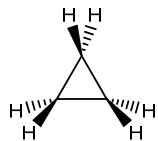
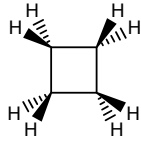


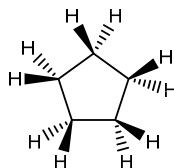
# Cycloalkanes



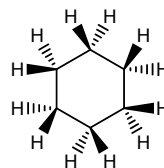
cyclopropane



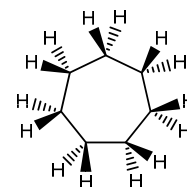
cyclobutane



cyclopentane



cyclohexane



cycloheptane



Although  $sp^3$  carbons would normally have bond angles of  $109.5^\circ$ , these bond-angle structures show C-C-C angles of

$60^\circ$   
(triangle)

$90^\circ$   
(square)

$108^\circ$   
(pentagon)

$120^\circ$   
(hexagon)

$129^\circ$   
(heptagon)

So what are they really,  
and what is the cost of them not being  $109.5^\circ$ ?

## Heats of Combustion for Cycloalkanes

*Some cycloalkanes have more energy stored in them (and are less stable) than others.*

For combustion,  $\text{C}_n\text{H}_{2n} + 3/2 n\text{O}_2 \longrightarrow n\text{CO}_2 + n\text{H}_2\text{O} \quad \Delta H_{\text{combustion}} < 0.$



$\Delta H_{\text{combustion}}$	-499 kcal/mol	-656 kcal/mol	-793 kcal/mol	-944 kcal/mol	-1108 kcal/mol
$\Delta H_{\text{combustion}}$ per $-\text{CH}_2-$	-167 kcal/mol	-164 kcal/mol	-159 kcal/mol	-157 kcal/mol	-158 kcal/mol
"ring strain" per $-\text{CH}_2-$	9.2 kcal/mol	6.6 kcal/mol	1.3 kcal/mol	0 kcal/mol	0.9 kcal/mol
total ring strain	27.6 kcal/mol	26.3 kcal/mol	6.5 kcal/mol	0 kcal/mol	6.4 kcal/mol

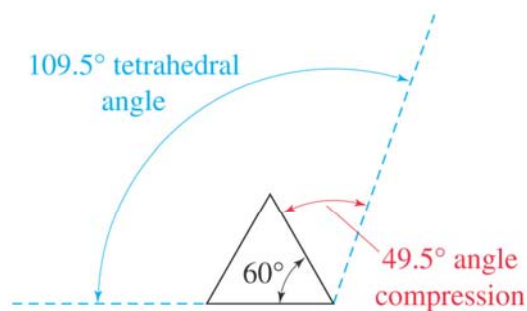
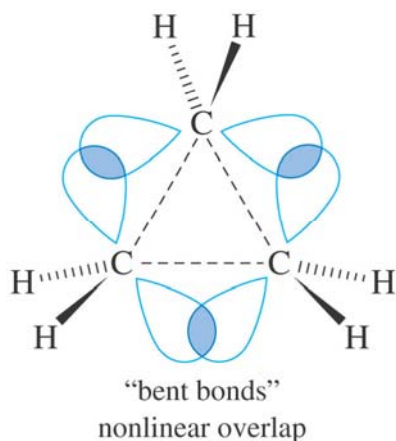
# Why Are Smaller Cycloalkanes So Unstable?

## 1. Angle strain.

Corresponds to difference between actual bond angle and  $sp^3$

$$\theta = 109.5^\circ.$$

For cyclopropane,



Poor orbital overlap leads to weaker bonds.

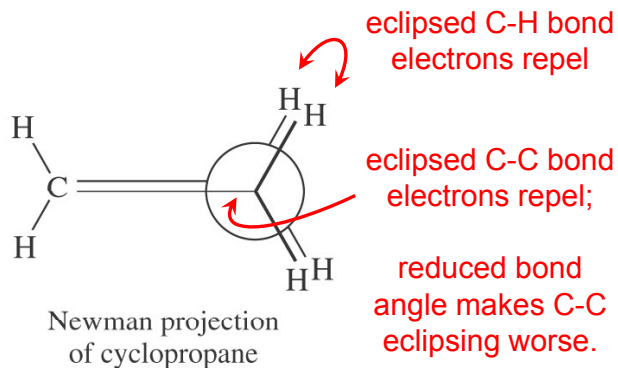
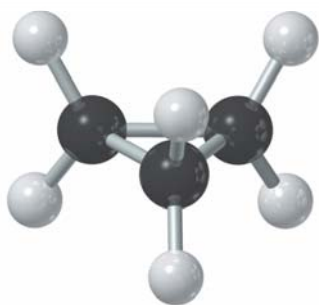
# Why Are Smaller Cycloalkanes So Unstable?

## 1. Angle strain.

$sp^3$  carbons want to have  $\theta = 109.5^\circ$ , but can't.

## 2. Torsional strain. (Eclipsing interactions.)

For cyclopropane,



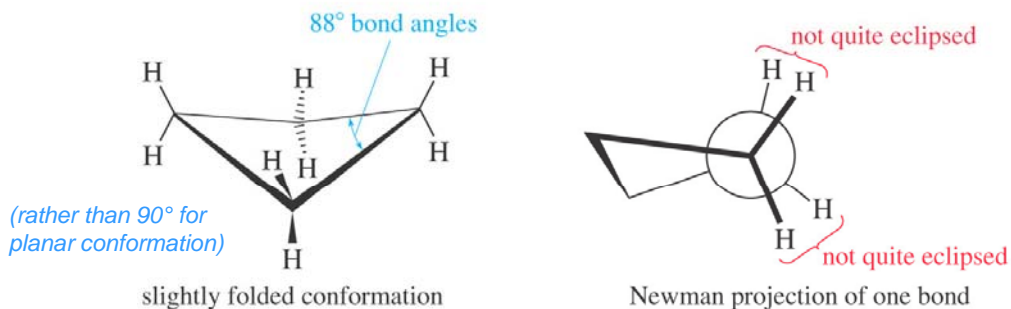
# Why Are Smaller Cycloalkanes So Unstable?

1. Angle strain.

$sp^3$  carbons want to have  $\theta = 109.5^\circ$ , but can't.

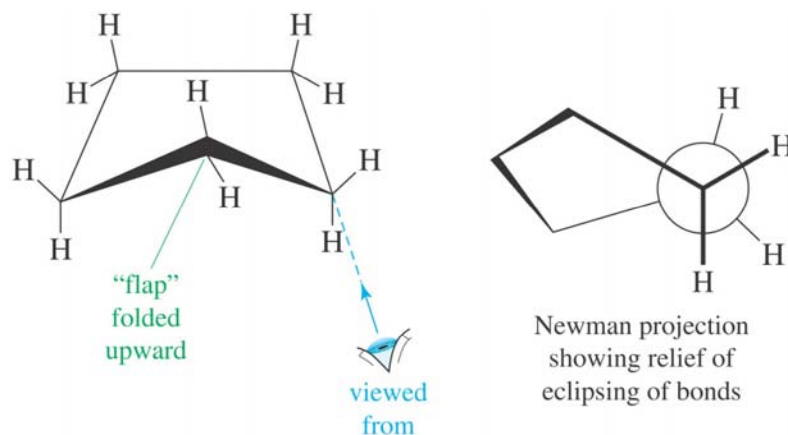
2. Torsional strain. (Eclipsing interactions.)

For **cyclobutane**, molecule folds/twists a bit to reduce eclipsing.



Molecule takes on additional angle strain to reduce torsional strain.

## Conformation of Cyclopentane



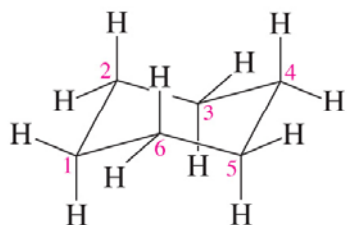
Cyclopentane assumes an "envelope" conformation.

A little bit of angle strain (in flap),

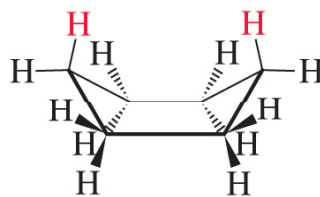
A little bit of torsional strain (in back).

# Conformations of Cyclohexane

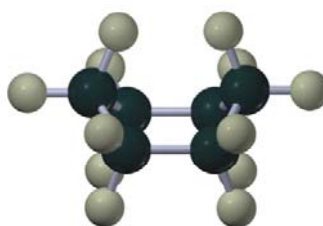
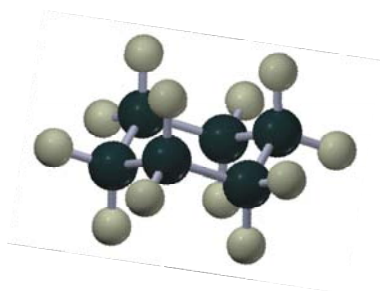
Preferred  $109.5^\circ$  bond angle is *smaller* than hexagon angle ( $120^\circ$ ).  
So, molecule buckles to accommodate.



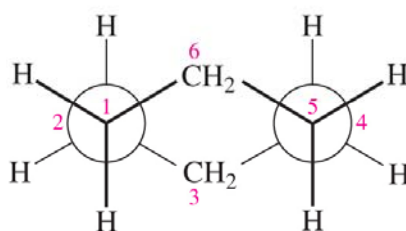
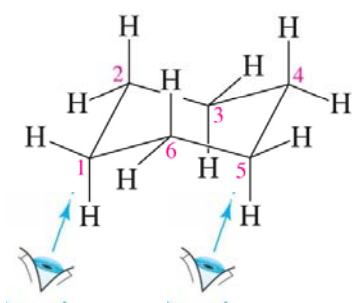
“chair” cyclohexane



“boat” cyclohexane



## “Chair” Cyclohexane



Newman projection



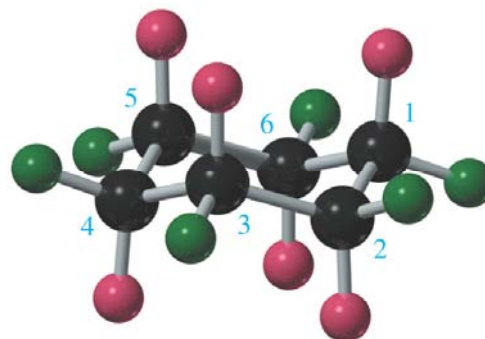
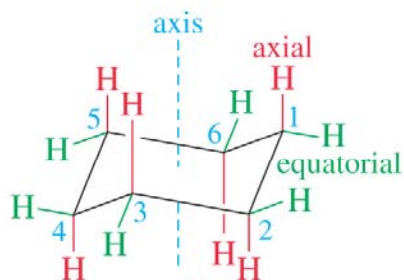
*all carbons tetrahedral!*

1. No angle strain.  
(All angles are  $109.5^\circ$ .)
2. No eclipsing interactions.

So, chair is the most stable conformation of cyclohexane.



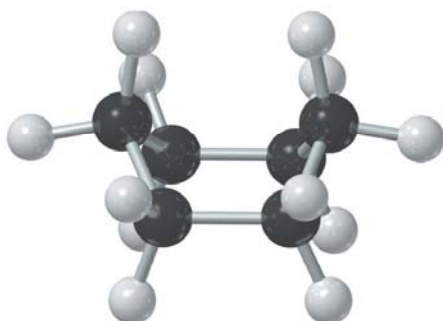
# Axial & Equatorial Hydrogens on Chair Cyclohexane



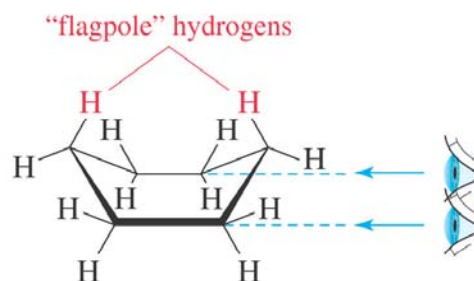
Drawing chair cyclohexane:

1. Chair is made of three pairs of parallel lines.
2. Each carbon has one equatorial and one axial hydrogen.
3. Equatorial H's are parallel to chair bonds.
4. Axial H's alternate up and down, same as carbons.

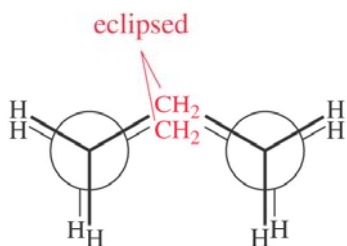
## “Boat” Cyclohexane



boat conformation



symmetrical boat



Newman projection

Boat conformers exhibit both steric interactions (from flagpole H's) and eclipsing interactions.

Boat is less stable than chair.

# Interconversion of Cyclohexane Conformations

