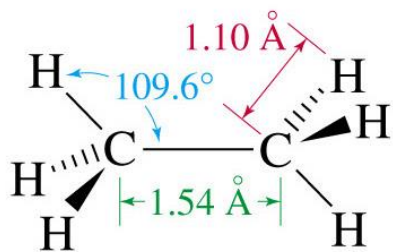


# Conformational Analysis

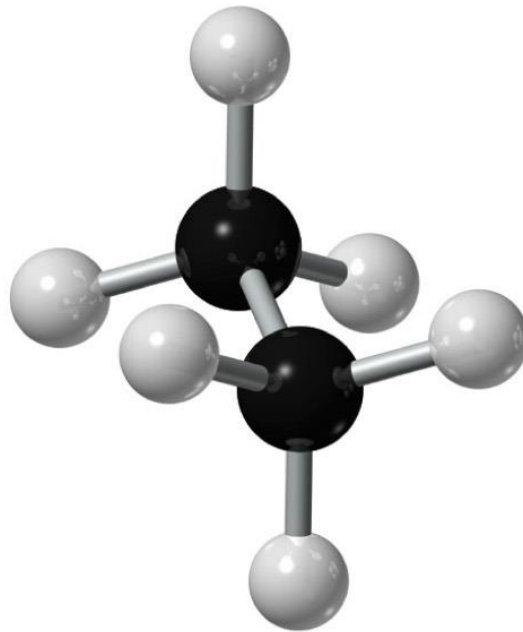
Cyclohexane Conformations

Alkane conformations

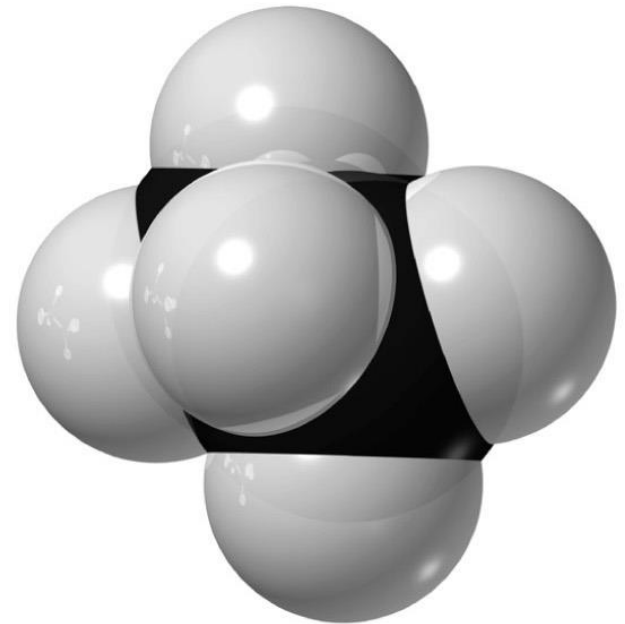
# Views of Ethane



ethane

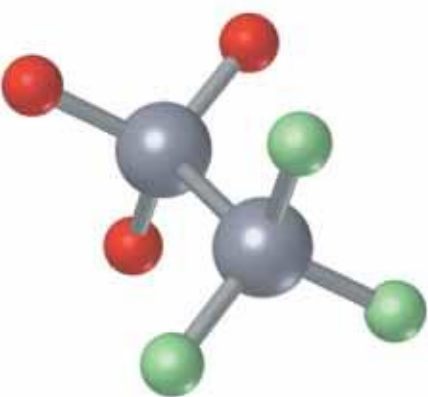


ethane

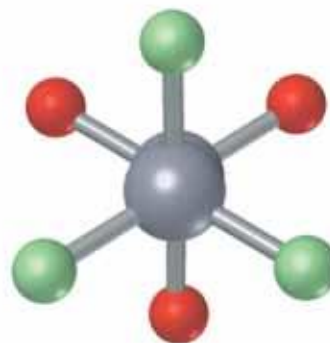
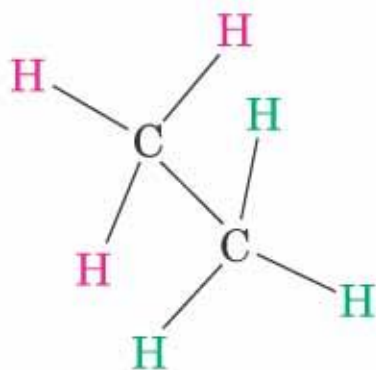


ethane

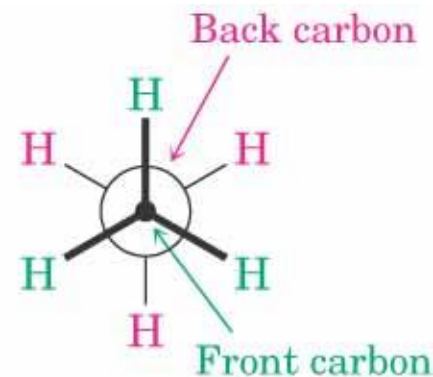
# The Newman Projection



**Sawhorse  
representation**

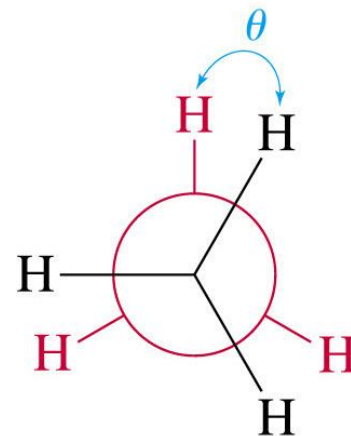
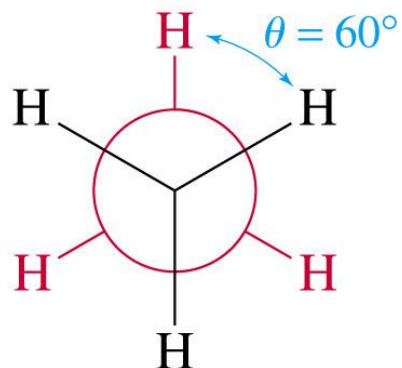
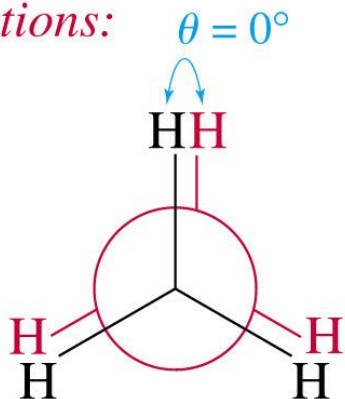


**Newman  
projection**

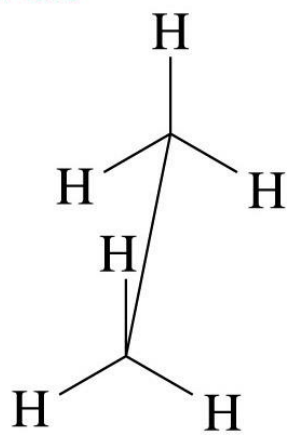


# Rotational Conformations of Ethane

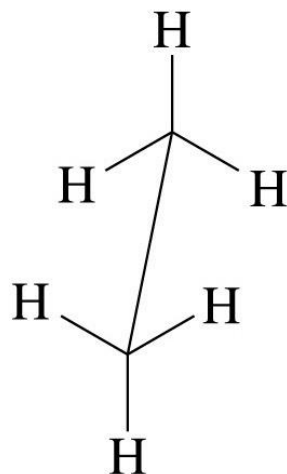
*Newman projections:*



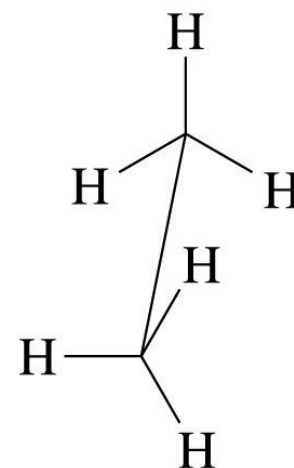
*Sawhorse structures:*



eclipsed,  $\theta = 0^\circ$



staggered,  $\theta = 60^\circ$



skew,  $\theta = \text{anything else}$

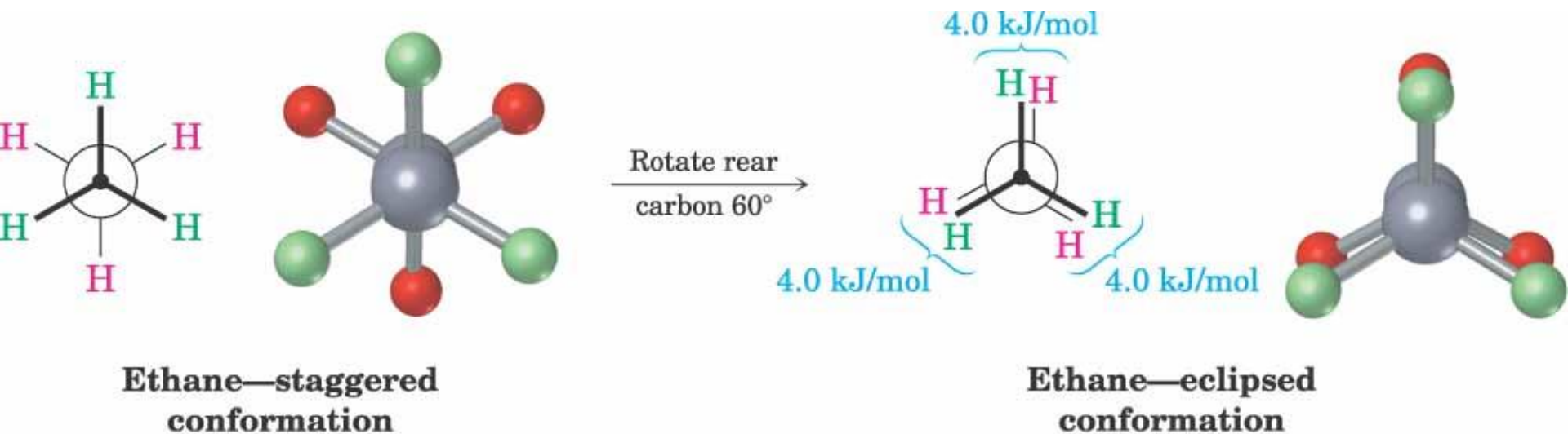
# Definitions

- **Conformations** - Different spatial arrangements that a molecule can adopt due to rotation about sigma bonds.
- **Staggered** - A low energy conformation where the bonds on adjacent atoms bisect each other ( $60^\circ$  dihedral angle), maximizing the separation.
- **Eclipsed** - A high energy conformation where the bonds on adjacent atoms are aligned with each other ( $0^\circ$  dihedral angle).

# Definitions

- **Anti** - Description given to two substituents attached to adjacent atoms when their bonds are at  $180^\circ$  with respect to each other.
- **Syn** - Description given to two substituents attached to adjacent atoms when their bonds are at  $0^\circ$  with respect to each other.
- **Gauche** - Description given to two substituents attached to adjacent atoms when their bonds are at  $60^\circ$  with respect to each other.

# 60° Rotation Causes Torsional or Eclipsing Strain

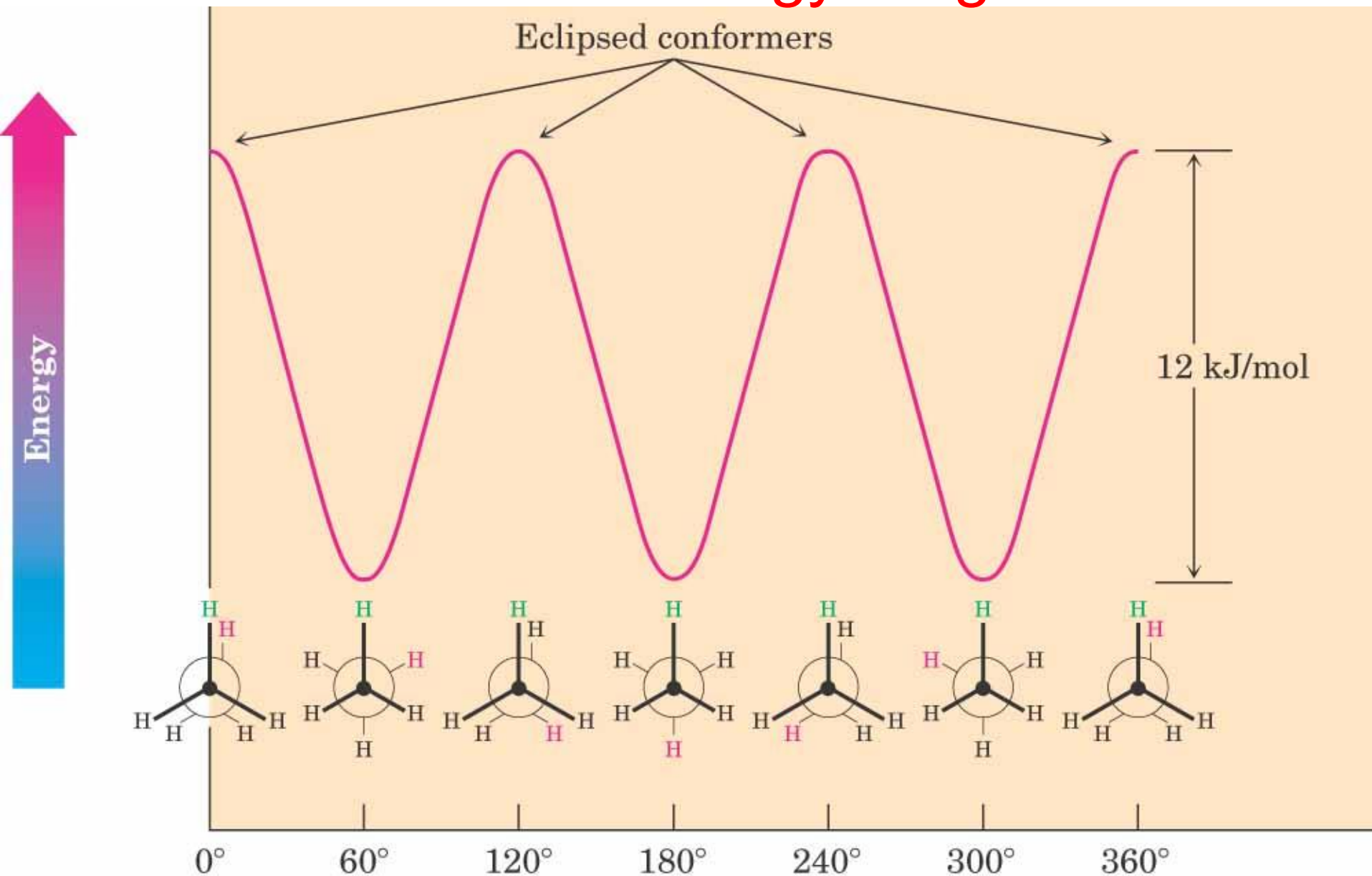


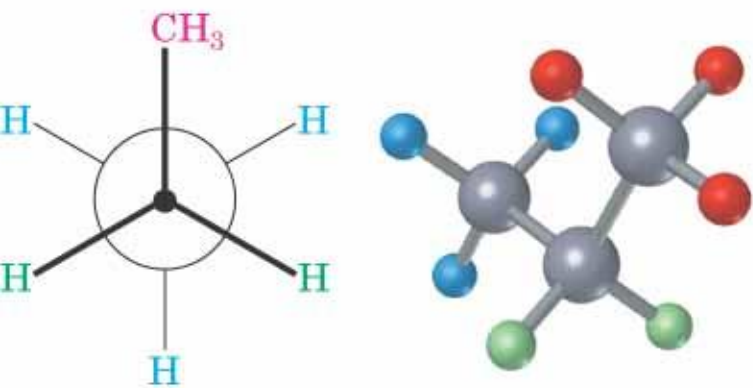
# Types of Strain

- **Steric** - Destabilization due to the repulsion between the electron clouds of atoms or groups. Groups try to occupy some common space.
- **Torsional** - Destabilization due to the repulsion between pairs of bonds caused by the electrostatic repulsion of the electrons in the bonds. Groups are eclipsed.
- **Angle** - Destabilisation due to distortion of a bond angle from its optimum value caused by the electrostatic repulsion of the electrons in the bonds. e.g. cyclopropane



# Potential Energy Diagram

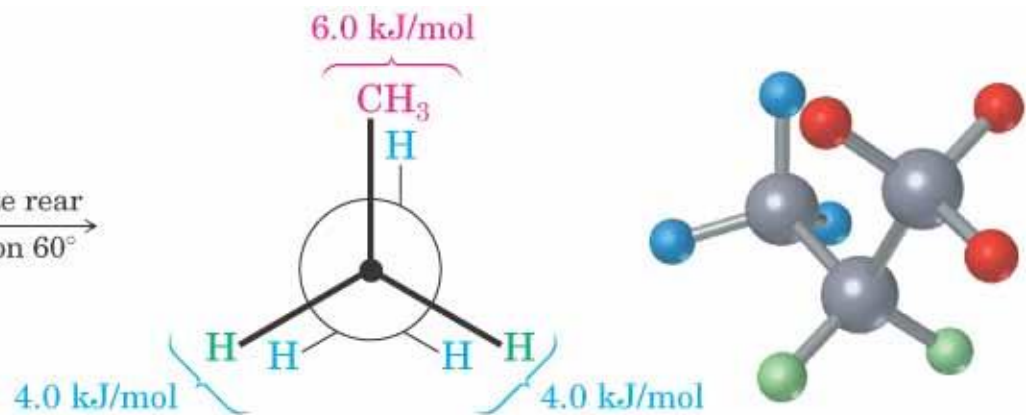




**Staggered propane**

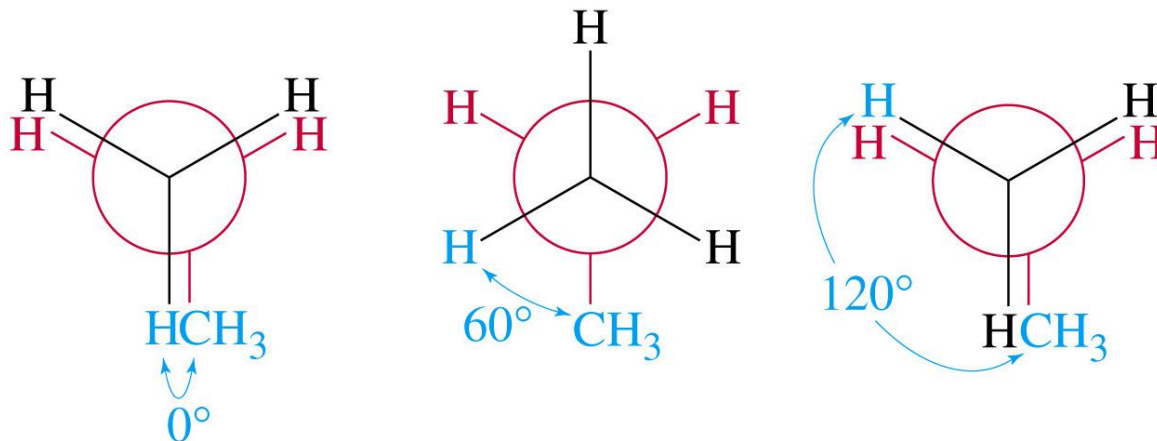
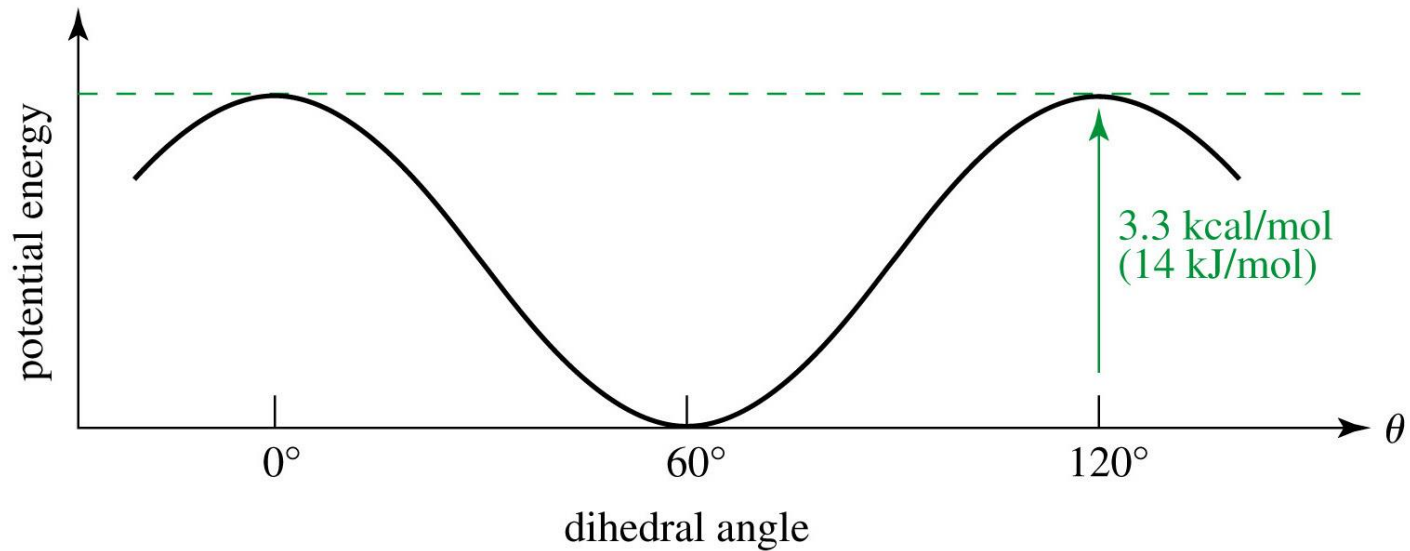
© 2004 Thomson/Brooks Cole

Rotate rear  
carbon 60°

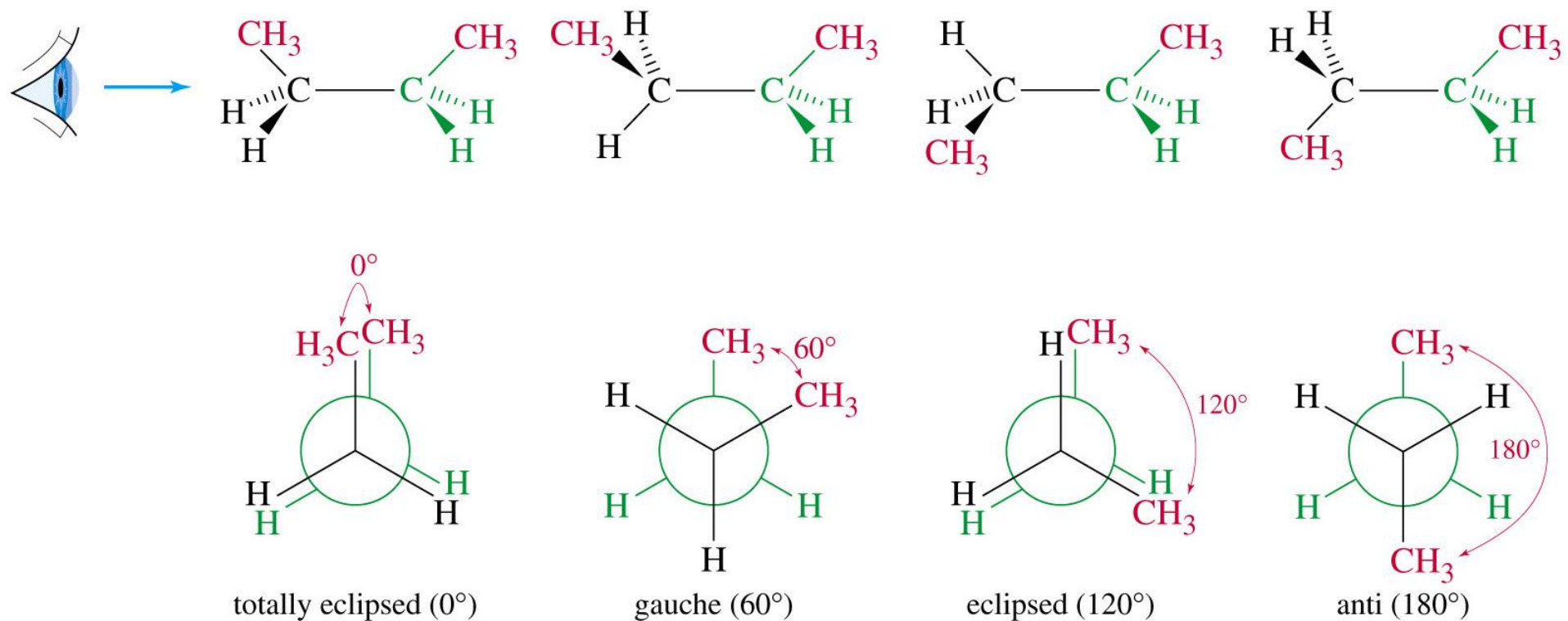


**Eclipsed propane**

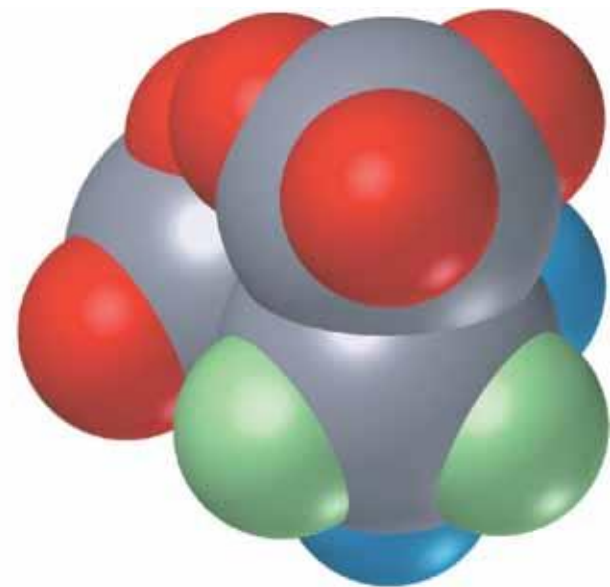
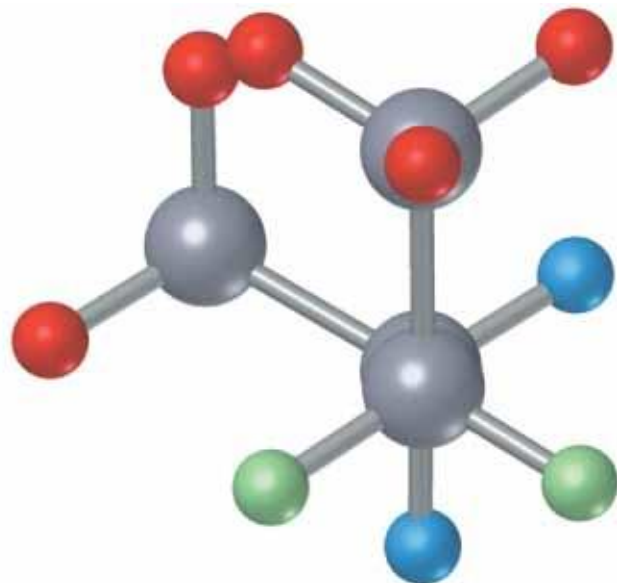
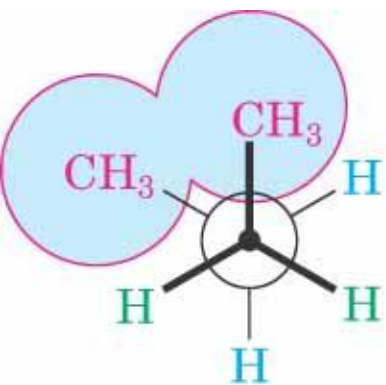
# Propane Conformations: Larger Barrier to Rotation



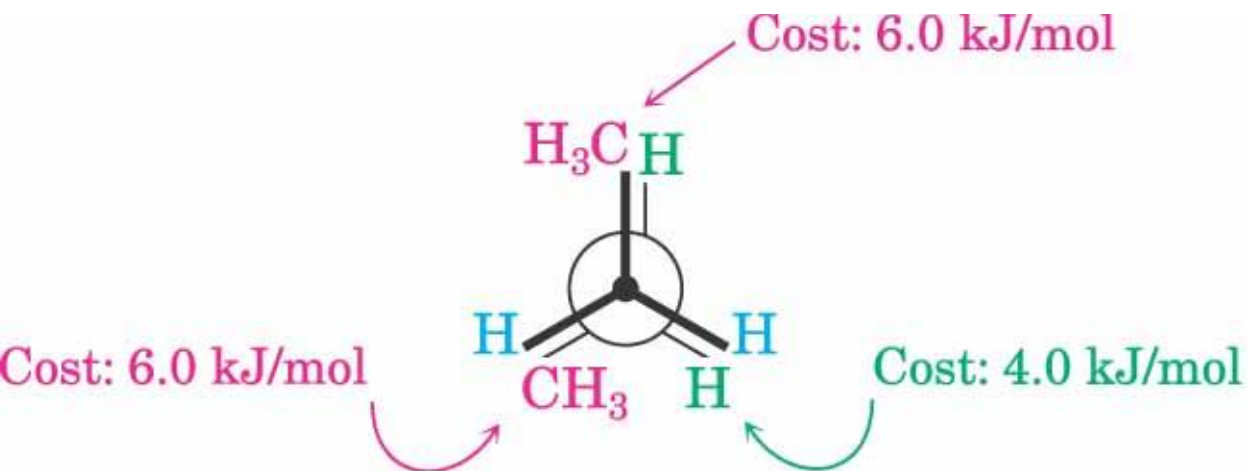
# Butane Conformations ( $C_2-C_3$ )



# Gauche Interaction in Butane

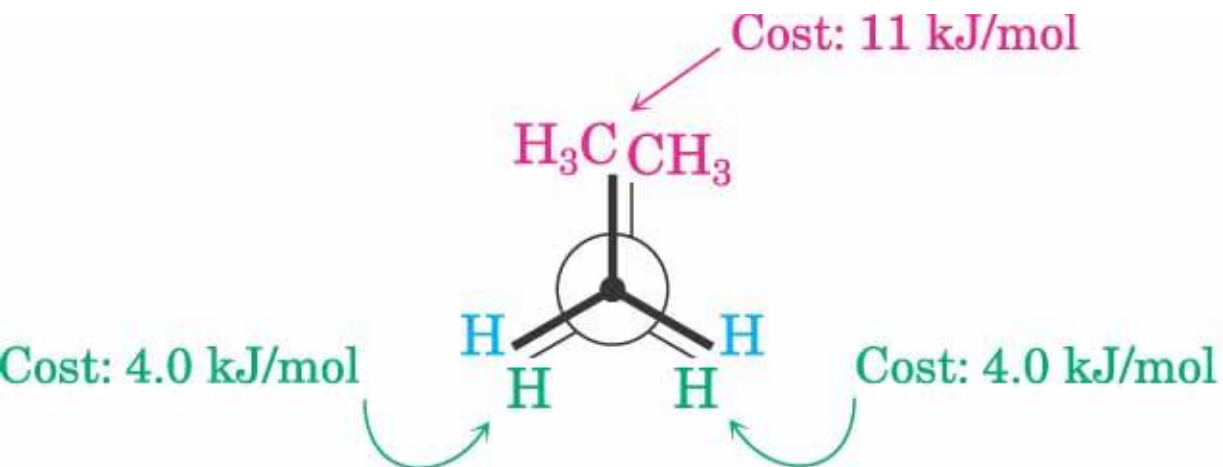


# 2 Different Eclipsed Conformations



**Total cost: 16 kJ/mol**

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**Total cost: 19 kJ/mol**

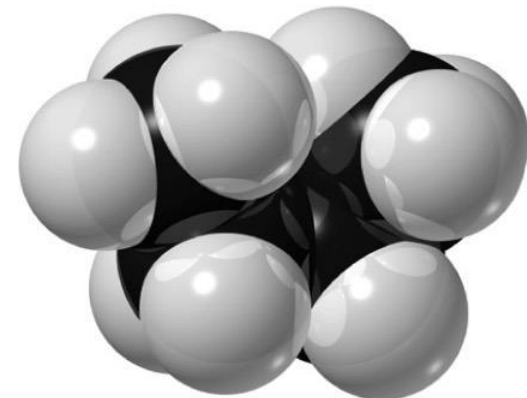
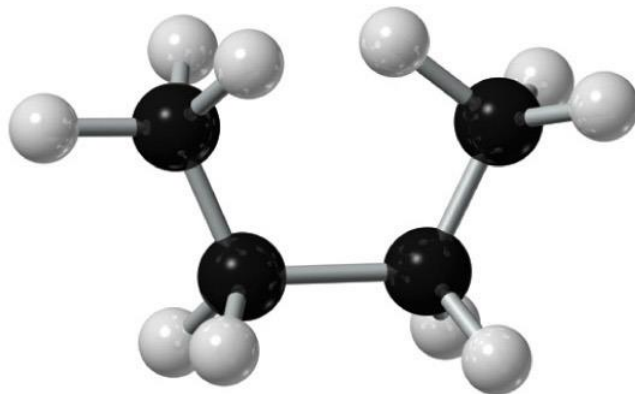
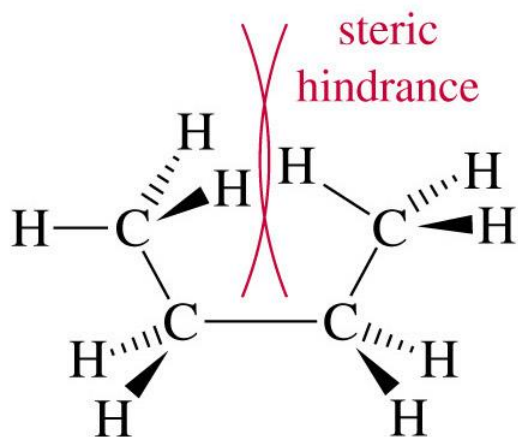
©2004 Thomson - Brooks/Cole

# Strain Energy can be Quantified

**TABLE 4.1** 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 <sub>3</sub> eclipsed	Mostly torsional strain	6.0	1.4
CH <sub>3</sub> ↔ CH <sub>3</sub> eclipsed	Torsional plus steric strain	11.0	2.6
CH <sub>3</sub> ↔ CH <sub>3</sub> gauche	Steric strain	3.8	0.9

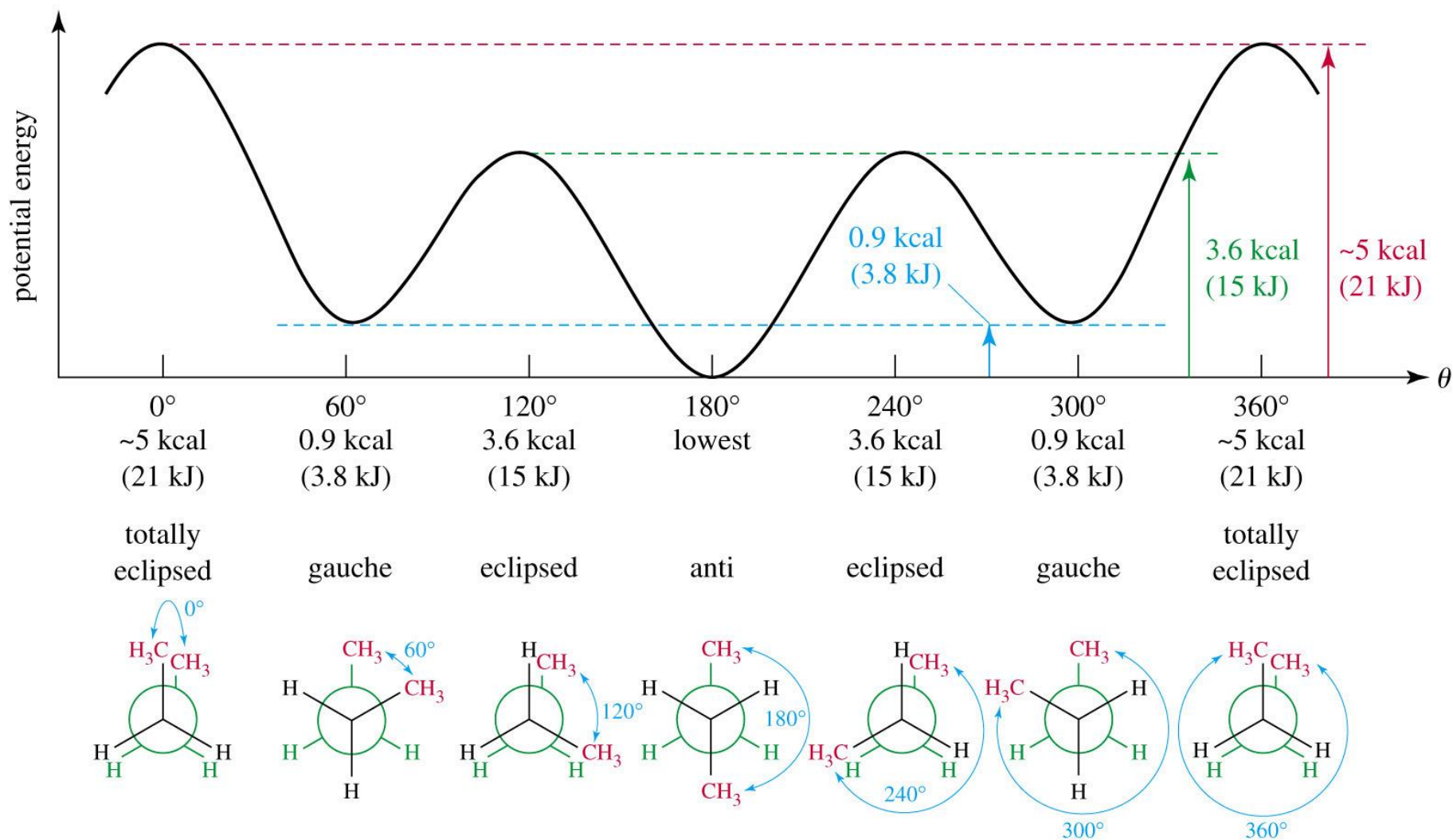
# Butane has Steric and Torsional Strain When Eclipsed

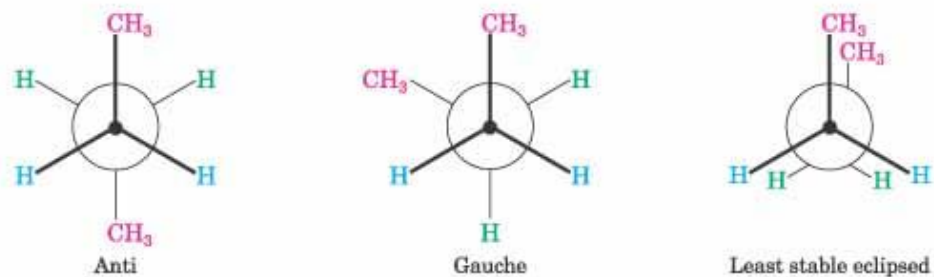
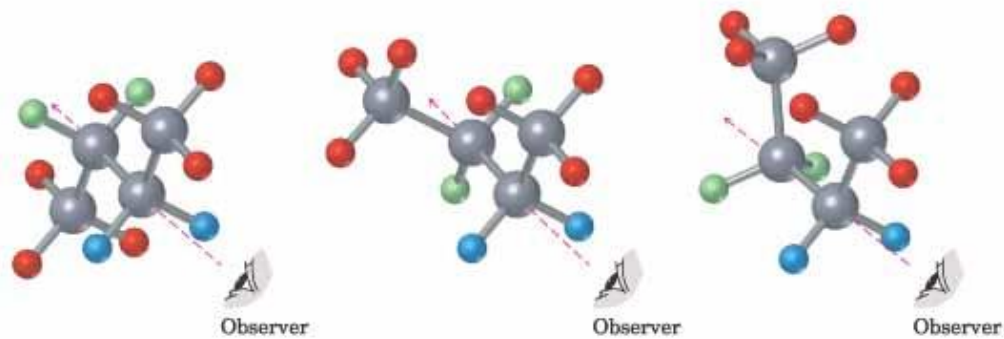
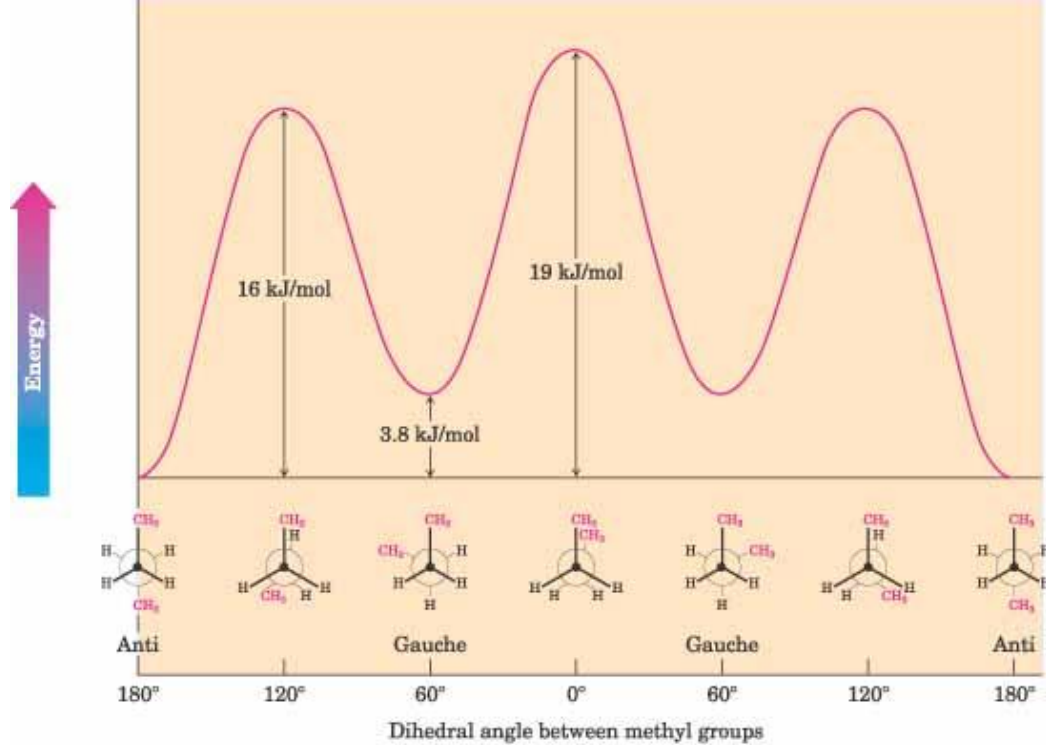


Totally eclipsed conformation of butane

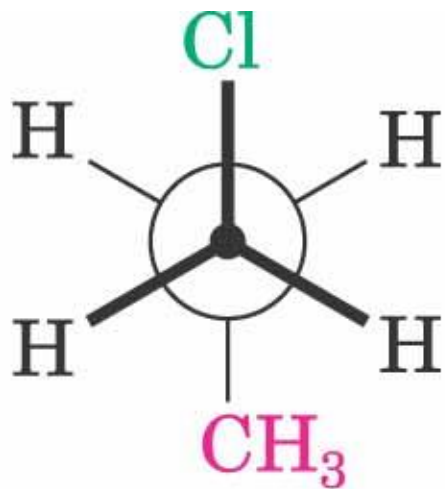


# PE Diagram for Butane ([link](#))

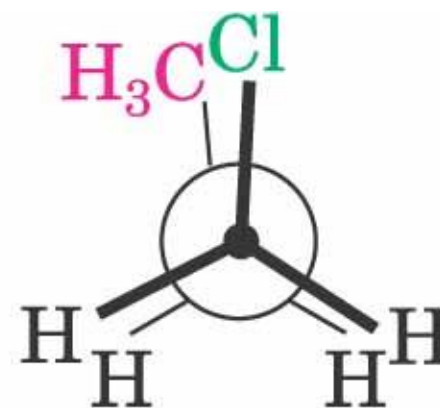




# 1-Chloropropane

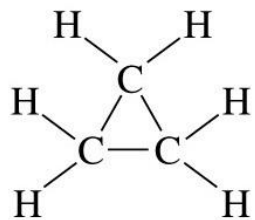


**Most stable (staggered)**



**Least stable (eclipsed)**

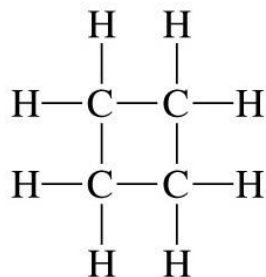
# Saturated Cyclic Compounds



or



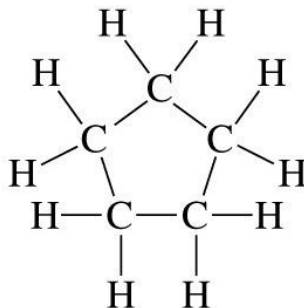
cyclopropane



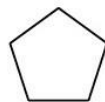
or



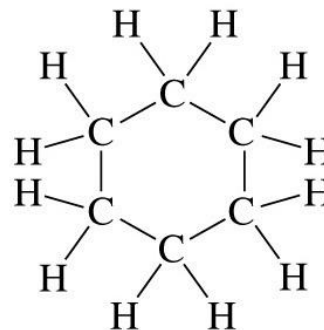
cyclobutane



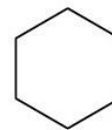
or



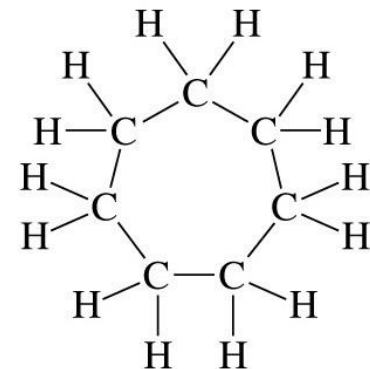
cyclopentane



or



cyclohexane

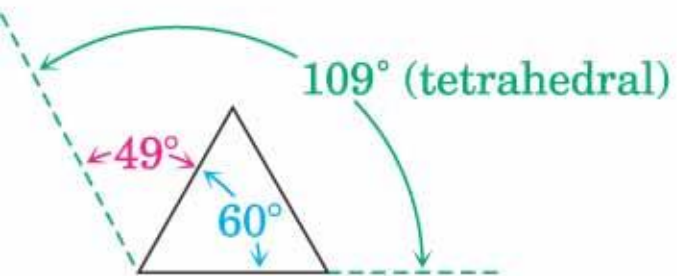


or



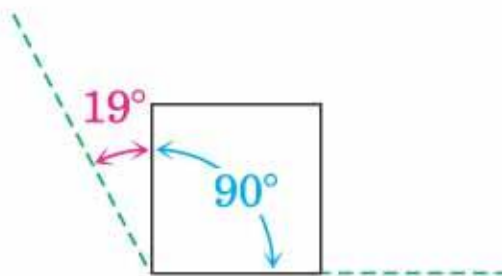
cycloheptane



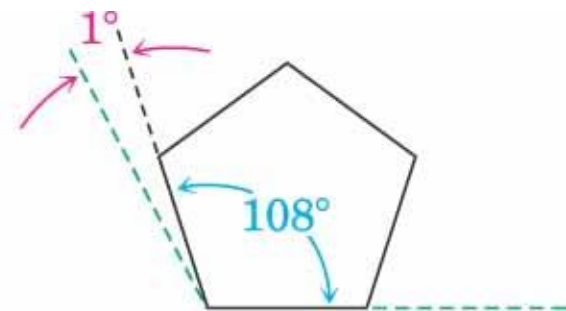


**Cyclopropane**

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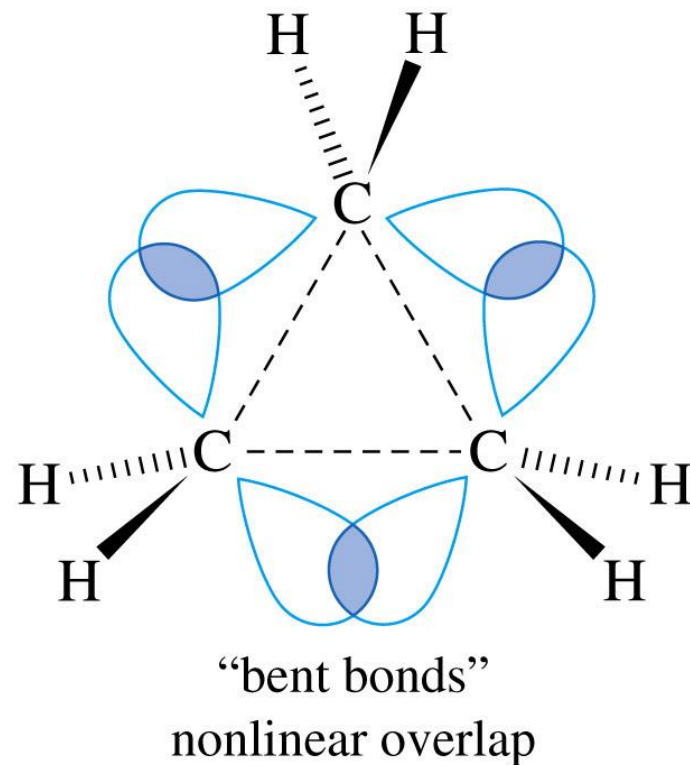
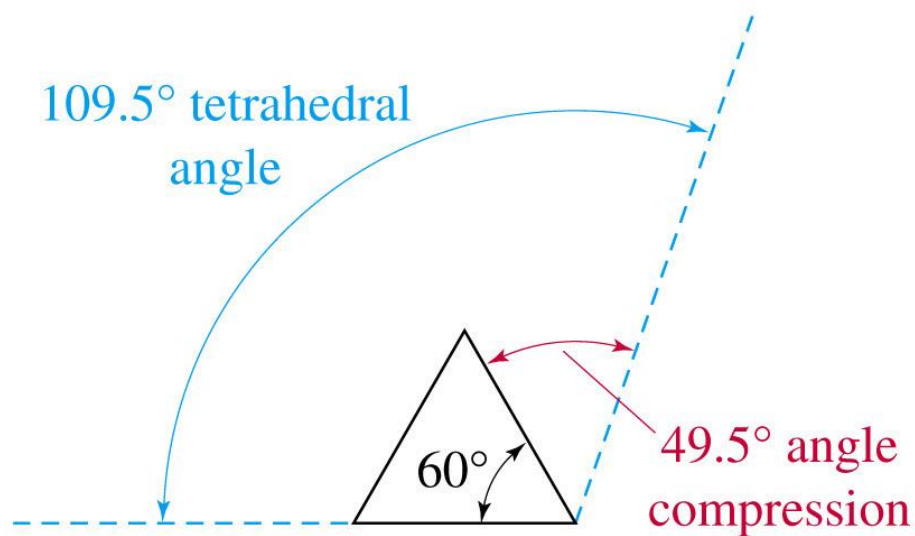
**Cyclobutane**



**Cyclopentane**

# Cyclopropane

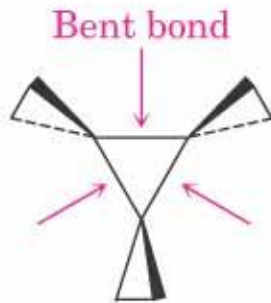
## Angle and Torsional Strain



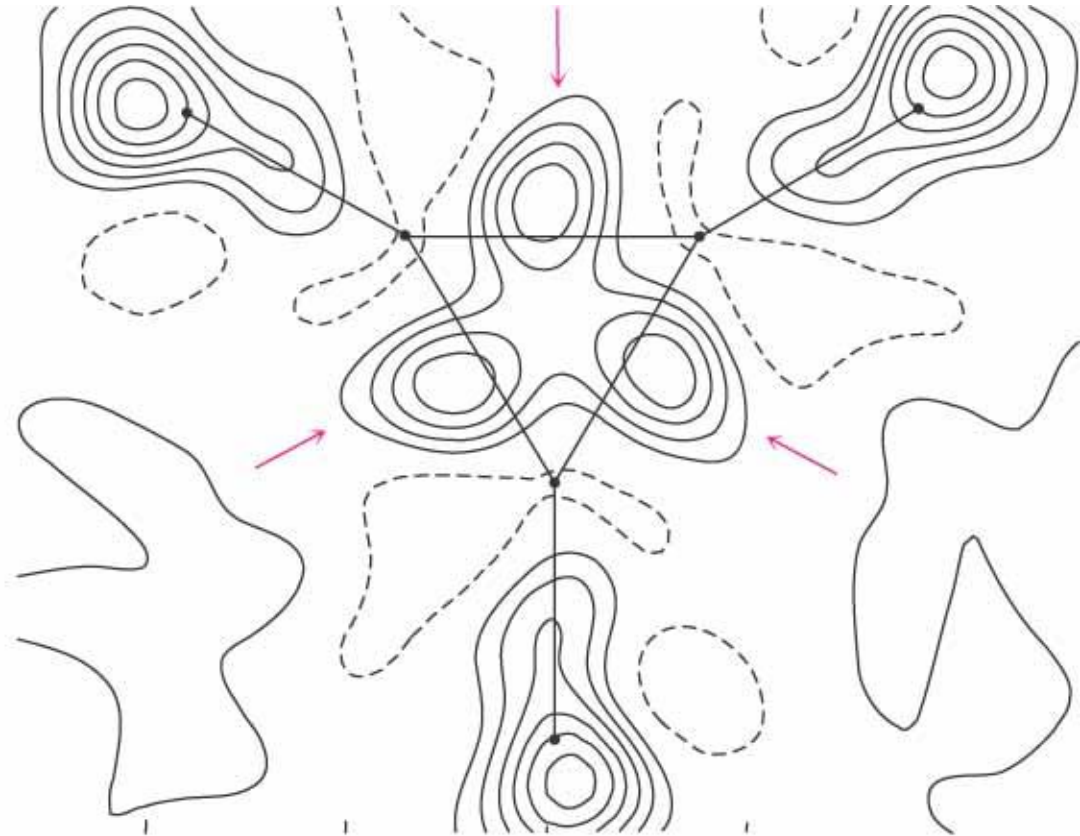
# Electron Density Map



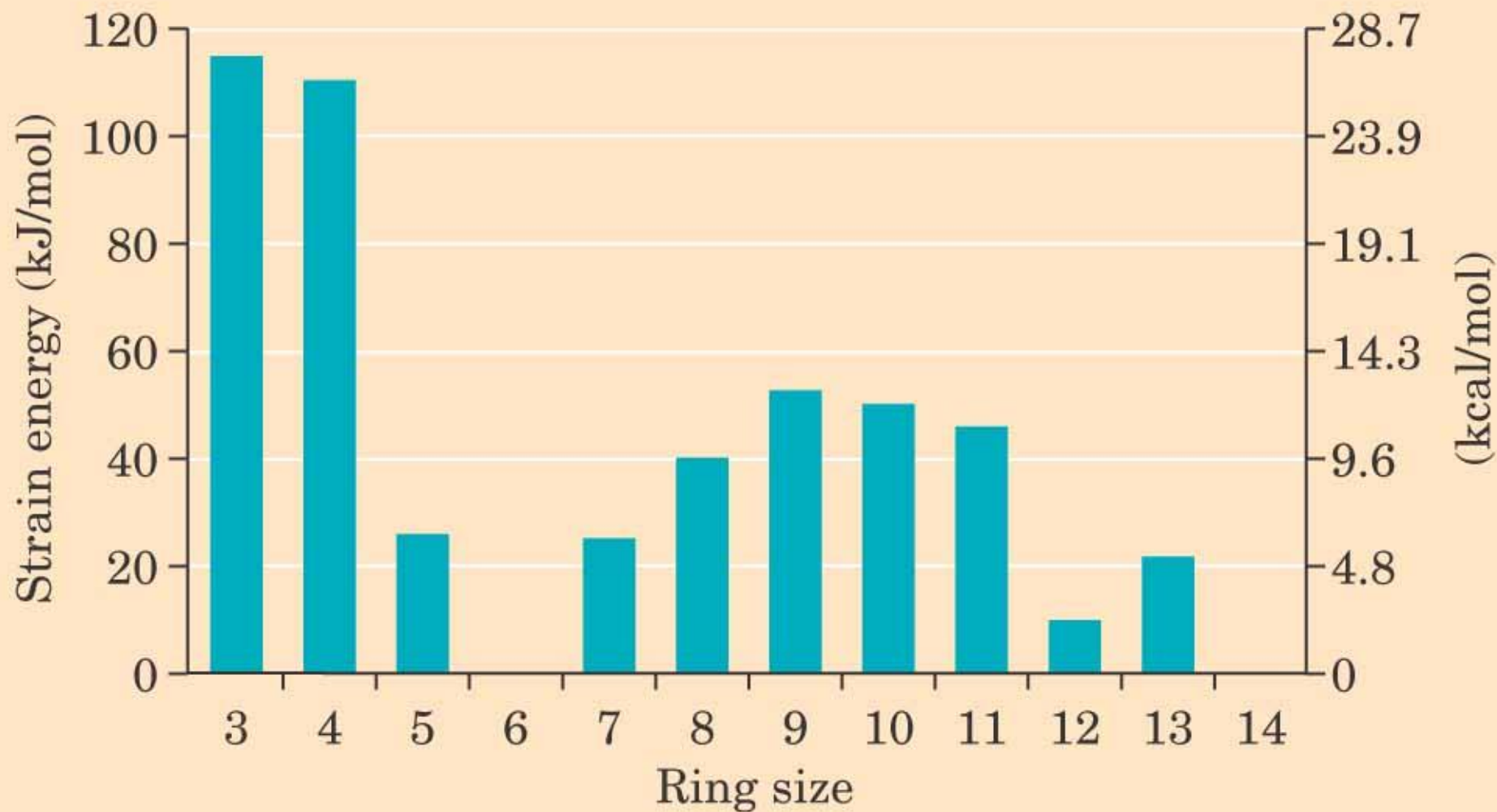
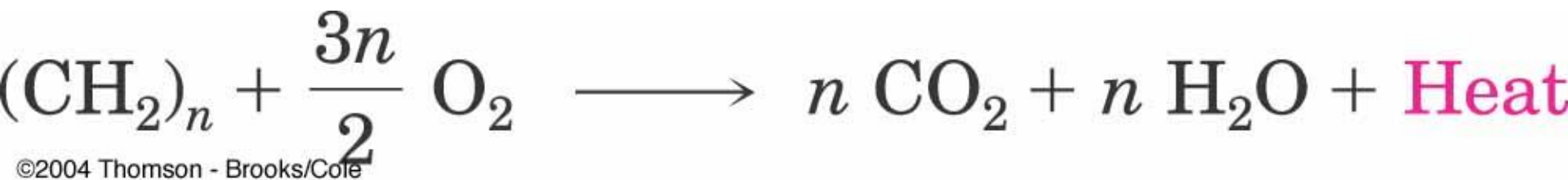
**Side view**



**Top view**

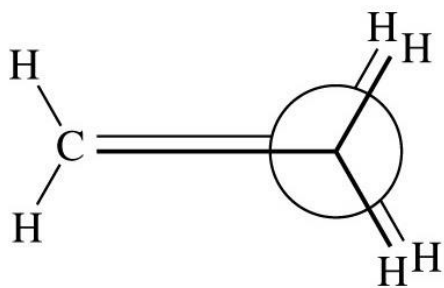




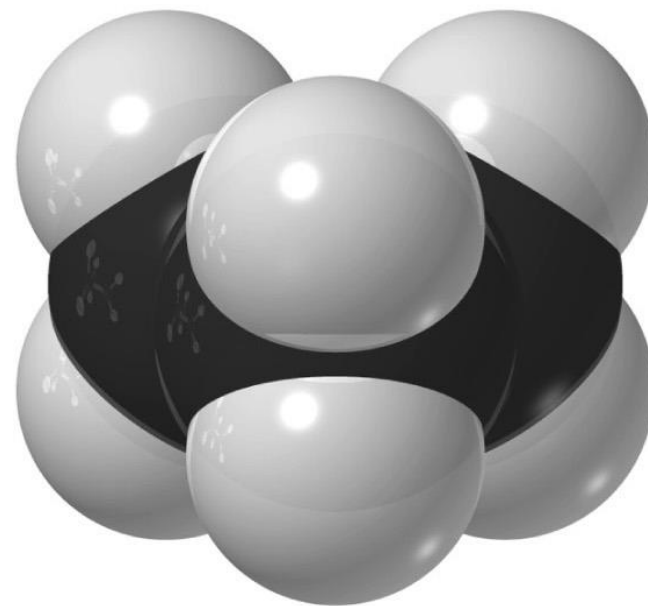
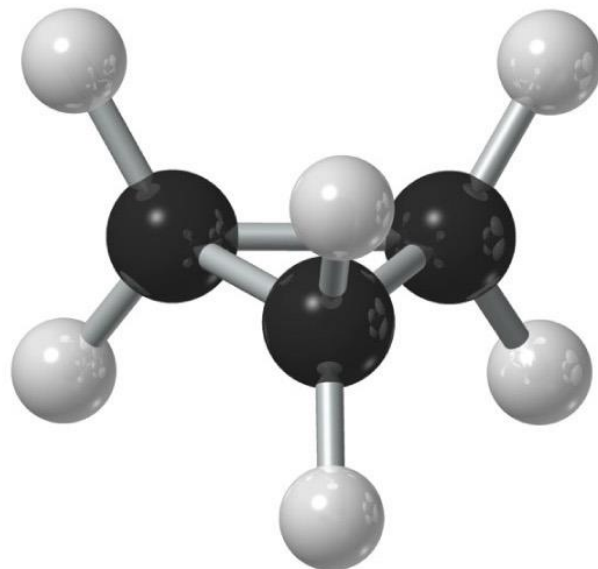




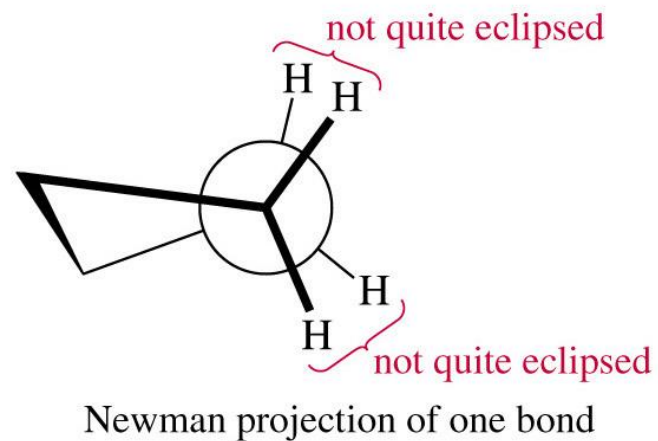
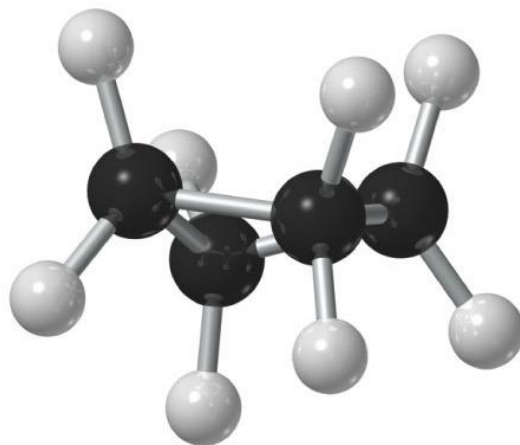
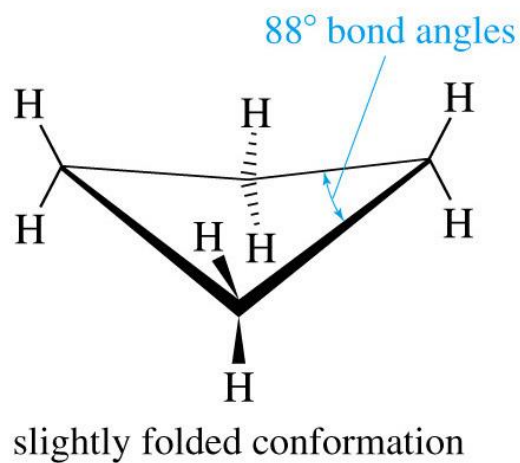
# All Dihedral Angles = $0^\circ$



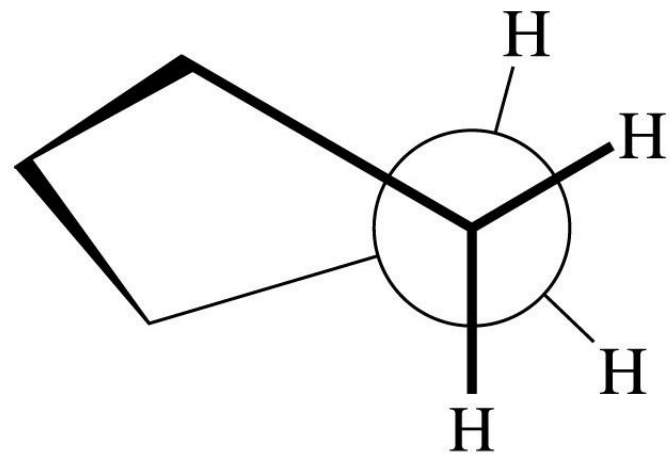
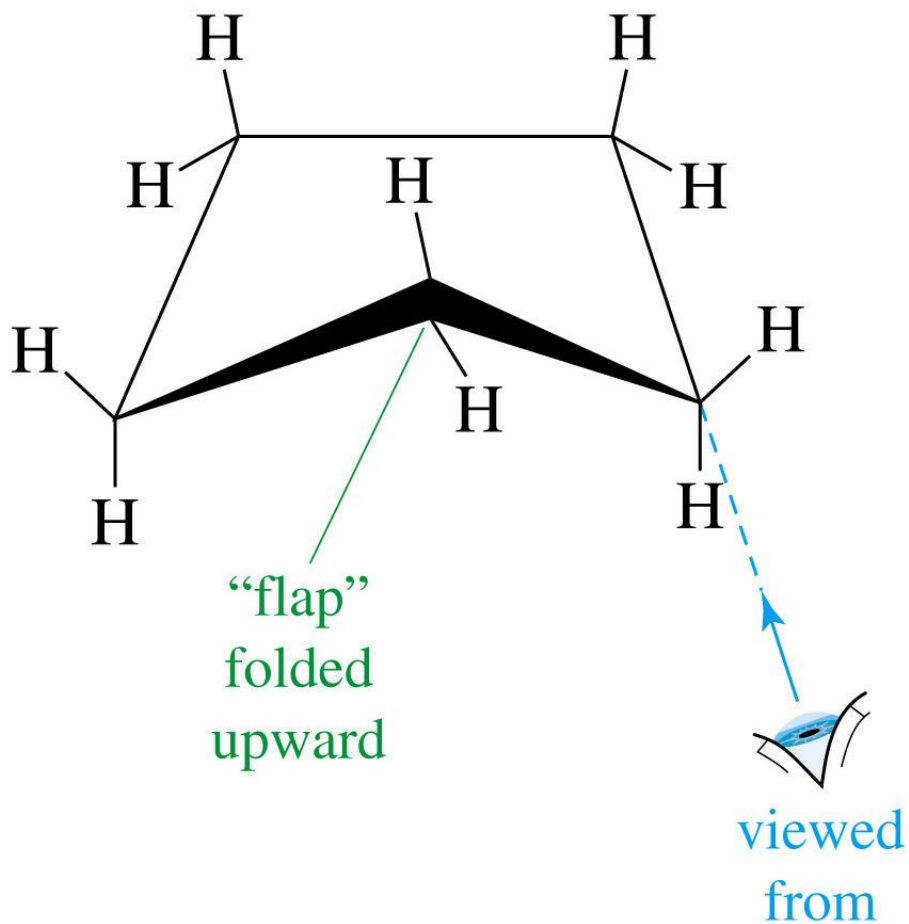
Newman projection  
of cyclopropane



# Cyclobutane is not Planar



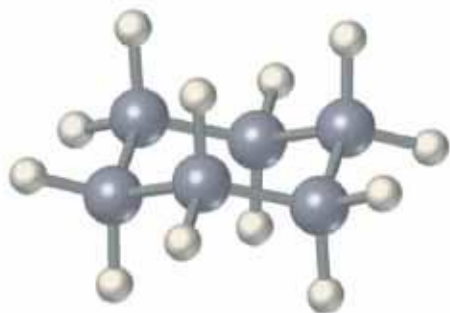
# Cyclopentane



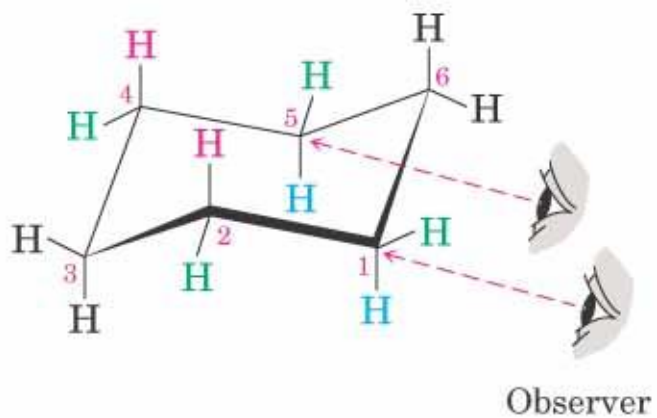
Newman projection  
showing relief of  
eclipsing of bonds

# Cyclohexane

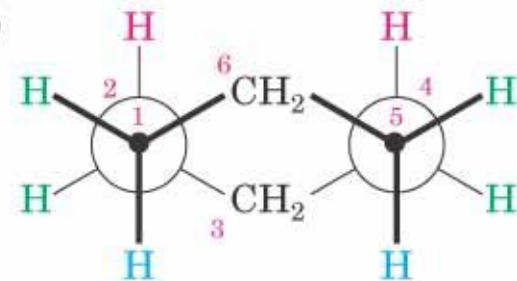
(a)  
b



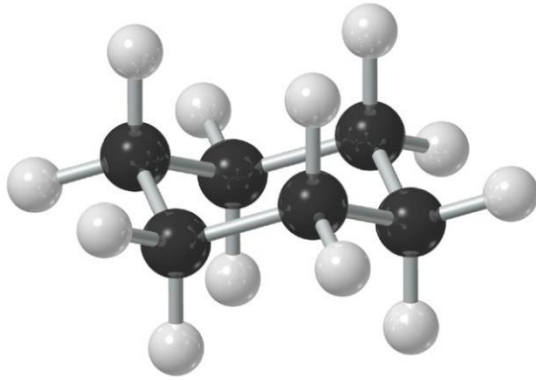
(b)



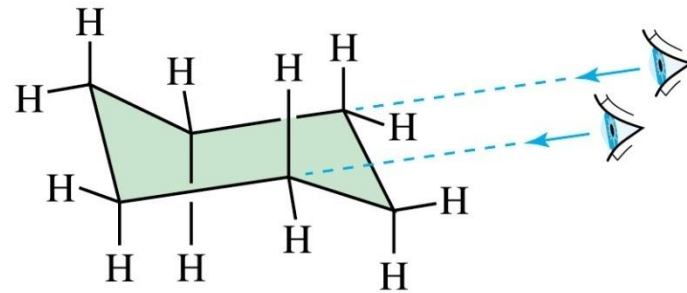
(c)



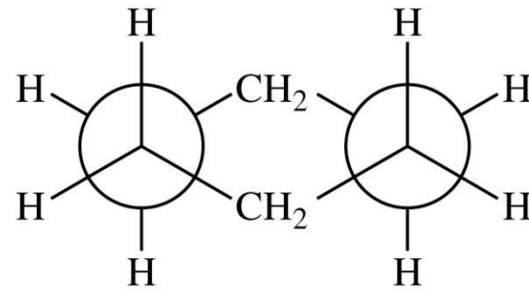
# Chair Conformation



chair conformation

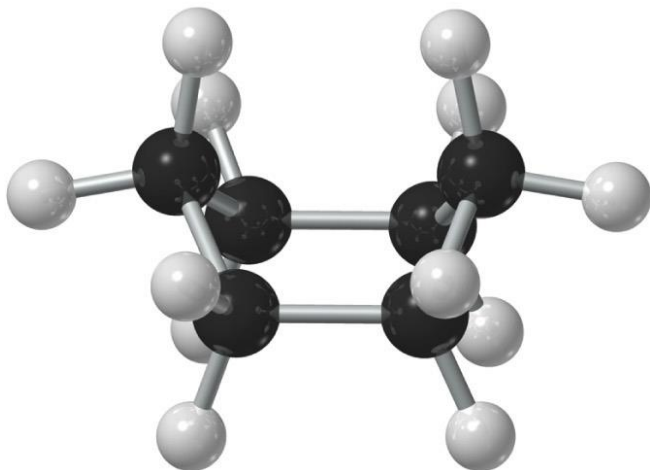


viewed along the "seat" bonds

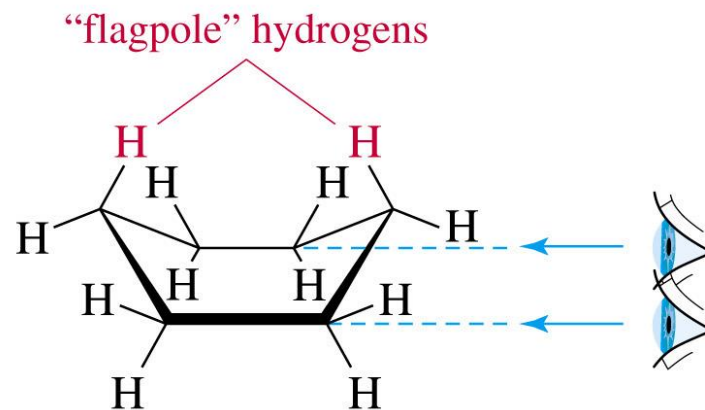


Newman projection

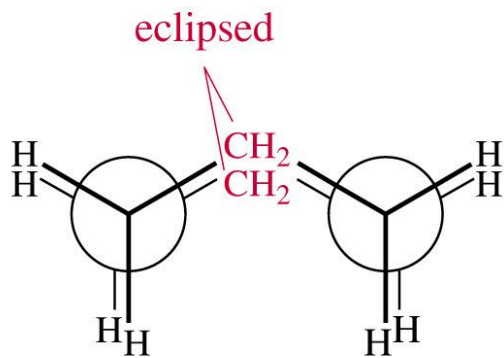
# Boat Conformation



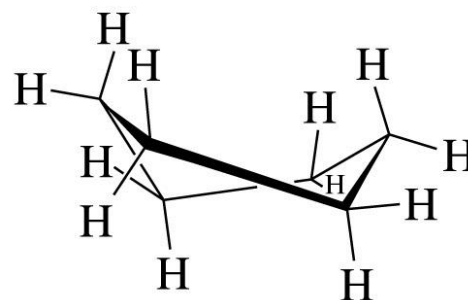
boat conformation



symmetrical boat

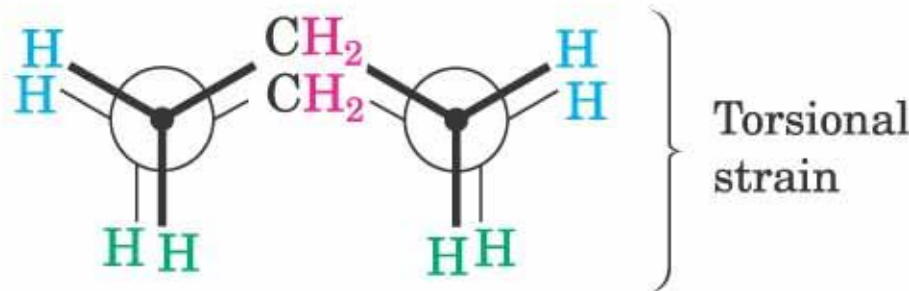
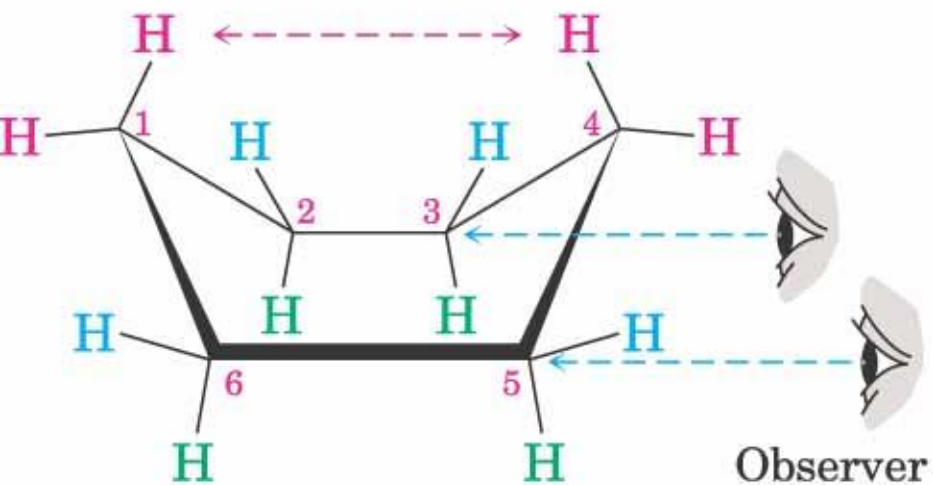


Newman projection



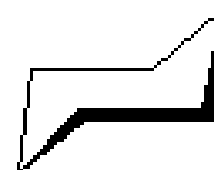
"twist" boat

### Steric strain of hydrogens at C1 and C4





adding "wedges" helps show the 3D structure



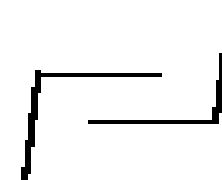
The chair can be obtained by drawing opposite sides as 3 sets of parallel lines



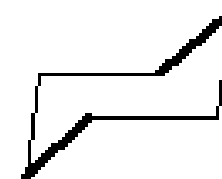
First draw the sides of the middle portion



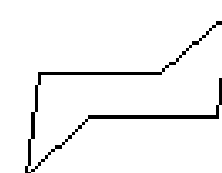
Next draw in the first half of each end



Finally complete the two ends



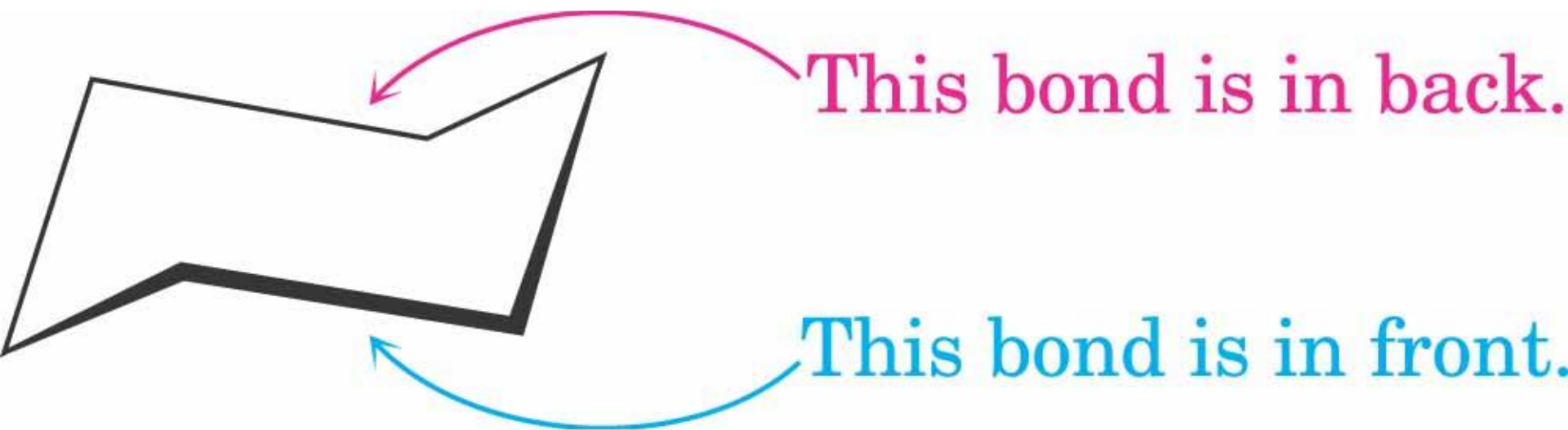
Done !

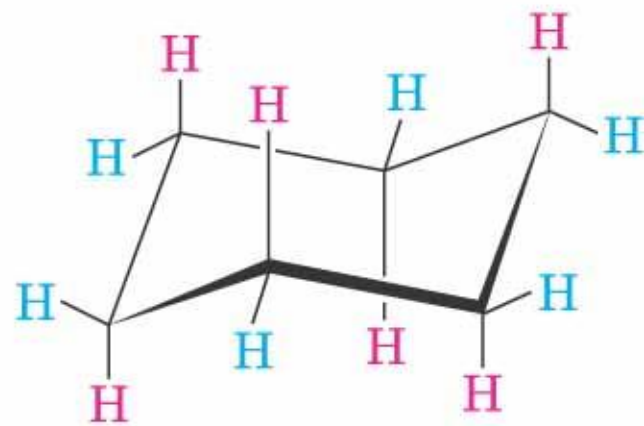
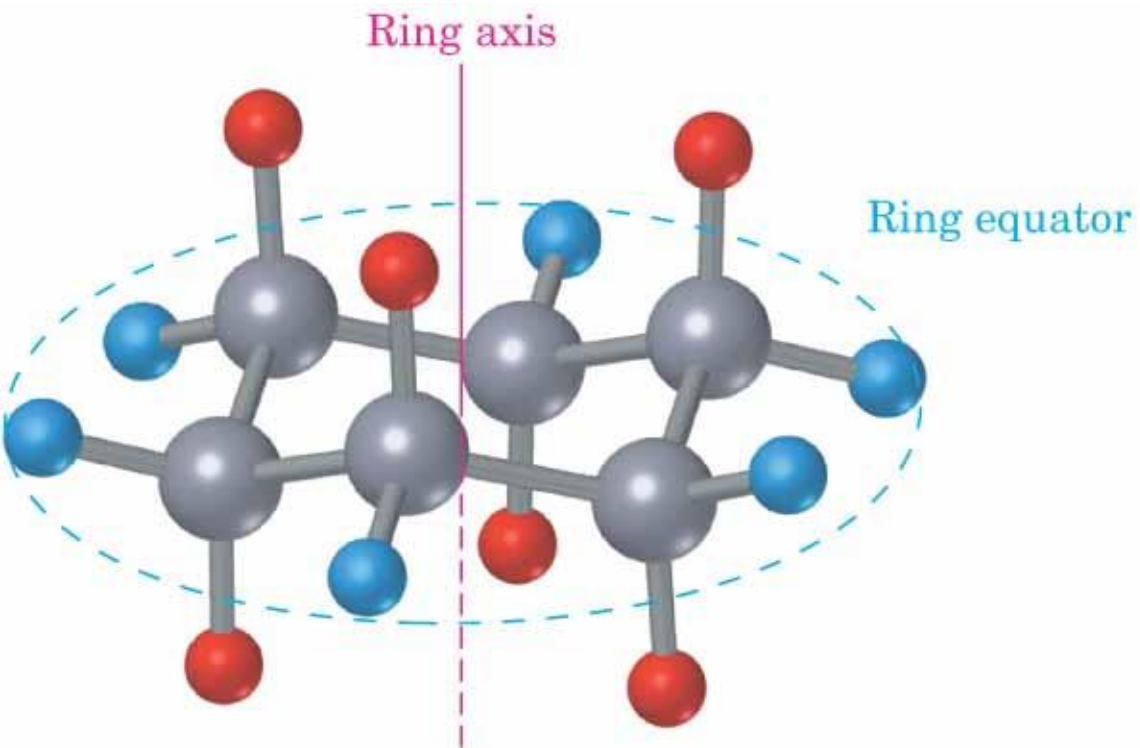


angled

horizontal

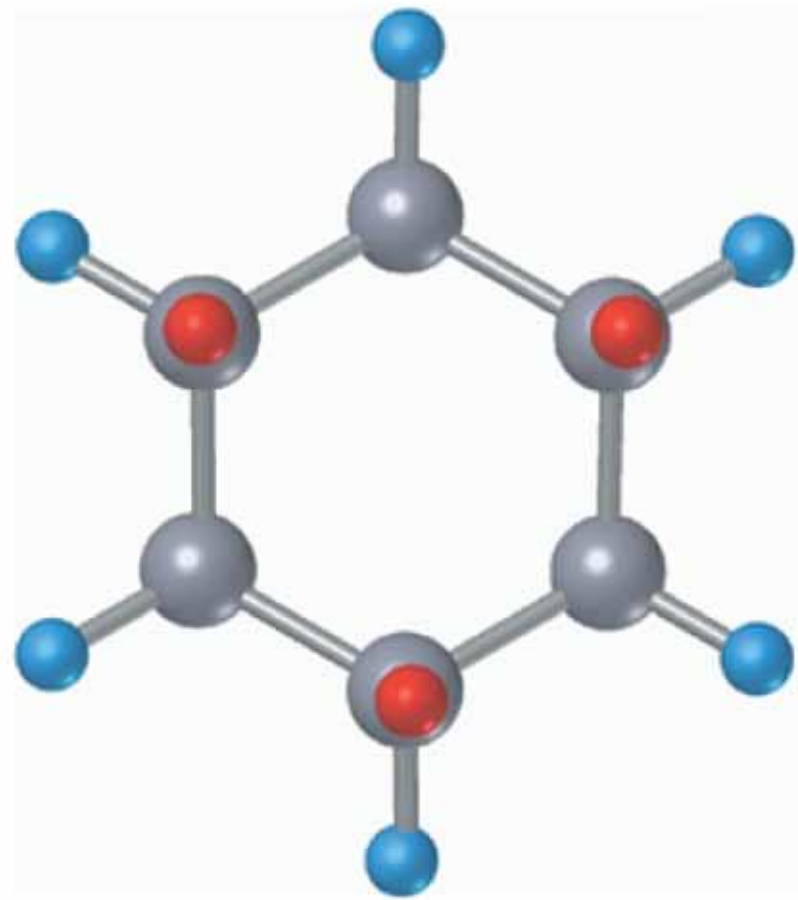
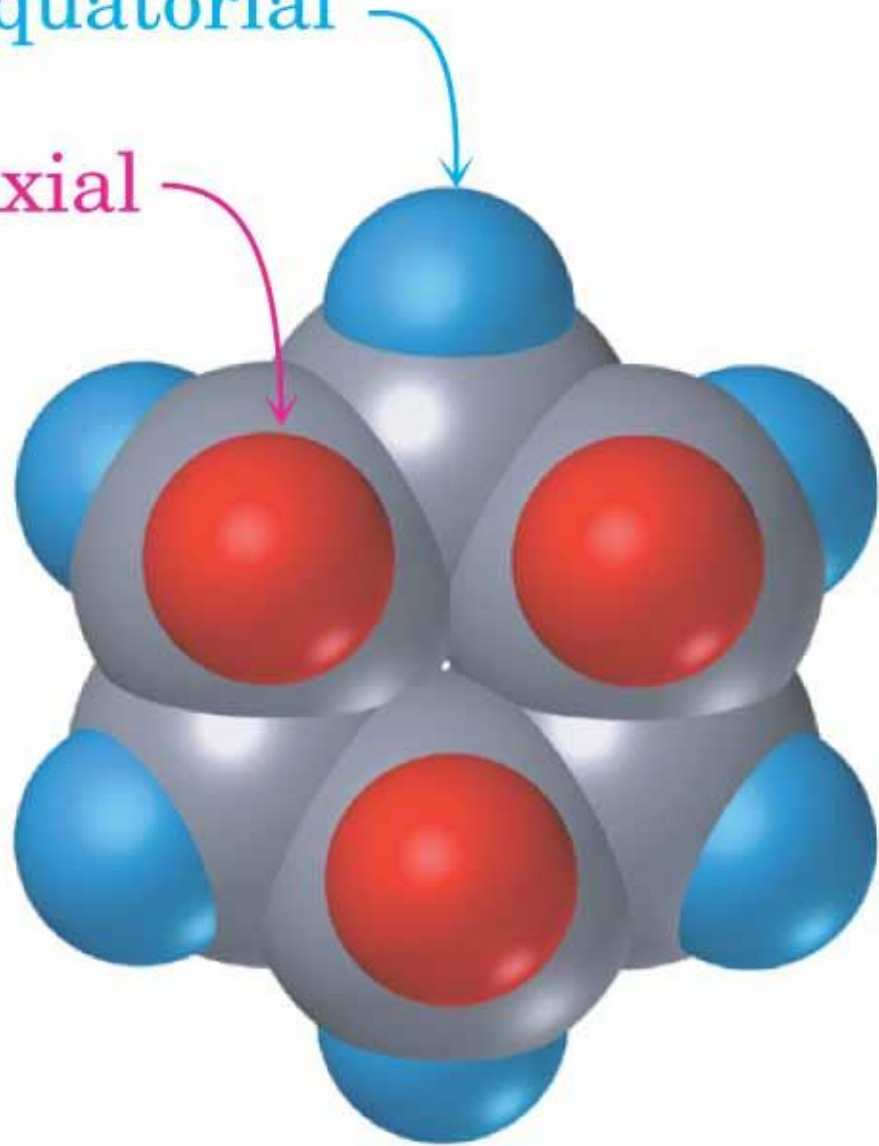






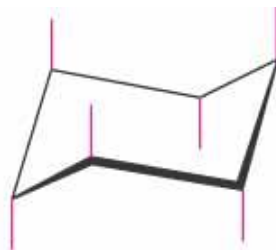
Equatorial

Axial



# Axial bonds and Equatorial bonds

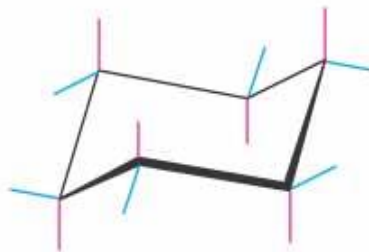
**Axial bonds:** The six axial bonds, one on each carbon, are parallel and alternate up–down.

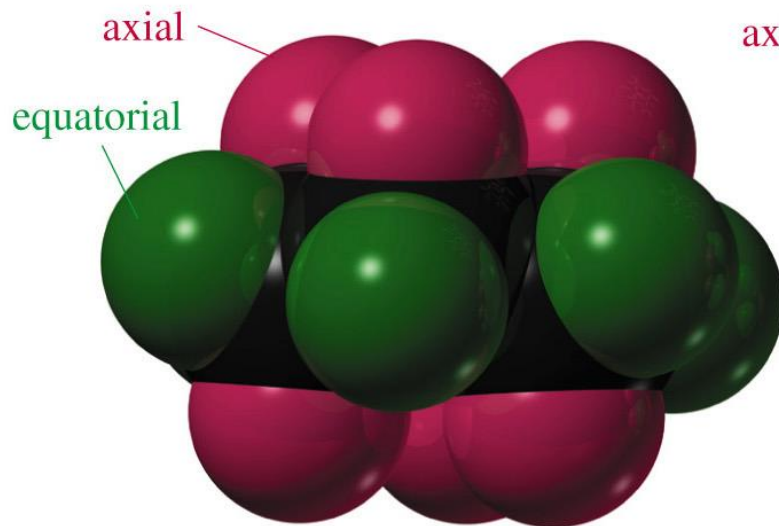
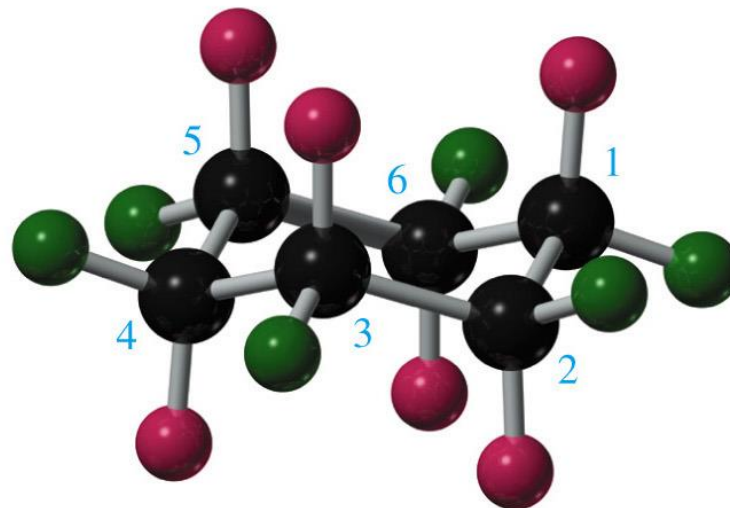
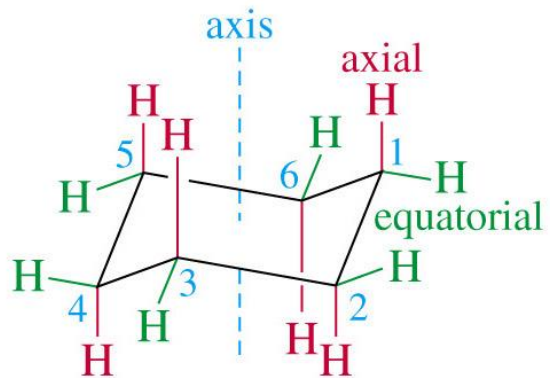


**Equatorial bonds:** The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.

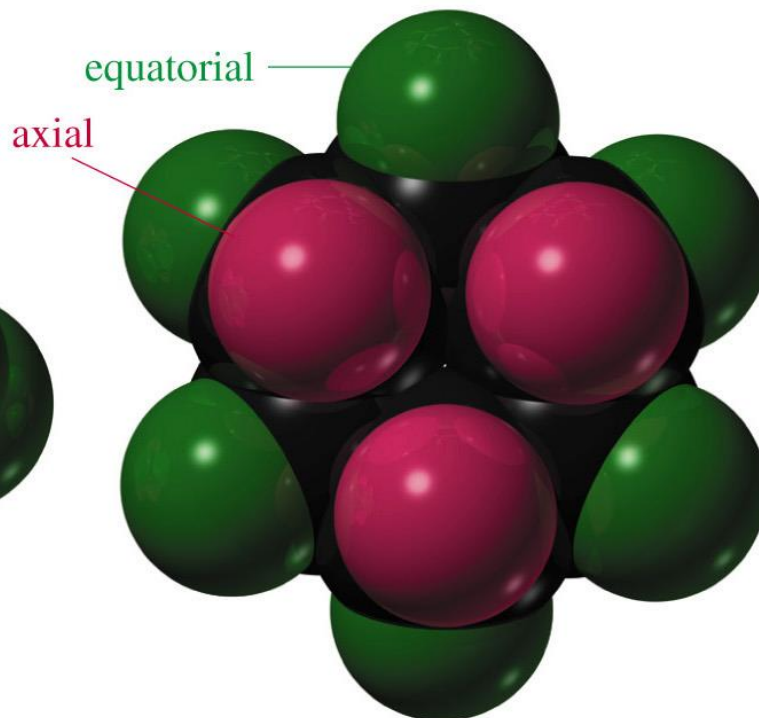


**Completed cyclohexane**



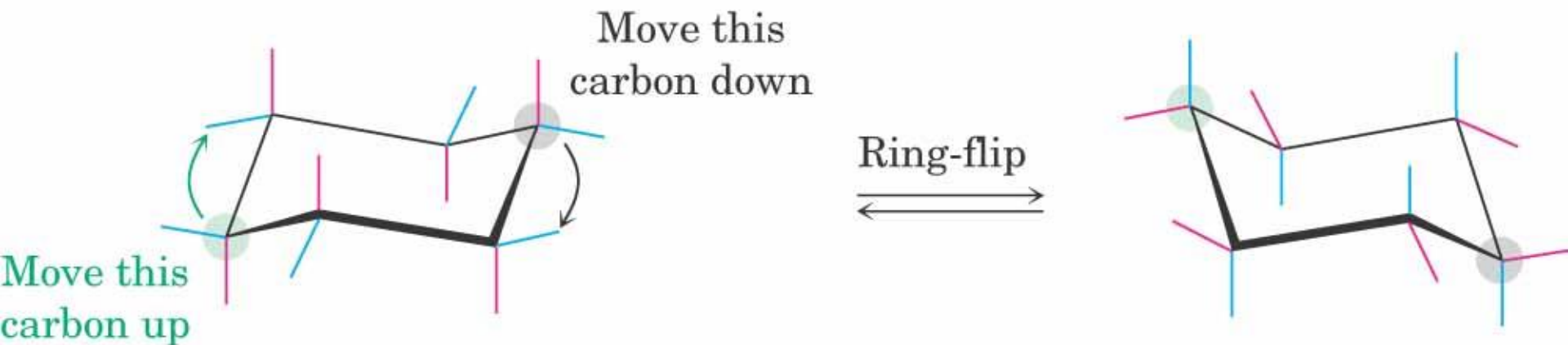
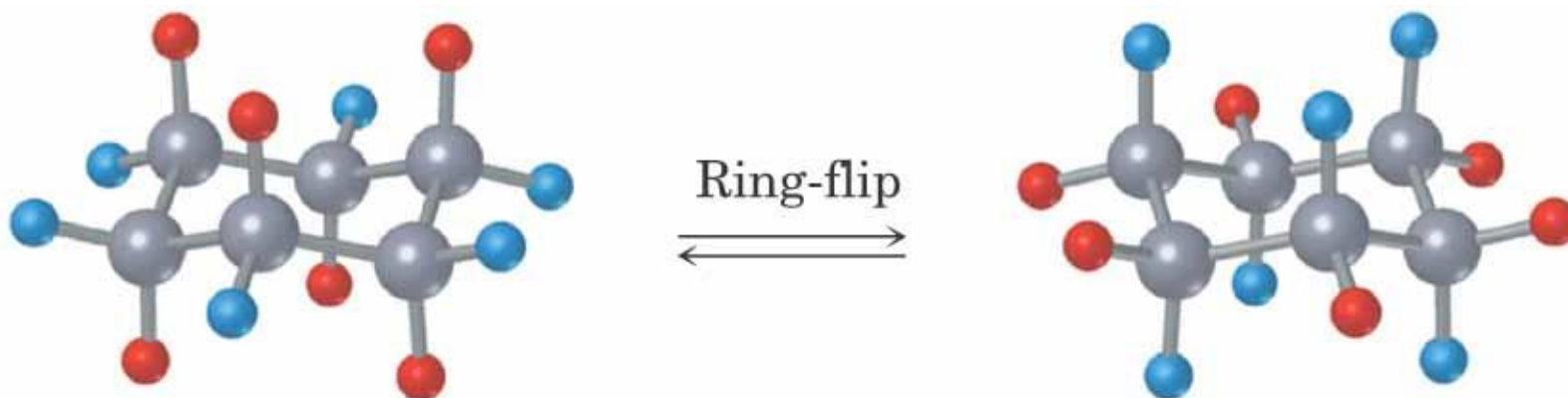


seen from the side



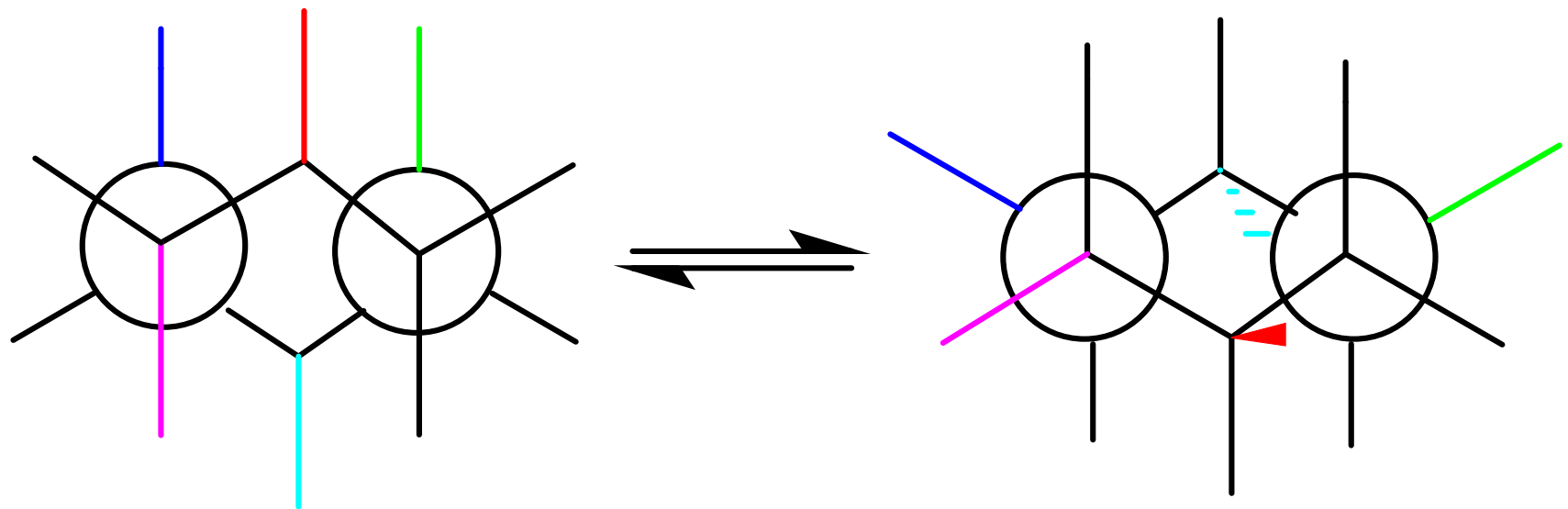
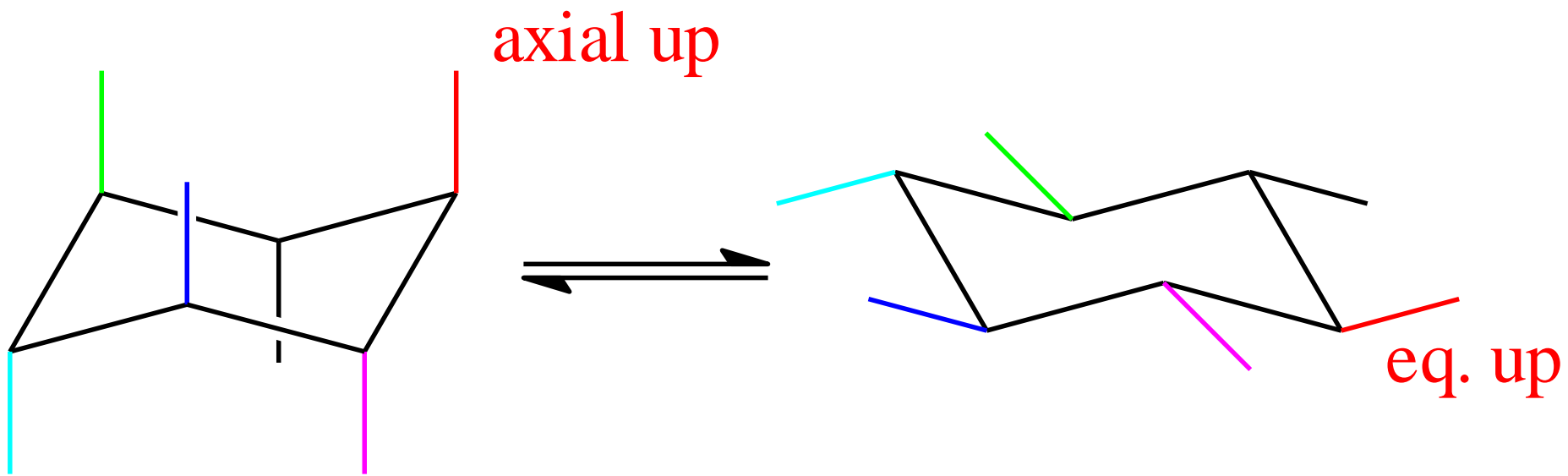
seen from above

# Rings can Flip from one Chair Conformation to Another



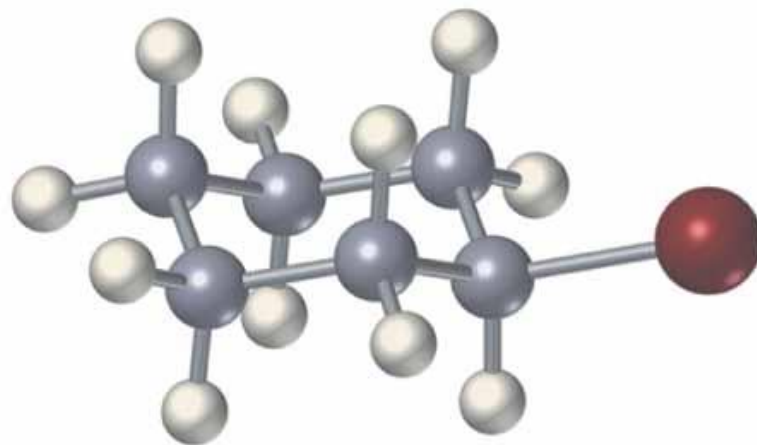
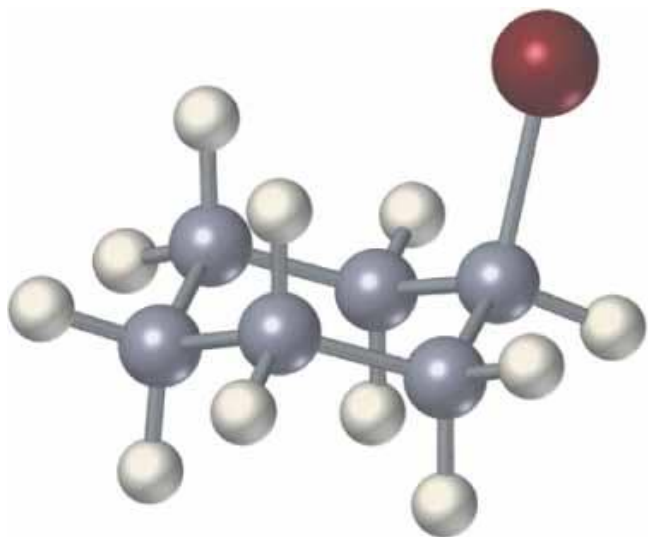
# Flipping Chair Conformations

- All axial bonds become equatorial
- All equatorial bonds become axial
- All “up” bonds stay up
- All “down” bonds stay down

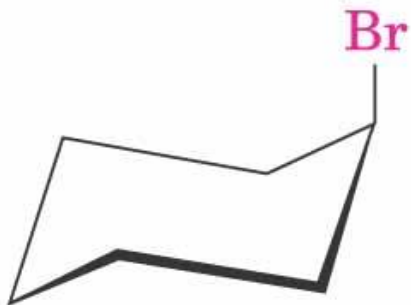




# Axial-up becomes Equatorial-up



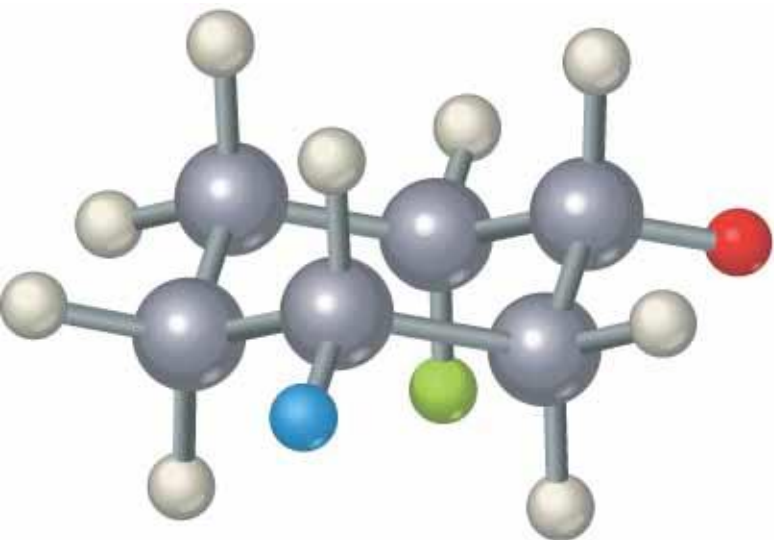
Ring-flip  
⇌



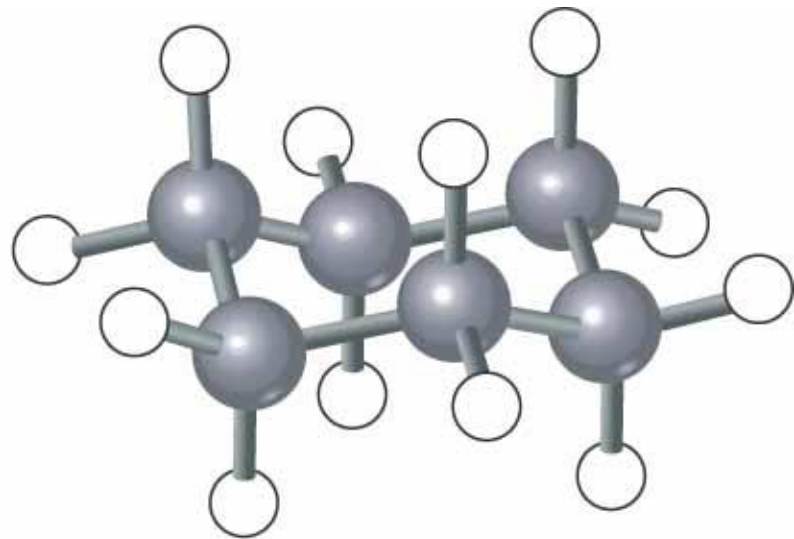
**Axial bromocyclohexane**



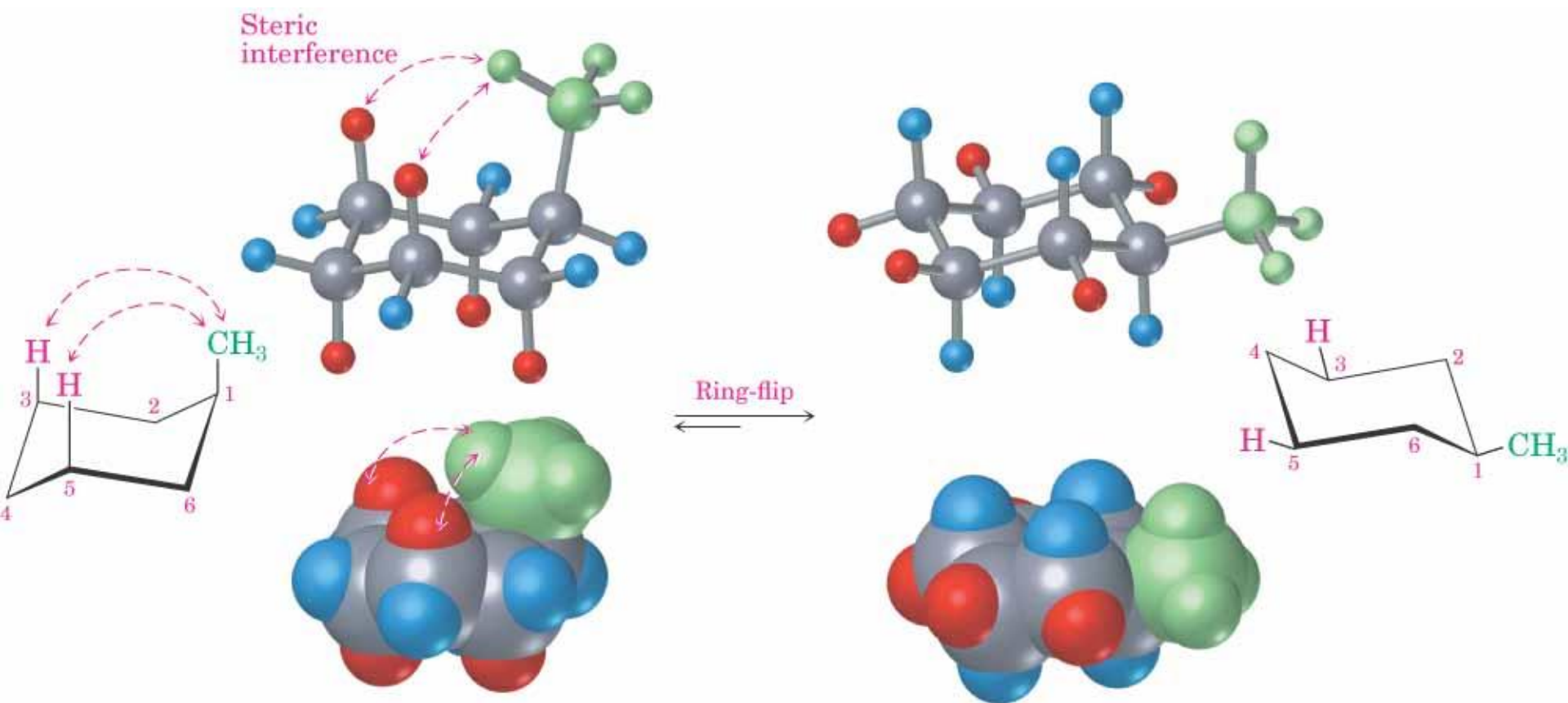
**Equatorial bromocyclohexane**



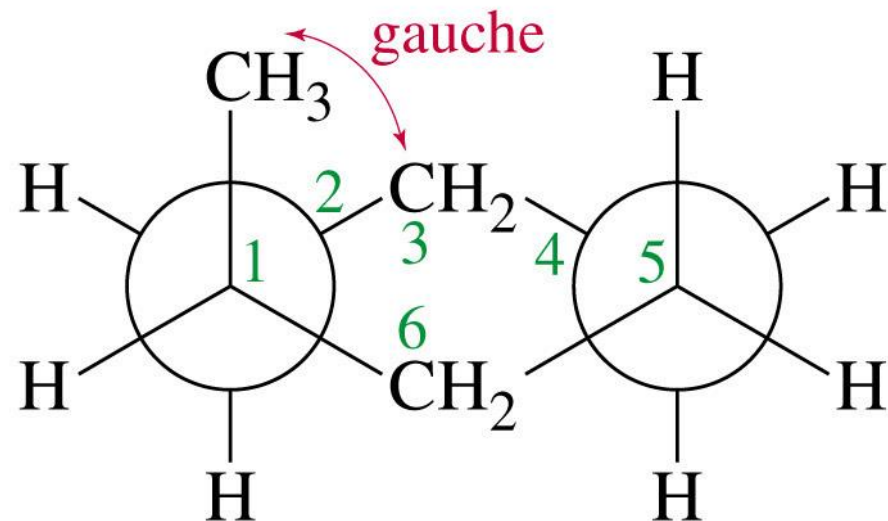
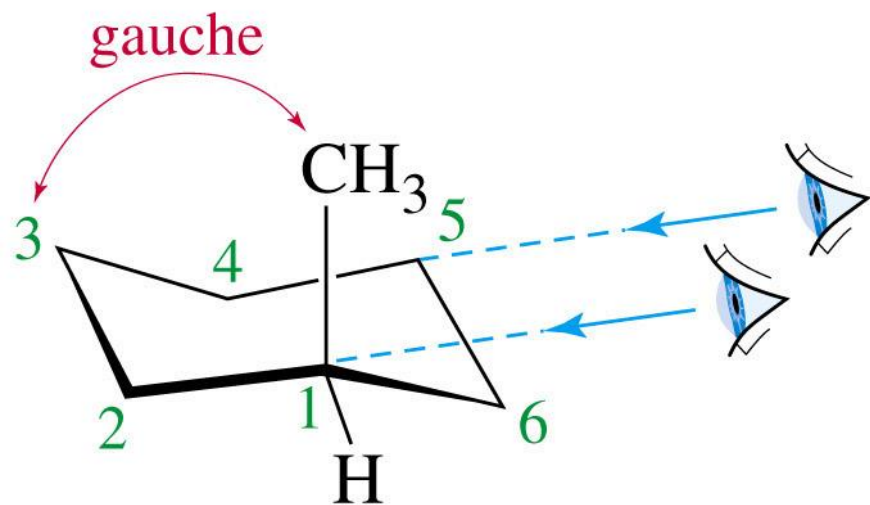
Ring-flip  
⇌



# Equatorial Conformation is Preferred ([link](#))



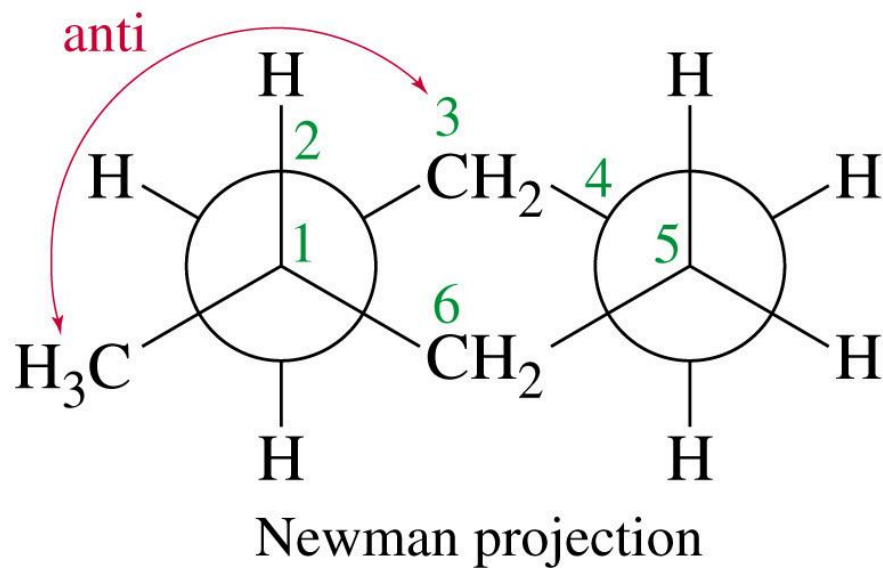
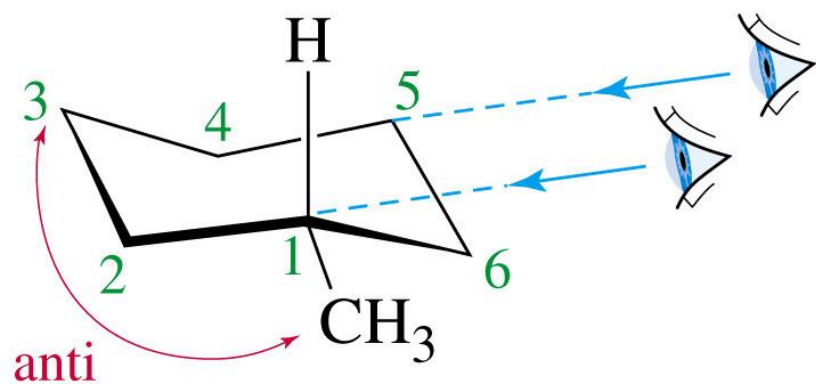
# Axial Methyl group is **Gauche** to **C<sub>3</sub>** in the ring



Newman projection

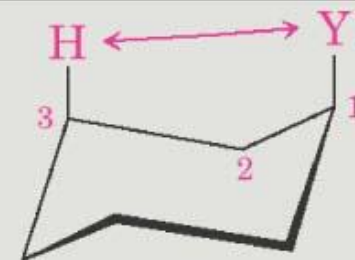
(a)

# Equatorial Methyl Group is Anti to C<sub>3</sub> in the ring

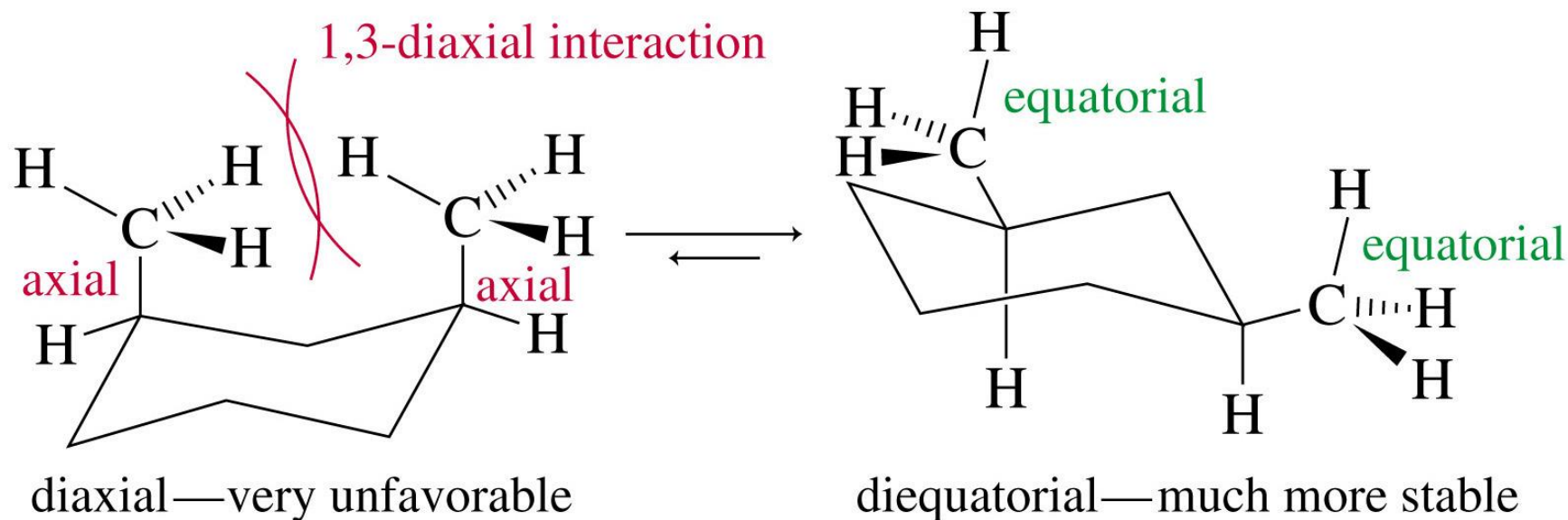


**TABLE 4.2** Steric Strain in Monosubstituted Cyclohexanes

Y	Strain of one H–Y 1,3-diaxial interaction	
	(kJ/mol)	(kcal/mol)
—F	0.5	0.12
—Cl	1.0	0.25
—Br	1.0	0.25
—OH	2.1	0.5
—CH <sub>3</sub>	3.8	0.9
—CH <sub>2</sub> CH <sub>3</sub>	4.0	0.95
—CH(CH <sub>3</sub> ) <sub>2</sub>	4.6	1.1
—C(CH <sub>3</sub> ) <sub>3</sub>	11.4	2.7
—C <sub>6</sub> H <sub>5</sub>	6.3	1.5
—CO <sub>2</sub> H	2.9	0.7
—CN	0.4	0.1

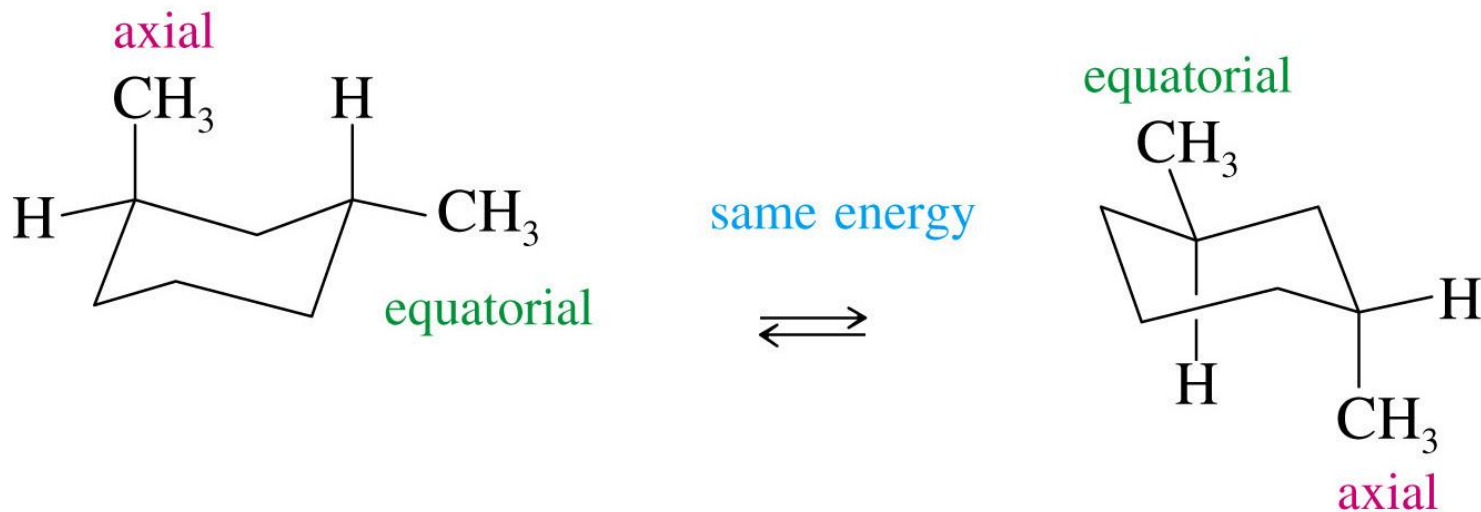


# *cis* 1,3-Dimethylcyclohexane



# *trans* 1,3-Dimethylcyclohexane

*Chair conformations of trans-1,3-dimethylcyclohexane*

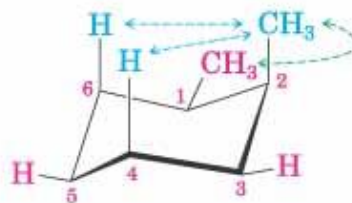




*cis*-1,2-Dimethylcyclohexane

One gauche  
interaction (3.8 kJ/mol)  
Two CH<sub>3</sub>-H diaxial  
interactions (7.6 kJ/mol)

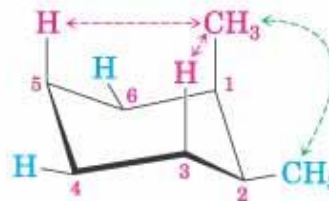
**Total strain: 3.8 + 7.6 = 11.4 kJ/mol**



Ring-flip

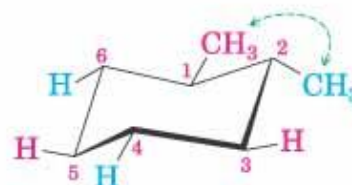
One gauche  
interaction (3.8 kJ/mol)  
Two CH<sub>3</sub>-H diaxial  
interactions (7.6 kJ/mol)

**Total strain: 3.8 + 7.6 = 11.4 kJ/mol**



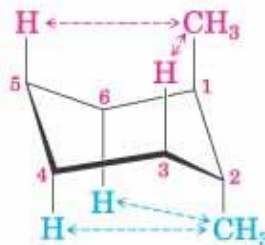
*trans*-1,2-Dimethylcyclohexane

One gauche  
interaction (3.8 kJ/mol)

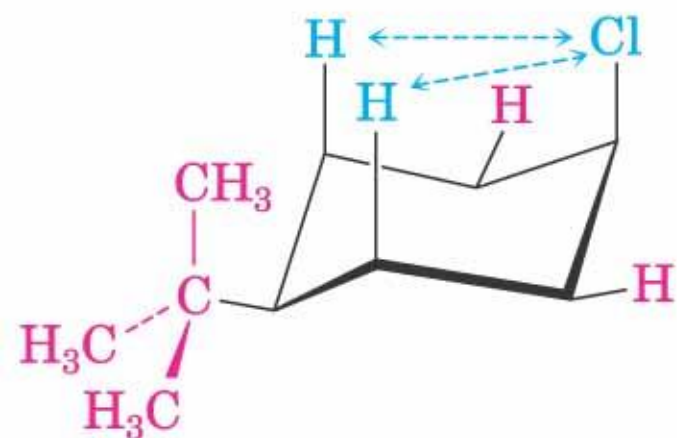


Ring-flip

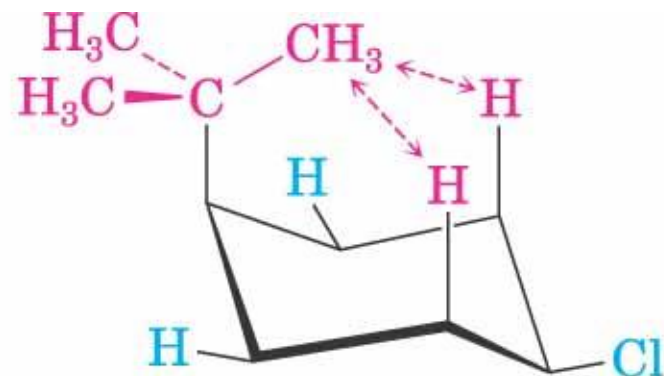
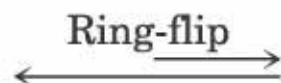
Four CH<sub>3</sub>-H diaxial  
interactions (15.2 kJ/mol)



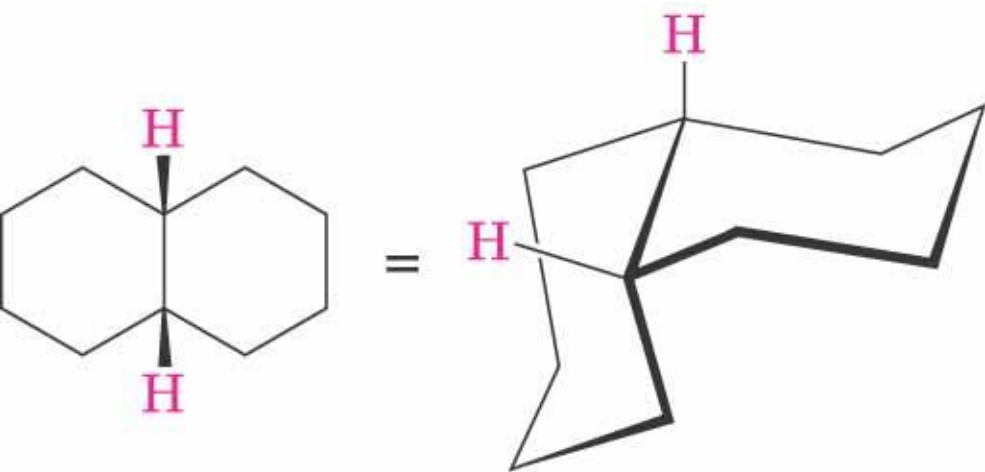
# *cis* 1-Chloro-4-*t*-butylcyclohexane



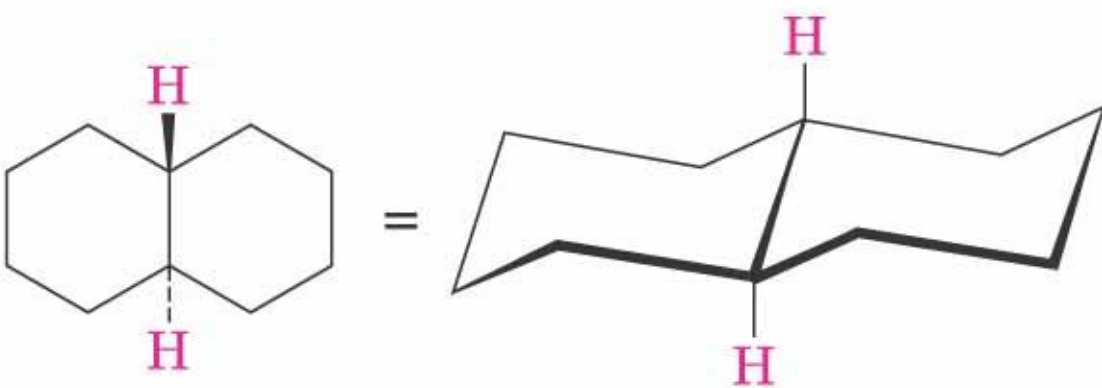
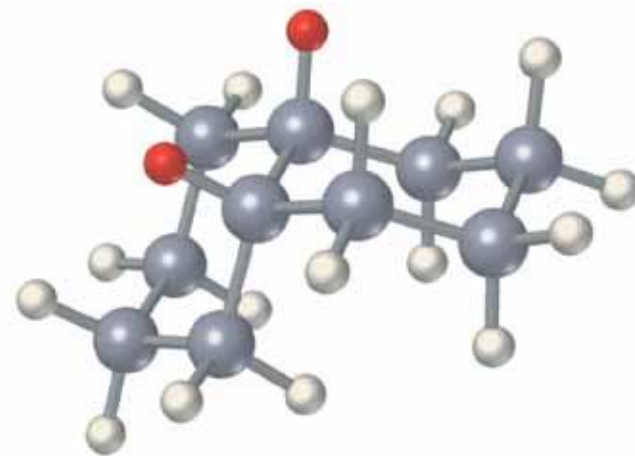
$2 \times 1.0 = 2.0$  kJ/mol steric strain



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



*cis-Decalin*



*trans-Decalin*

