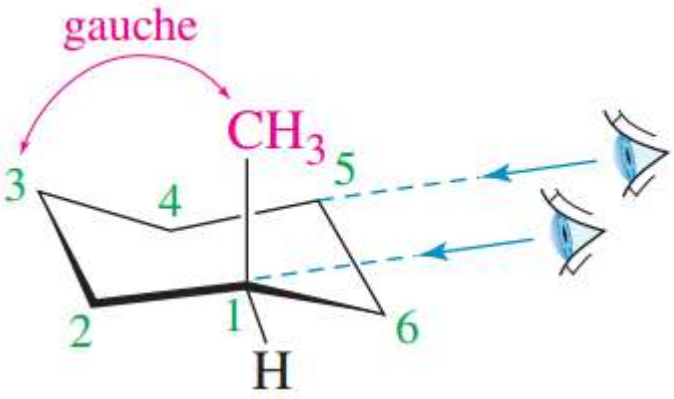
LEARN THE STRATEGY

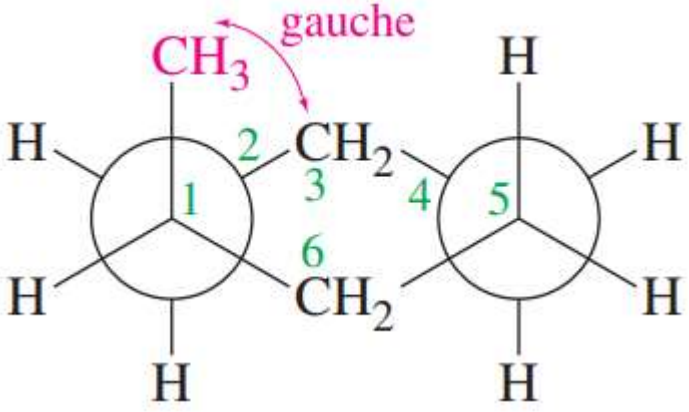
$$K_{eq} = \frac{\text{[equatorial conformer]}}{\text{[axial conformer]}} = \frac{18}{1}$$

$$\%\text{ of equatorial conformer} = \frac{\text{[equatorial conformer]}}{\text{[equatorial conformer]} + \text{[axial conformer]}} \times 100$$

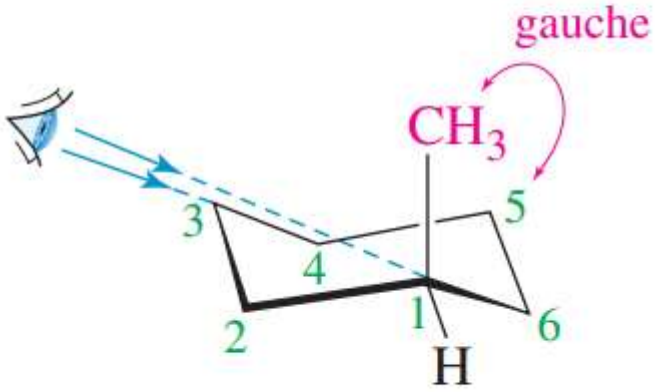
$$\%\text{ of equatorial conformer} = \frac{18}{18 + 1} \times 100 = 95\%$$

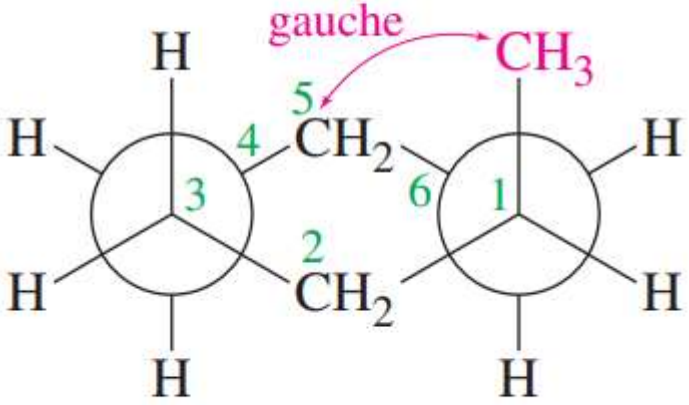
Two gauche interactions for axial methylcyclohexane is more clearly shown in the next slide





Newman projection
(a)



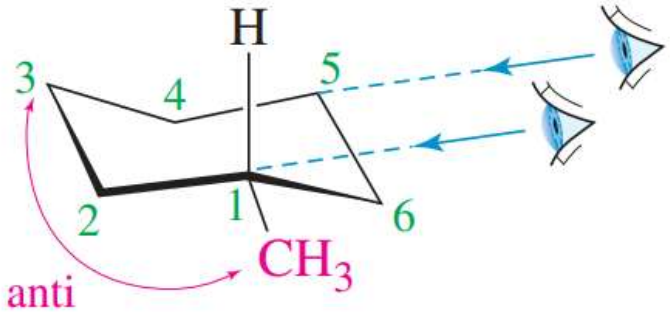


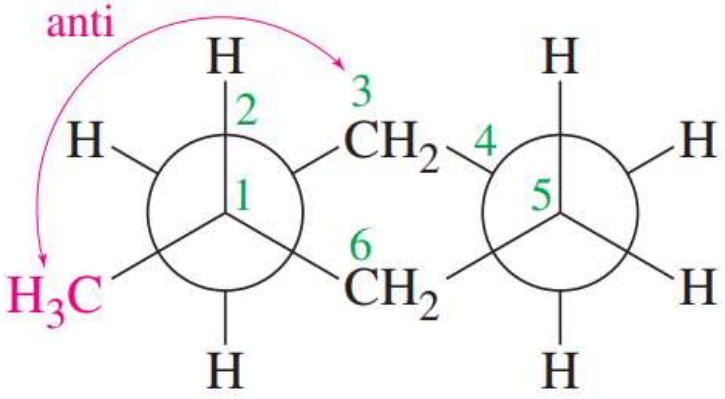
Newman projection
(b)

(a) When the methyl substituent is in an axial position on C1, it is gauche to C3.

(b) The axial methyl group on C1 is also gauche to C5 of the ring.

Anti methyl to C3 for equatorial methylcyclohexane is more clearly shown in the next slide



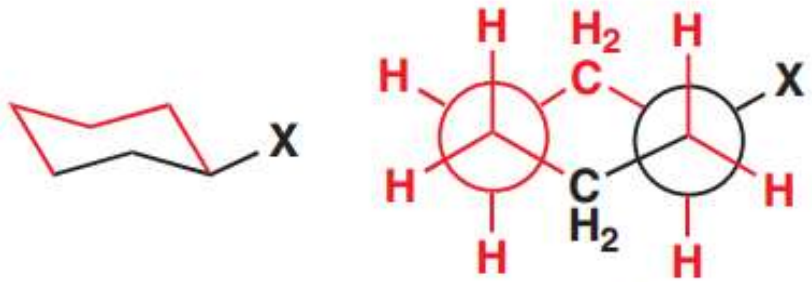


Newman projection

Looking down the C1-C2 bond of the equatorial conformation. Notice that the methyl group is anti to C3.

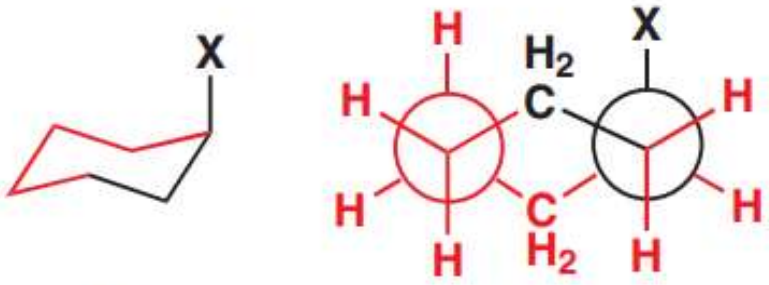
Summary

equatorially substituted cyclohexane:



the black bonds are anti-periplanar
(only one pair shown for clarity)

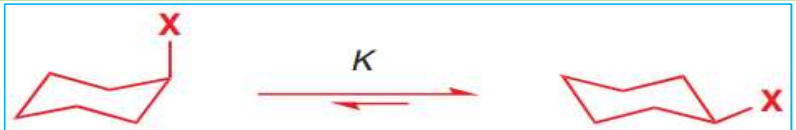
axially substituted cyclohexane:



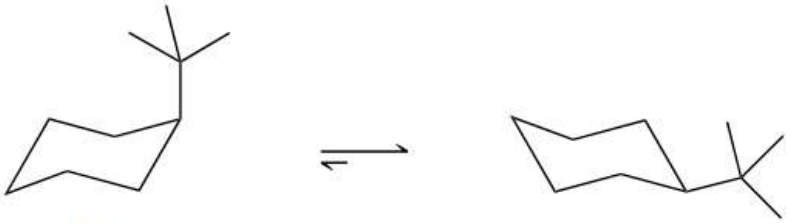
the black bonds are synclinal (gauche)
(only one pair shown for clarity)

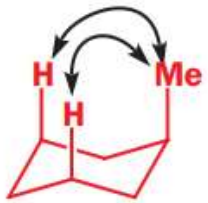
4.12 Equilibrium Constants for Several Monosubstituted Cyclohexanes at 25 °C

Substituent	$K_{eq} = \frac{[\text{equatorial}]}{[\text{axial}]}$
H	1
CH_3	18
CH_3CH_2	21
$CH_3CH(CH_3)$	35
$CH_3C(CH_3)_2$	4800
CN	1.4
F	1.5
Cl	2.4
Br	2.2
I	2.2
HO	5.4

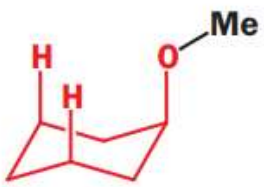


$$K = \frac{\text{concentration of equatorial conformer}}{\text{concentration of axial conformer}}$$

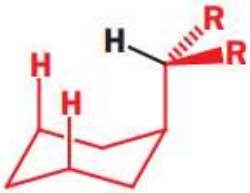




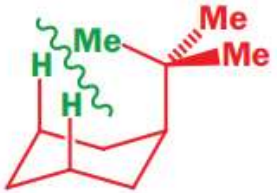
in the axial conformer of methylcyclohexane, there is a direct interaction between the methyl group and the axial hydrogen atoms



in methoxyclohexane, the methyl group is removed somewhat from the ring

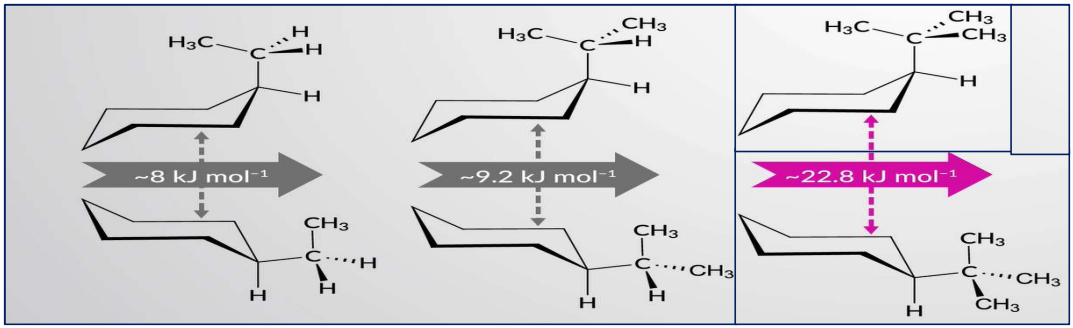


when a methyl, ethyl or *i*-propyl group is axial, only a hydrogen atom need lie directly over the ring

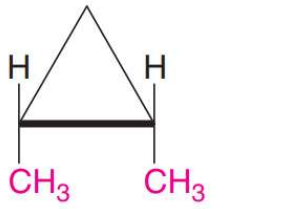


the steric requirements for putting a *t*-butyl group axial are enormous since now there is a severe interaction between a methyl group and the axial protons

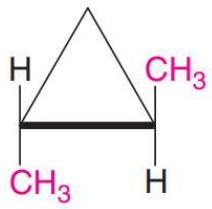
X	Equilibrium constant, *K*
OMe	2.7
Ph	110



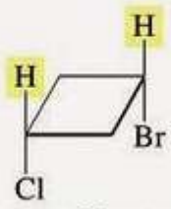
4.13 Disubstituted Cycloalkanes: *Cis–Trans* Isomerism



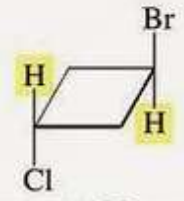
***cis*-1,2-Dimethylcyclopropane**



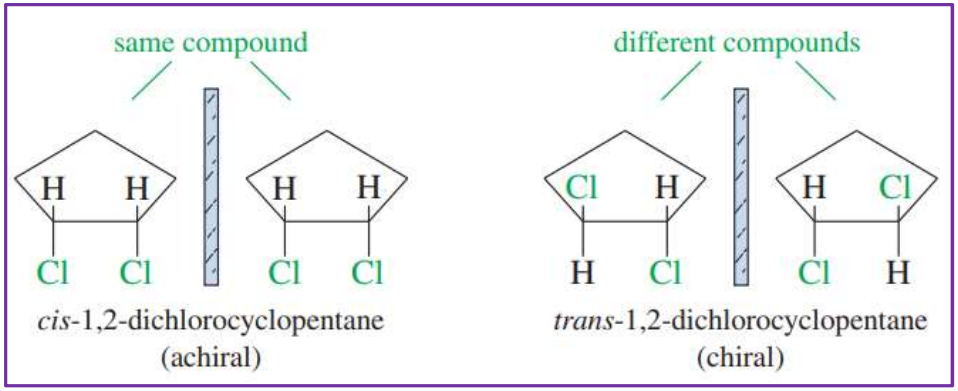
***trans*-1,2-Dimethylcyclopropane**



***cis*-1-bromo-3-chlorocyclobutane**



***trans*-1-bromo-3-chlorocyclobutane**

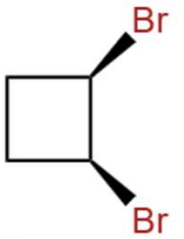


cis-1,2-dichlorocyclopentane (achiral)

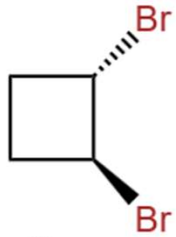
trans-1,2-dichlorocyclopentane (chiral)

Chemists class rings as small, normal, medium, or large depending on their size.

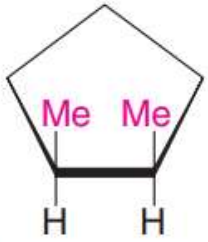
small, $n = 3$ or 4
normal, $n = 5$, 6, or 7
medium, $n = 8$ to about 14
large, $n >$ about 14



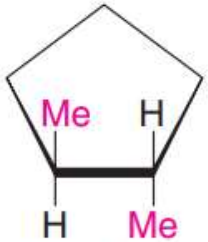
cis-1,2-dibromocyclobutane



trans-1,2-dibromocyclobutane



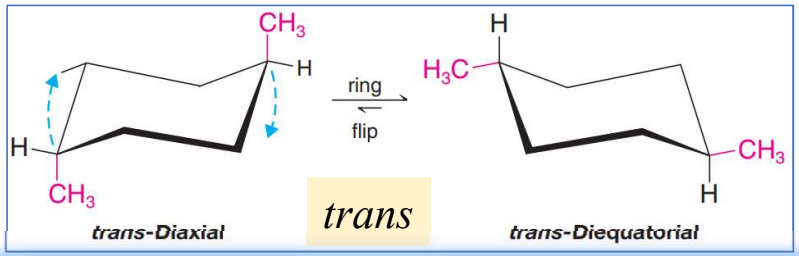
***cis*-1,2-Dimethylcyclopentane (C_7H_{14})**

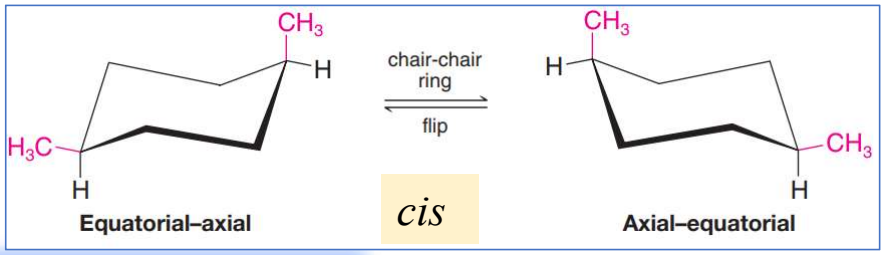


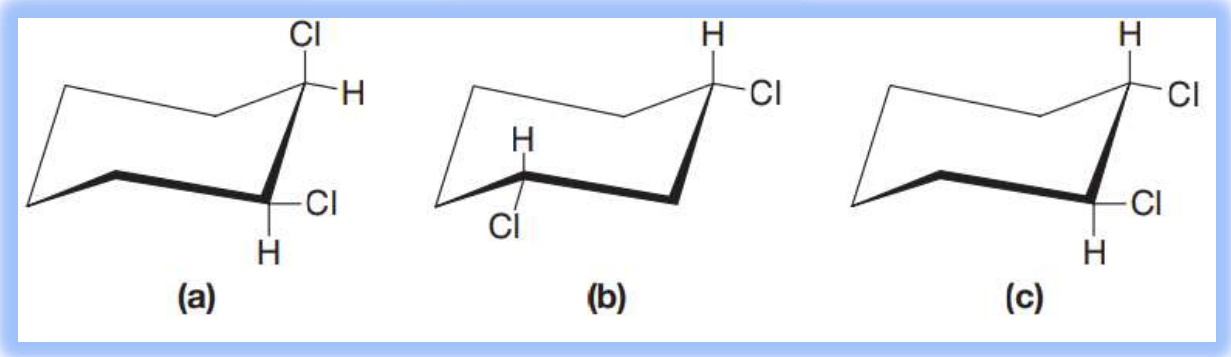
***trans*-1,2-Dimethylcyclopentane (C_7H_{14})**

Cis and trans cycloalkane isomers are diastereomers.

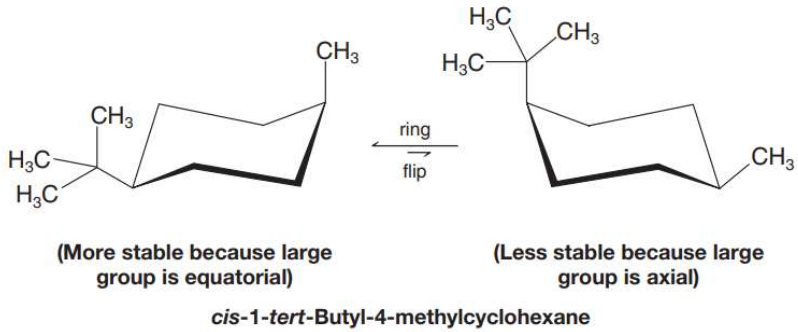
4.13 Disubstituted Cyclohexane: 1,4-Disubstituted Cyclohexanes

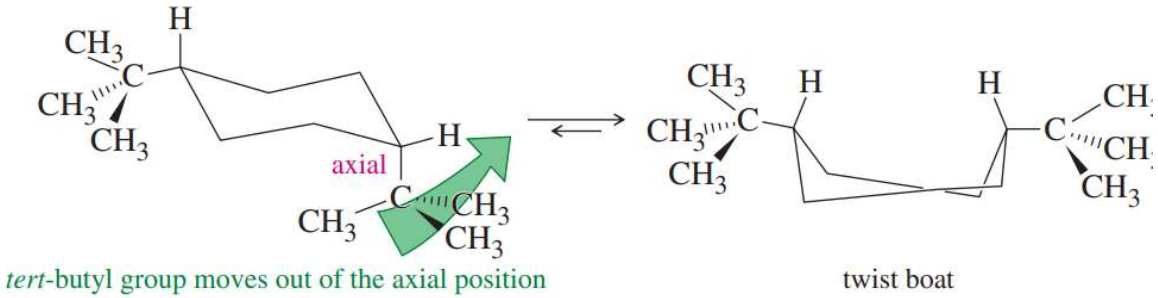






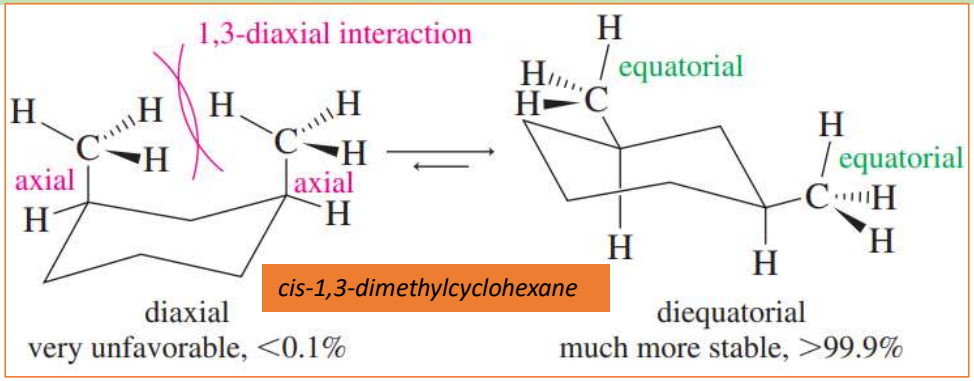
Consider each of the following conformational structures and tell whether each is cis or trans?

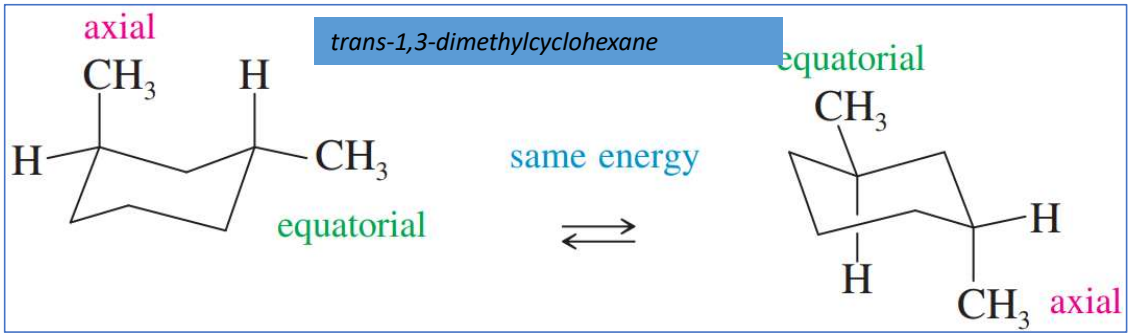




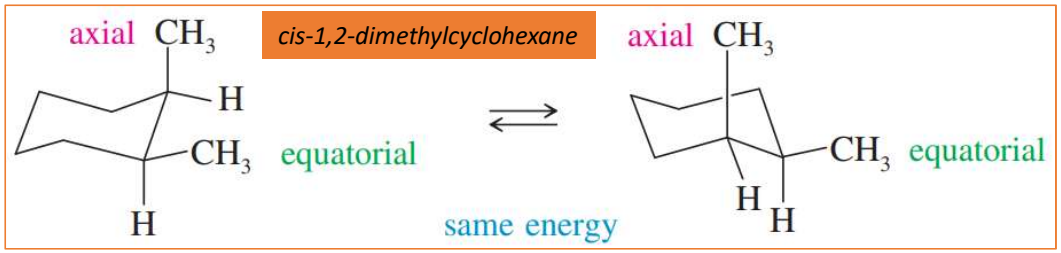
Cis-1,4 ditert-Butyl cyclohexane

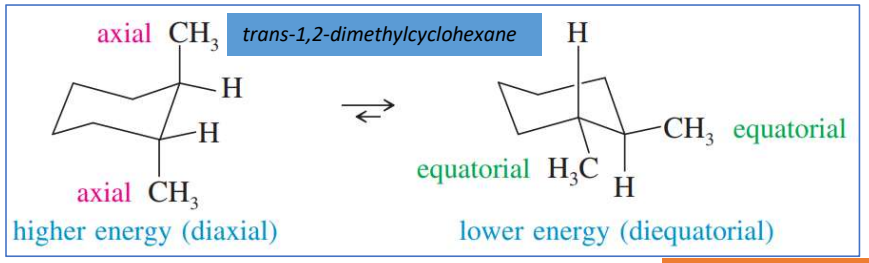
4.13 Disubstituted Cyclohexane: 1,3-Disubstituted Cyclohexanes

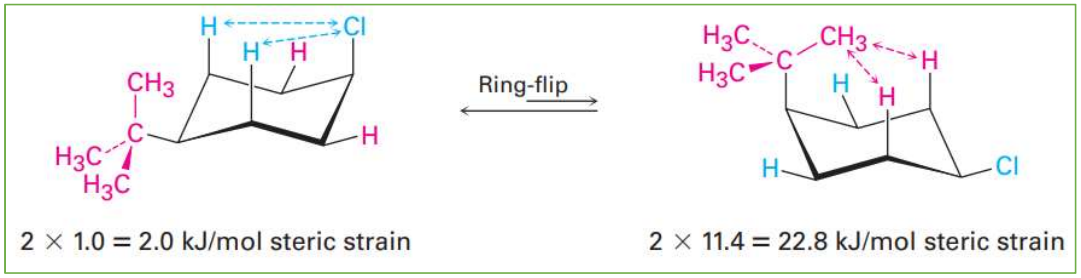




4.13 Disubstituted Cyclohexane: 1,2-Disubstituted Cyclohexanes

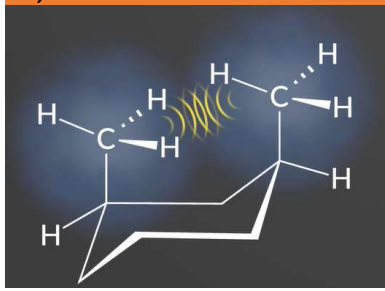




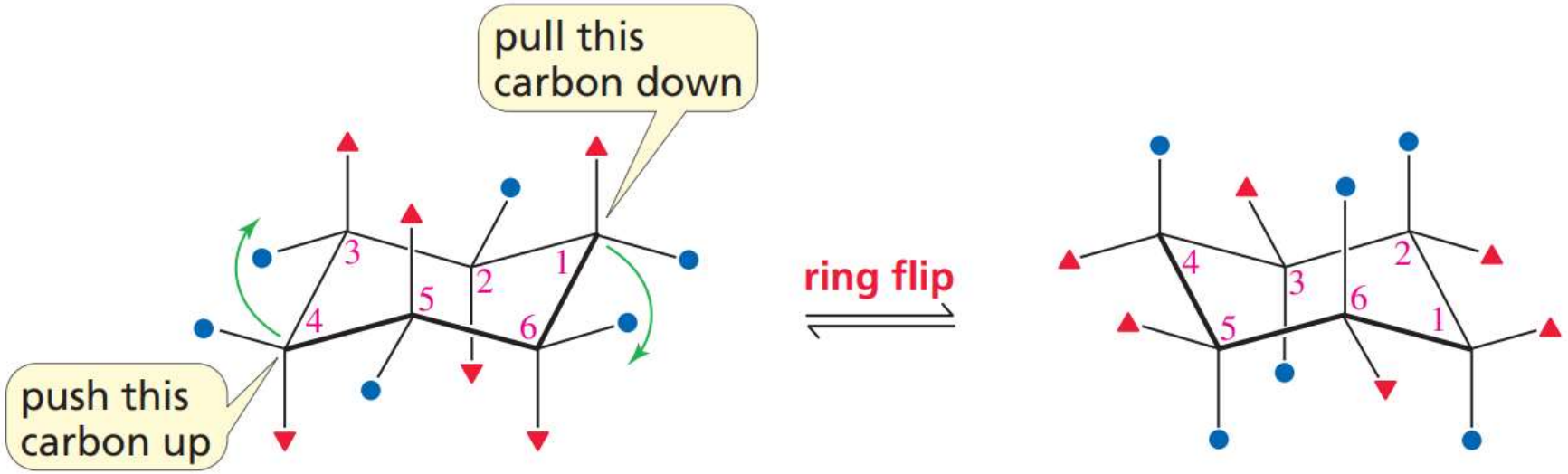


cis-1-chloro, 4tert-Butylcyclohexane

1,3 diaxial interaction



@ Ring Flipping and its consequences



@ Ring flipping does not disturb the α and β orientations

@ Ring flipping does not change the configurational nomenclature (*R*, *S*)

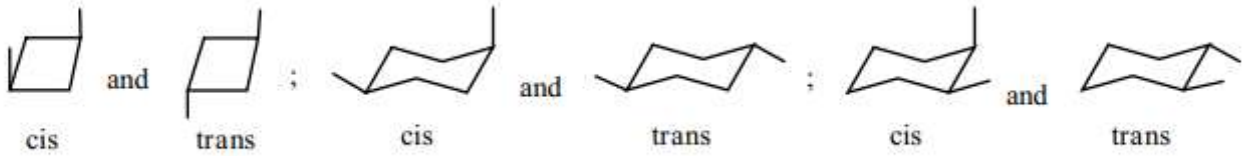
@ Ring flipping only results interchange of equatorial and axial bonds

@ Conformational and Configurational Isomers

Configurational Diastereomers (e): Examples

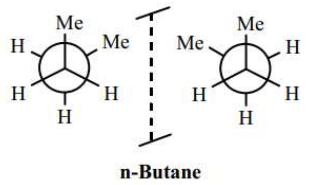
(Anisometric) Relative positions of all atoms – not same

(2S, 3R)-3-Bromo-2-butanol **(2S, 3S)-3-Bromo-2-butanol**

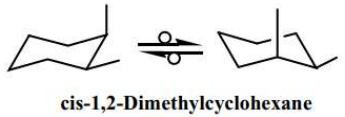


All physical and chemical properties are different

Conformational Enantiomers (d)

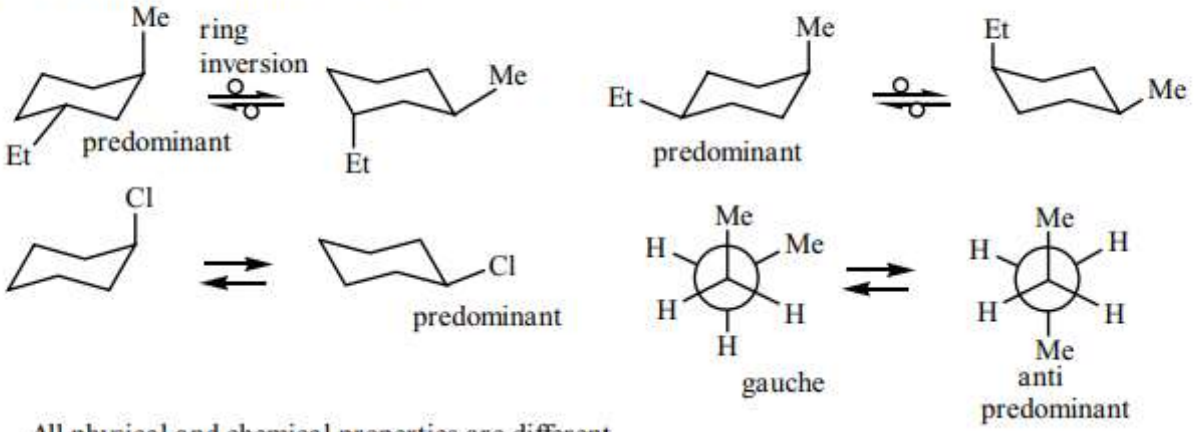


n-Butane



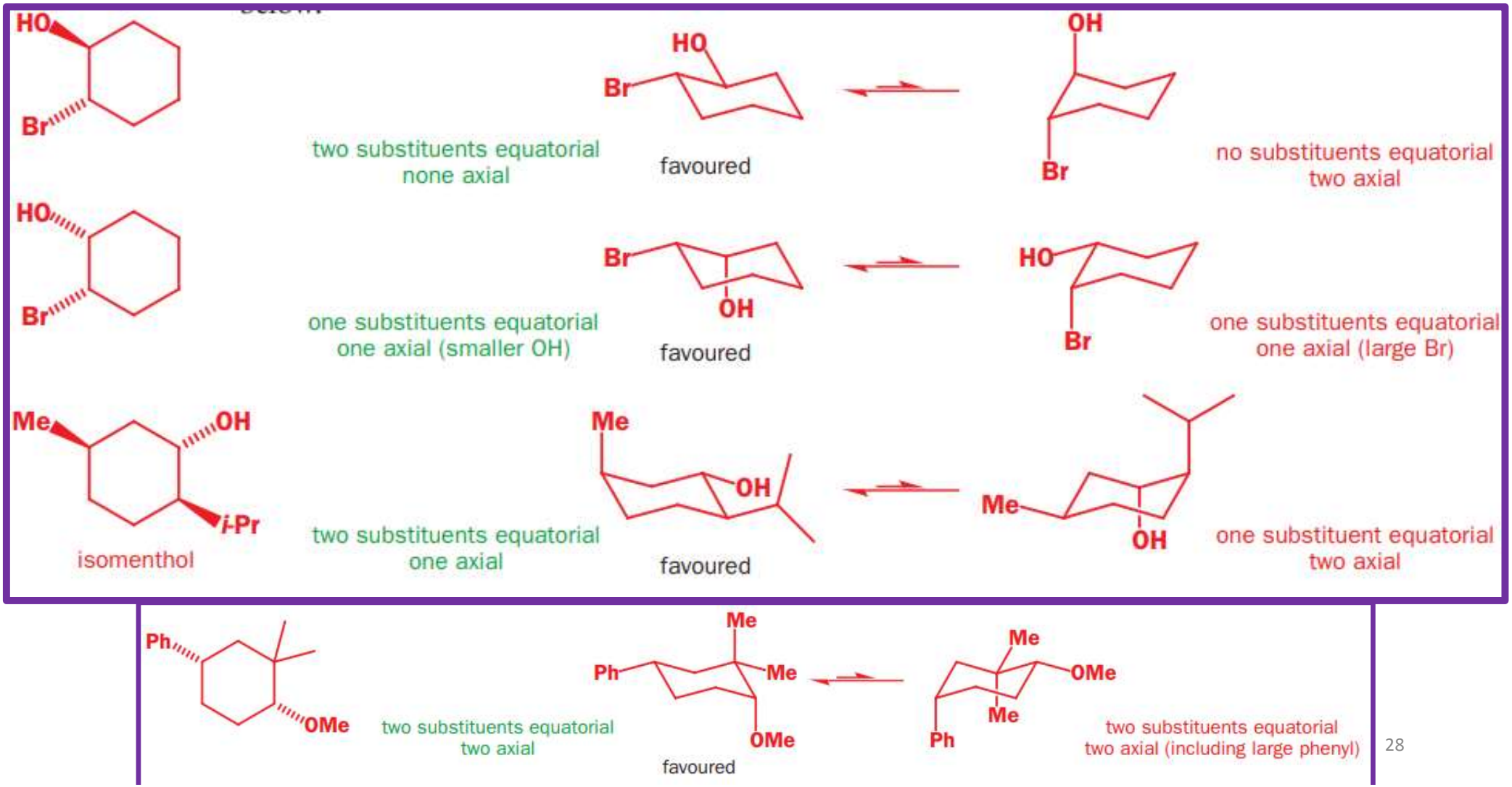
cis-1,2-Dimethylcyclohexane

(f) Conformational Diastereomers



All physical and chemical properties are different

Conformers Drawing in chair: Favored Conformer



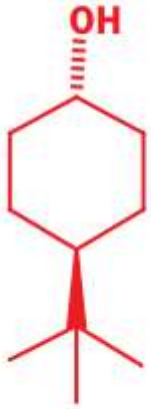
Conformers Drawing in chair: Favored Conformer

cis-4-*t*-butylcyclohexanol

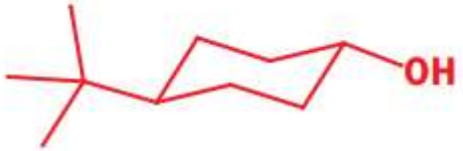
in the *cis* diastereoisomer, the hydroxyl group is forced into an axial position

in both compounds, the *t*-butyl group is equatorial

trans-4-*t*-butylcyclohexanol



in the *trans* diastereoisomer, the hydroxyl group is forced into an equatorial position

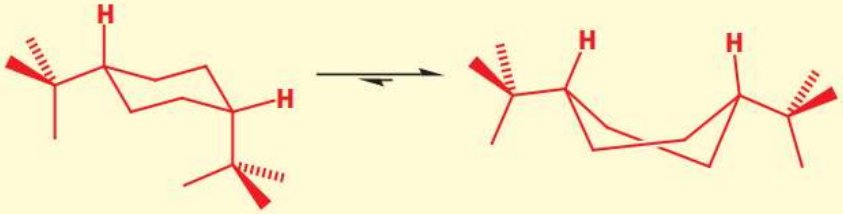


in both compounds, the *t*-butyl group is equatorial

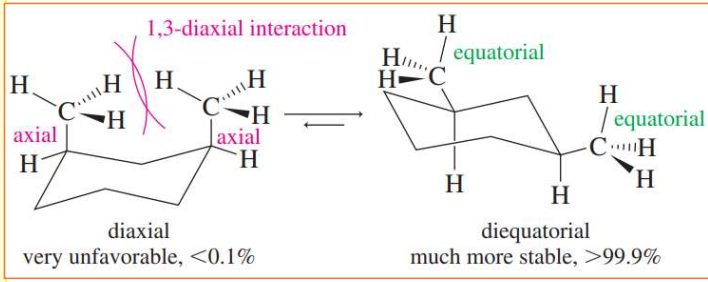
Cis-1,4-di-*t*-butylcyclohexane

An axial *t*-butyl group really is very unfavourable. In *cis*-1,4-di-*t*-butylcyclohexane, one *t*-butyl group would be forced axial if the compound existed in a chair conformation. To avoid this, the compound prefers to pucker into a twist boat so that the two large groups can both be in equatorial positions (or 'pseudoequatorial', since this is not a chair).

cis-1,4-di-*t*-butylcyclohexane



the twist-boat conformer (with both *t*-butyl groups in pseudoequatorial positions) is lower in energy than the chair conformer.



cis-1,3-dimethylcyclohexane