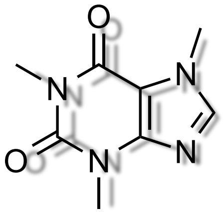
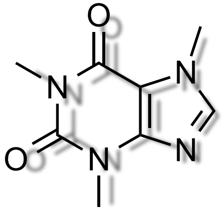


Chemistry 2500

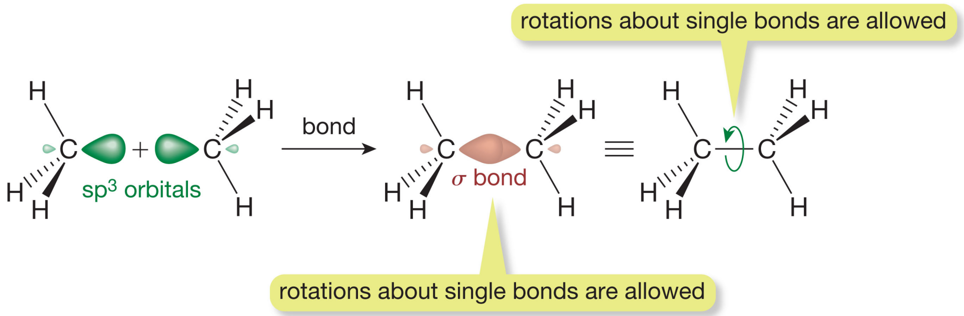
Chapter 3

Conformations by Rotations

Rotations About Single Bonds

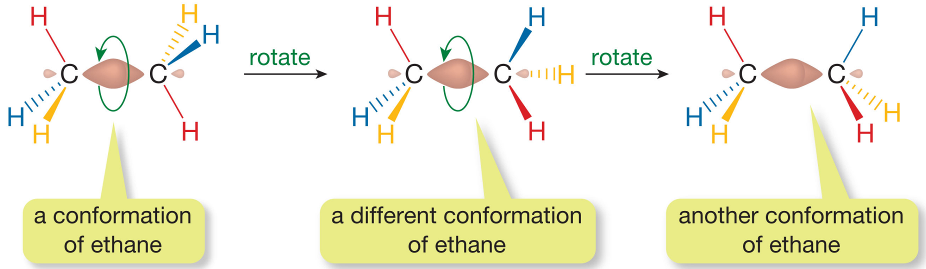


- It is important to understand that under normal conditions, STP, molecules are in constant motion and that atoms move relative to each other – rotation about single bonds.
- Rotation about a C-C bond does not change the overlap between the orbitals therefore the σ bond remains intact.
- The different spatial arrangements produced by rotation about single bonds are called ***conformations***.



rotations about single bonds are allowed

rotations about single bonds are allowed



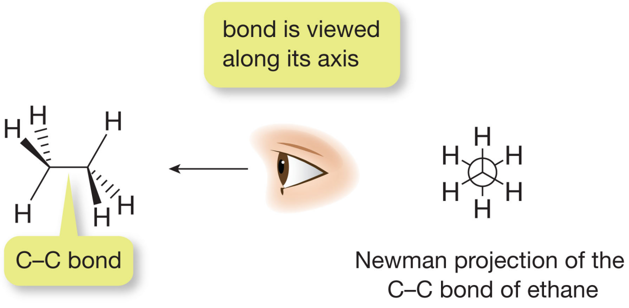
a conformation of ethane

a different conformation of ethane

another conformation of ethane

Newman Projections

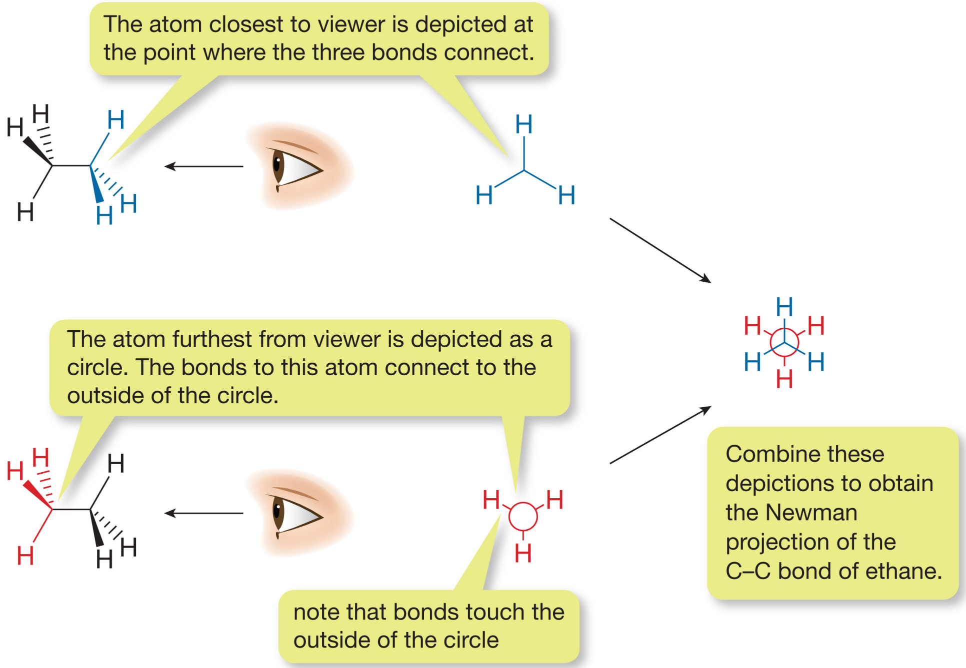
- ***Newman Projections*** are used to clearly show the arrangement around a single bond.



bond is viewed along its axis

C–C bond

Newman projection of the C–C bond of ethane



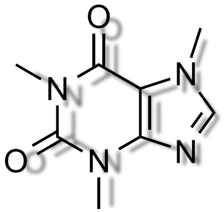
The atom closest to viewer is depicted at the point where the three bonds connect.

The atom furthest from viewer is depicted as a circle. The bonds to this atom connect to the outside of the circle.

note that bonds touch the outside of the circle

Combine these depictions to obtain the Newman projection of the C–C bond of ethane.

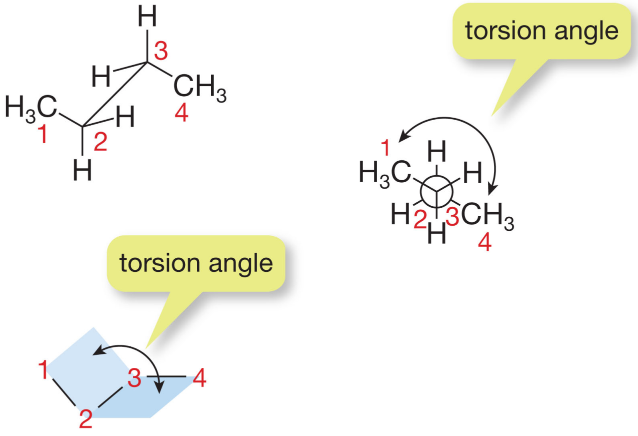
Staggered and Eclipsed Conformations

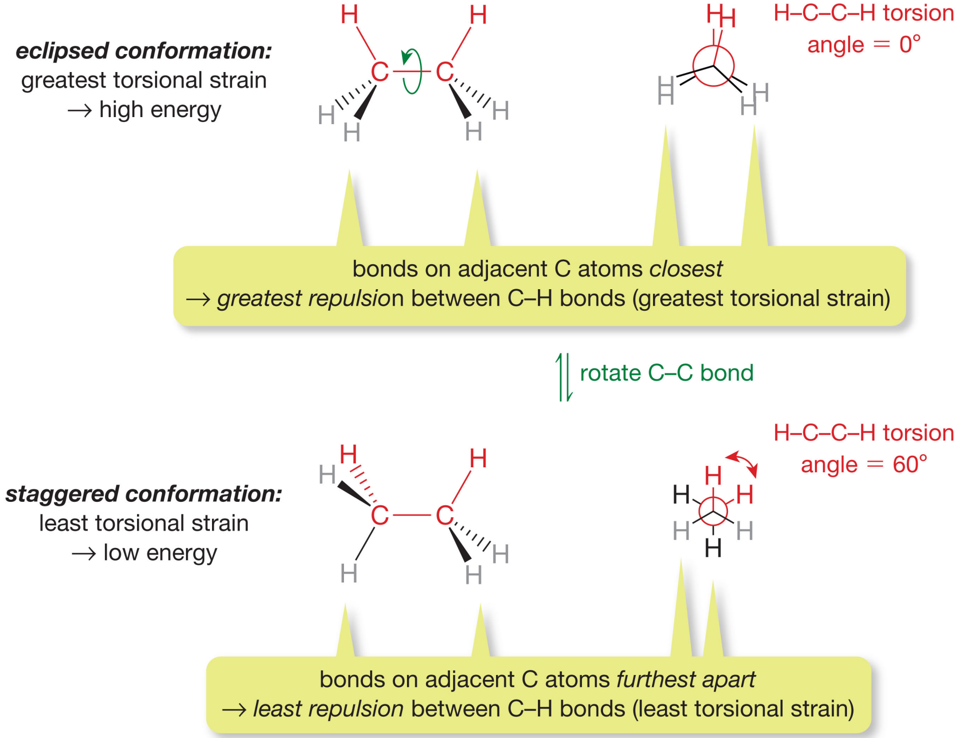


- Different conformations have different energies. Rotation about a particular bond is described by its ***torsion*** or ***dihedral angle***.
- When the bonds of the front carbon atom align (or eclipse) with those of the back carbon atom, they form what is called a ***eclipsed conformation***.
- Repulsion between the adjacent bonds create torsion strain, raising the energy of the conformation.
- Further rotation about the C-C bond moves the atoms and bonds farther apart, reducing the torsion strain and lower the its energy.
- The torsional strain is at a minimum in a ***staggered conformation*** – when the groups in front and back are as far apart as possible.

Staggered and Eclipsed Conformations

- The greater the torsion angle, the less torsional strain.





eclipsed conformation:
greatest torsional strain
→ high energy

H–C–C–H torsion
angle = 0°

bonds on adjacent C atoms *closest*
→ *greatest repulsion* between C–H bonds (greatest torsional strain)

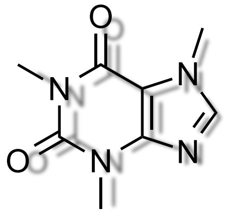
rotate C–C bond

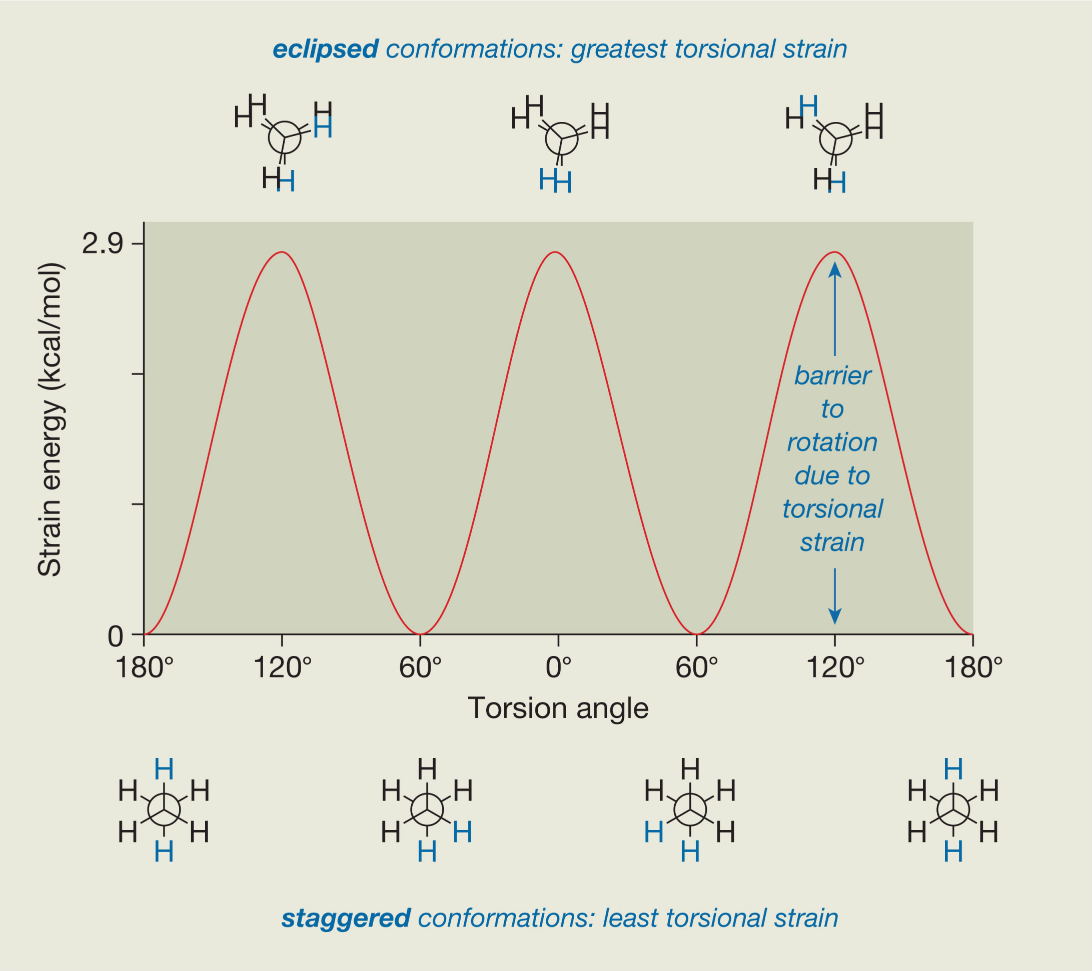
staggered conformation:
least torsional strain
→ low energy

H–C–C–H torsion
angle = 60°

bonds on adjacent C atoms *furthest apart*
→ *least repulsion* between C–H bonds (least torsional strain)

Staggered and Eclipsed Conformations





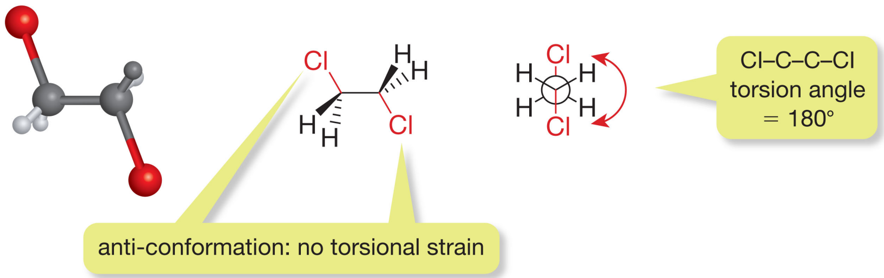
eclipsed *conformations: greatest torsional strain*

barrier to rotation due to torsional strain

staggered *conformations: least torsional strain*

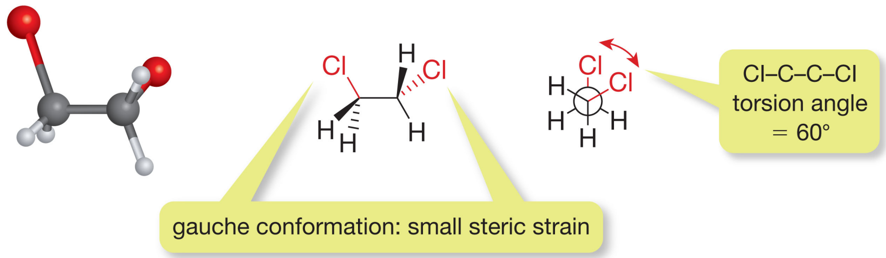
Steric Strain

- ***Steric strain*** is defined as a repulsive force between the electron clouds of atoms that are close to each other but not directly bonded.



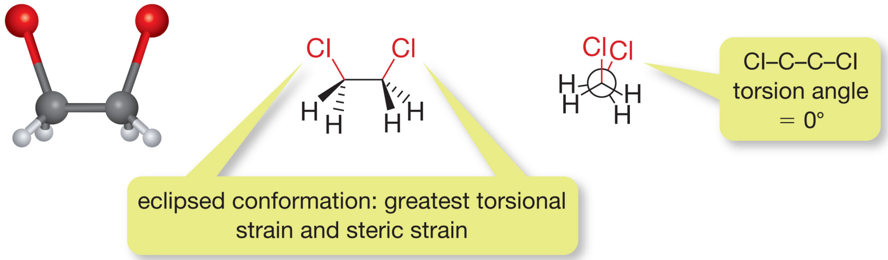
anti-conformation: no torsional strain

Cl–C–C–Cl torsion angle = 180°



gauche conformation: small steric strain

Cl–C–C–Cl torsion angle = 60°

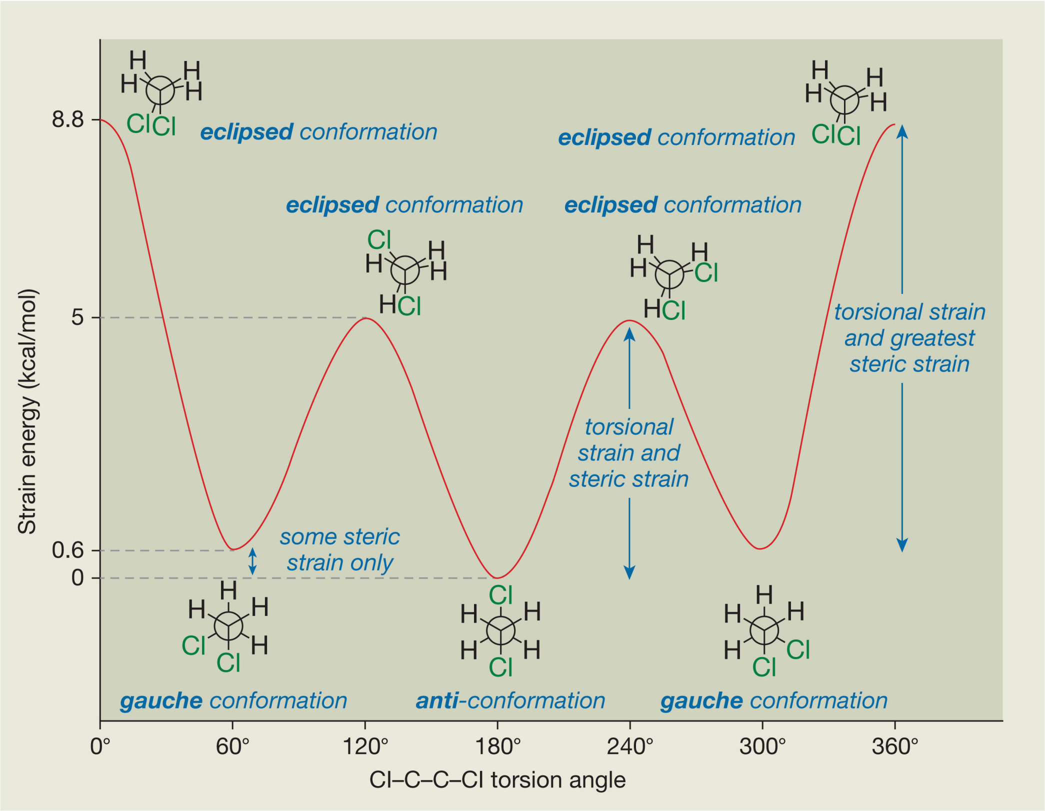


eclipsed conformation: greatest torsional strain and steric strain

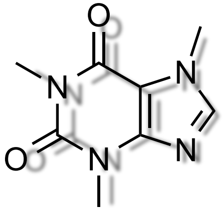
Cl–C–C–Cl torsion angle = 0°

Steric Strain

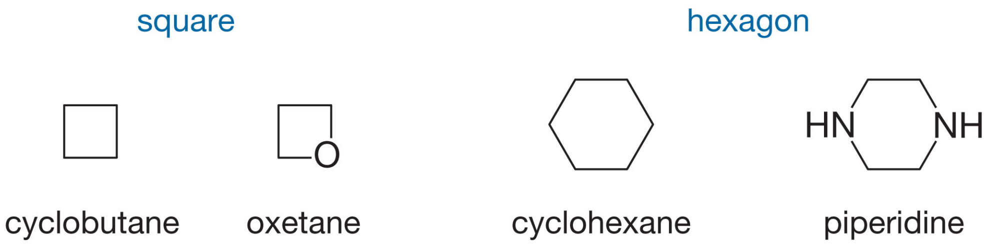
- The bigger the group (i.e. the bigger the electron cloud), the more steric strain the molecule will experience.



Strain in Cyclic Molecules

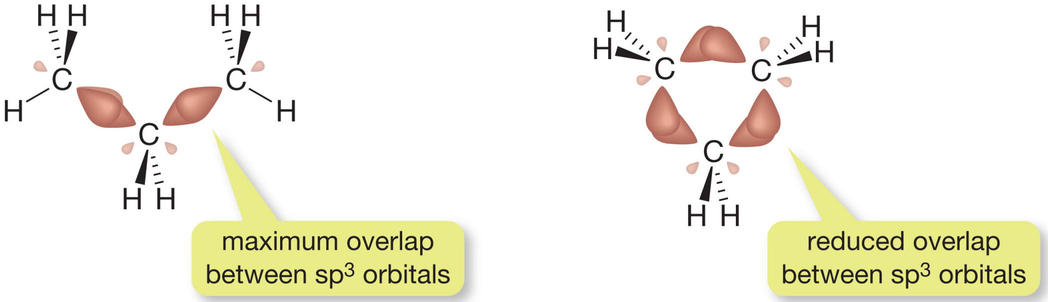


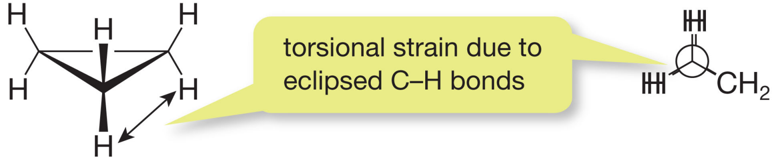
- Cyclic molecules are often depicted as simple polygons, neglecting their true 3-dimentional structure.
- ***Angle strain*** arises from bond angles that do not permit maximum orbital overlap between atoms of a molecule.



3-Membered Rings

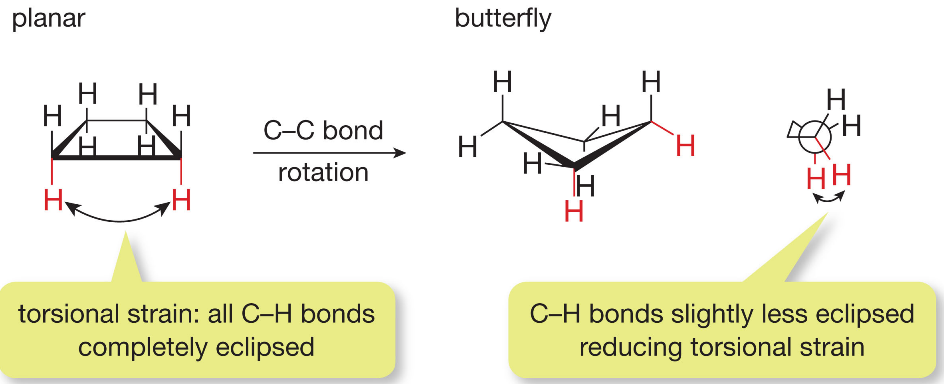
- 3-membered rings possess the most strain, experiencing angle, steric, and torsional strain.
- Despite their inherent strain, 3-membered rings do occur in nature.



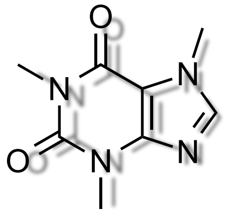


4-Membered Rings

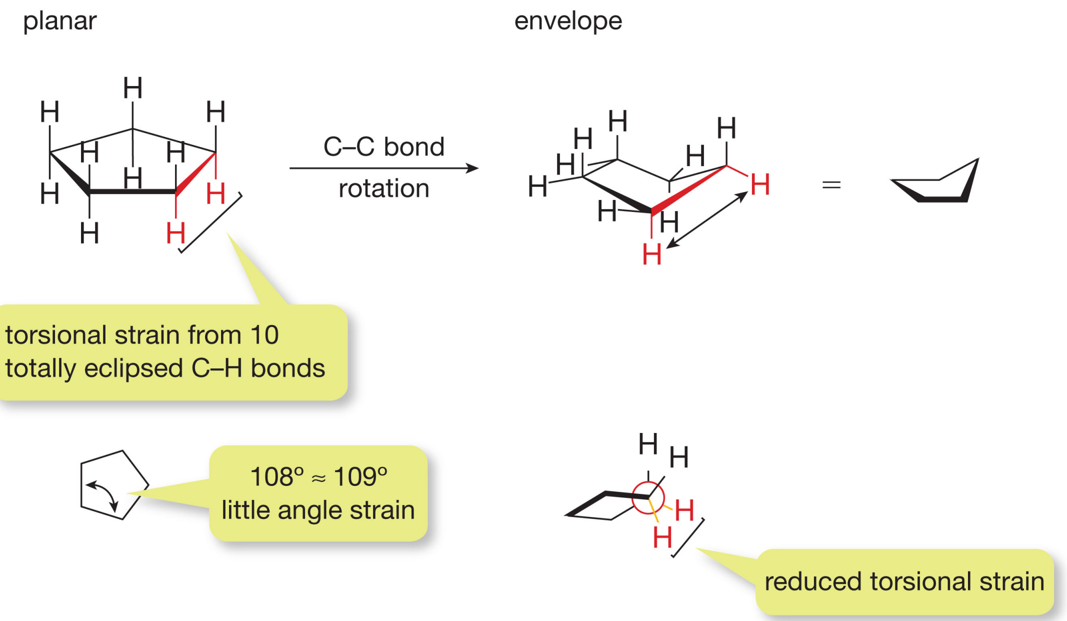
- 4-membered rings have non-planar conformations, which reduces the amount of inherent strain within the molecule.
- With less angle, torsion, and steric strain, 4-membered rings are inherently more stable than 3-membered rings.



5-Membered Rings



- The most stable conformation for 5-membered rings is the ***envelope conformation***.
- With even less strain, 5-membered rings are inherently more stable than 4- and 3-membered rings and are frequently found in nature.



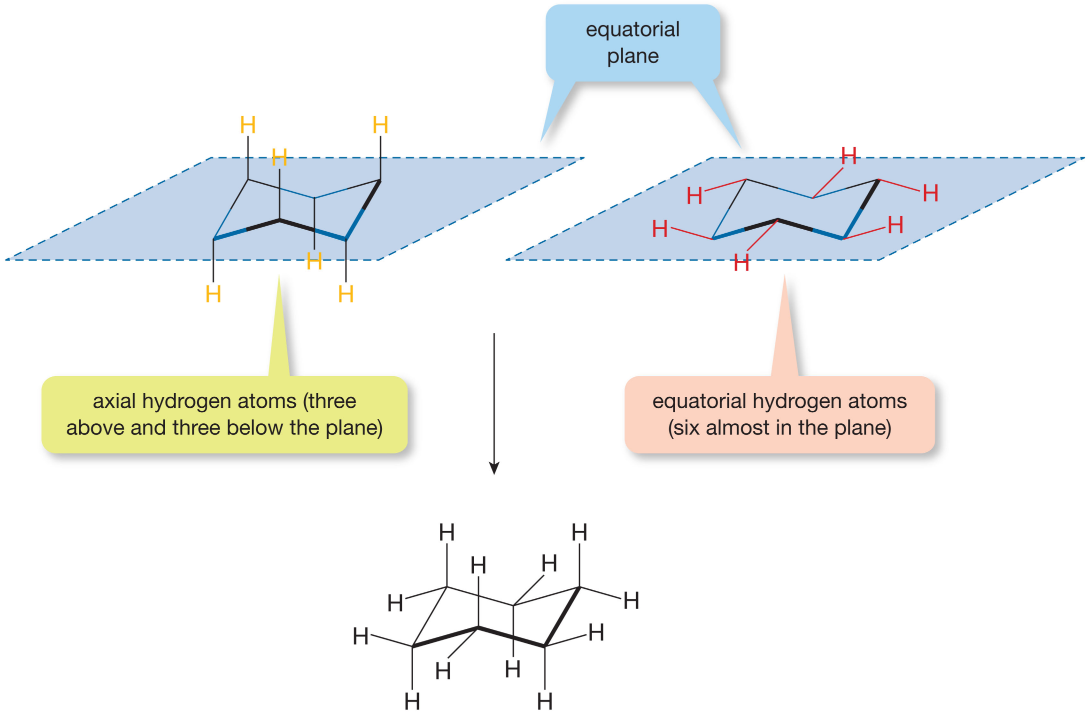
torsional strain from 10 totally eclipsed C–H bonds

108° ≈ 109°
little angle strain

reduced torsional strain

6-Membered Rings

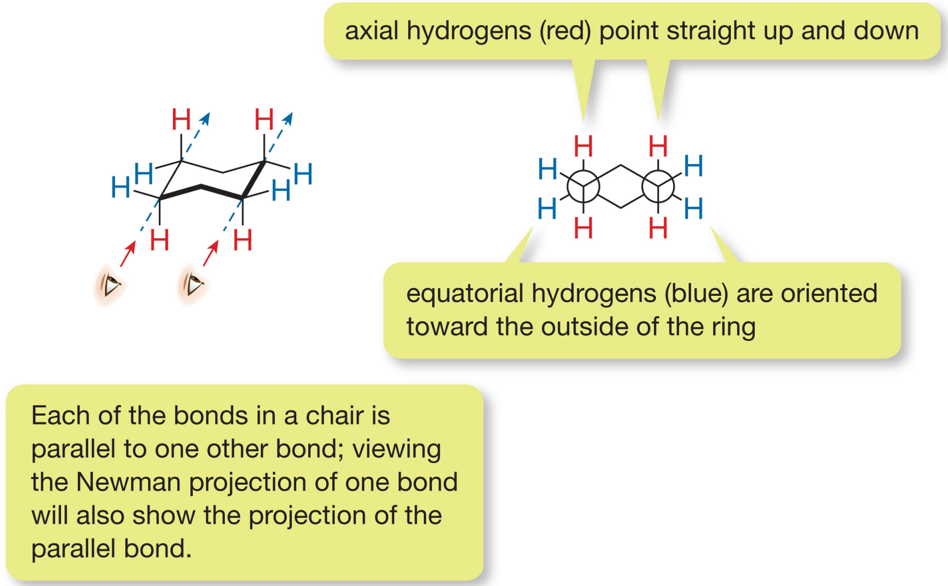
- Cyclohexane is the only ring under 14 carbon atoms that is relatively free from strain.
- The ***chair conformation*** is by far the most common conformation for 6-membered rings.



equatorial plane

axial hydrogen atoms (three above and three below the plane)

equatorial hydrogen atoms (six almost in the plane)

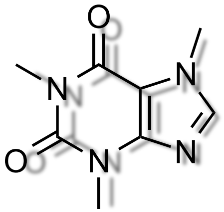


axial hydrogens (red) point straight up and down

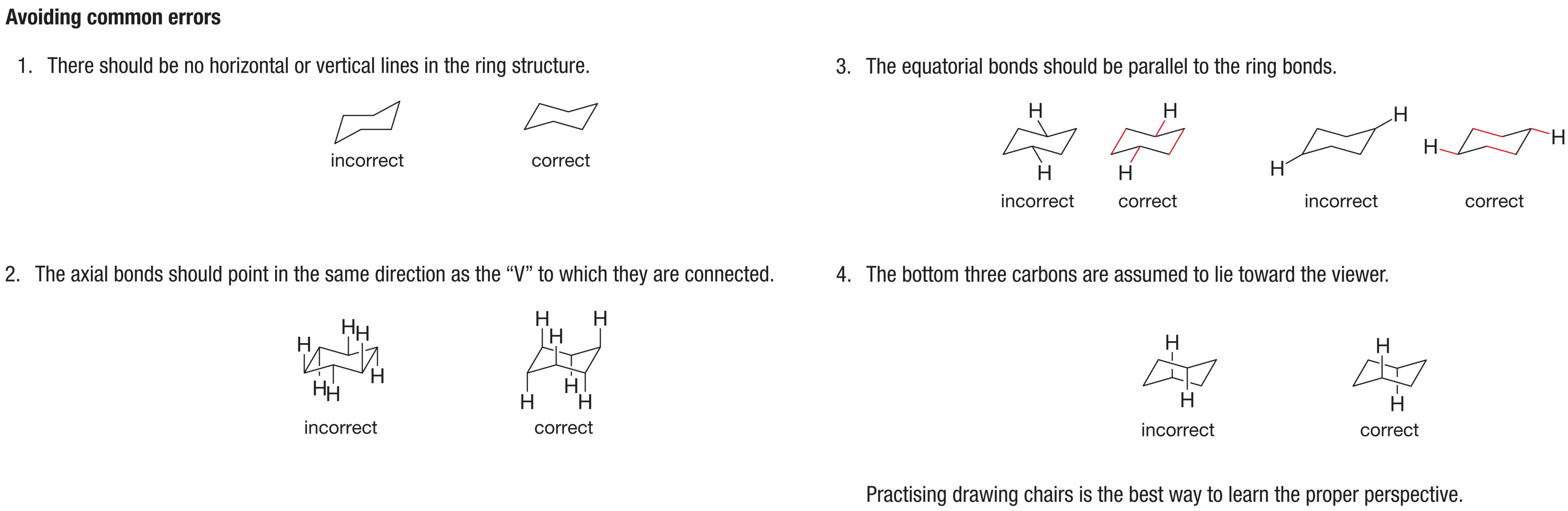
equatorial hydrogens (blue) are oriented toward the outside of the ring

Each of the bonds in a chair is parallel to one other bond; viewing the Newman projection of one bond will also show the projection of the parallel bond.

6-Membered Rings – Chair Conformations



- It is ***imperative*** that you learn how to properly draw chair conformations – refer to section 3.5.1 of your text.



Avoiding common errors

1. There should be no horizontal or vertical lines in the ring structure.

2. The axial bonds should point in the same direction as the “V” to which they are connected.

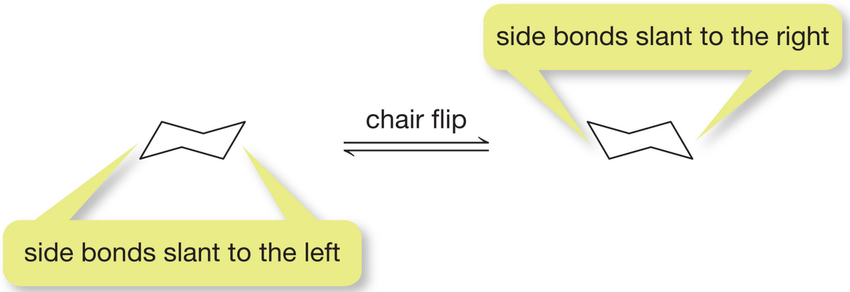
3. The equatorial bonds should be parallel to the ring bonds.

4. The bottom three carbons are assumed to lie toward the viewer.

Practising drawing chairs is the best way to learn the proper perspective.

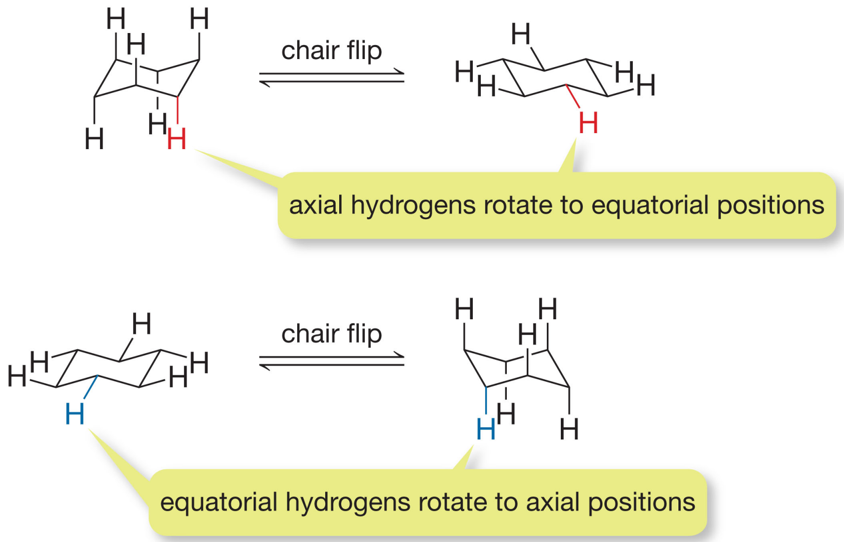
6-Membered Rings – Chair Conformations

- There are 2 different chair conformations that interconvert through a process called a ***ring flip*** or ***chair flip***.
- For cyclohexane, both conformers resulting from the ring flip have the same energy.



side bonds slant to the right

side bonds slant to the left

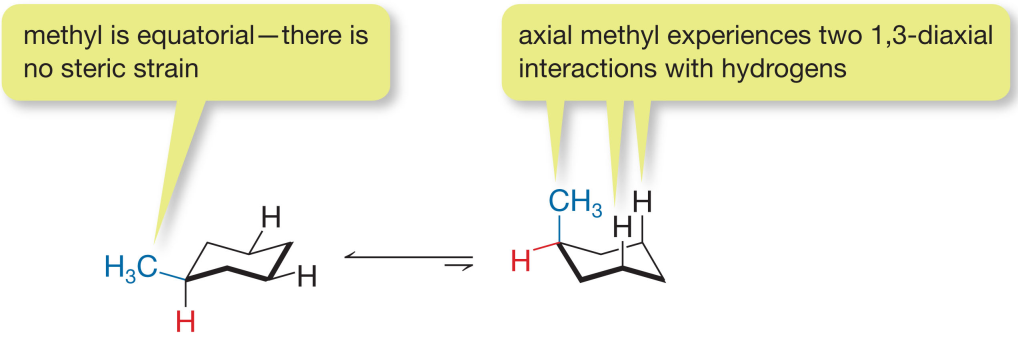


axial hydrogens rotate to equatorial positions

equatorial hydrogens rotate to axial positions

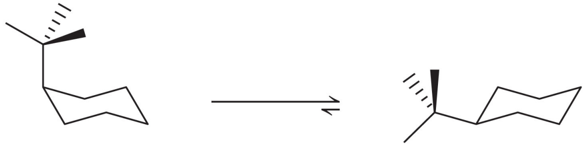
Substituted 6-Membered Rings

- When a substituent is added to a 6-membered ring, the 2 conformers do ***NOT*** have the same energy.
- Substituents found in the axial position are less favorable due to ***1,3-diaxial interactions***.
- Steric strain from 1,3-diaxial interactions generally increases as the size of the substituent increases.

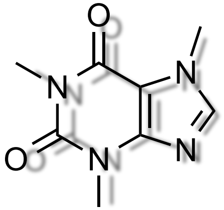


methyl is equatorial—there is no steric strain

axial methyl experiences two 1,3-diaxial interactions with hydrogens



Substituted 6-Membered Rings



- In general, the more stable chair conformer is the one where more of the larger substituents are placed in the equatorial position.

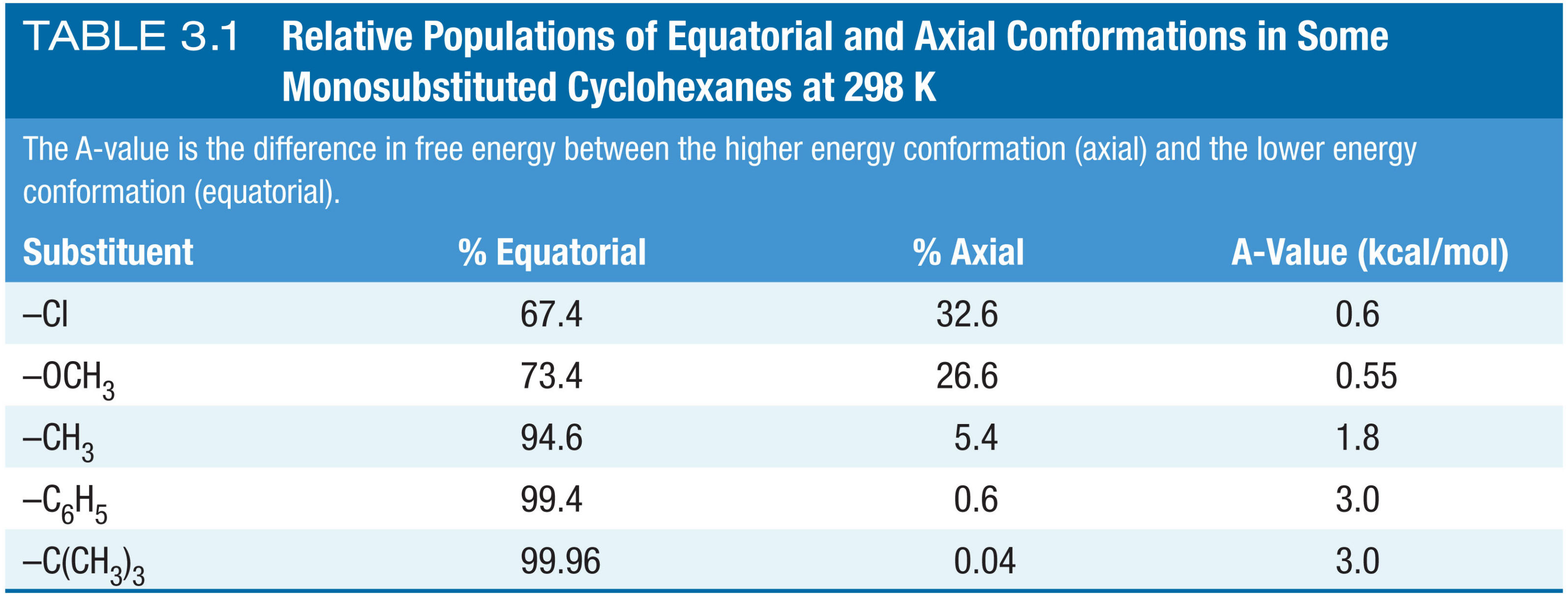


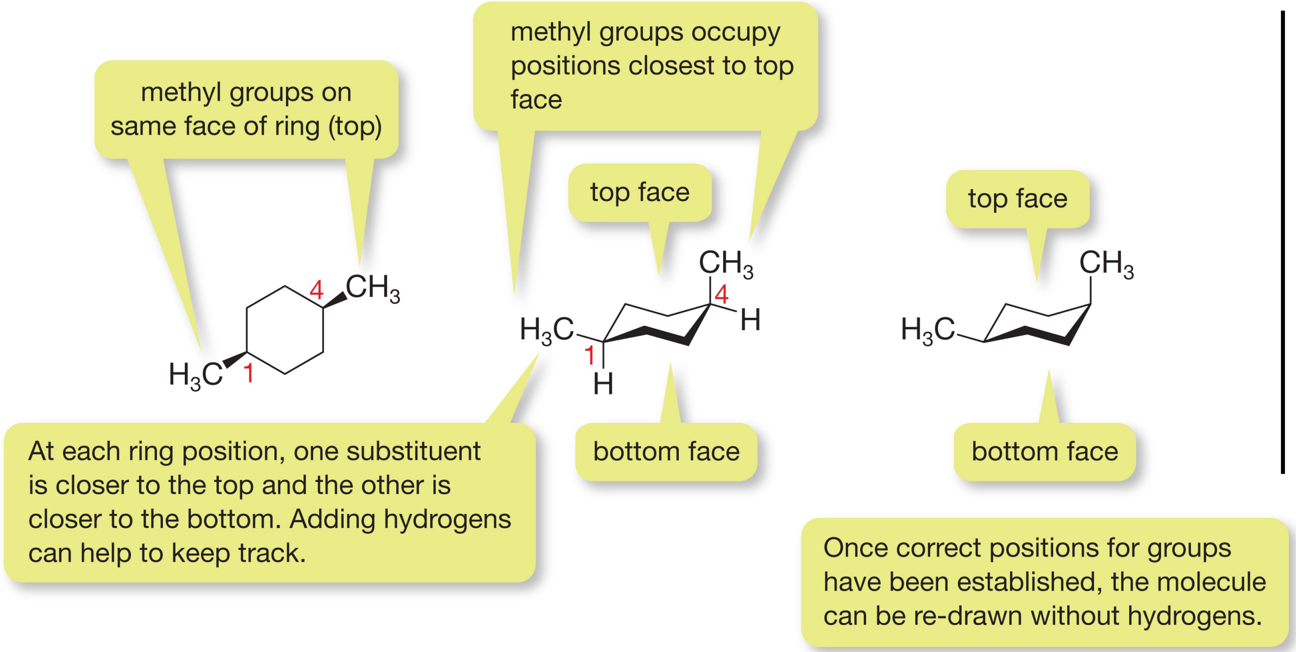
TABLE 3.1 Relative Populations of Equatorial and Axial Conformations in Some Monosubstituted Cyclohexanes at 298 K

The A-value is the difference in free energy between the higher energy conformation (axial) and the lower energy conformation (equatorial).

Substituent	% Equatorial	% Axial	A-Value (kcal/mol)
–Cl	67.4	32.6	0.6
$-OCH_3$	73.4	26.6	0.55
$-CH_3$	94.6	5.4	1.8
$-C_6H_5$	99.4	0.6	3.0
$-C(CH_3)_3$	99.96	0.04	3.0

Disubstituted 6-Membered Rings

- When more than one substituent attached to a 6-membered ring, the position of the substituents need to be analyzed in order to determine the most stable conformer.



methyl groups on same face of ring (top)

methyl groups occupy positions closest to top face

top face

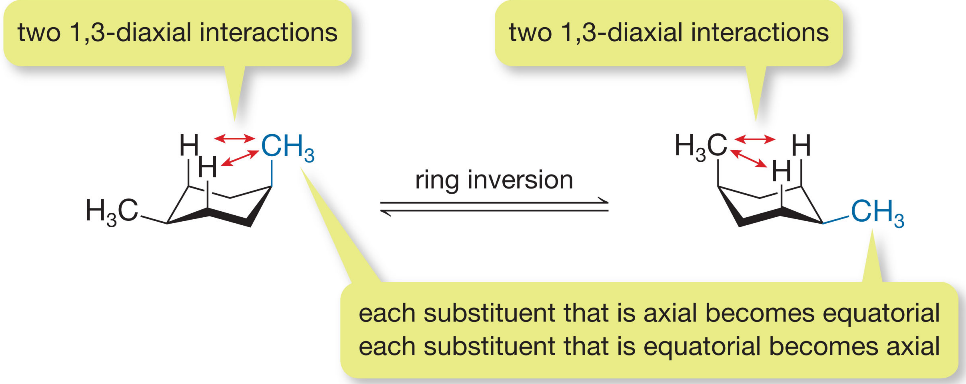
bottom face

At each ring position, one substituent is closer to the top and the other is closer to the bottom. Adding hydrogens can help to keep track.

top face

bottom face

Once correct positions for groups have been established, the molecule can be re-drawn without hydrogens.



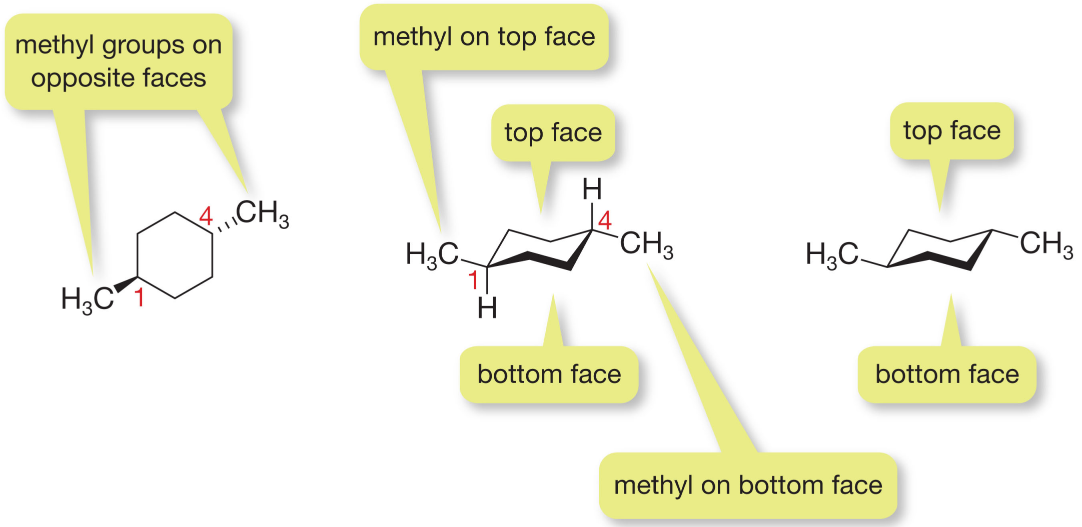
two 1,3-diaxial interactions

two 1,3-diaxial interactions

each substituent that is axial becomes equatorial
each substituent that is equatorial becomes axial

Disubstituted 6-Membered Rings

- Keep in mind that dashes/wedges are completely independent of whether the group is axial or equatorial.



methyl groups on opposite faces

methyl on top face

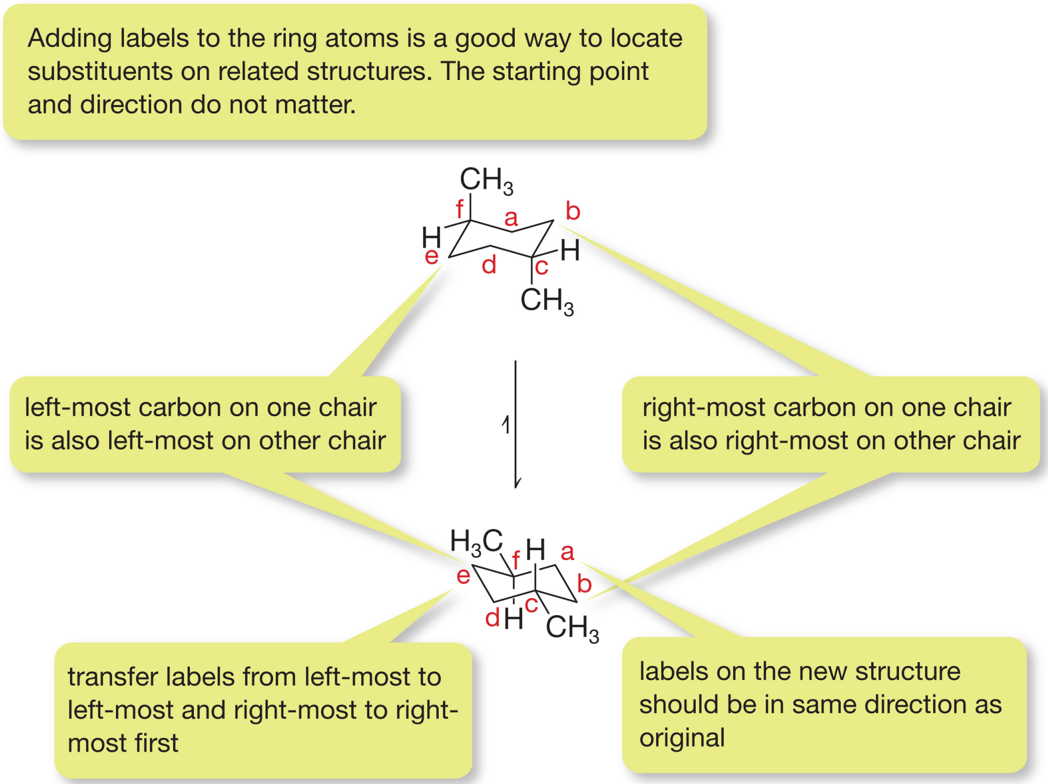
top face

bottom face

methyl on bottom face

top face

bottom face



Adding labels to the ring atoms is a good way to locate substituents on related structures. The starting point and direction do not matter.

left-most carbon on one chair is also left-most on other chair

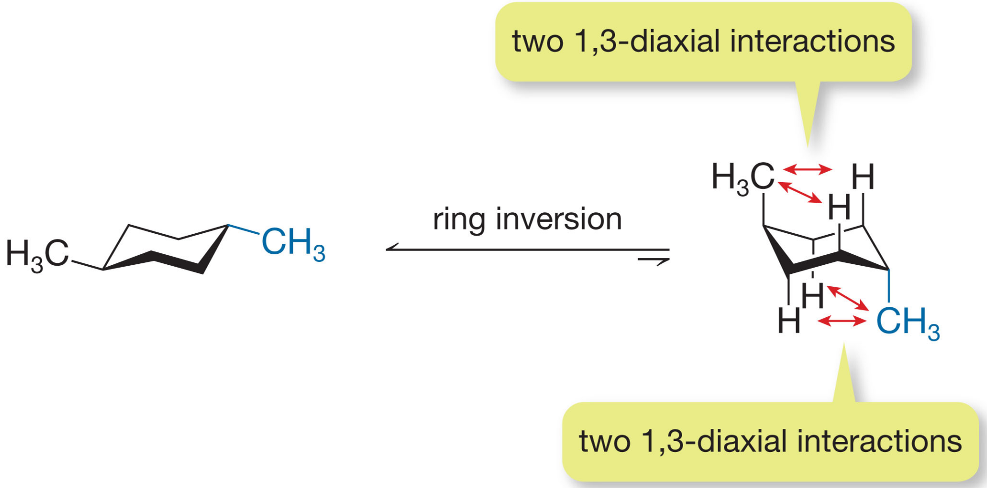
right-most carbon on one chair is also right-most on other chair

transfer labels from left-most to left-most and right-most to right-most first

labels on the new structure should be in same direction as original

Disubstituted 6-Membered Rings

- In general, the more stable conformer is the one with more substituents in the equatorial position.



two 1,3-diaxial interactions

two 1,3-diaxial interactions