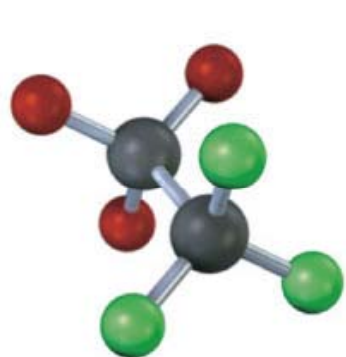
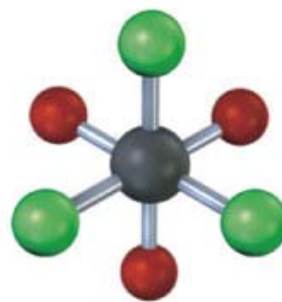
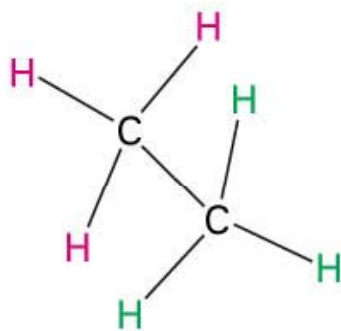


Conformational Isomers

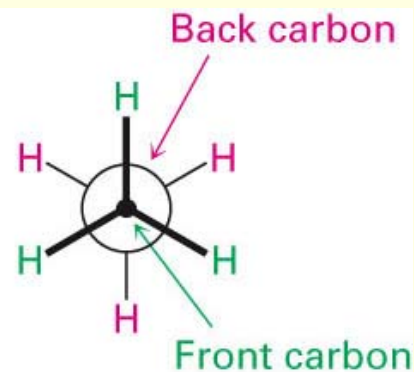
- Isomers that differ as a result of sigma bond rotation of C-C bond in alkanes



**Sawhorse
representation**

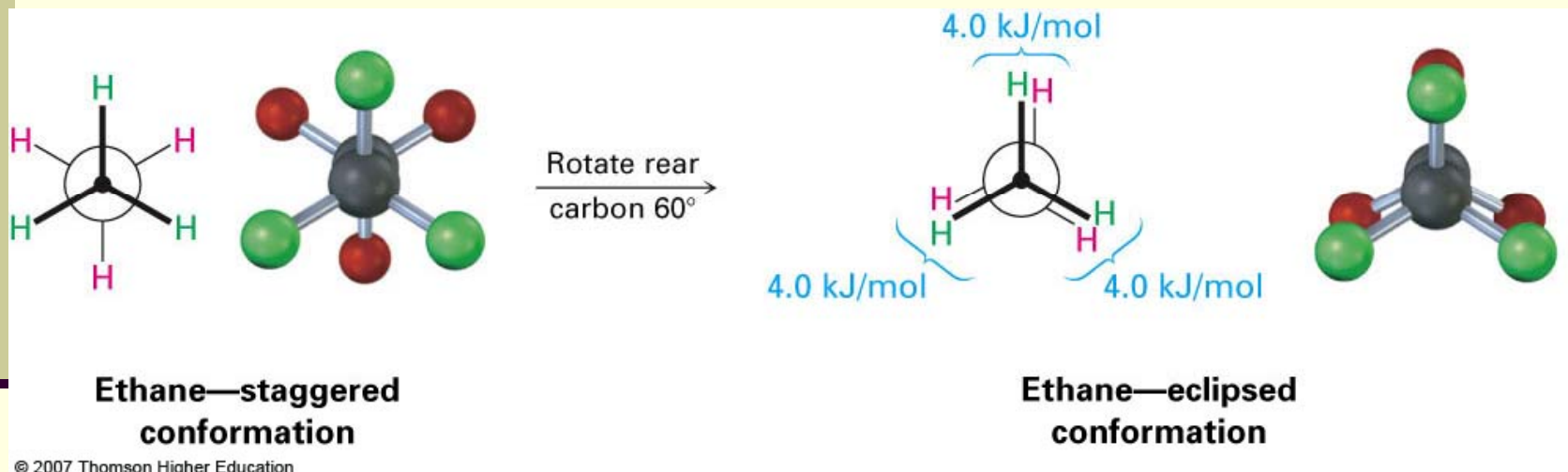


**Newman
projection**



Bond Rotation and Newman Projections

- As carbon-carbon bond rotates, interconvert between staggered and eclipsed conformers

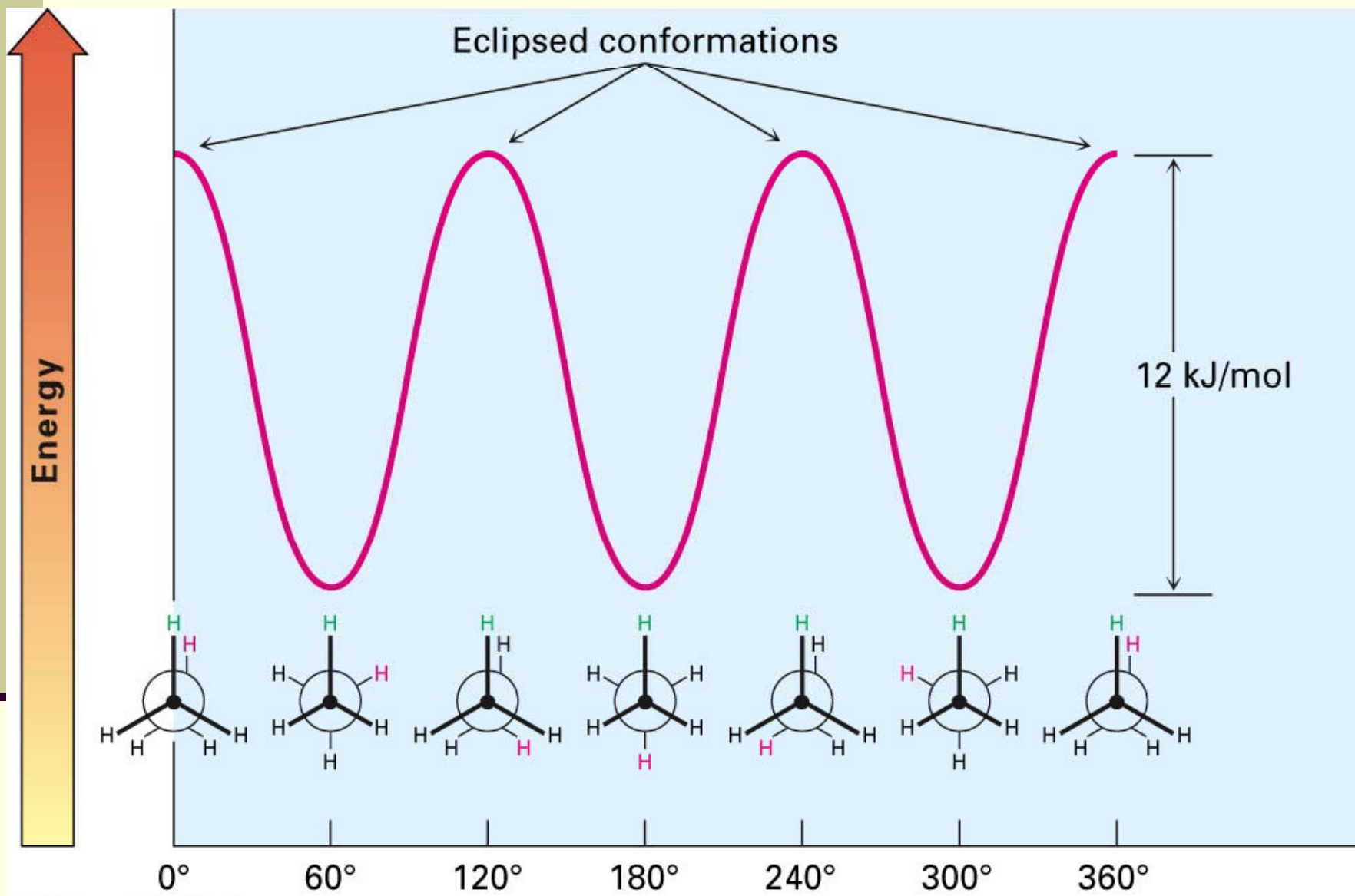


Eclipsed conformer is 12.0 kJ/mol higher in energy ('free' rotation at room temperature)

Torsional Strain Energy

Force that opposes rotation due to the repulsion of bonding electrons

- We do not observe perfectly free rotation
- There is a barrier to rotation, and some conformers are more stable than others
- Small energy barrier easily overcome at RT
- **Each eclipsed H-H costs 4 kJ/mol of Torsional Energy**



Strain Energy in Alkanes

- **Torsional Strain**
- **Steric strain-** repulsive interaction occurring between atoms that are forced closer together than their atomic radii allow

Table 3.5 | Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost	
		(kJ/mol)	(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	2.6
CH ₃ ↔CH ₃ gauche	Steric strain	3.8	0.9

In Class: Conformations of Higher and Branched Alkanes

- Propane
 - Butane
 - 2-methylbutane
 - 2-chlorobutane
-
- draw conformers (id most/least stable)
 - define anti and gauche staggered conformers
 - predict relative energies and draw diagrams
 - determine relative percentages of conformers

What does ΔE tell us?

- $\Delta G = -RT \ln K$
 $= -2.303RT \log K$

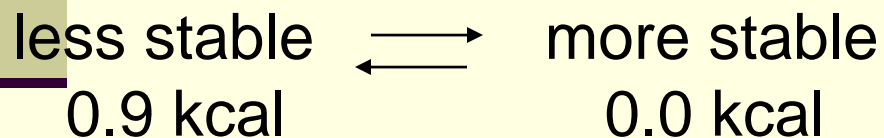
- which can rearrange to

$$\log K = -\Delta G / 1.36 \quad \text{where } R = 0.001987 \text{ kcal/K}^* \text{mol}$$

or $T = 298 \text{ K}$

(1 kcal = 4.14 kJ)

$$K = 10^{-(\Delta G / 1.36)}$$

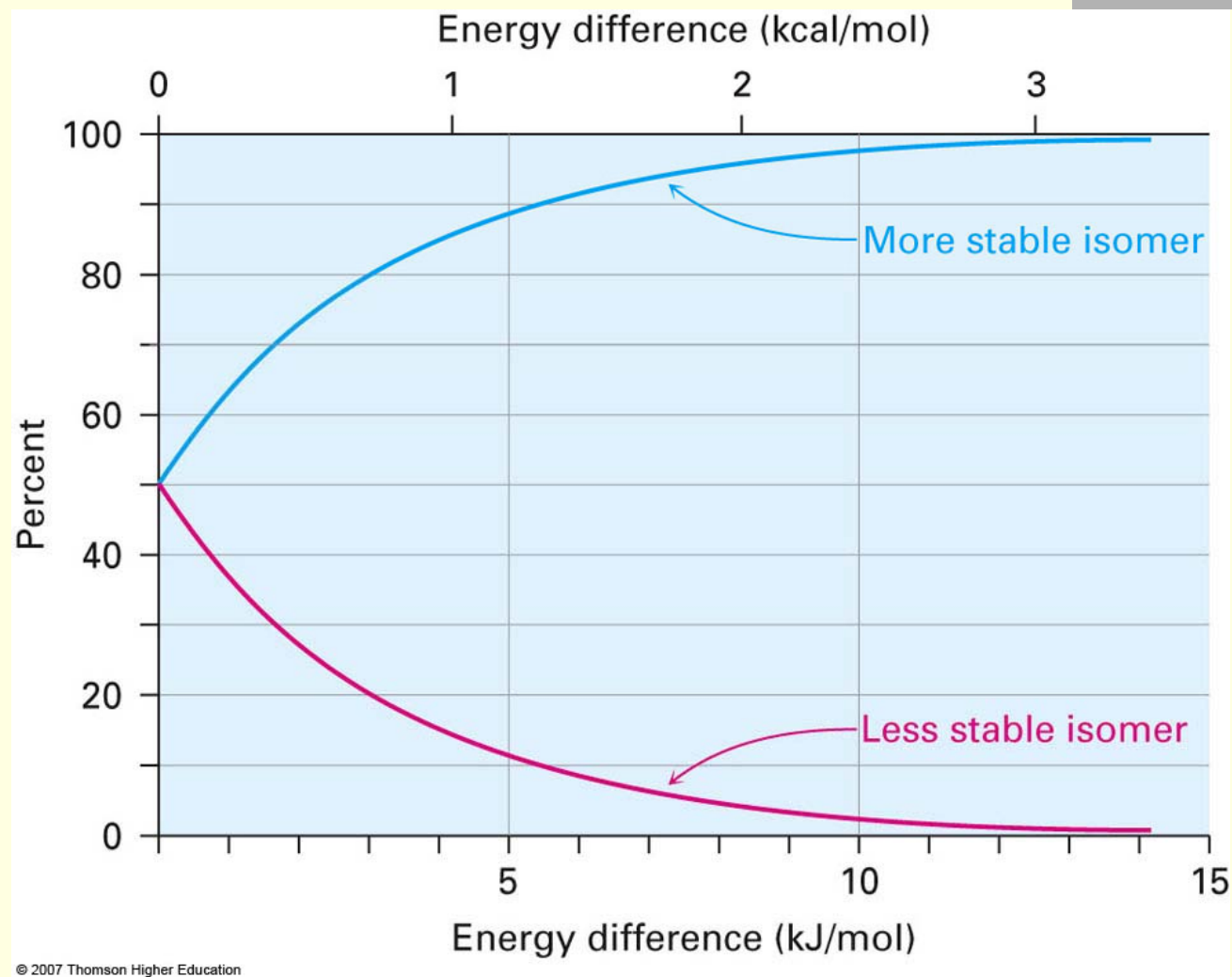


$$K = 10^{-(-0.9/1.36)} = 4.5$$

$\Delta G = -0.9 \text{ kcal/mol}$
(product - reactant)

so product : reactant is 4.5:1
or **82% pdt** and **18% reactant**

What does ΔE tell us?



Cycloalkanes

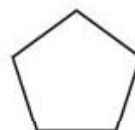
- **Cycloalkanes** are alkanes that have carbon atoms that form a ring (called alicyclic compounds)
- Simple cycloalkanes rings of —CH₂— units, (CH₂)_n, or C_nH_{2n}



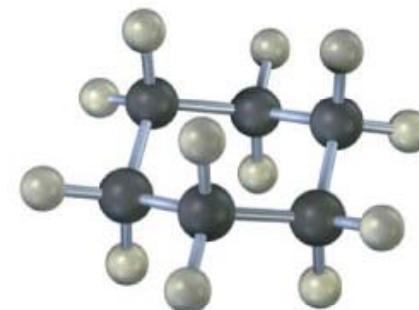
Cyclopropane



Cyclobutane



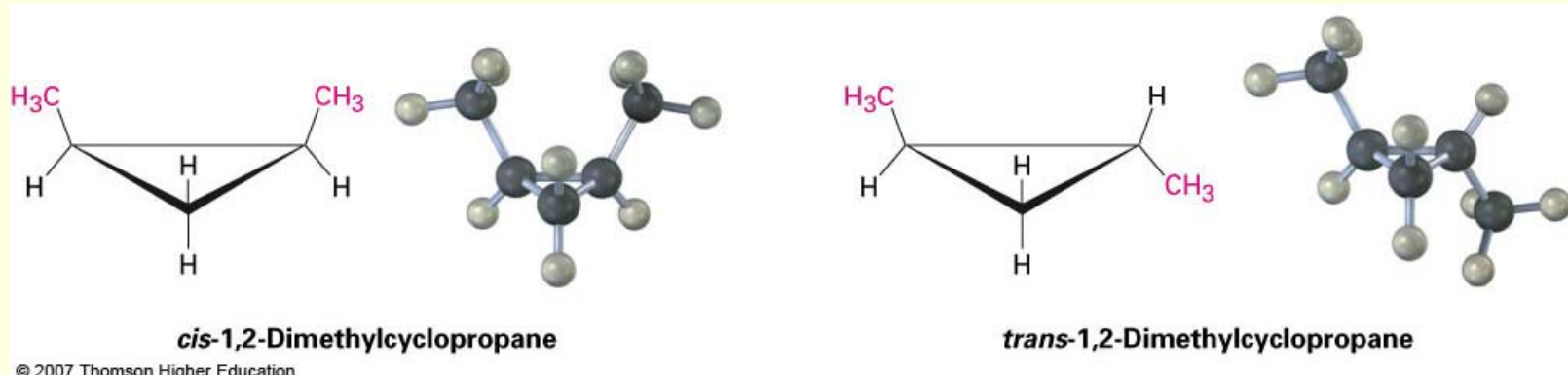
Cyclopentane



Cyclohexane

Cis-Trans Isomerism in Cycloalkanes

- Rotation about C-C bonds in cycloalkanes is limited by the ring structure
- Rings have two “faces” and substituents are labeled as to their relative facial positions
- There are two different 1,2-dimethyl-cyclopropane isomers, one with the two methyls on the same side (cis) of the ring and one with the methyls on opposite sides (trans)



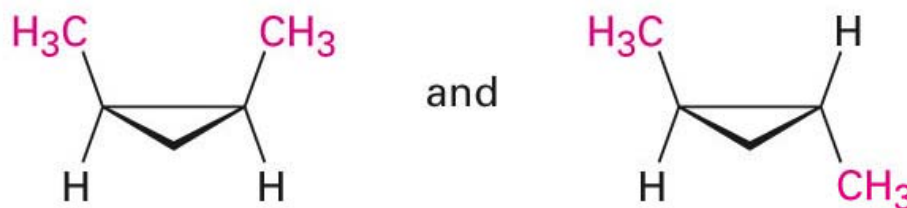
Stereoisomers

- Compounds with atoms connected in the same order but which differ in three-dimensional orientation, are **stereoisomers**
- The terms “cis” and “trans” should be used to specify stereoisomeric ring structures

Constitutional isomers
(different connections
between atoms)

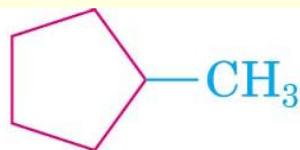


Stereoisomers
(same connections
but different three-
dimensional geometry)

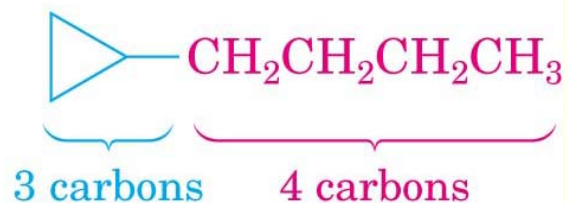


Naming Cycloalkanes

- Count the number of carbon atoms in the ring and the number in the largest substituent chain. If the number of carbon atoms in the ring is equal to or greater than the number in the substituent, the compound is named as an alkyl-substituted cycloalkane
- For an alkyl- or halo-substituted cycloalkane, start at a point of attachment as C1 and number the substituents on the ring so that the *second* substituent has as low a number as possible.
- If choice, give substituent that comes first alphabetically lower number
- Number the substituents and write the name adding prefix "cyclo"



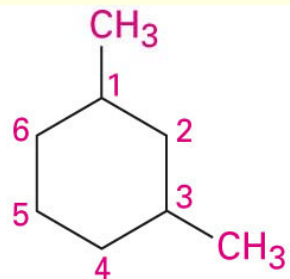
BUT



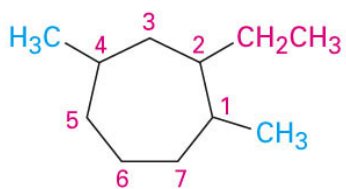
Methylcyclopentane

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1-Cyclopropylbutane



1,3-Dimethylcyclohexane

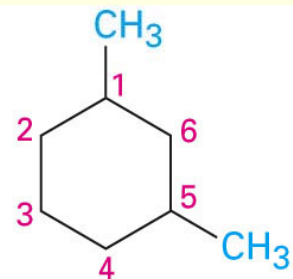


2-Ethyl-1,4-dimethylcycloheptane

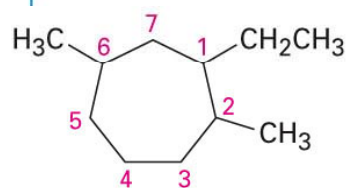
↑
Lower

↑
Lower

NOT

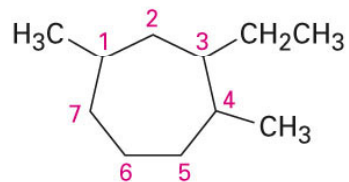


1,5-Dimethylcyclohexane



1-Ethyl-2,6-dimethylcycloheptane

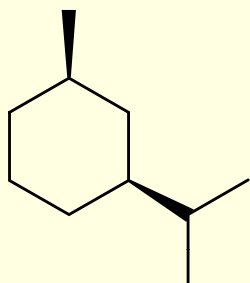
↑
Higher



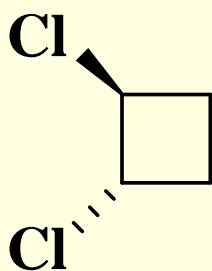
3-Ethyl-1,4-dimethylcycloheptane

↑
Higher

NOT



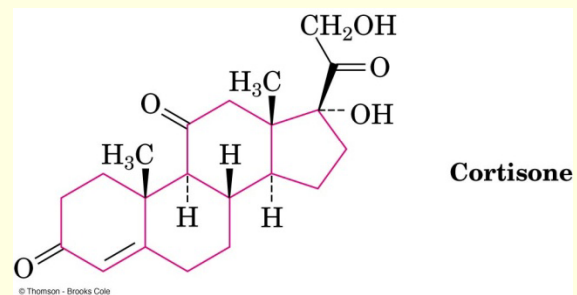
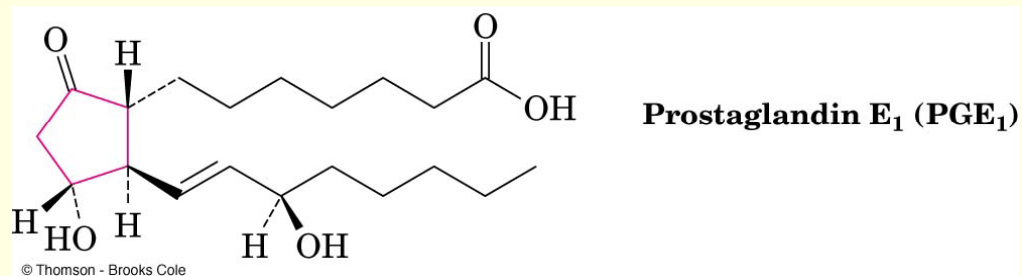
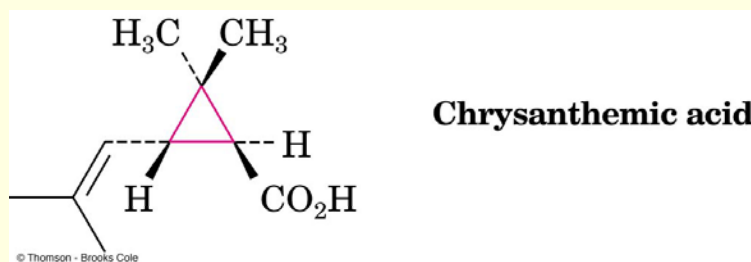
cis-1-isopropyl-3-methylcyclohexane



trans-1,2-dichlorocyclobutane

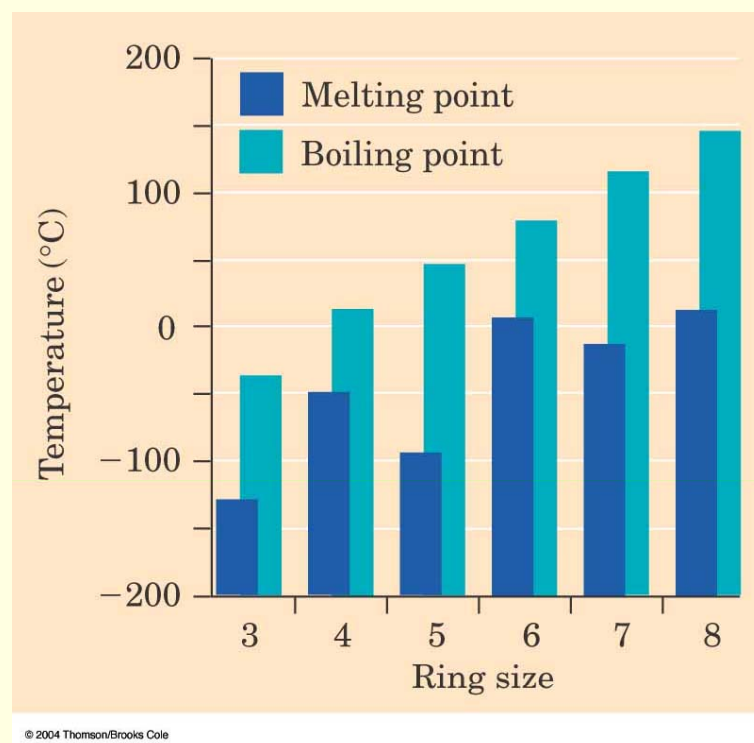
Complex Cycloalkanes

- Naturally occurring materials contain cycloalkane structures
- Examples: chrysanthemic acid (cyclopropane), prostaglandins (cyclopentane), steroids (cyclohexanes and cyclopentane)



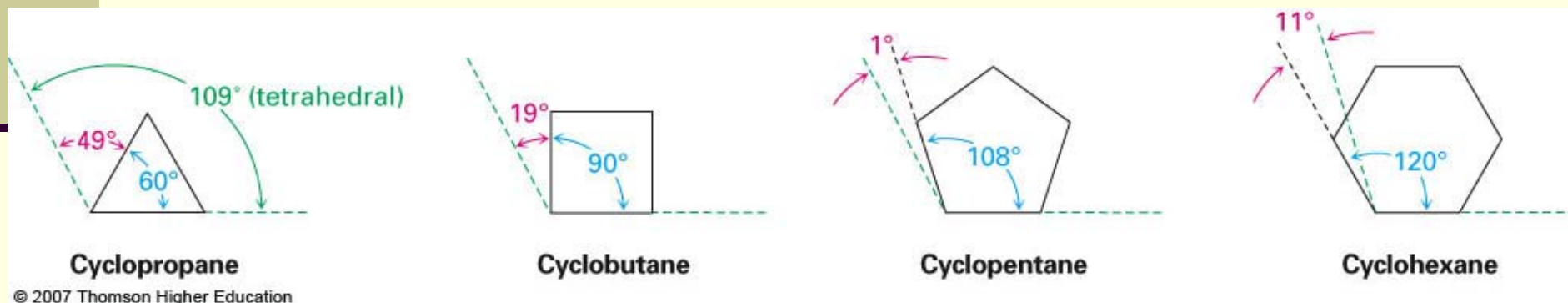
Properties of Cycloalkanes

- Melting points are affected by the shapes and the way that crystals pack so they do not change uniformly



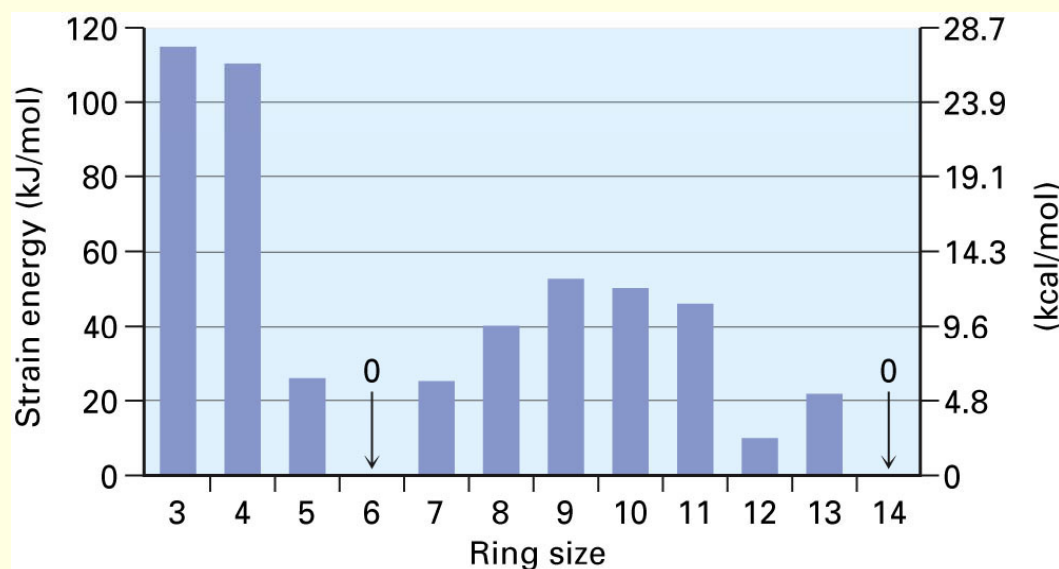
Stability of Cycloalkanes: Ring Strain

- Rings larger than 3 atoms are not flat
- **Cyclic molecules** can assume nonplanar conformations to minimize angle strain and torsional strain by ring-puckering
- Larger rings have many more possible conformations than smaller rings and are more difficult to analyze



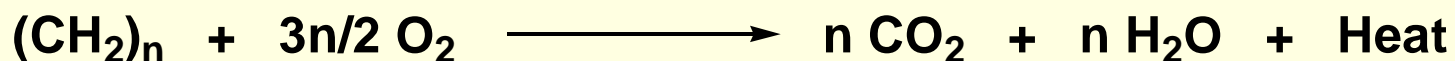
Stability of Cycloalkanes: The Baeyer Strain Theory

- Baeyer (1885): since carbon prefers to have bond angles of approximately 109° , ring sizes other than five and six may be too *strained* to exist
- Rings from 3 to 30 C's do exist but are strained due to bond bending distortions and steric interactions



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$$[\Delta H/\text{CH}_2(\text{ring}) - \Delta H/\text{CH}_2(\text{acyclic})] * n$$



Summary: Types of Strain

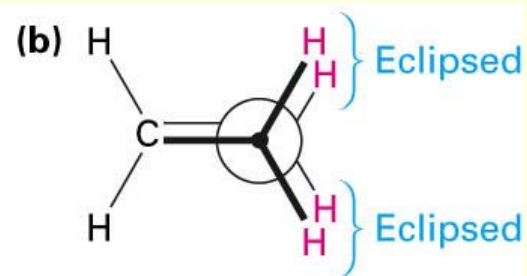
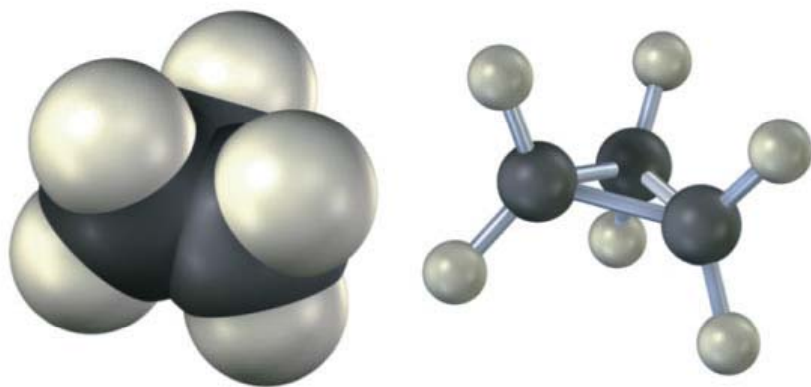
- **Angle strain** - expansion or compression of bond angles away from most stable
- **Torsional strain** - eclipsing of bonds on neighboring atoms
- **Steric strain** - repulsive interactions between nonbonded atoms in close proximity
- **RING STRAIN** = combination of Angle Strain + Torsional Strain

Conformations of Cycloalkanes

Cyclopropane

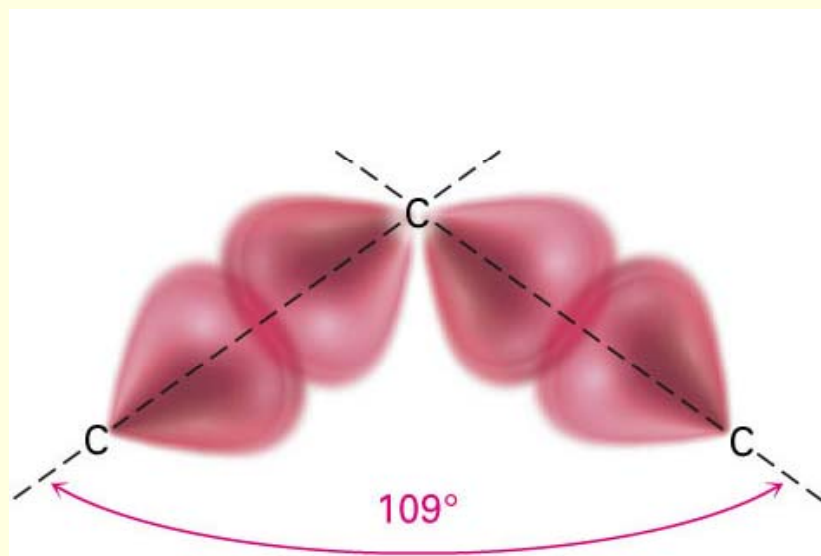
- 3-membered ring must have planar structure
- Symmetrical with C–C–C bond angles of 60°
- Requires that sp^3 based bonds are bent (and weakened)
- All C-H bonds are eclipsed

(a)



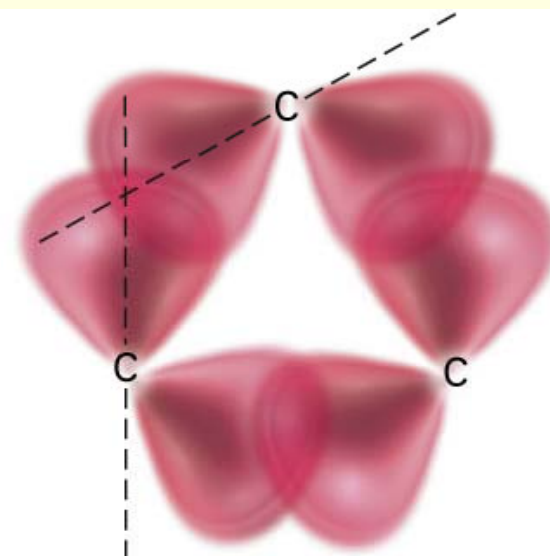
Bent Bonds of Cyclopropane

- In cyclopropane, the C-C bond is displaced outward from internuclear axis



Typical alkane C-C bonds

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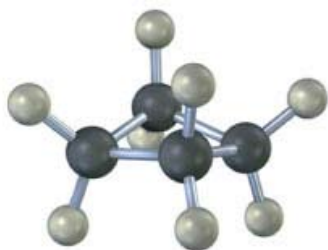


Typical bent cyclopropane C-C bonds

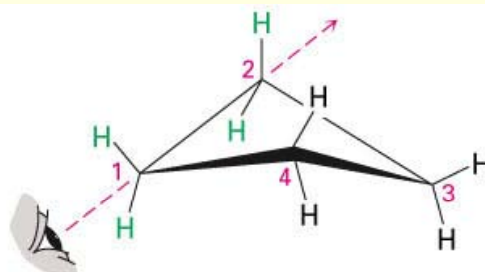
Cyclobutane

- Cyclobutane has less angle strain than cyclopropane but more torsional strain because of its larger number of ring hydrogens
- Cyclobutane is slightly bent out of plane - one carbon atom is about 25° above
 - The bend *increases* angle strain but *decreases* torsional strain

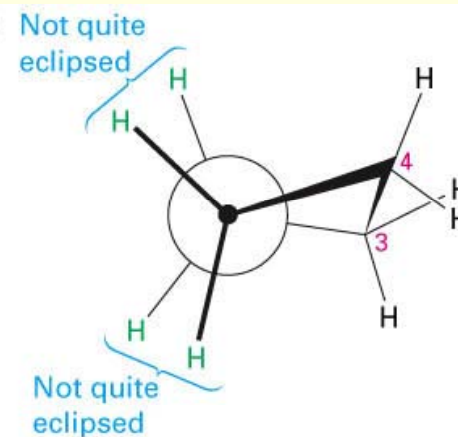
(a)



(b)

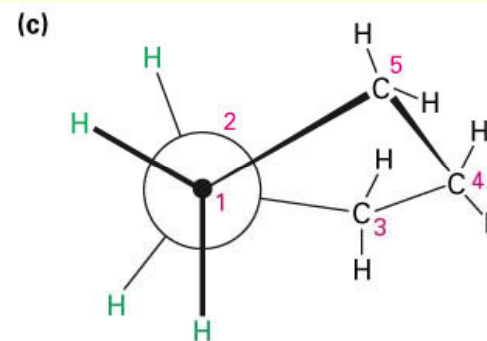
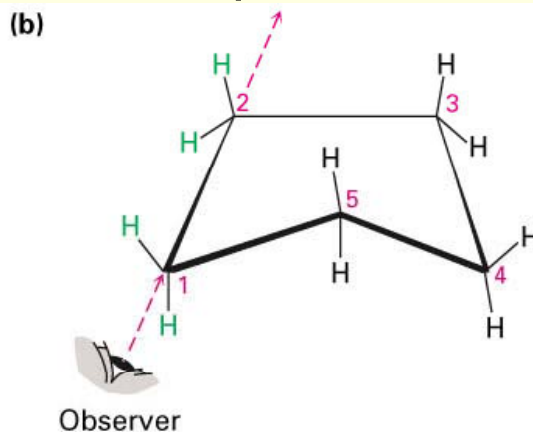
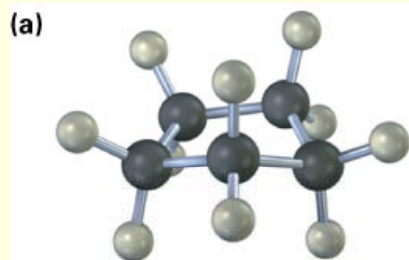


(c)



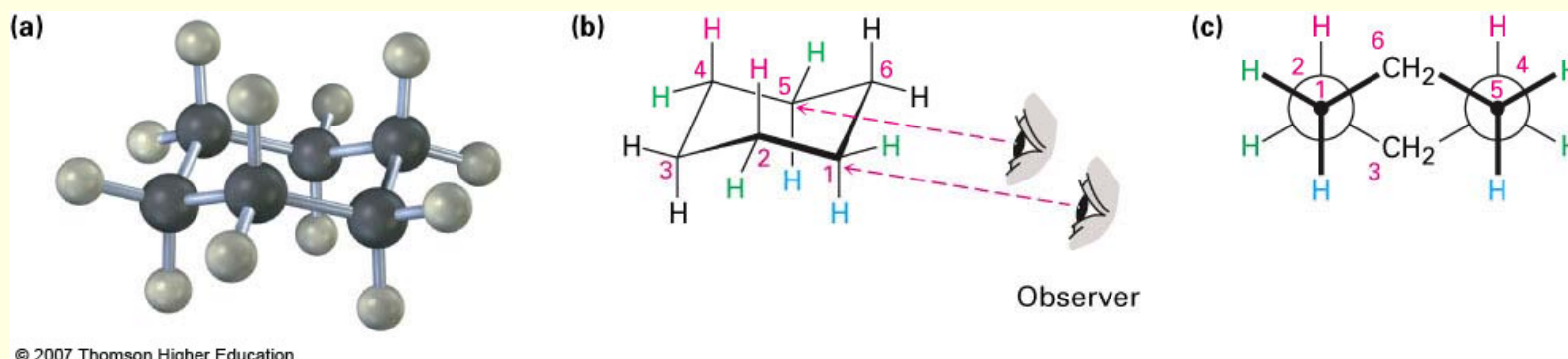
Cyclopentane

- Planar cyclopentane would have no angle strain but very high torsional strain
- Actual conformations of cyclopentane are nonplanar, reducing torsional strain
- Four carbon atoms are in a plane
 - The fifth carbon atom is above or below the plane – looks like an envelope



Conformations of Cyclohexane

- Substituted cyclohexanes occur widely in nature
- The cyclohexane ring is free of angle strain and torsional strain
- The conformation is has alternating atoms in a common plane and tetrahedral angles between all carbons
- This is called a **chair conformation**



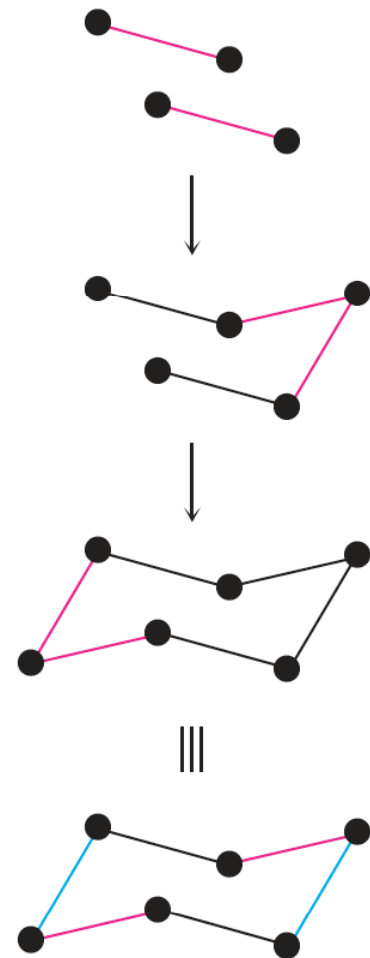
All bond angles 109.5° , and all hydrogens staggered

How to Draw Chair Cyclohexane

Step 1 Draw two parallel lines, slanted downward and slightly offset from each other. This means that four of the cyclohexane carbons lie in a plane.

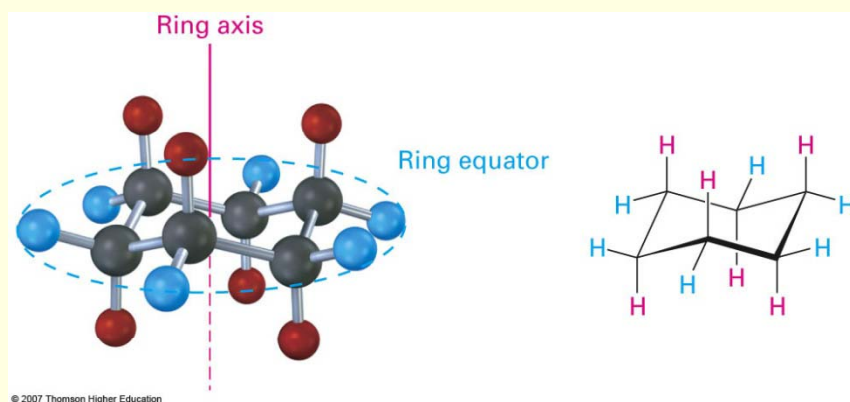
Step 2 Place the topmost carbon atom above and to the right of the plane of the other four, and connect the bonds.

Step 3 Place the bottommost carbon atom below and to the left of the plane of the middle four, and connect the bonds. Note that the bonds to the bottommost carbon atom are parallel to the bonds to the topmost carbon.



Axial and Equatorial Bonds in Cyclohexane

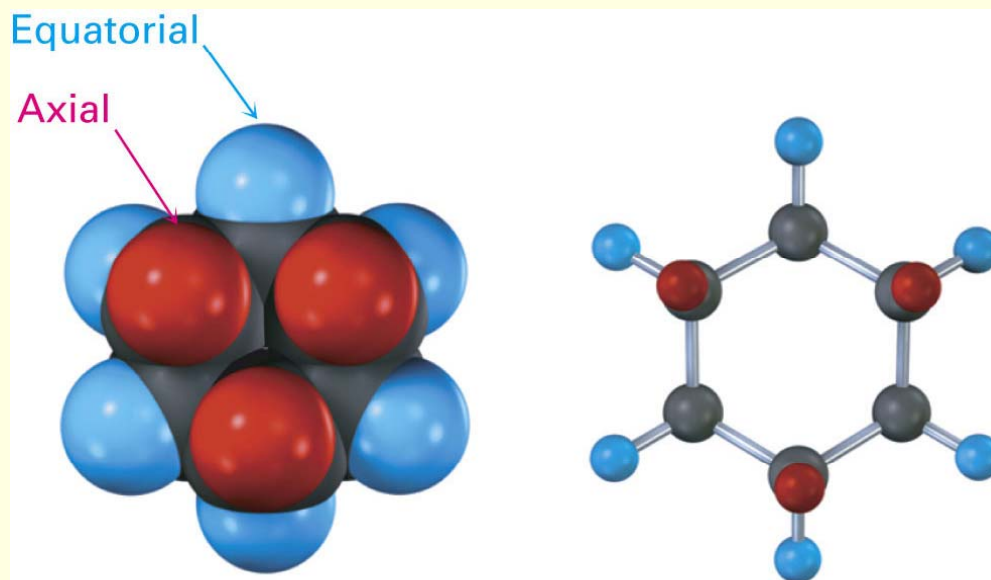
- The chair conformation has two kinds of positions for substituents on the ring: **axial** positions and **equatorial** positions
- Chair cyclohexane has six **axial** hydrogens perpendicular to the ring (parallel to the ring axis) and six **equatorial** hydrogens near the plane of the ring



You must be able to clearly indicate axial and equatorial positions

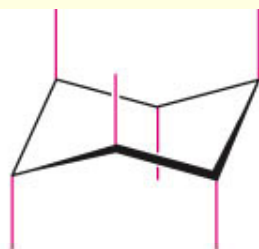
Axial and Equatorial Positions

- Each carbon atom in cyclohexane has one axial and one equatorial hydrogen
- Each face of the ring has three axial and three equatorial hydrogens in an alternating arrangement



Drawing the Axial and Equatorial Hydrogens

Axial bonds: The six axial bonds, one on each carbon, are parallel and alternate up-down.



Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.

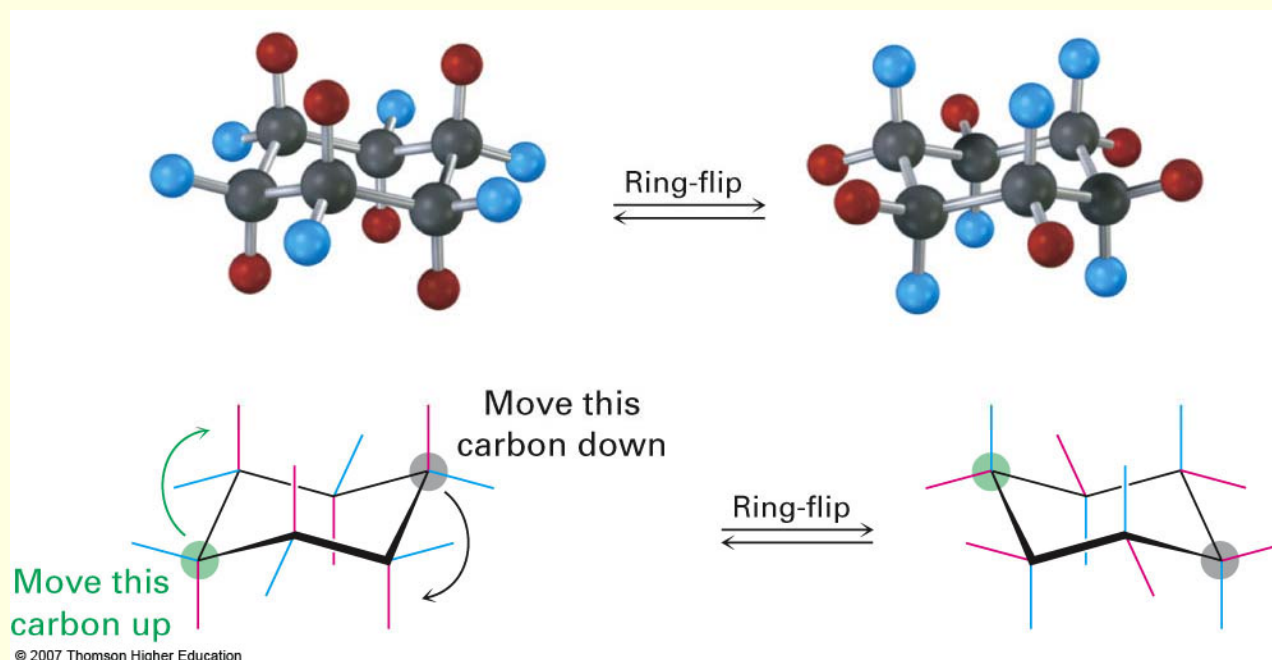


Completed cyclohexane



Conformational Mobility of Cyclohexane

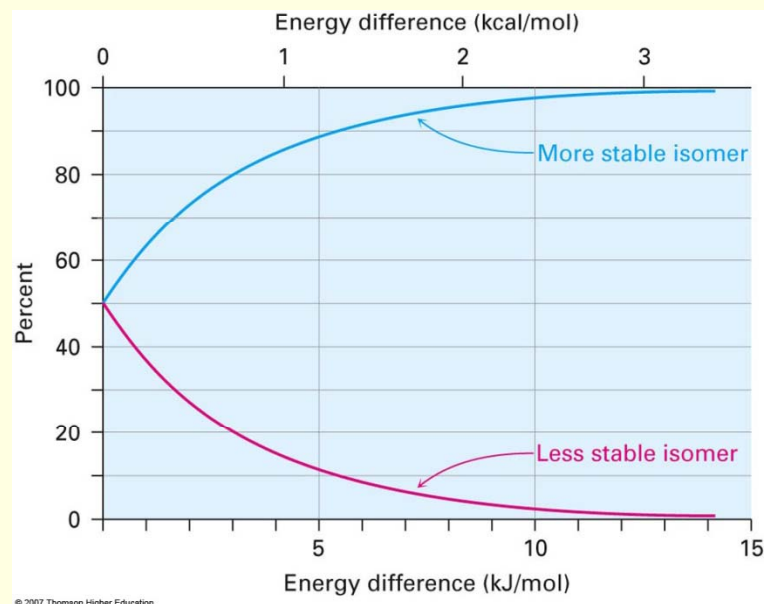
- Chair conformations readily interconvert, resulting in the **exchange** of axial and equatorial positions by a **ring-flip**



If only H's present, these two structures are identical

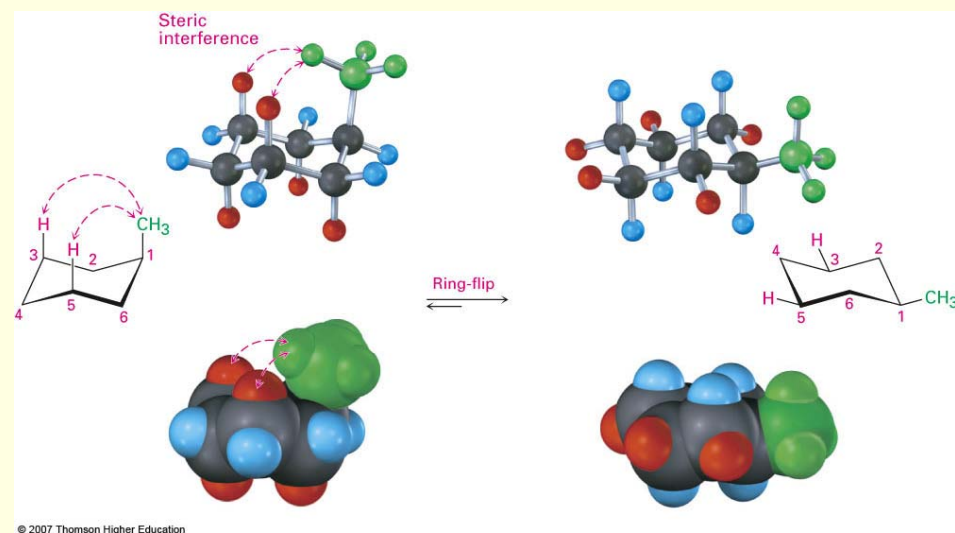
Conformations of Monosubstituted Cyclohexanes

- Cyclohexane ring rapidly flips between chair conformations at room temp.
- Two conformations of **monosubstituted** cyclohexane **aren't equally stable**.
- The equatorial conformer of methyl cyclohexane is more stable than the axial by 7.6 kJ/mol



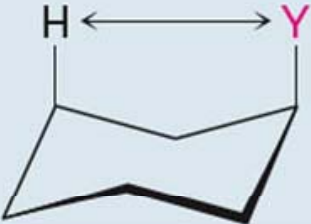
1,3-Diaxial Interactions

- Difference between axial and equatorial conformers is due to steric strain caused by **1,3-diaxial interactions**
- Hydrogen atoms of the axial methyl group on C1 are too close to the axial hydrogens three carbons away on C3 and C5, resulting in 7.6 kJ/mol of steric strain



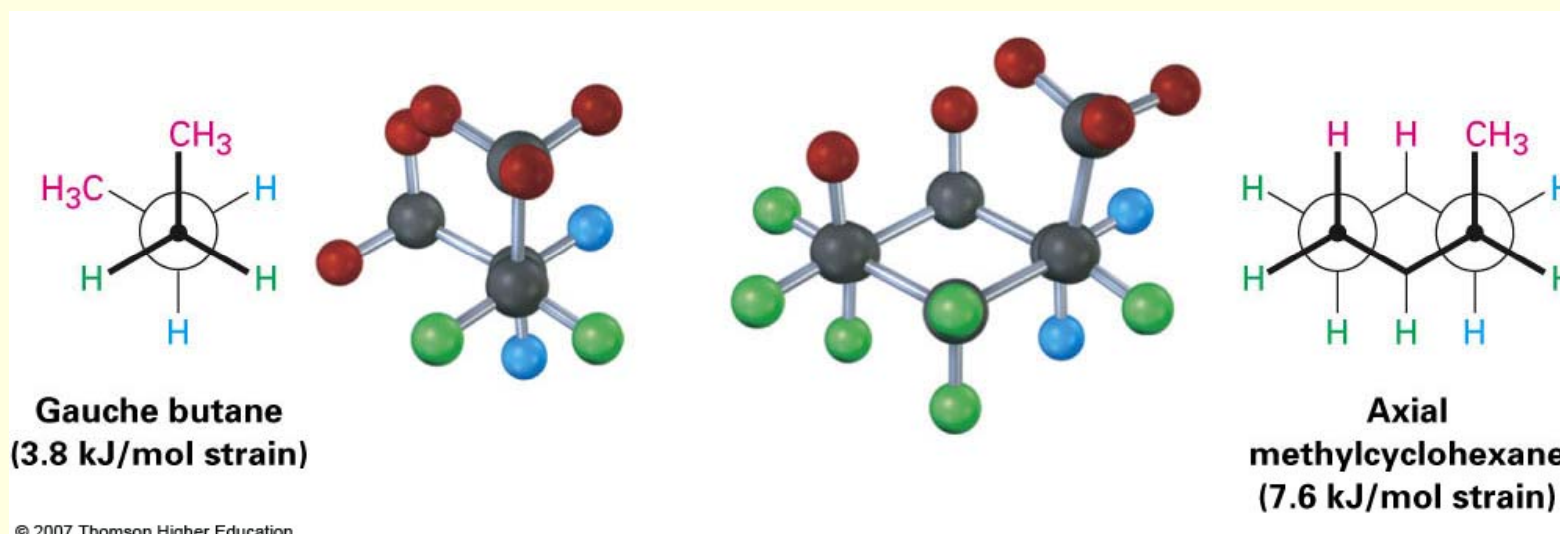
7.6 kJ/mol higher
in energy

Table 4.1 Steric Strain in Monosubstituted Cyclohexanes

Y	1,3-Diaxial strain		
	(kJ/mol)	(kcal/mol)	
F	0.5	0.12	
Cl, Br	1.0	0.25	
OH	2.1	0.5	
CH ₃	3.8	0.9	
CH ₂ CH ₃	4.0	0.95	
CH(CH ₃) ₂	4.6	1.1	
C(CH ₃) ₃	11.4	2.7	
C ₆ H ₅	6.3	1.5	
CO ₂ H	2.9	0.7	
CN	0.4	0.1	

Relationship to Gauche Butane Interactions

- Gauche butane is less stable than anti butane by 3.8 kJ/mol because of steric interference between hydrogen atoms on the two methyl groups
- The four-carbon fragment of axial methylcyclohexane and gauche butane have the same steric interaction
- In general, equatorial positions give more stable isomer



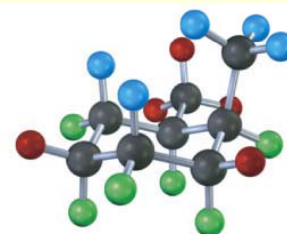
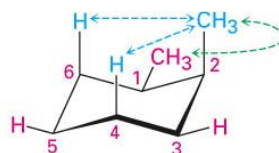
Conformational Analysis of Disubstituted Cyclohexanes

- In disubstituted cyclohexanes the steric effects of both substituents must be taken into account in both conformations
- There are two isomers of 1,2-dimethylcyclohexane. *cis* and *trans*
- In the *cis* isomer, both methyl groups are on the same face of the ring, and compound can exist in two chair conformations
- Consider the sum of all interactions
- In *cis*-1,2, both conformations are equal in energy

cis-1,2-Dimethylcyclohexane

One gauche interaction (3.8 kJ/mol)
Two CH₃ ↔ H diaxial interactions (7.6 kJ/mol)

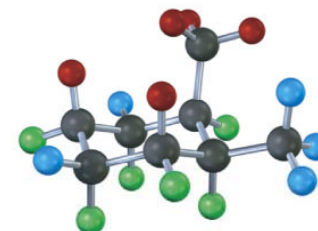
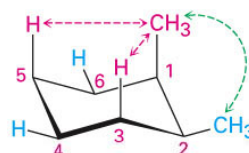
Total strain: 3.8 + 7.6 = 11.4 kJ/mol



Ring-flip

One gauche interaction (3.8 kJ/mol)
Two CH₃ ↔ H diaxial interactions (7.6 kJ/mol)

Total strain: 3.8 + 7.6 = 11.4 kJ/mol

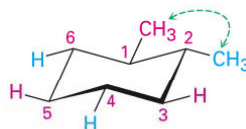


Trans-1,2-Dimethylcyclohexane

- Methyl groups are on opposite faces of the ring
- One trans conformation has both methyl groups equatorial and only a gauche butane interaction between methyls (3.8 kJ/mol) and no 1,3-diaxial interactions
- The ring-flipped conformation has both methyl groups axial with four 1,3-diaxial interactions
- Steric strain of $4 \times 3.8 \text{ kJ/mol} = 15.2 \text{ kJ/mol}$ makes the diaxial conformation 11.4 kJ/mol less favorable than the diequatorial conformation
- *trans*-1,2-dimethylcyclohexane will exist almost exclusively (>99%) in the diequatorial conformation

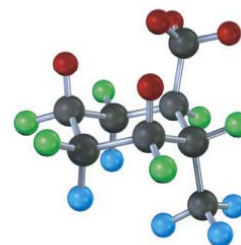
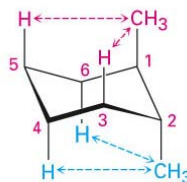
trans-1,2-Dimethylcyclohexane

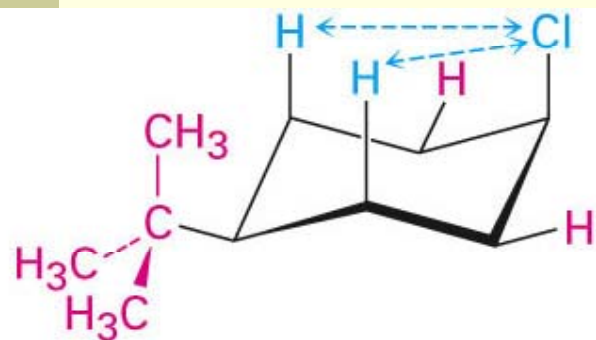
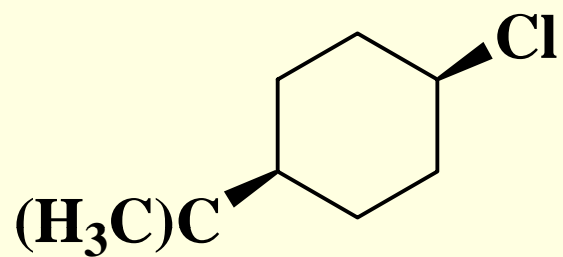
One gauche interaction (3.8 kJ/mol)



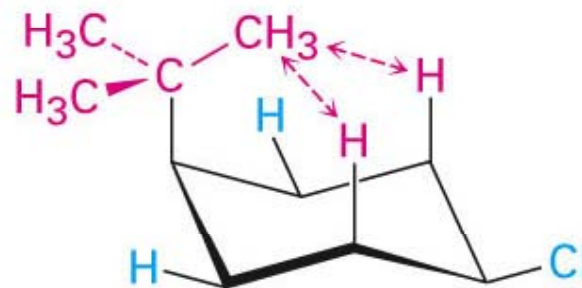
Ring-flip

Four CH₃ ↔ H diaxial interactions (15.2 kJ/mol)





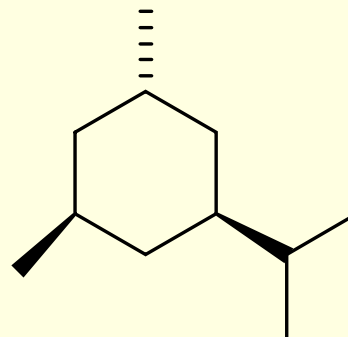
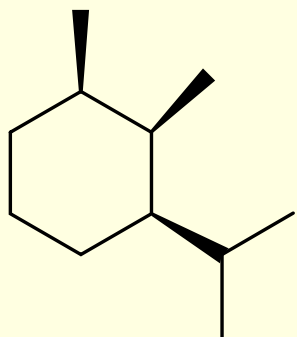
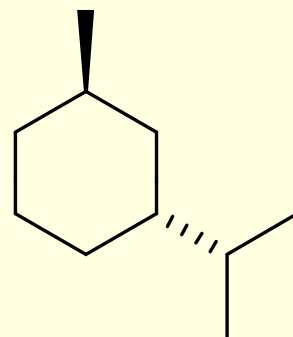
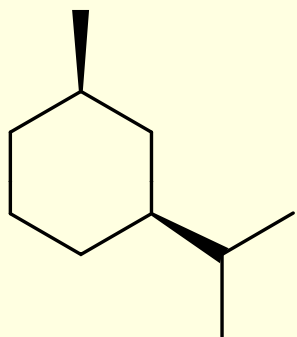
Ring-flip
↔



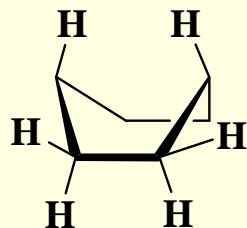
$2 \times 1.0 = 2.0$ kJ/mol steric strain

$2 \times 11.4 = 22.8$ kJ/mol steric strain

Draw the two chair conformers and calculate the strain energy for each chair. Which is more stable?

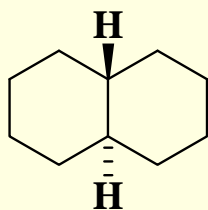


Additional Cyclic Structures

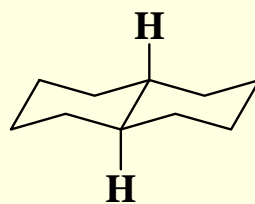


Boat Cyclohexane

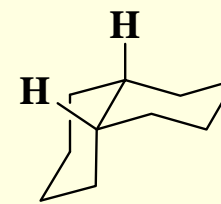
Fused Polycycles



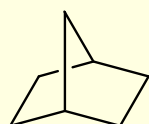
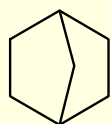
trans-decalin



cis-decalin



Bridged Polycycles



bicyclo[2.2.1]heptane