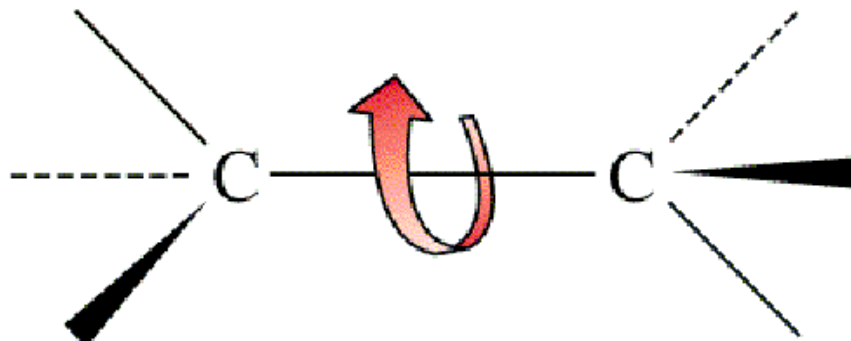


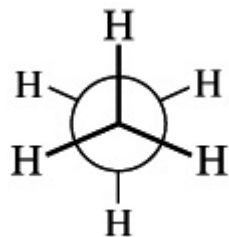
Conformations of Alkanes: Rotation about C-C Single Bonds

- Different spatial arrangements of atoms that result from rotation about carbon-carbon single bonds are known as **conformations**
- Different conformations also are called **conformational isomers** or **conformers**



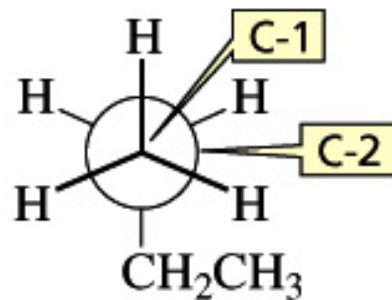
Newman Projections

- A convenient way to describe conformation isomers is to look at the molecule along the axis of the bond of interest
- A **Newman projection** is a graphical representation of such a view

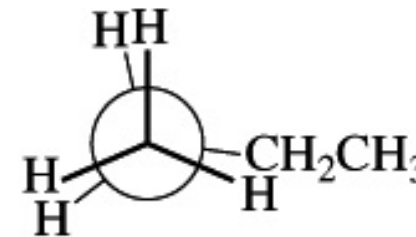


Conformations of Alkanes: Rotation About C-C Single Bonds

- When ethane molecules rotate about the carbon-carbon bond there are two extremes:
 - **staggered conformation**
 - **eclipsed conformation**



staggered conformation for rotation about the C-1—C-2 bond in butane



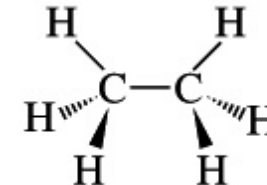
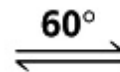
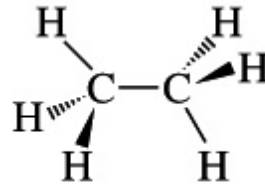
eclipsed conformation for rotation about the C-1—C-2 bond in butane

Conformations of Alkanes: Rotation About C-C Single Bonds

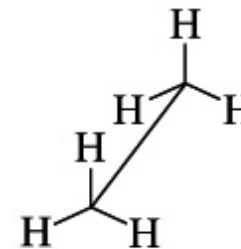
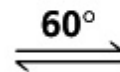
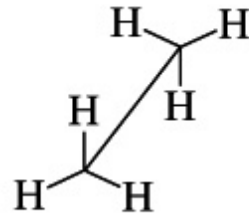
staggered conformation
for rotation about the carbon-carbon
bond in ethane

eclipsed conformation
for rotation about the carbon-carbon
bond in ethane

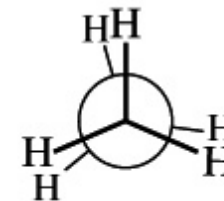
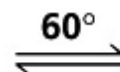
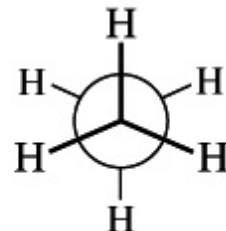
perspective
formulas



sawhorse
projections



Newman
projections

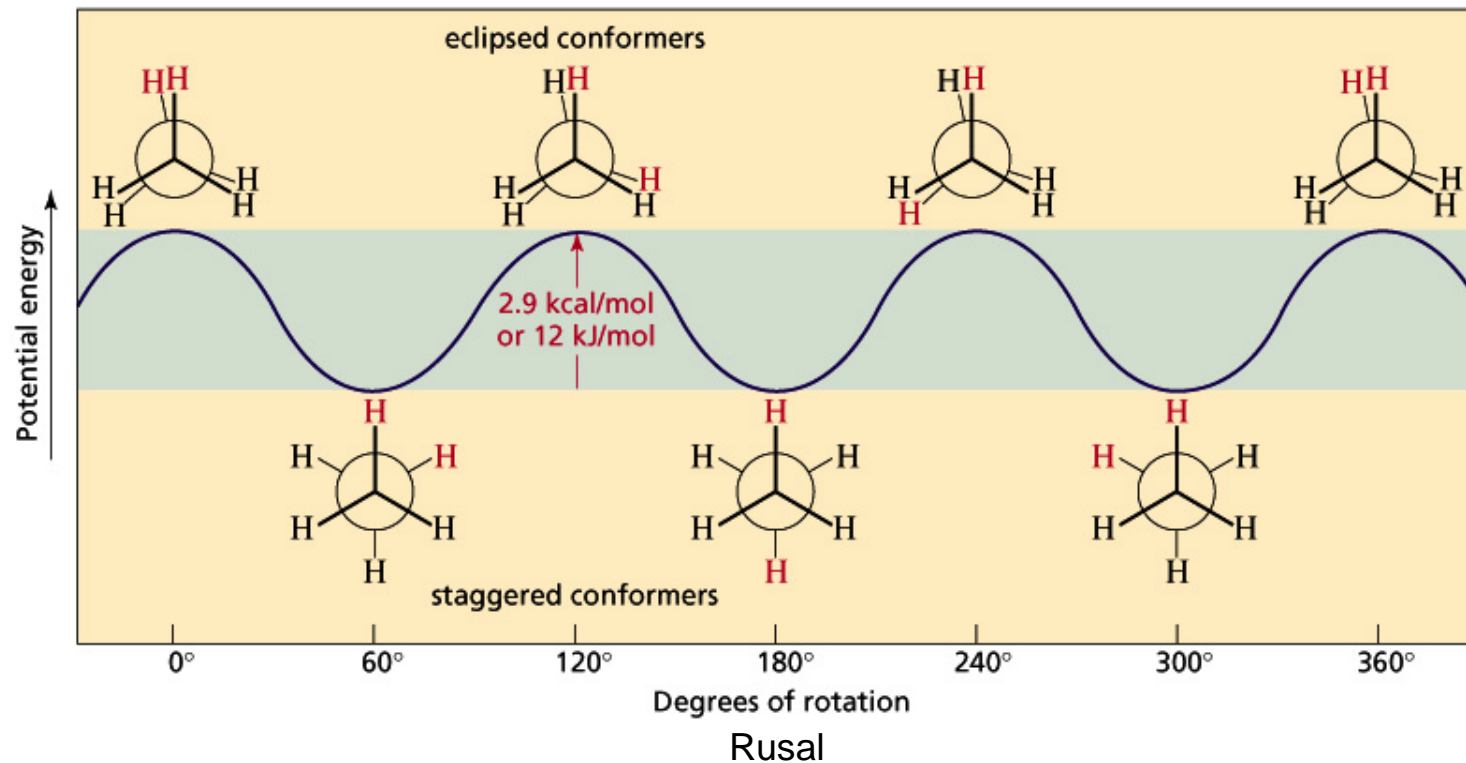


Conformations of Alkanes: Rotation About C-C Single Bonds

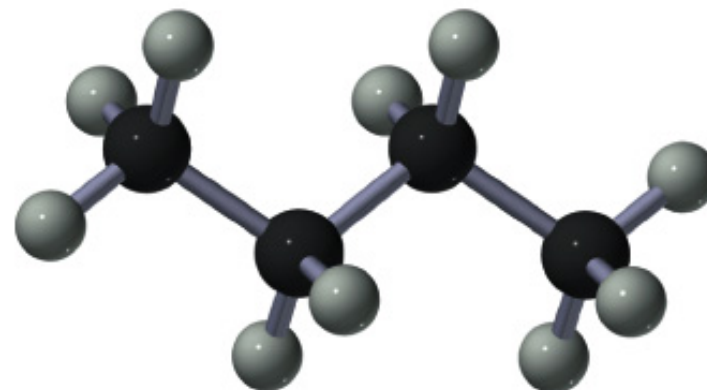
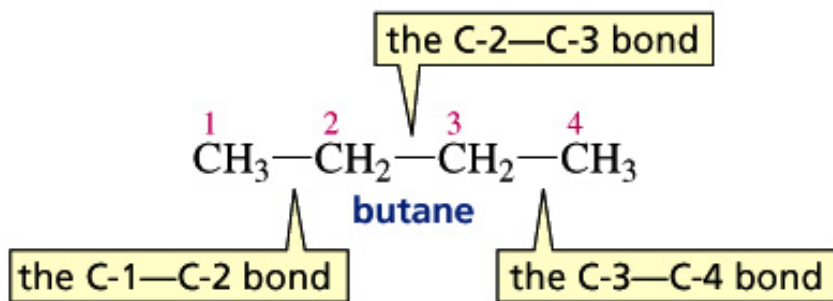
- Rotation about the C-C bond of ethane is not completely free
- Electrons of C-H bonds repel electrons of other C-H bonds if they get too close together
- For these reasons the eclipsed conformation is not as stable as the staggered conformation

Conformations of Alkanes: Rotation About C-C Single Bonds

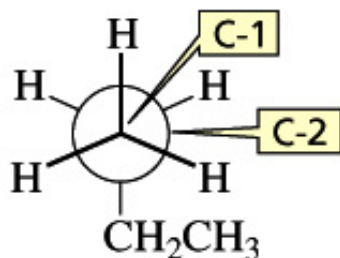
- The extra energy of the eclipsed conformation is called **Torsional Strain**



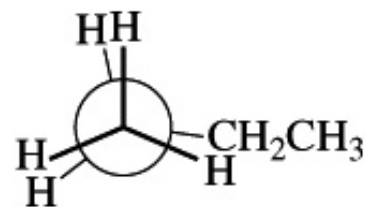
Conformations of Butane: Rotation About the C₂-C₃ Single Bond



ball-and-stick model of butane

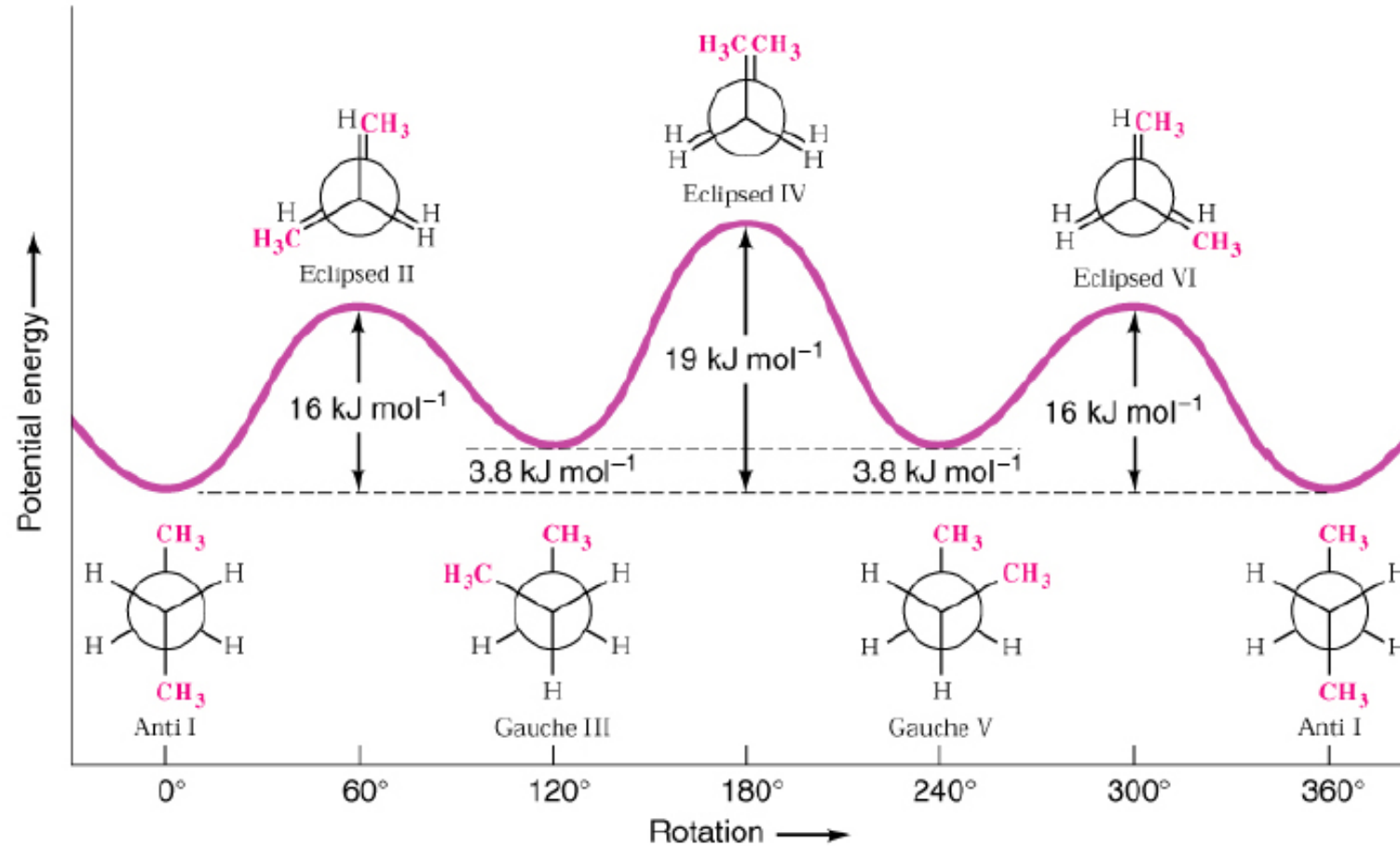


staggered conformation for rotation about the C-1—C-2 bond in butane



eclipsed conformation for rotation about the C-1—C-2 bond in butane

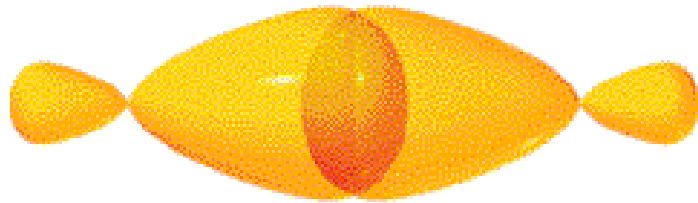
Conformations of Butane: Rotation About the C₂-C₃ Single Bond



Cycloalkanes: Ring Strain

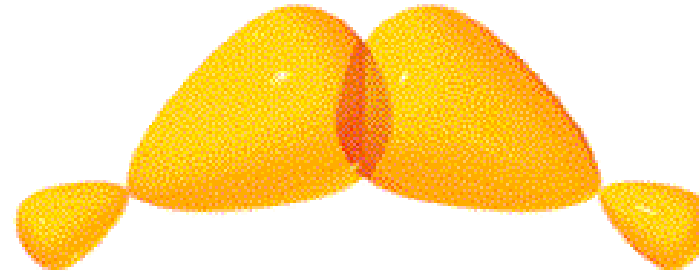
- Most ring compounds found in nature are 5- and 6-membered rings
- There is some stability in 5- and 6- membered rings
- Smaller rings such as 3- and 4- membered rings are considerably less stable
- Deviation of C-C-C bond angles from the tetrahedral value of 109.5° known as **angle strain**
- Bonds in smaller rings take on a bent appearance, and are **banana bonds**

Cycloalkanes: Ring Strain



**good overlap
strong bond**

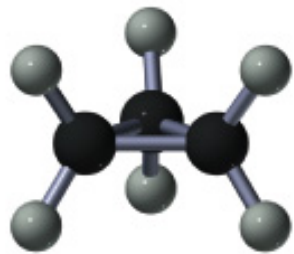
(a)



**poor overlap
weak bond**

(b)

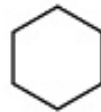
Cycloalkanes: Ring Strain



cyclopropane



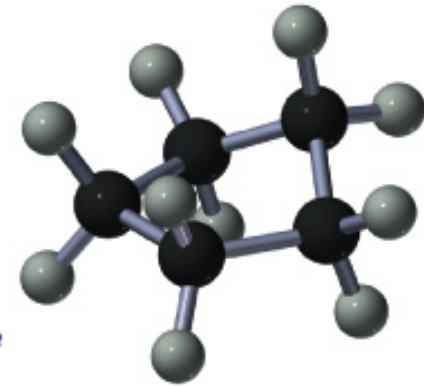
"planar" cyclopentane
bond angles = 108°



"planar" cyclohexane
bond angles = 120°



"planar" cycloheptane
bond angles = 128.6°



cyclopentane



Cycloalkanes

- **Angle strain** is strain that results from deviations from the ideal e.g. tetrahedral angle of 109.5°
- **Torsional strain** is strain that results from repulsion between bonding electrons of one substituent and a neighboring substituent
- **Steric strain** is the strain that results from atoms or groups of atoms approaching each other too closely

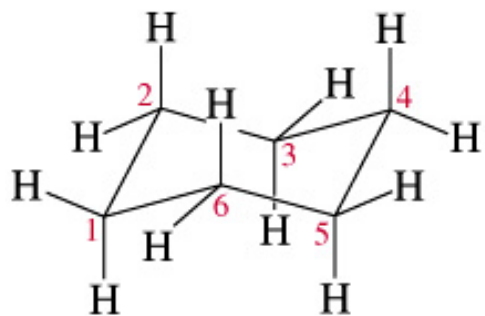
Conformations of Cyclohexane

- 6-membered rings are almost free of strain in a Chair conformation

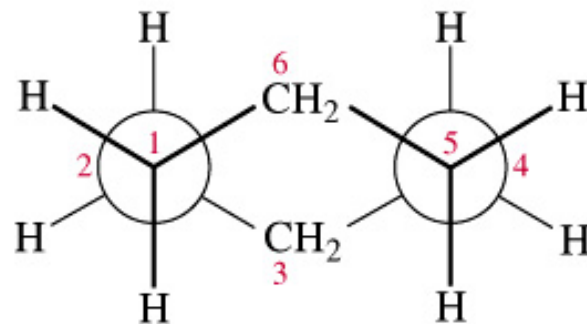
Table 2.9 Heats of Formation and Total Strain Energies of Cycloalkanes

	Heat of formation		"Strainless" Heat of formation		Total strain energy	
	(kcal/mol)	(kJ/mol)	(kcal/mol)	(kJ/mol)	(kcal/mol)	(kJ/mol)
	cyclopropane	+12.7	53.1	-14.6	-61.1	27.3
cyclobutane	+6.8	24.5	-19.7	-82.4	26.5	101.9
cyclopentane	-18.4	-77.0	-24.6	-102.9	6.2	25.9
cyclohexane	-29.5	-123.4	-29.5	-123.4	0	0
cycloheptane	-28.2	-118.0	-34.4	-143.9	6.2	25.9
cyclooctane	-29.7	-124.3	-39.4	-164.8	9.7	40.6
cyclononane	-31.7	-132.6	-44.3	-185.4	12.6	52.7
cyclodecane	-36.9	-154.4	-49.2	-205.9	12.3	51.5
cycloundecane	-42.9	-179.5	-54.1	-226.4	11.2	46.9

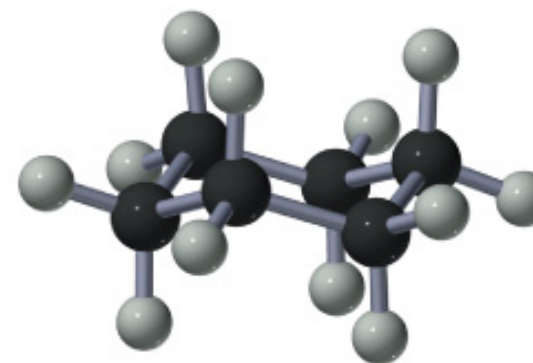
Chair Conformation of Cyclohexane



chair conformer of cyclohexane

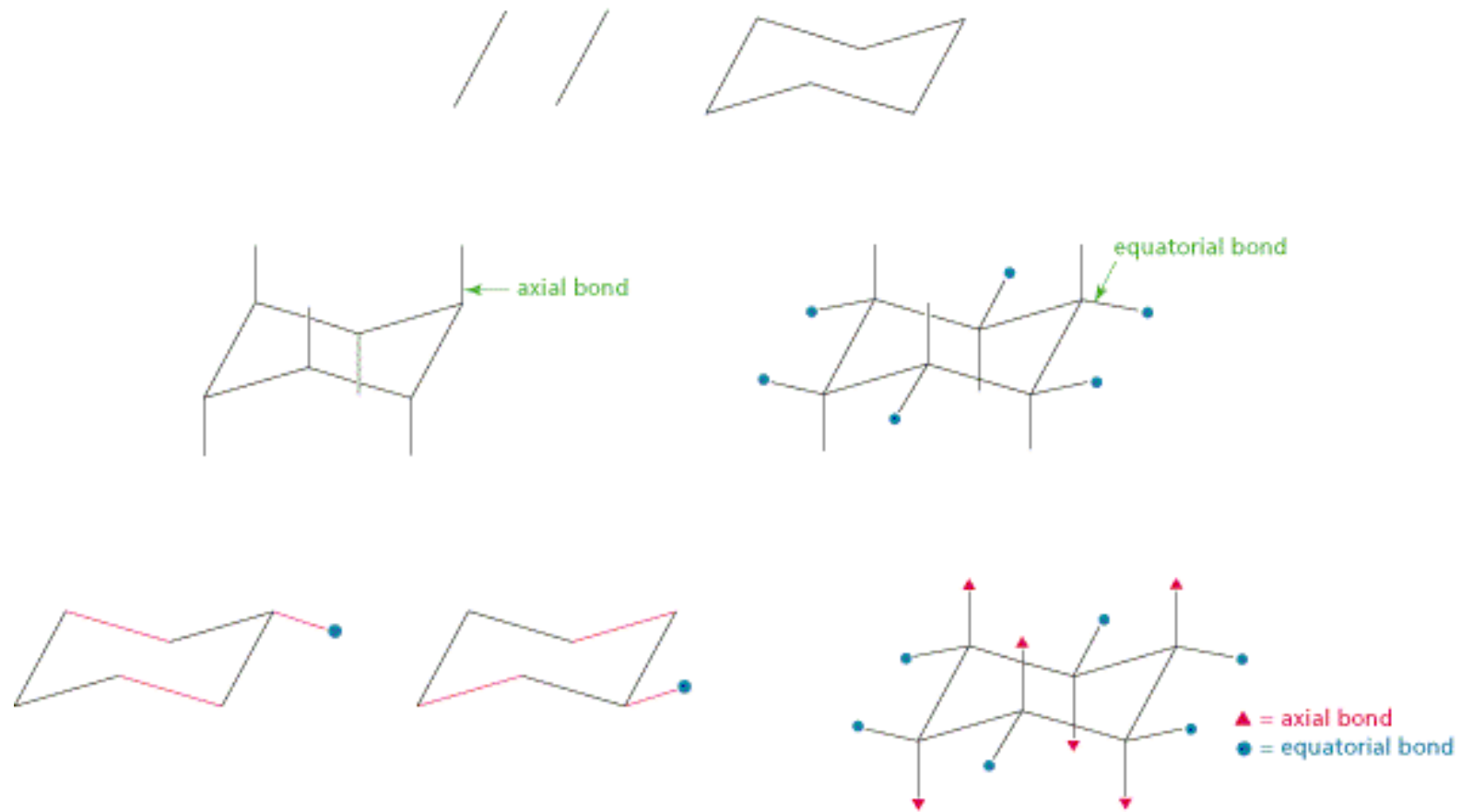


Newman projection of the chair conformer



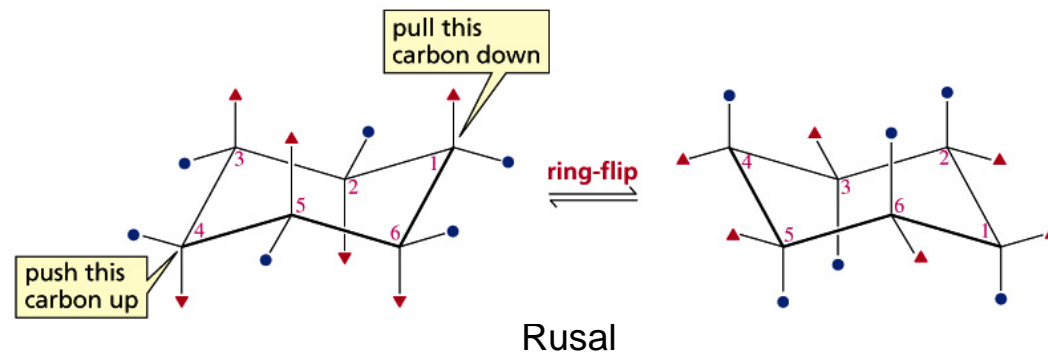
ball-and-stick model of the chair conformer of cyclohexane

Drawing Cyclohexane in the Chair Conformation



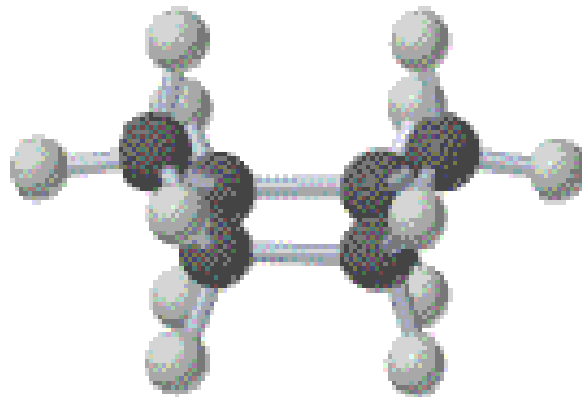
Interconversion of Cyclohexane Conformations

- As a result of simultaneous rotation about all C-C bonds, a chair conformation of cyclohexane can interconvert to another chair conformation by a **ring-flip**
- In the process, equatorial bonds become axial and vice versa



Conformations of Cyclohexane

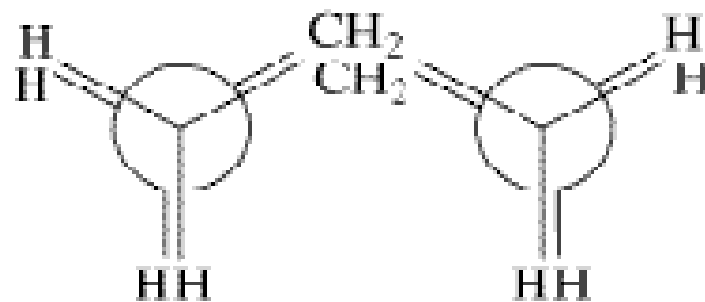
- There is another conformation for cyclohexane - the **boat conformation**



ball-and-stick model of the boat conformer of cyclohexane

Conformations of Cyclohexane

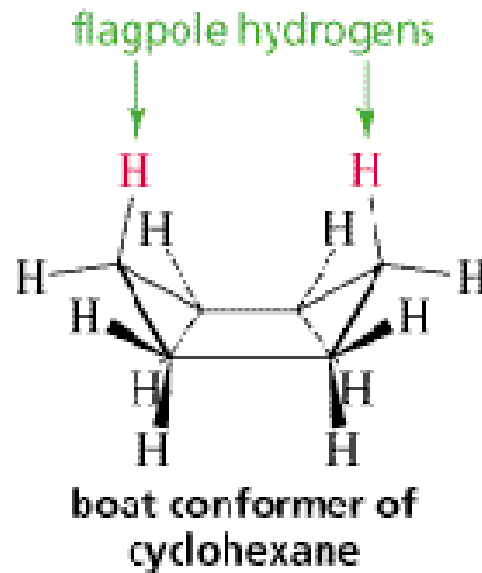
- While all hydrogens in the **chair conformation** are staggered, four hydrogens are eclipsed in the **boat conformation**, which is less stable



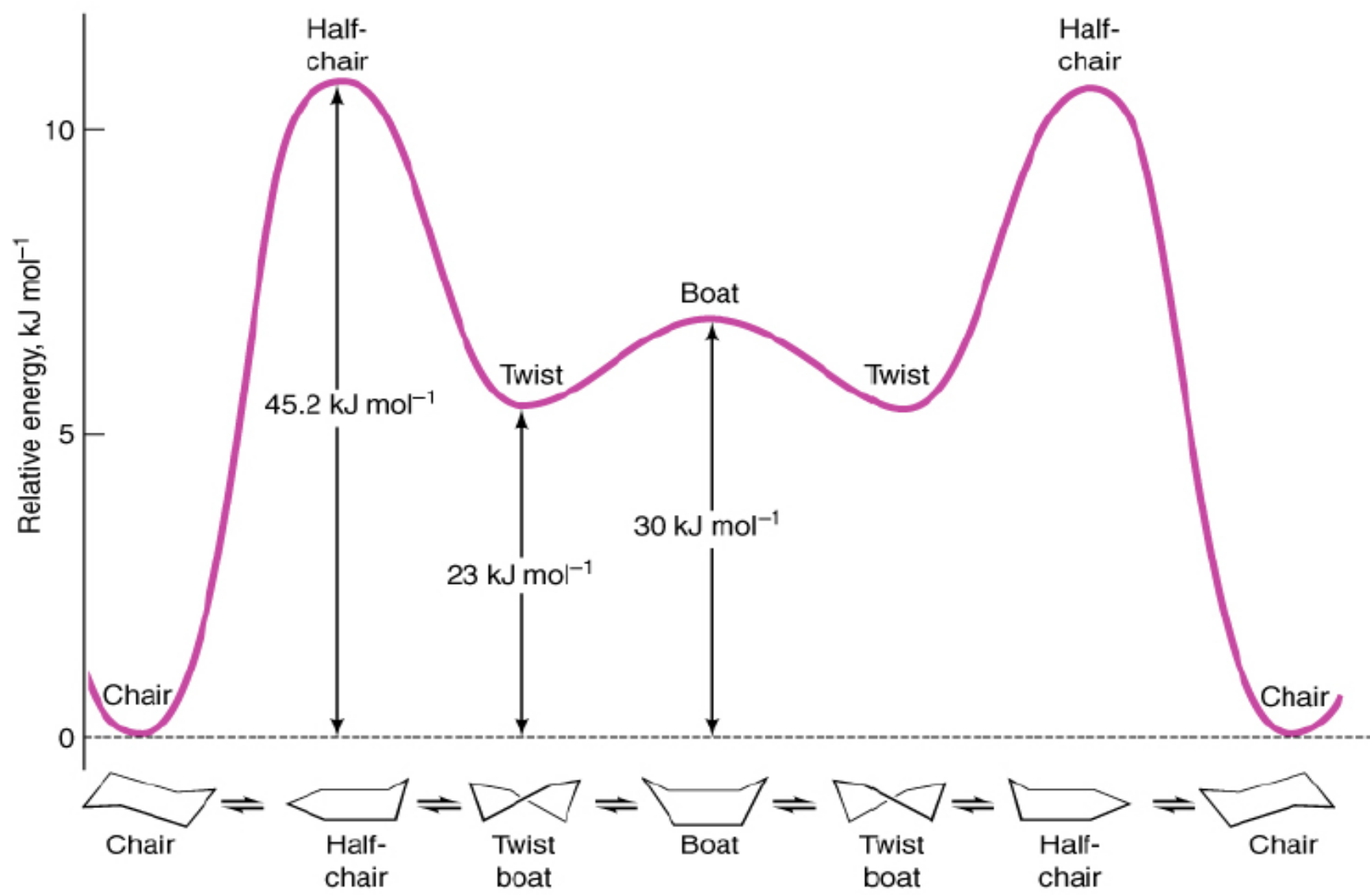
Newman projection of
the boat conformer

Conformations of Cyclohexane

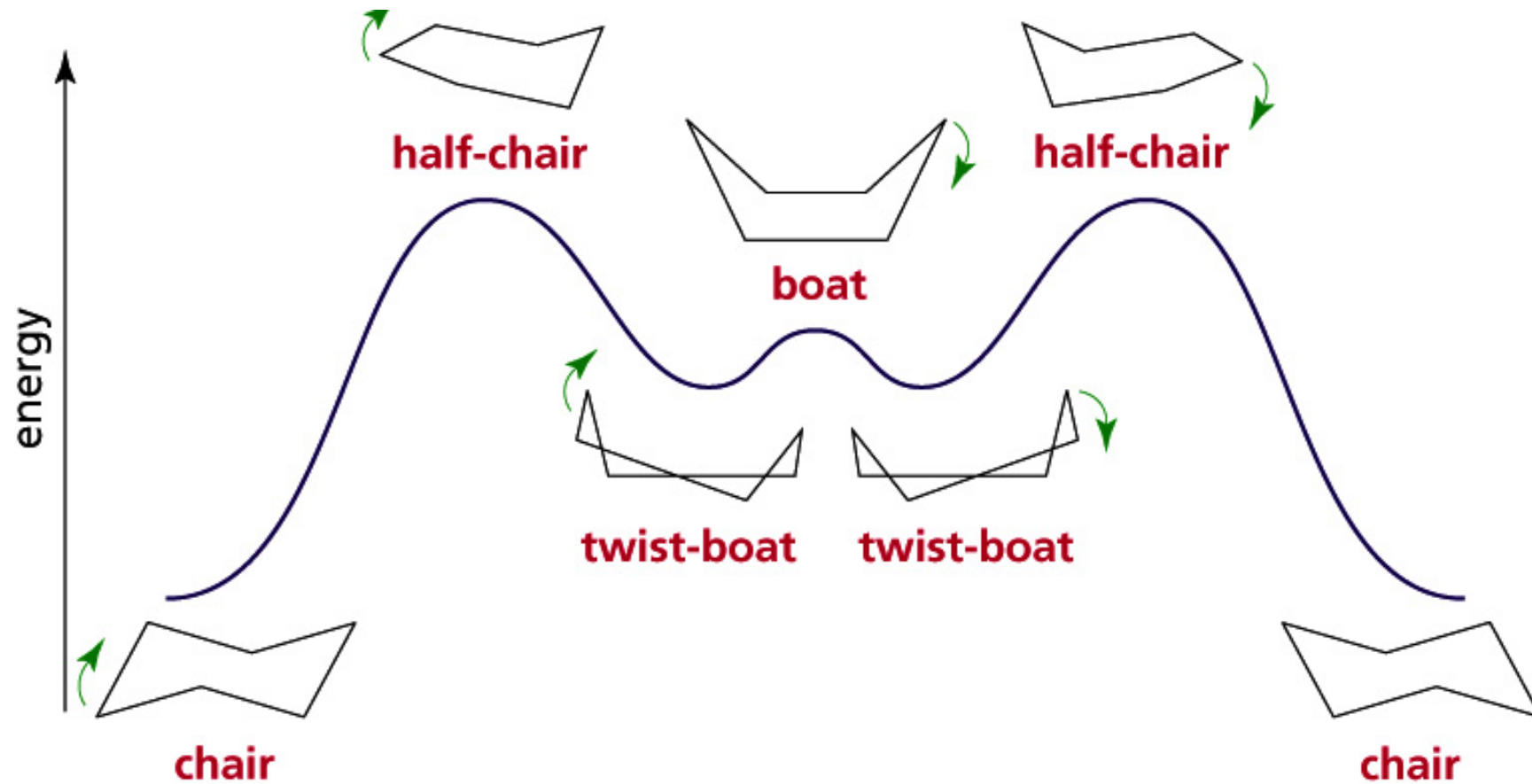
- Another destabilizing feature is the fact that two of the “axial” hydrogens become **flagpole** hydrogens



Rusal

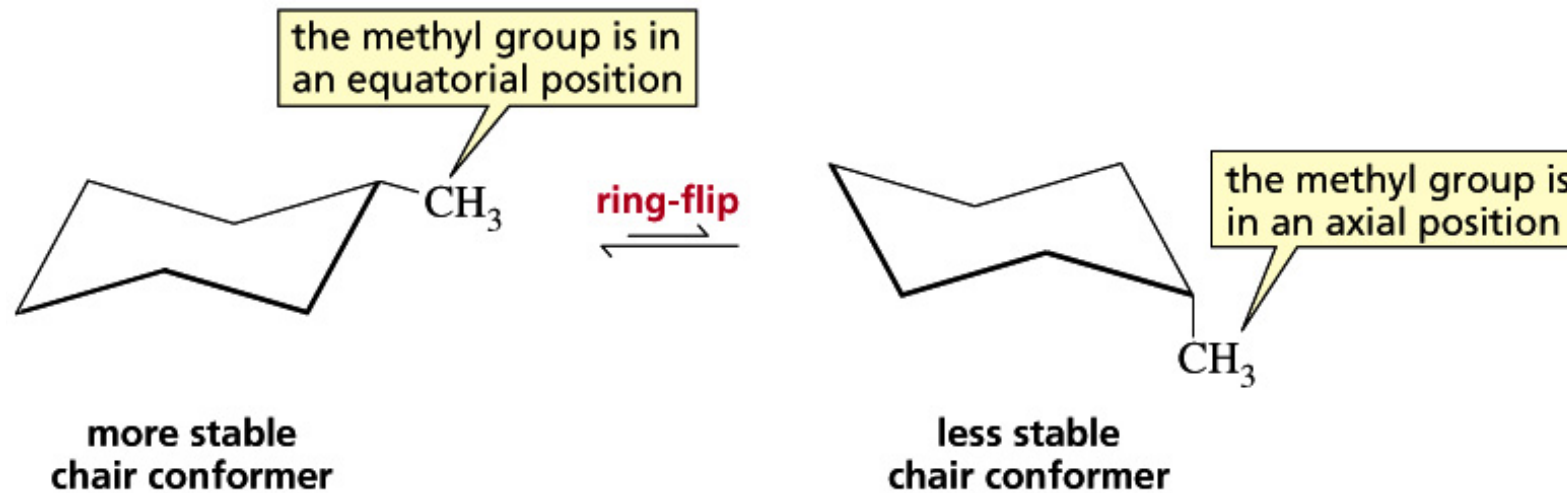


Interconversion of Cyclohexane Conformations



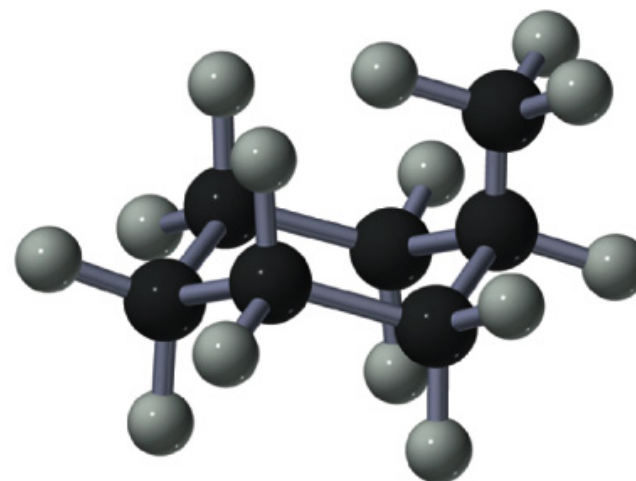
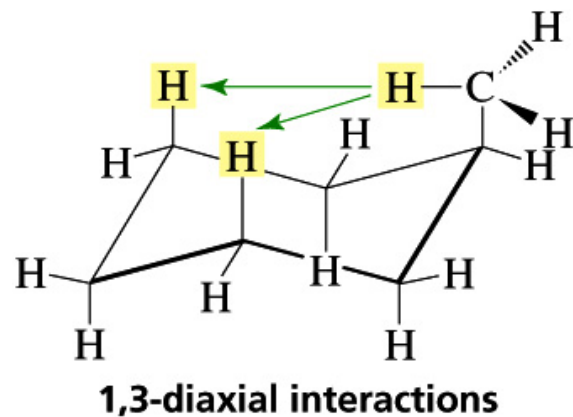
Monosubstituted Cyclohexanes

- When there is one substituent on the cyclohexane ring, the two chair conformations are no longer equivalent



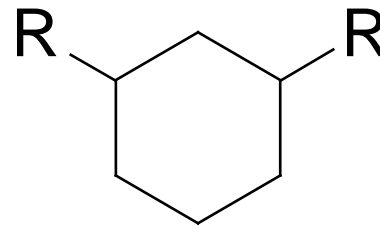
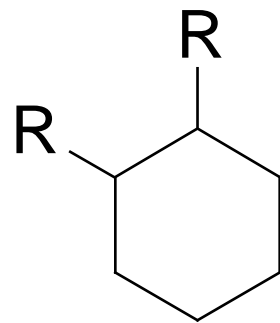
Monosubstituted Cyclohexanes

- In an axial position there are close approaches from the hydrogens (or other substituents) located at the axial positions two carbons away
- These are called the **1,3-diaxial interactions**

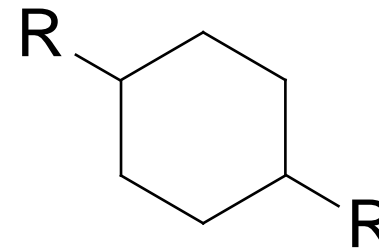


Conformations of Disubstituted Cyclohexanes

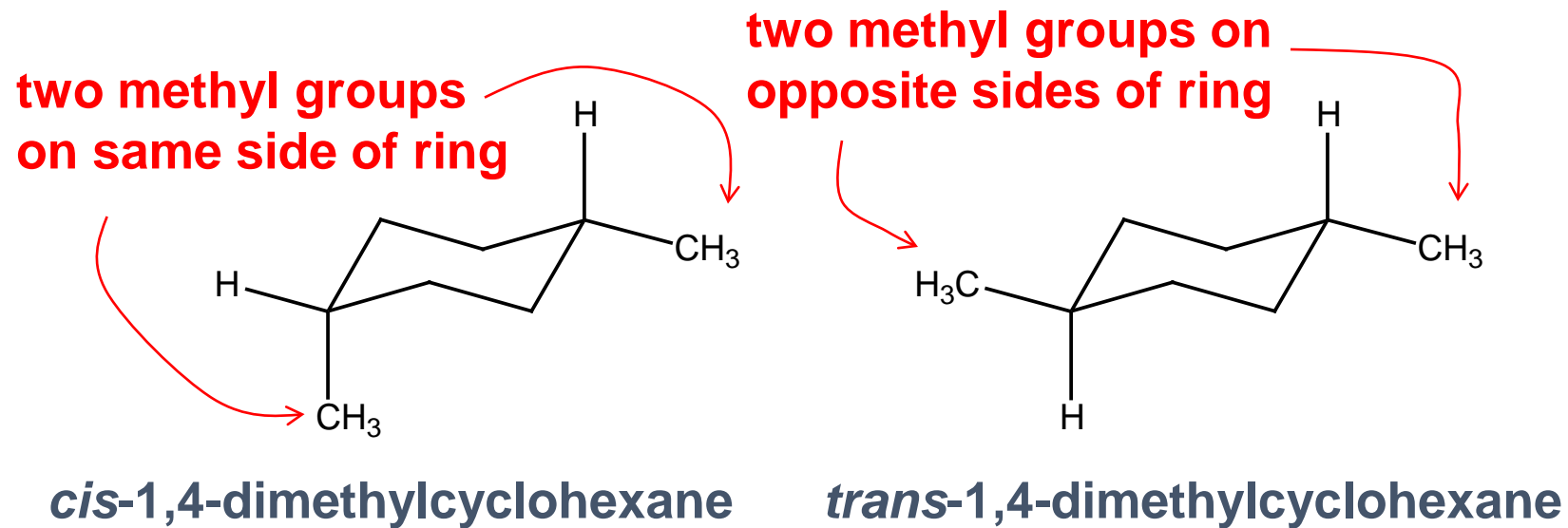
- If there are two substituents on a cyclohexane ring, both substituents must be considered when determining which of the two chair conformations is more stable



Rusal

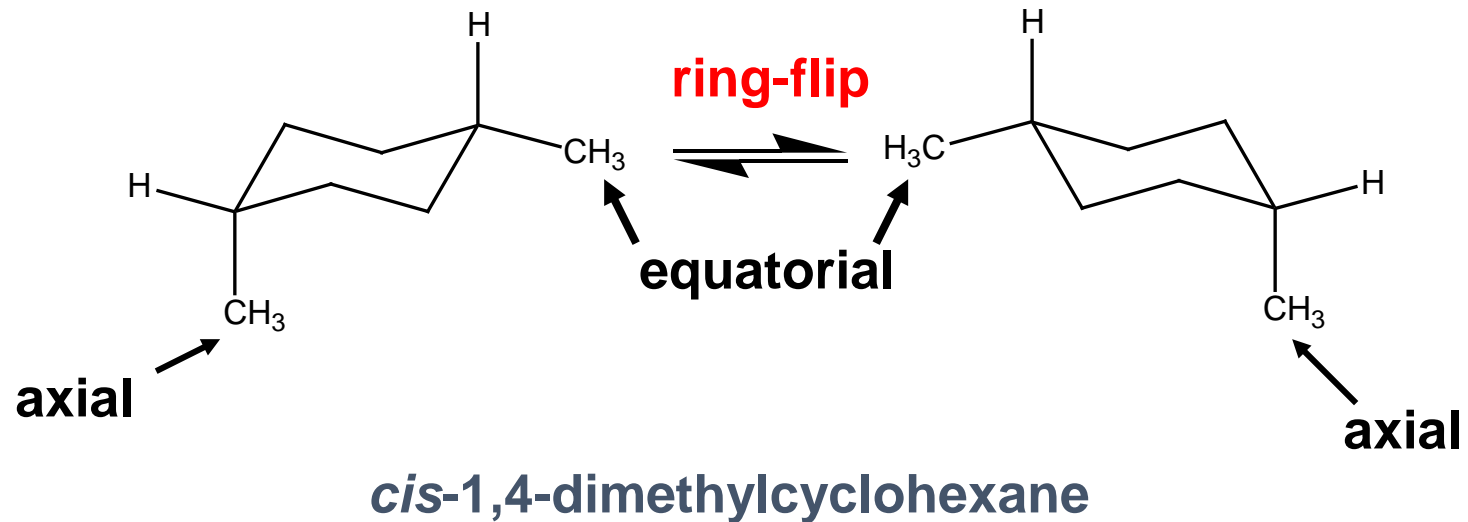


Conformations of 1,4-Disubstituted Cyclohexanes



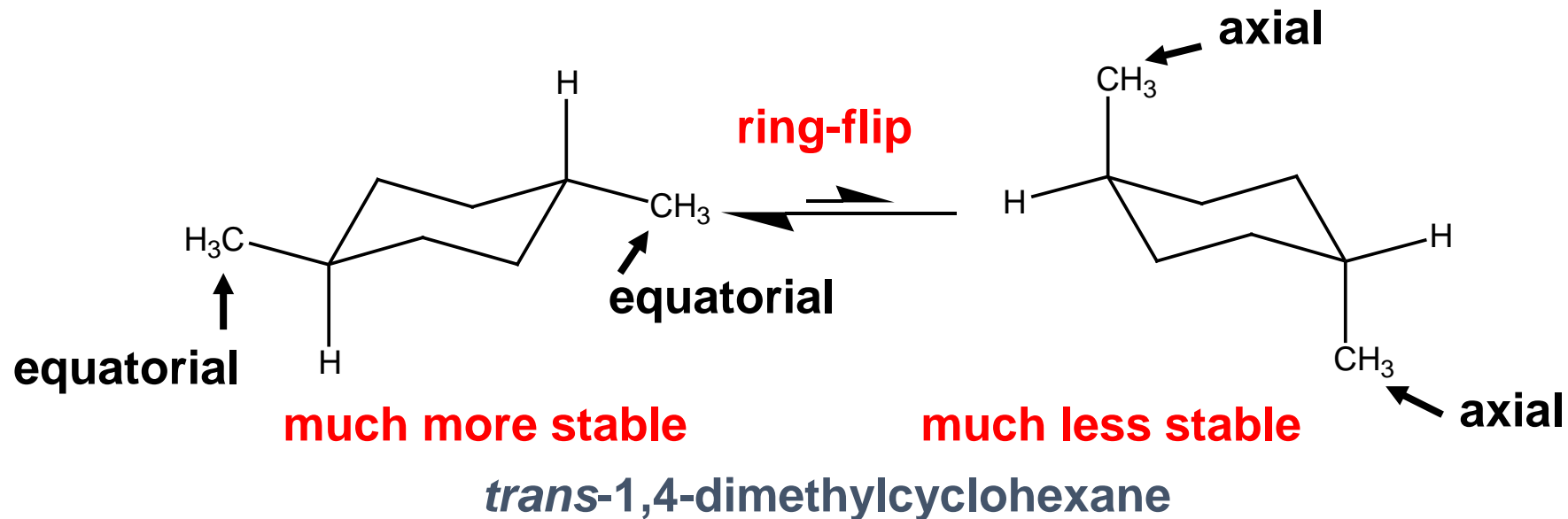
Conformations of 1,4-Disubstituted Cyclohexanes

- The cis isomer must have one substituent in an axial position and one in an equatorial position

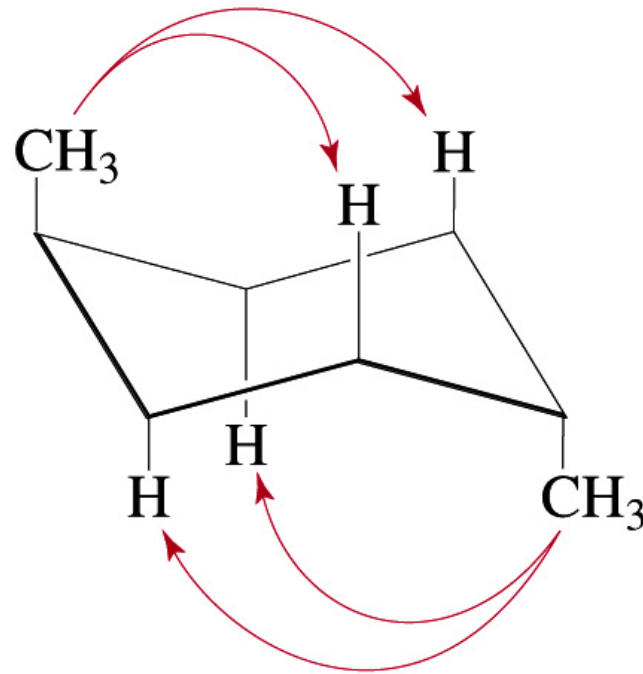


Conformations of 1,4-Disubstituted Cyclohexanes

- The trans isomer has both substituents in either the equatorial or in the axial positions
- Conformations of 1,4-Disubstituted Cyclohexanes, Of the two isomers, the trans isomer is the more stable



Conformations of Disubstituted Cyclohexanes

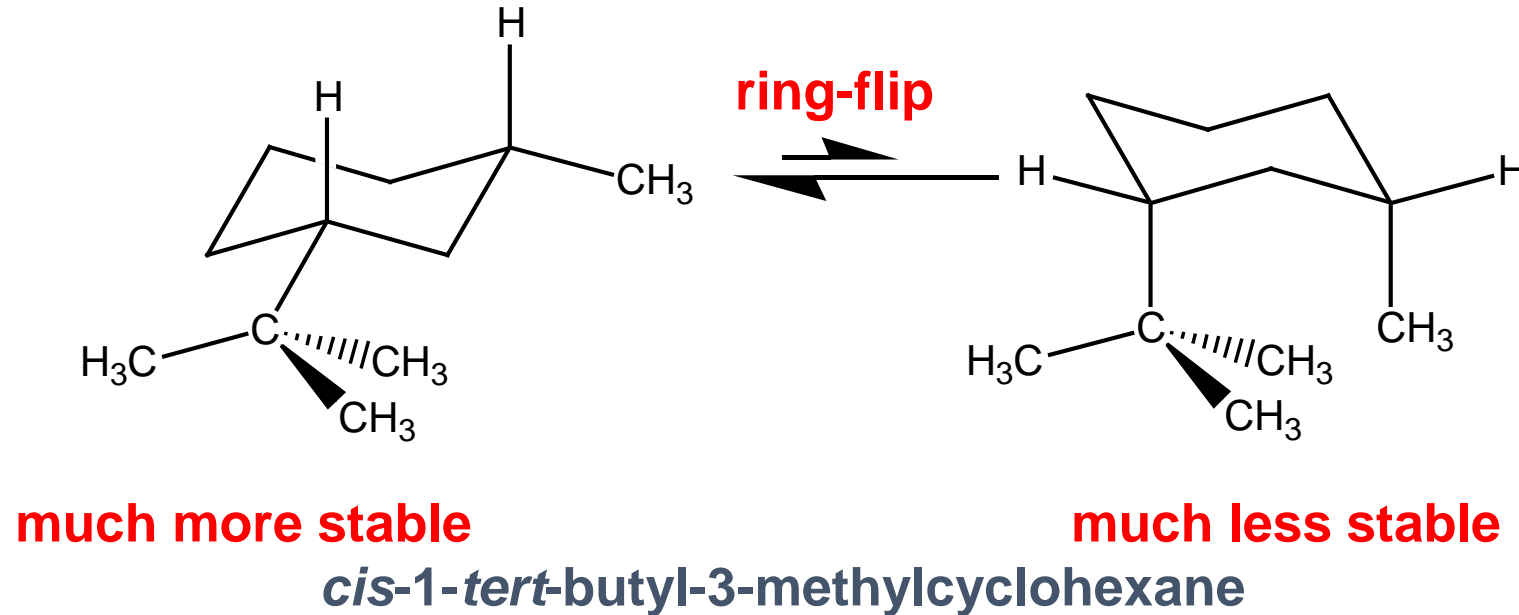


**steric interactions
make this
conformation very
unstable**

**This chair conformer has
four 1,3-diaxial interactions.**

Conformations of *cis*-1,3-Disubstituted Cyclohexanes

- A *cis*-1,3-disubstituted cyclohexane can exist in one of two conformations



Conformations of *trans*-1,3-Disubstituted Cyclohexanes

- Both conformers of *trans*-1-*tert*-butyl-3-methylcyclohexane have one substituent in an axial position and one in an equatorial position

