

Organic Chemistry 1

Lecture 6

Instructor: Prof. Duncan Wardrop

Time/Day: T & R, 12:30-1:45 p.m.

January 28, 2010

Self Test Question

Which form of strain occurs in cycloalkanes when bond angles are distorted from their natural preference?

steric strain
groups close in space

eclipsed bonds
angle strain

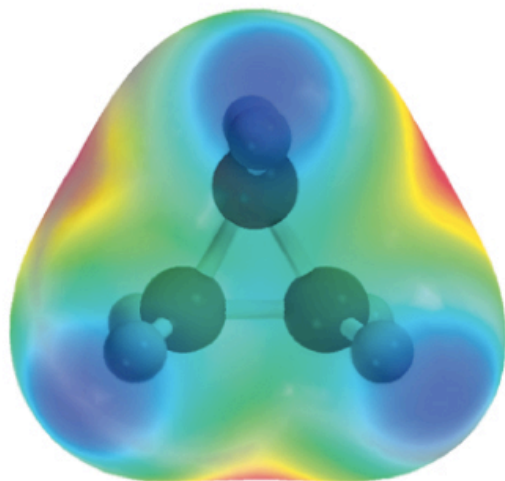
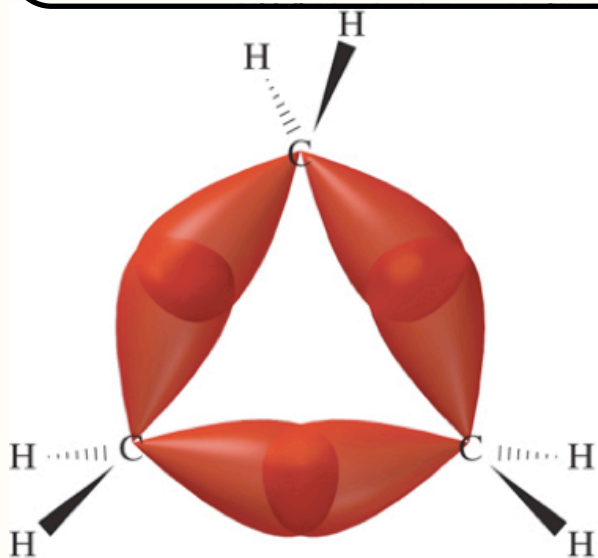
- A. van der Waals strain
- B. steric strain
- C. compression strain
- D. torsional strain
- E. Baeyer strain

The Answer is E. Factors A, B, D and E all potentially contribute to the strain energy in cyclohexanes, but that arising from bond angle deformations is termed Baeyer strain.

Summary of Strain Energy

strain energy: additional potential energy associated with unfavorable interactions in different conformations

1. Angle strain (Baeyer strain): increase in energy associated with deviation of natural bond angles (i.e. predicted by VSEPR).

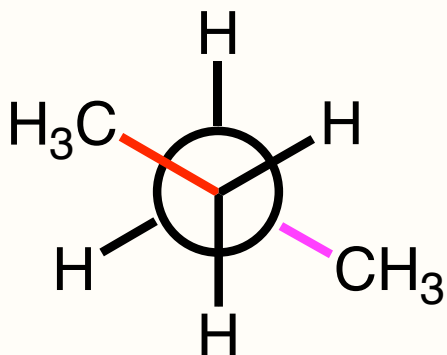


natural bond angle for sp³ carbon = 109.5°
actual bond angle in cyclopropane = 60°

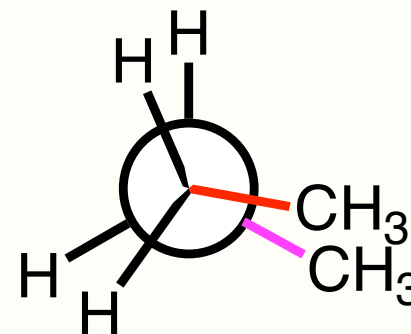
Summary of Strain Energy

strain energy: additional potential energy associated with unfavorable interactions in different conformations

2. Torsional strain: increase in energy associated with eclipsed electron pairs (typically in covalent bonds).



- staggered conformation
- all groups gauche ($\theta = 60^\circ$) or anti, ($\theta = 180^\circ$)
- lowest energy (most stable)

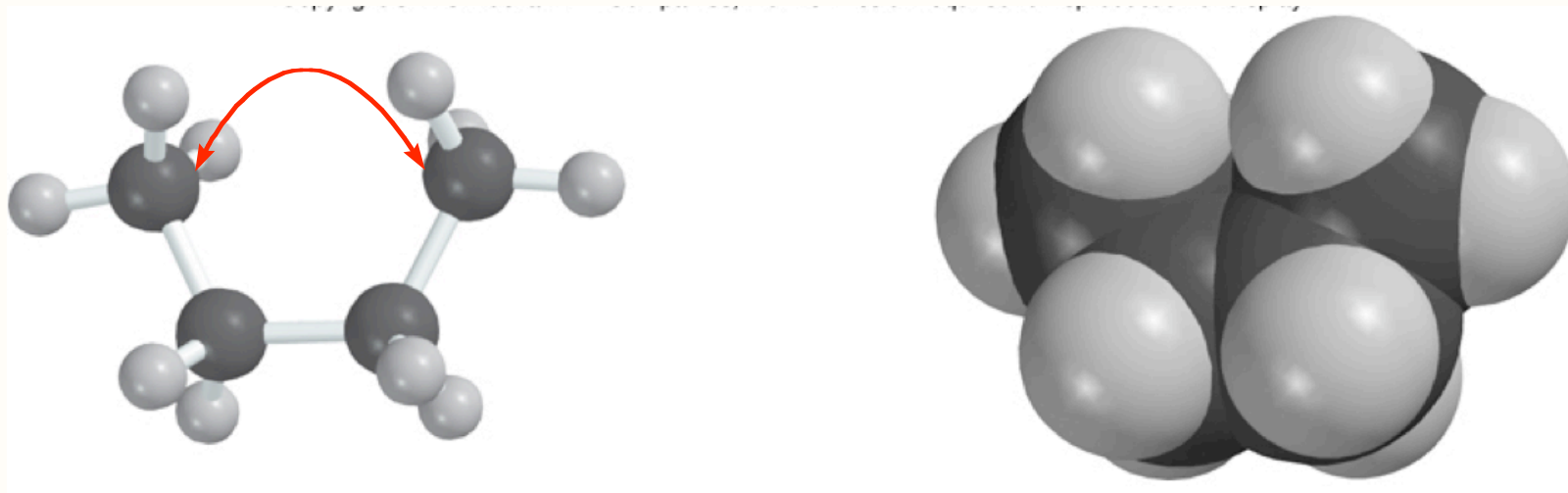


- eclipsed conformation
- all groups eclipsed ($\theta = 0^\circ$)
- highest energy (least stable)

Summary of Strain Energy

strain energy: additional potential energy associated with unfavorable interactions in different conformations

3. Steric strain (van der Waals strain): increase in energy associated adjacent groups being close together (i.e. overlapping van der Waals radii); most pronounced for large groups (i.e. two eclipsed -CH_3)



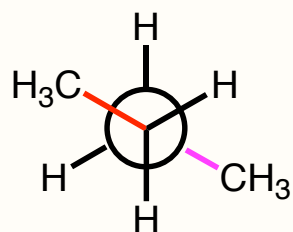
- no steric strain between adjacent hydrogen atoms
- slight steric strain between adjacent H & CH_3 groups (~ 1.4 kcal/mol)
- large steric strain between adjacent, eclipsed CH_3 groups (~ 3.1 kcal/mol)

Conformational Analysis: Combined Energy "Costs" in Alkanes

total energy cost = sum of steric strain and torsional strain

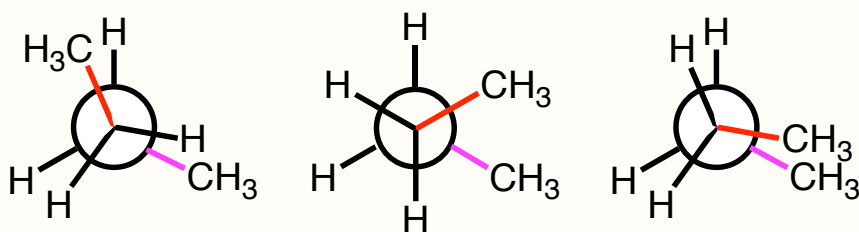
$$1 \text{ kcal} = 4.1868 \text{ kJ}$$

most stable
(lowest NRG)



anti

least stable
(highest NRG)



syn

individual
components of
total energy
cost for each
conformation

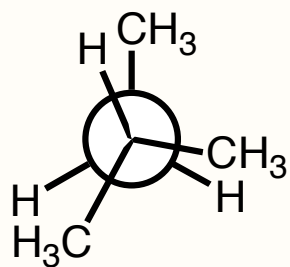
1(1.0) = 1.0	1(0.9) = 0.9	2(1.0) = 2.0
2(1.4) = 2.8		1(3.1) = 3.1
<hr/>	<hr/>	<hr/>
tot = 3.8 kcal/mol	tot = 0.9 kcal/mol	tot = 5.1 kcal/mol

Adjacent Groups	Relationship	Strain energy
H - H	gauche	0
H - CH ₃	gauche	0
CH ₃ - CH ₃	gauche	0.9 kcal/mol
H - H	eclipsed	1.0 kcal/mol
H - CH ₃	eclipsed	1.4 kcal/mol
CH ₃ - CH ₃	eclipsed	3.1 kcal/mol

Self Test Question

Rank the following conformations of isobutane in order of *increasing* energy?

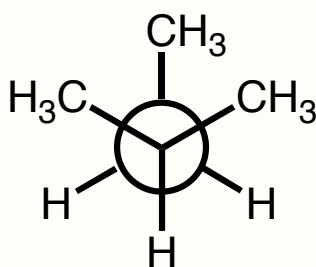
a.



$$\underline{3(1.4) = 3.1}$$

tot = 3.1
kcal/mol

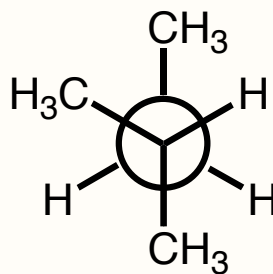
b.



$$\underline{2(0.9) = 1.8}$$

tot = 1.8
kcal/mol

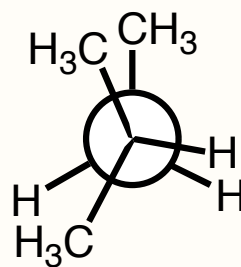
c.



$$\underline{1(0.9) = 0.9}$$

tot = 0.9
kcal/mol

d.



$$1(3.1) = 3.1$$

$$\underline{2(1.4) = 2.8}$$

tot = 5.9
kcal/mol

A. a, b, c, d

B. b, c, a, d

C. c, b, a, d

D. d, a, b, c

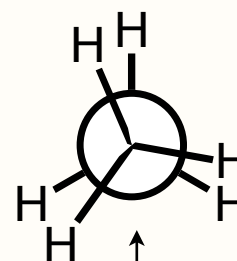
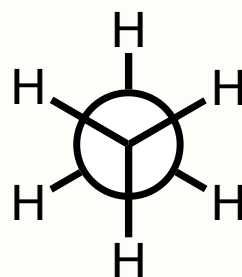
E. d, b, a, c

The Answer is C. Employing the table on Slide 6, determine the number of syn and significant gauche interactions (i.e. ignore H-H and H-Me gauche interactions, but not Me-Me ones) and sum the associated strain energies. You will not be expected to remember these specific numbers, but will be expected to know how to employ them to determine strain energy.

Self Test Question

Using the table below, estimate the difference in energy (ΔE) between the eclipsed and staggered conformations of ethane?

Adjacent Groups	Relationship	Strain Energy
H - H	gauche	0
H - CH ₃	gauche	0
CH ₃ - CH ₃	gauche	0.9 kcal/mol
H - H	eclipsed	1.0 kcal/mol
H - CH ₃	eclipsed	1.4 kcal/mol
CH ₃ - CH ₃	eclipsed	3.1 kcal/mol



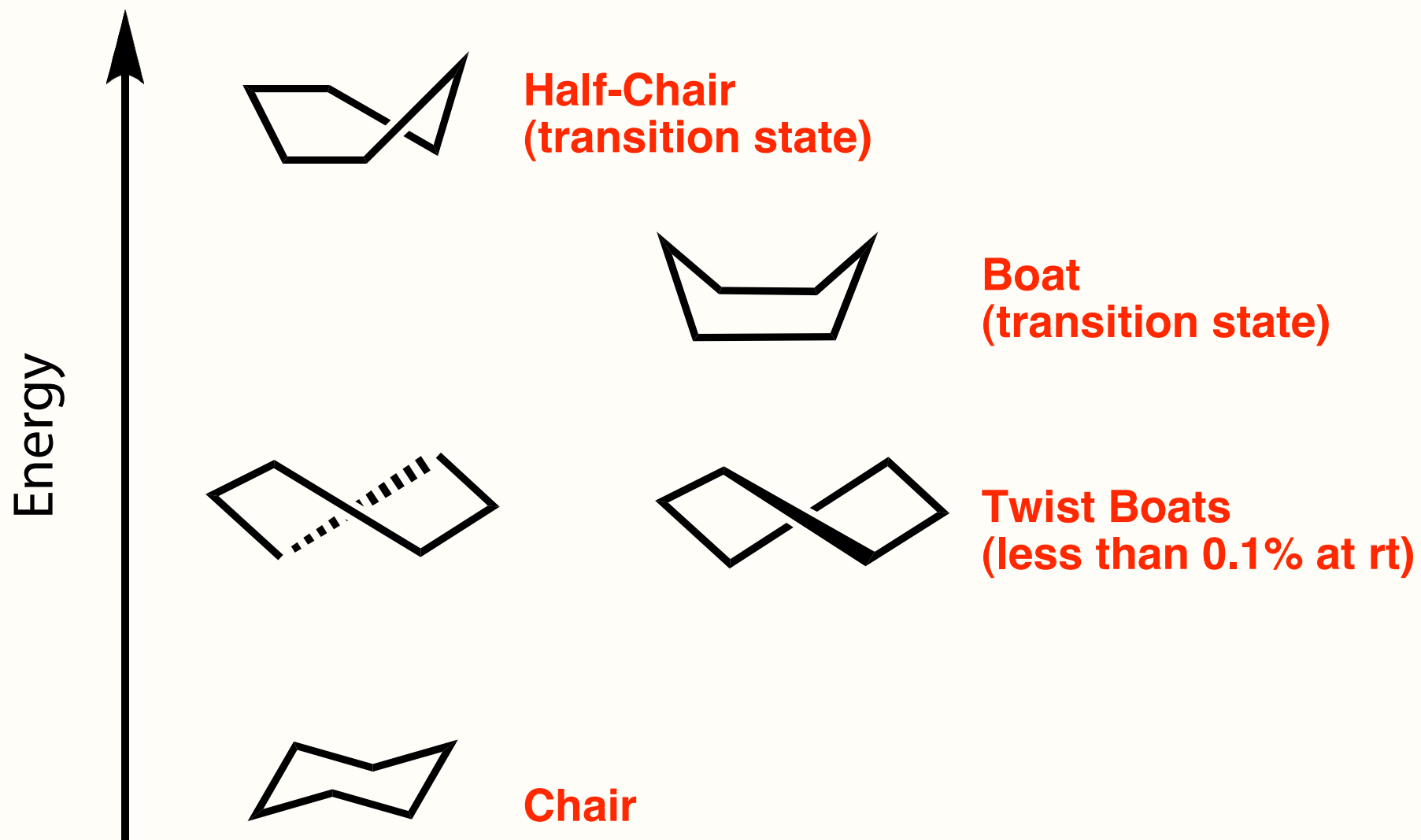
3 x 1.0 =
3.0 kcal/mol
higher in energy

- A. 6.9 kcal/mol
- B. 3.0 kcal/mol**
- C. 2.4 kcal/mol
- D. 1.0 kcal/mol
- E. no difference

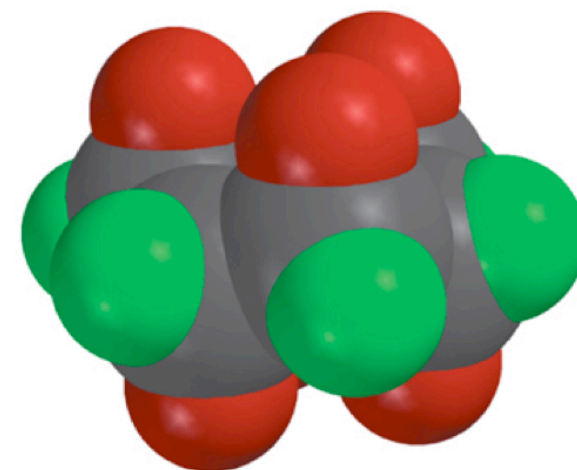
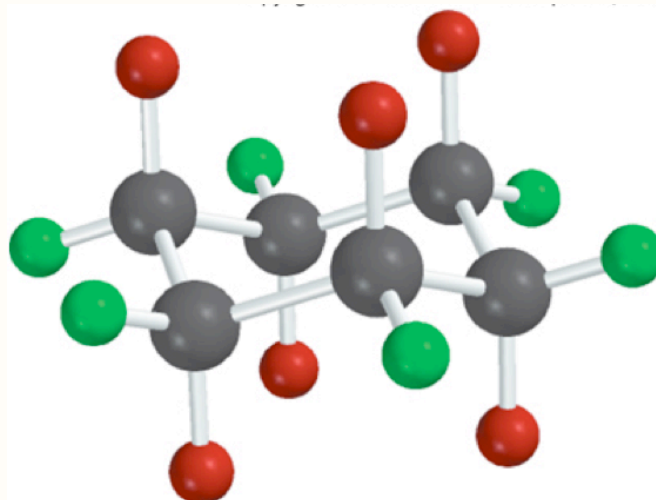
Conformations of Cyclohexane

Sections 3.7-3.9

Conformers of Cyclohexane

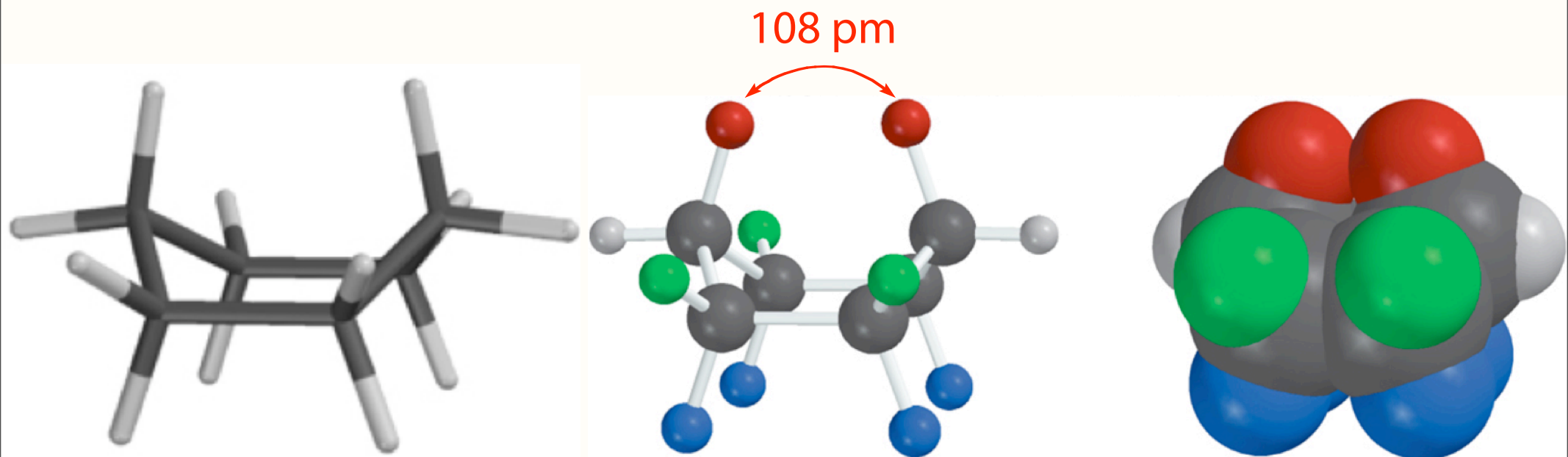


"Chair" Conformation of Cyclohexane



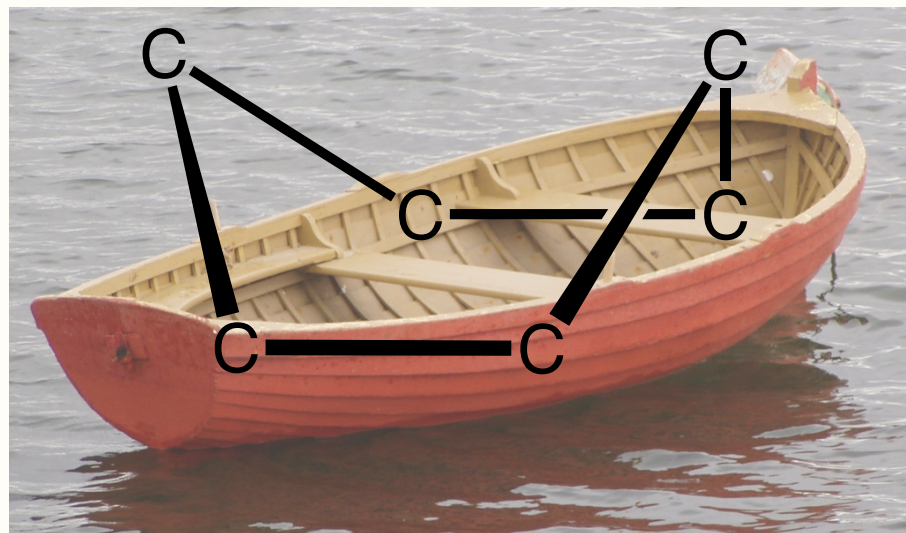
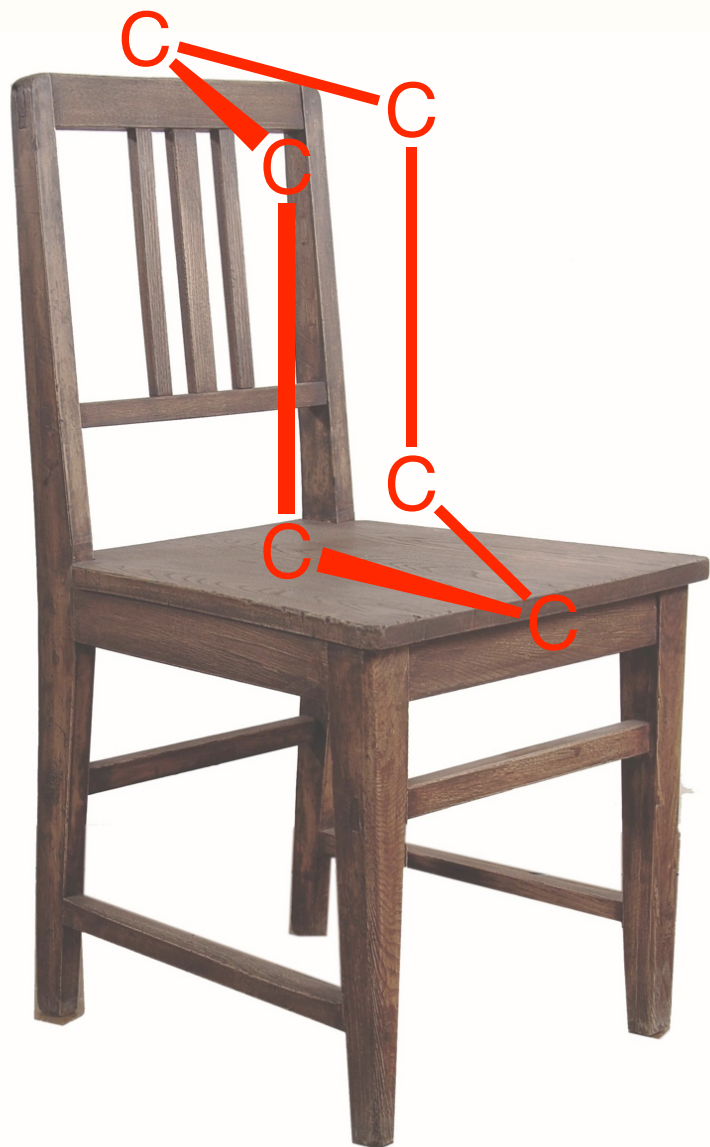
- most stable (lowest energy conformation)
- all vicinal C-C & C-H bonds are *gauche* (dihedral angle = 60°)
- bond angles at carbon are close to 109.5°

“Boat” Conformation of Cyclohexane



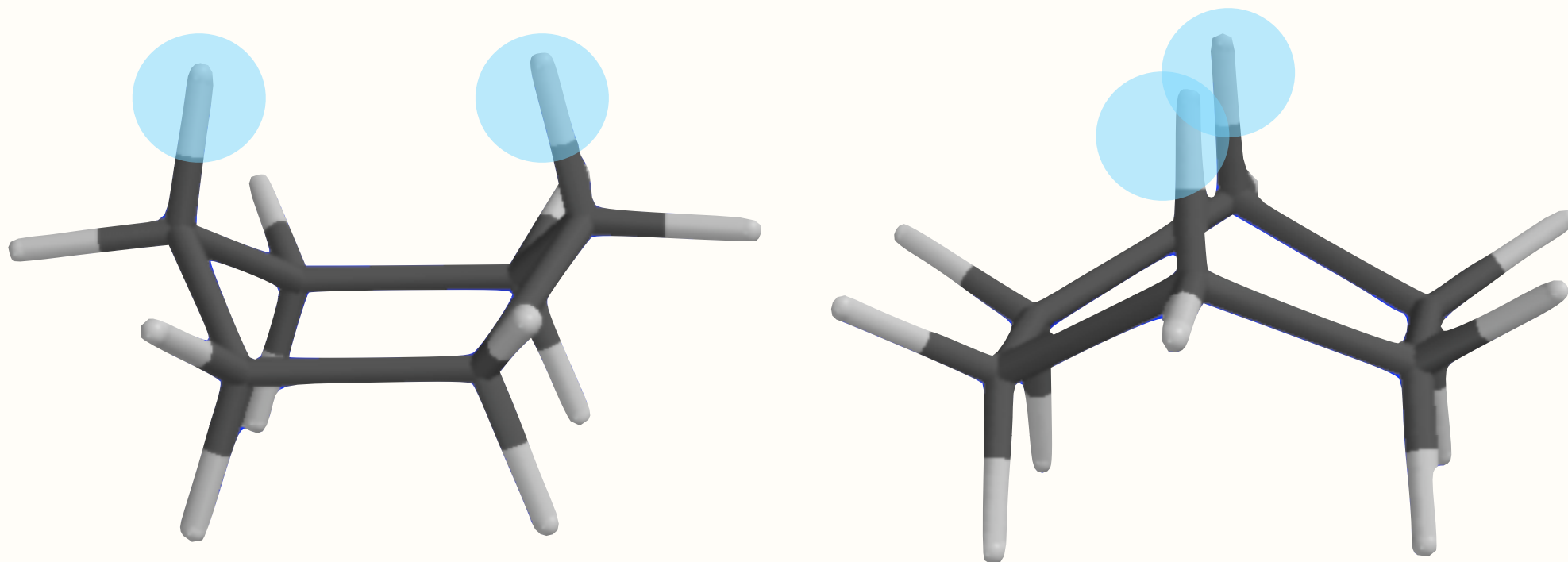
- least stable conformation
- all bond angles close to tetrahedral (109.5°)
- steric strain: repulsion between “flagpole” hydrogens
- torsional strain: eclipsed bonds

Why "Chair" and "Boat"?



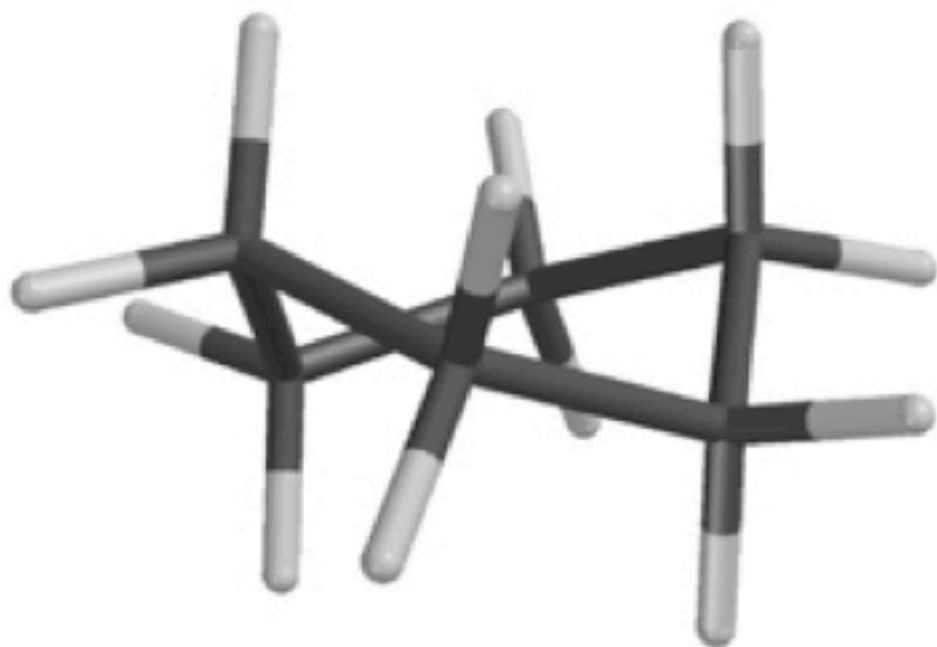
Boat Conformer is Less Stable Than Chair

Another View:

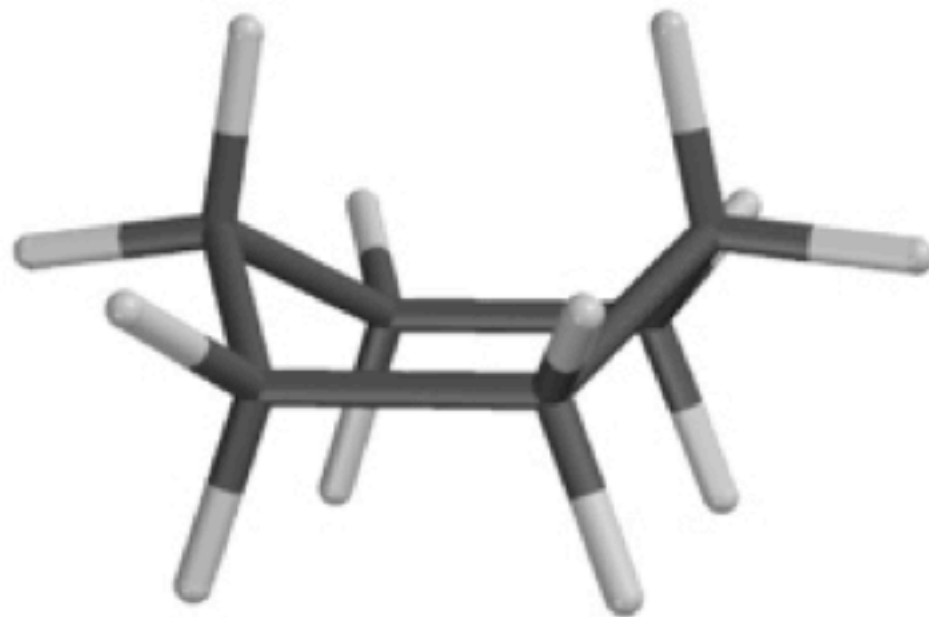


- eclipsed bonds produce torsional strain (raise energy)
- Steric strain (van der Waals strain) of flagpole hydrogens

Twist Boat is Slightly More Stable Than Boat



Skew boat

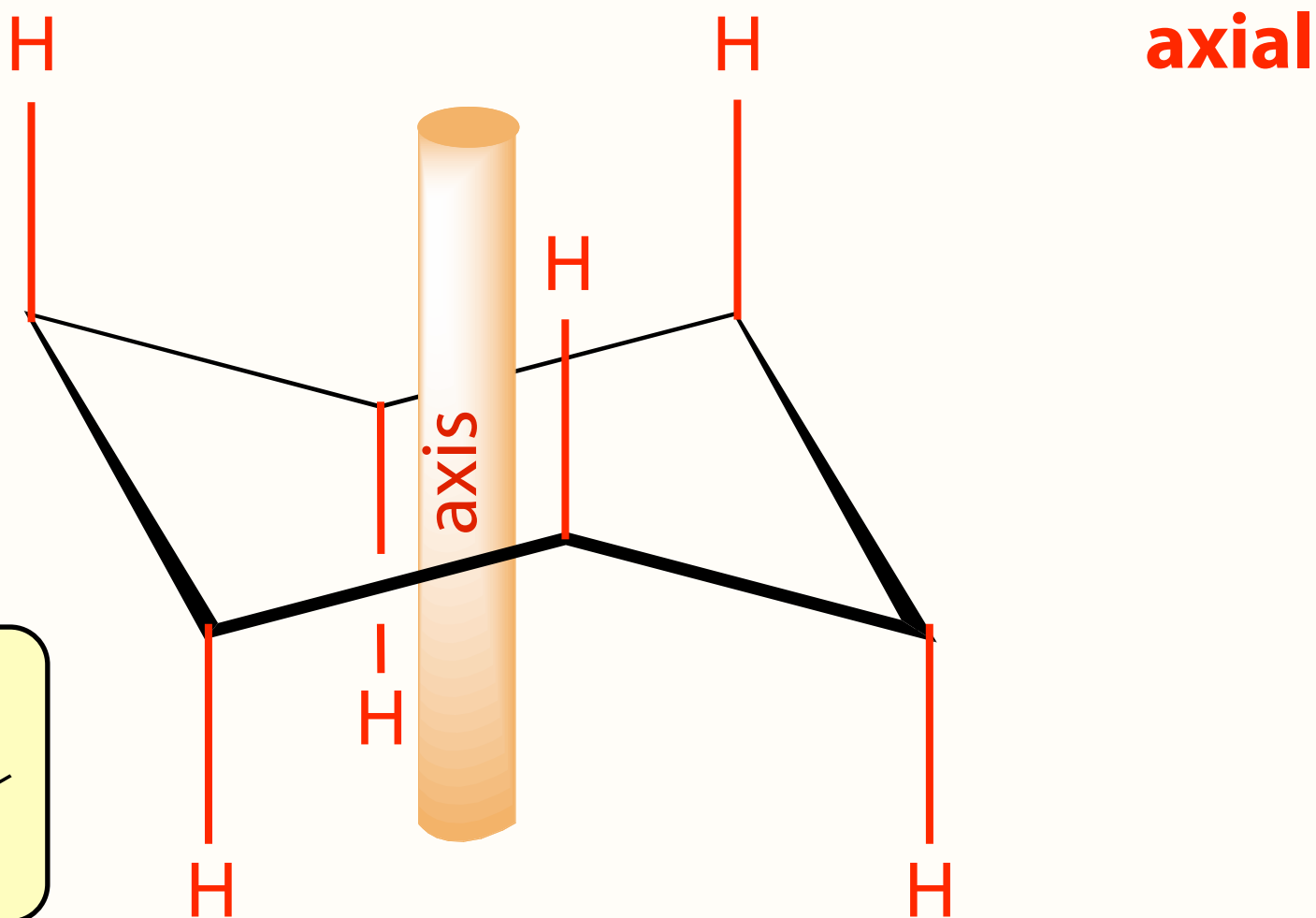


Boat

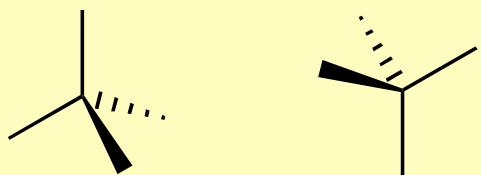
- less steric strain (van der Waals strain)
- less torsional strain; fewer eclipsed bonds

Axial & Equatorial Bonds in Cyclohexane

12 C-H bonds can be divided into 2 sets:

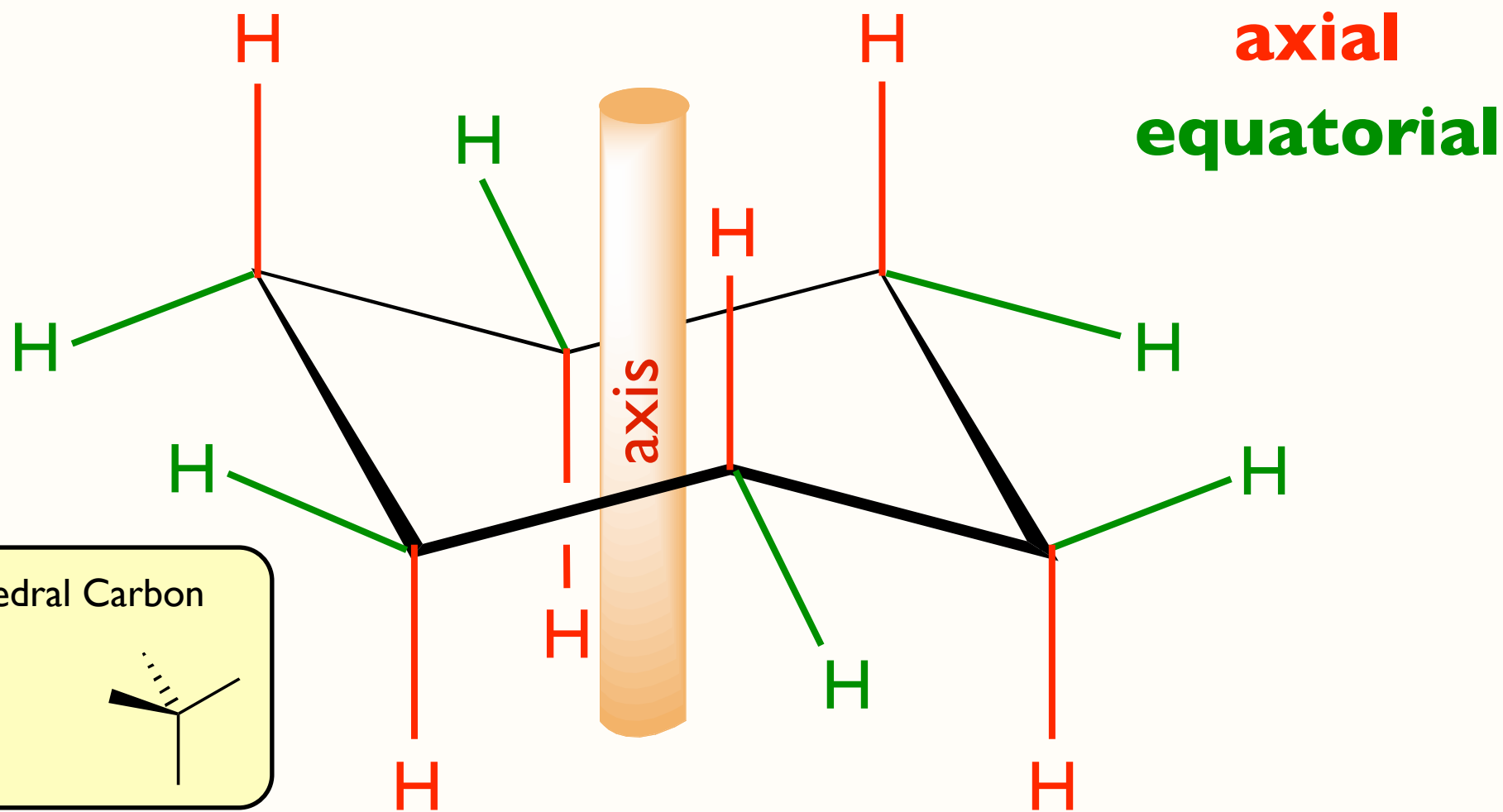


Tetrahedral Carbon

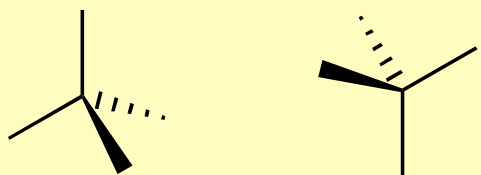


Axial & Equatorial Bonds in Cyclohexane

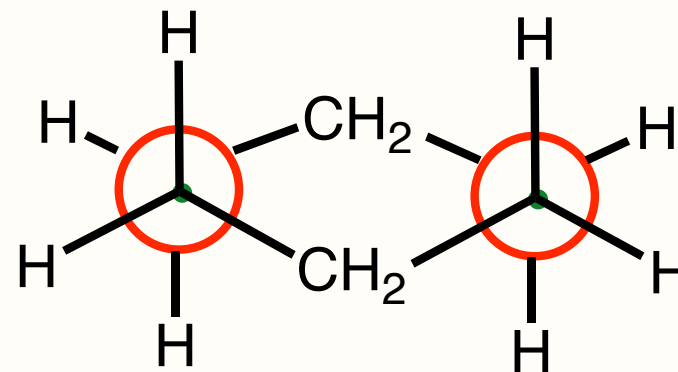
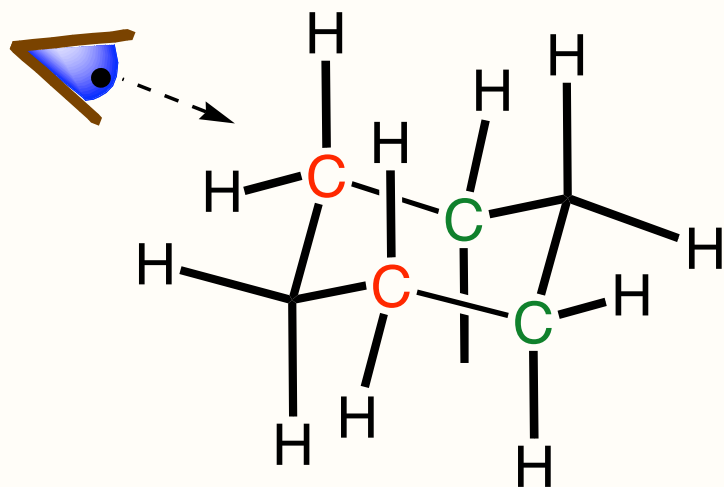
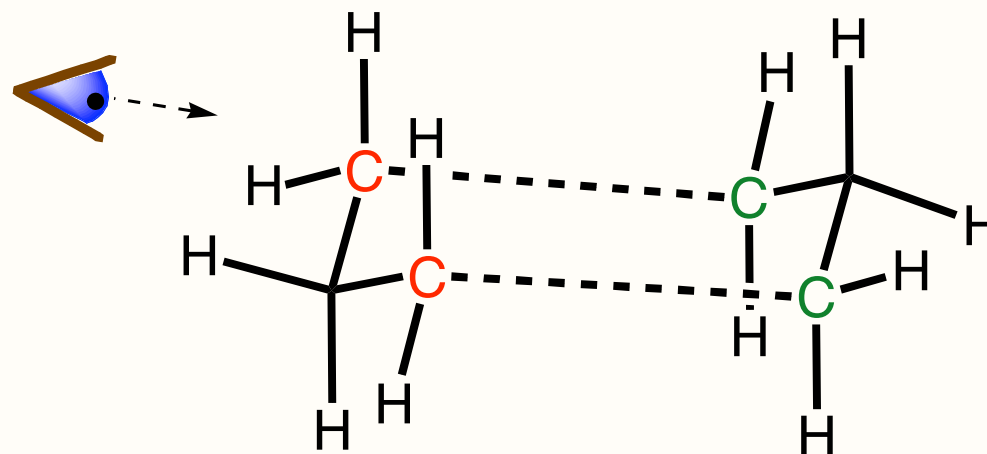
12 C-H bonds can be divided into 2 sets:



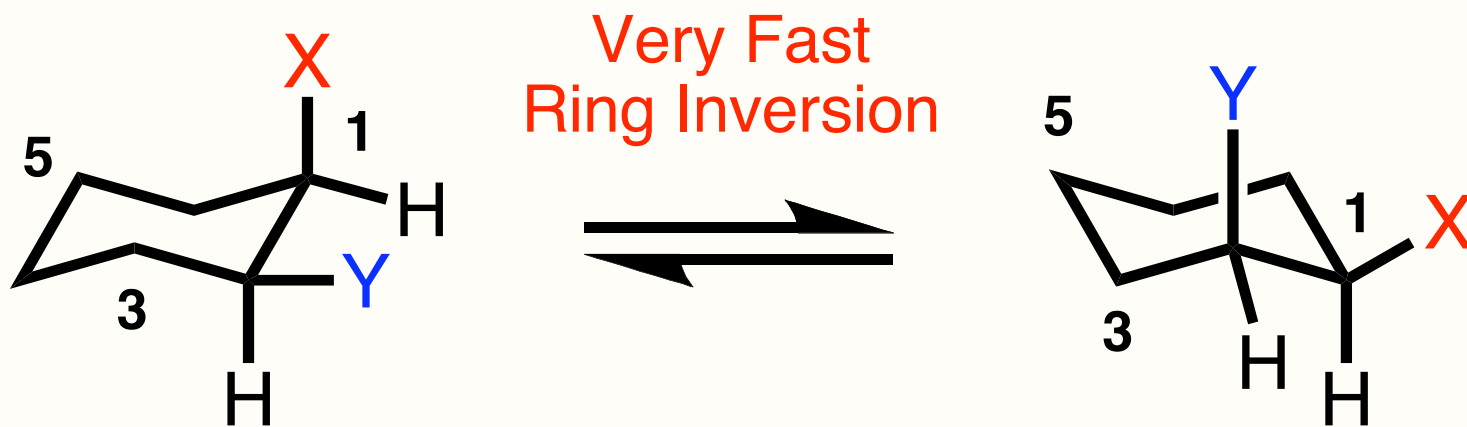
Tetrahedral Carbon



Sawhorse and Newman Projection of Cyclohexane Chair



Conformational Inversion is Rapid

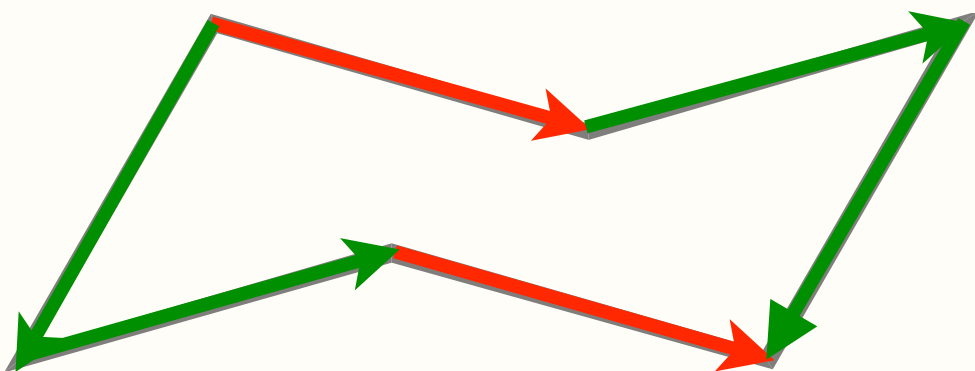


X axial; Y equatorial

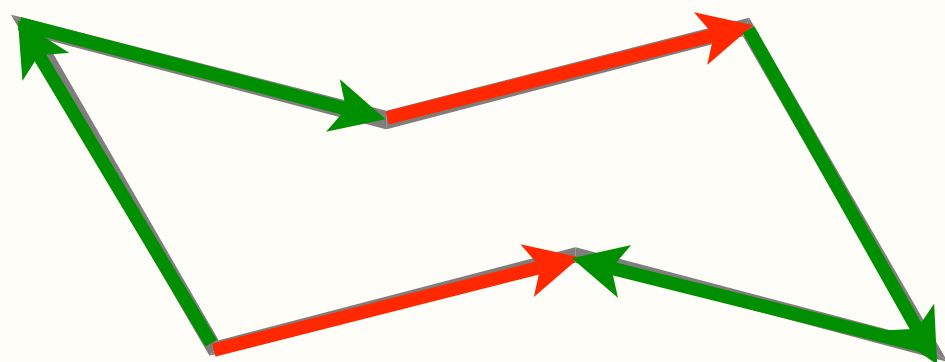
X equatorial; Y axial

- ring flipping = conformational inversion of cyclohexane
- chair-to-chair: all axial become equatorial and vice versa
- both chairs have equal energy ($K_{eq} = 1$)
- activation energy = 10.8 kcal/mol (45 kJ/mol)

How to Cyclohexane Skeleton...

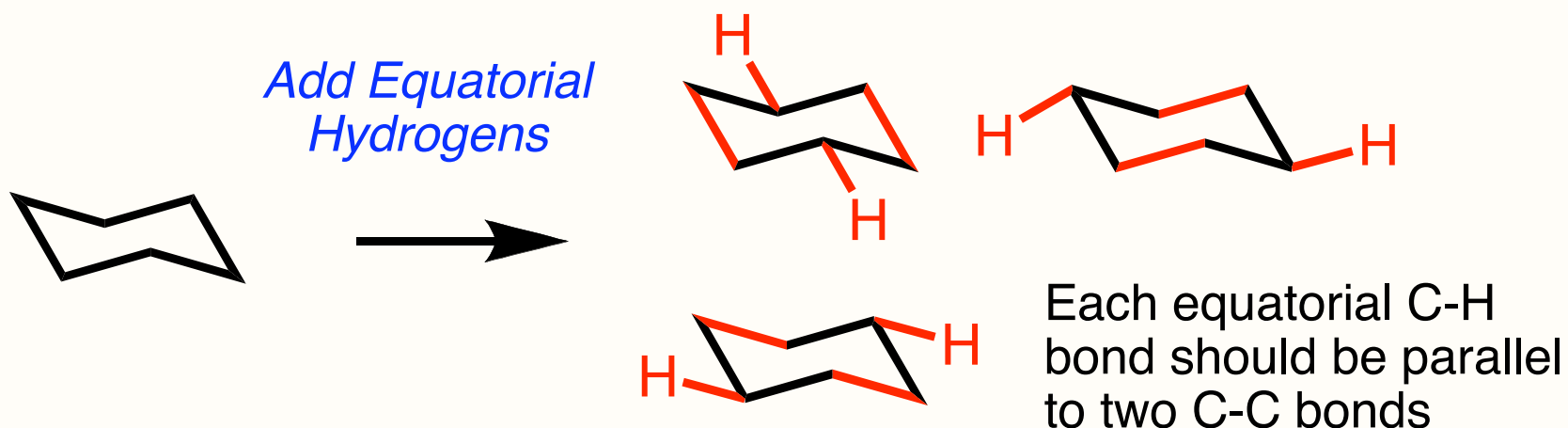
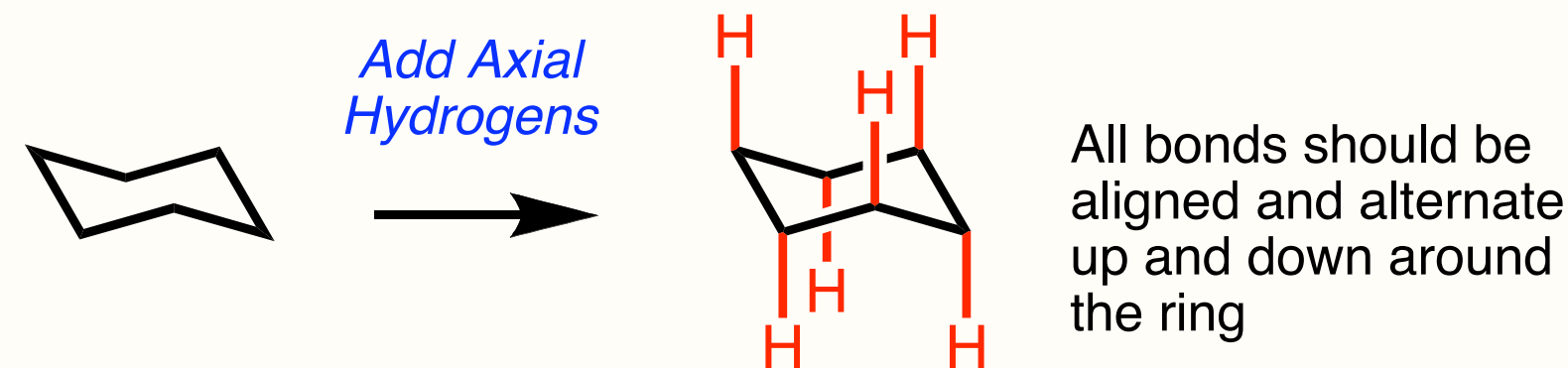


1. Draw two parallel lines that are offset and at approximately 45° from any axis.

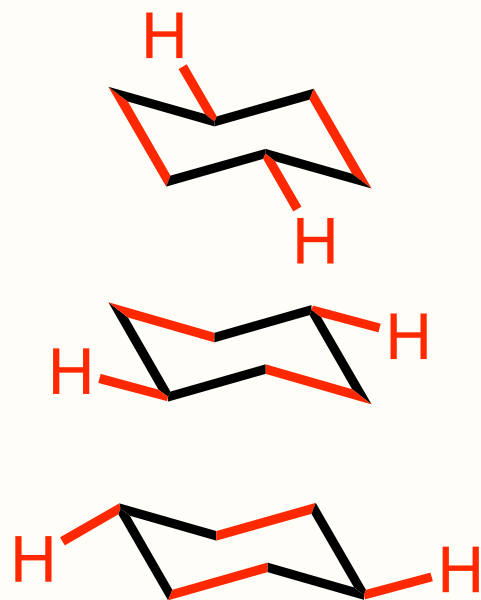


2. Connect the offset ends of the lines with the equilateral sides of an isosceles triangle.

Now Add the Hydrogen Atoms...

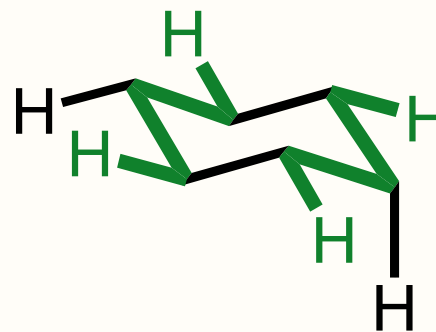


Finally, Put It All Together....

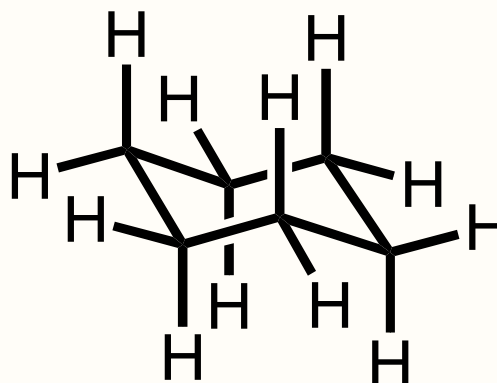


*Add all
6 C-H Bonds*

Notice the "W" shape here.....

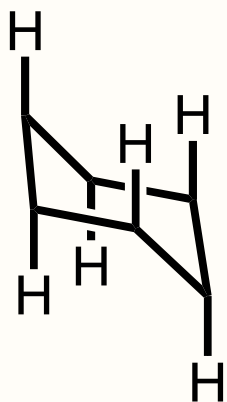


.....and the "M" shape here

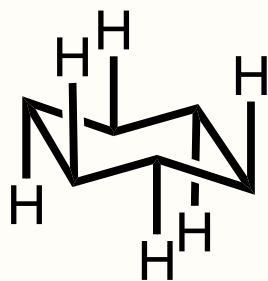


Common Mistakes

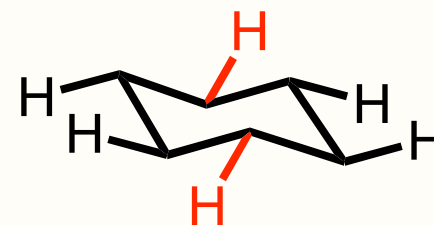
How not to draw cyclohexanes.....



the chair has been drawn with the middle bonds horizontal, so the upper points of the chair are not level. Axial bonds cannot be drawn vertically

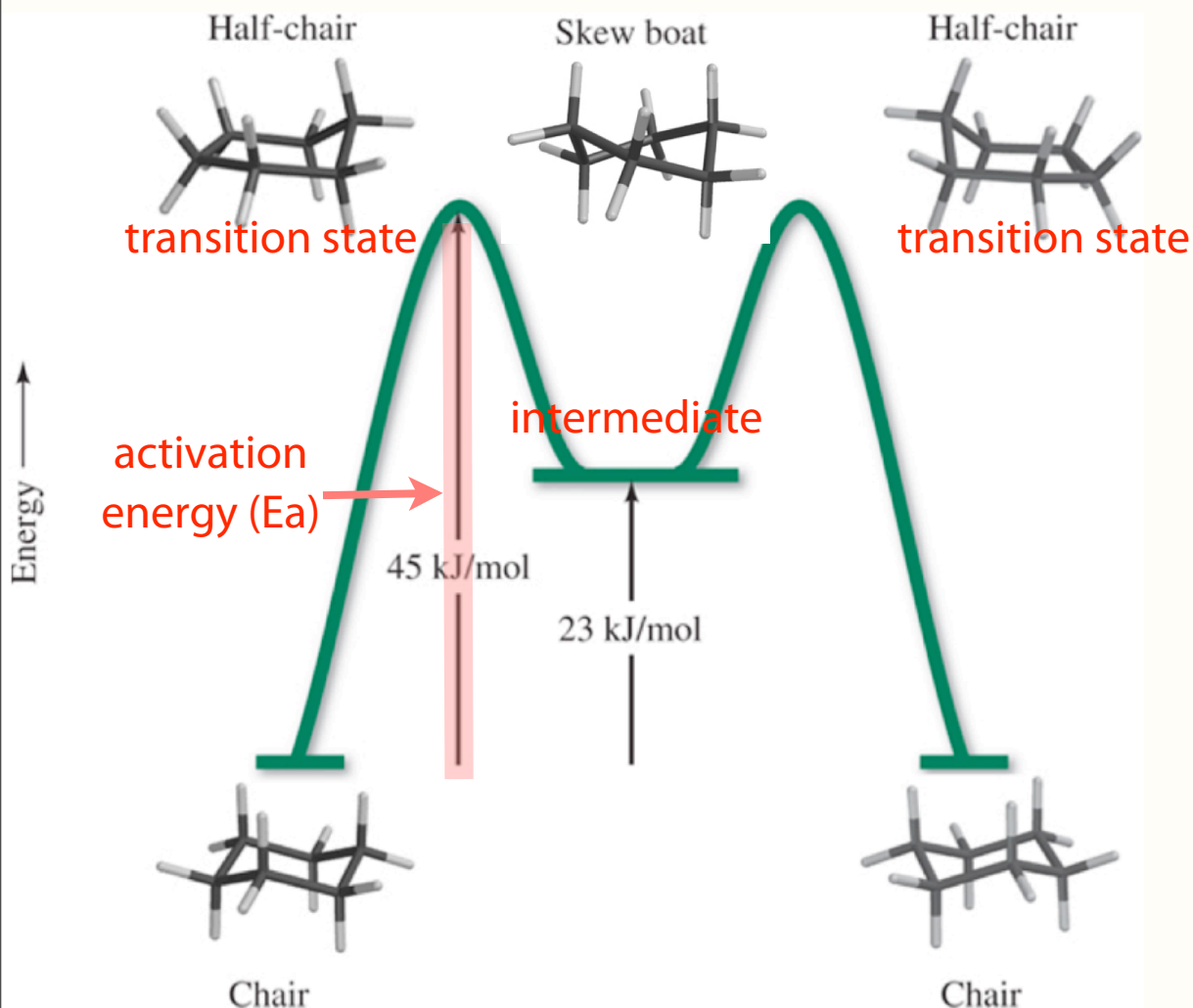


the axial hydrogens have been drawn alternating up and down on the wrong carbons - none of the C-centers are tetrahedral!



the red hydrogens have been drawn at the wrong angles - notice the lack of "W" and "M"

Mechanism of Ring-Flipping (No Boat Required)



Intermediate

local minimum energy species on the potential energy profile

TS (transition state)

local maximum energy species on the potential energy profile

H_{act} (activation energy)

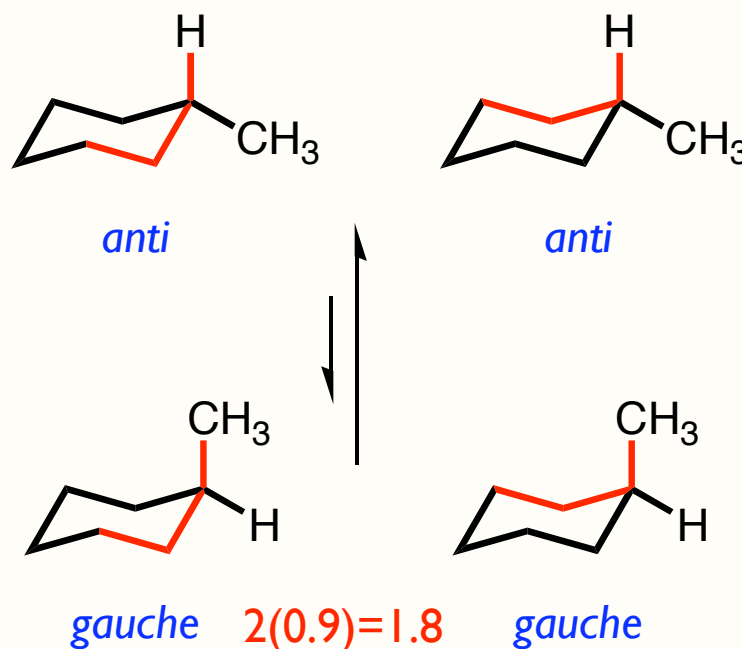
energy required to reach the transition state

Self Test Question

Using the table below, estimate the difference in energy (ΔE) between the two conformations of methyl-cyclohexane?

Use a model to determine the # of gauche & eclipsed relationships

Adjacent Groups	Relationship	Strain Energy
H - H	gauche	0
H - CH ₃	gauche	0
CH ₃ - CH ₃	gauche	0.9 kcal/mol
H - H	eclipsed	1.0 kcal/mol
H - CH ₃	eclipsed	1.4 kcal/mol
CH ₃ - CH ₃	eclipsed	3.1 kcal/mol



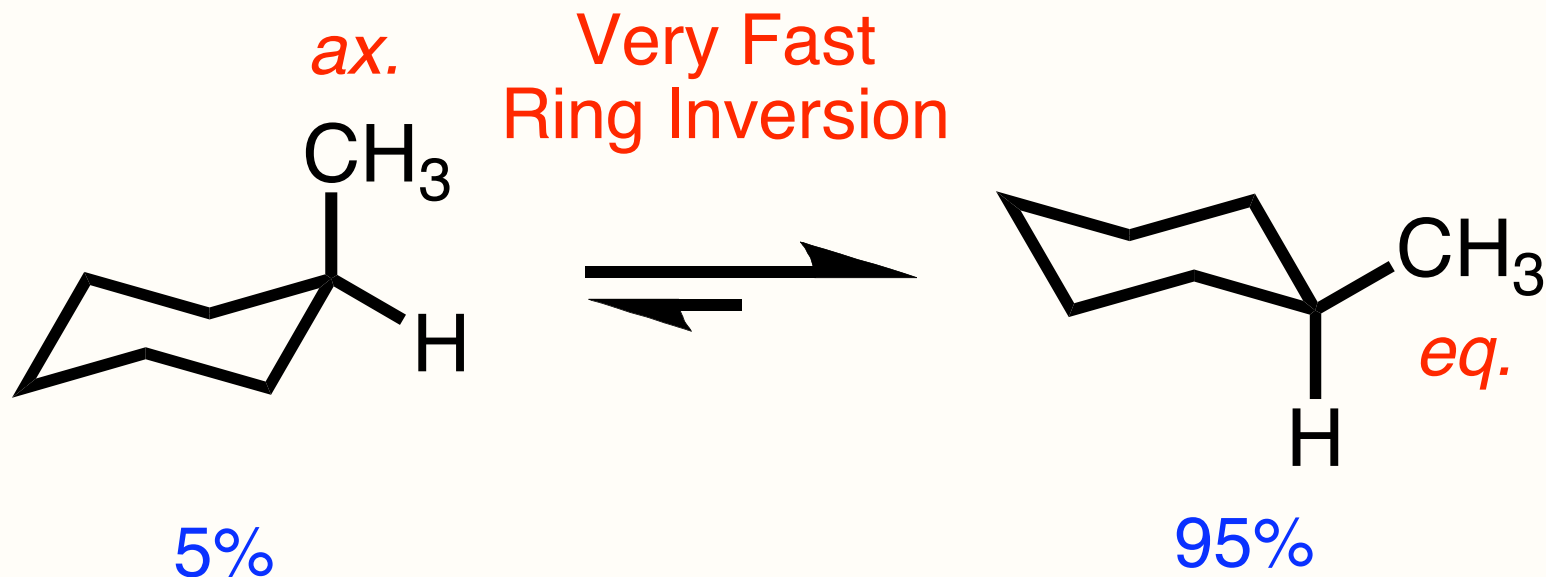
- A. 3.1 kcal/mol
- B. 2.8 kcal/mol
- C. 1.8 kcal/mol**
- D. 1.0 kcal/mol
- E. no difference

The Answer is C. As before, determine the strain energy of the axial conformer by identifying “bad” gauche interactions (Me-CH₂) and summing their contributions to strain energy. In the case of the axial conformer of methylcyclohexane, you must consider the gauche interaction between Me-(C1)-(C2)-(C3) as well as between Me-(C1)-(C6)-(C5).

Conformational Analysis of Monosubstituted Cyclohexanes

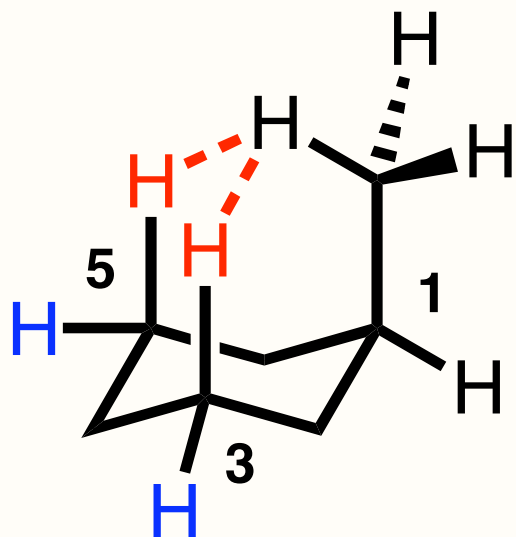
Section 3.10

Methylcyclohexane

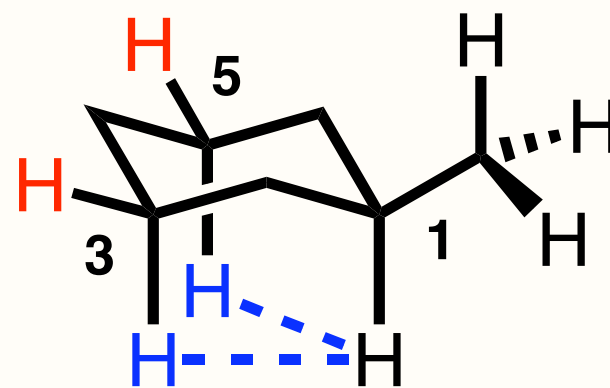


- conformer with equatorial methyl is more stable by 7.3 kJ/mol
- although ring flipping occurs, at any given moment 95% of conformers have the methyl group equatorial ($K = 19$)
- axial methyl group is crowded (steric strain)

Steric Strain: 1,3-Diaxial Repulsions



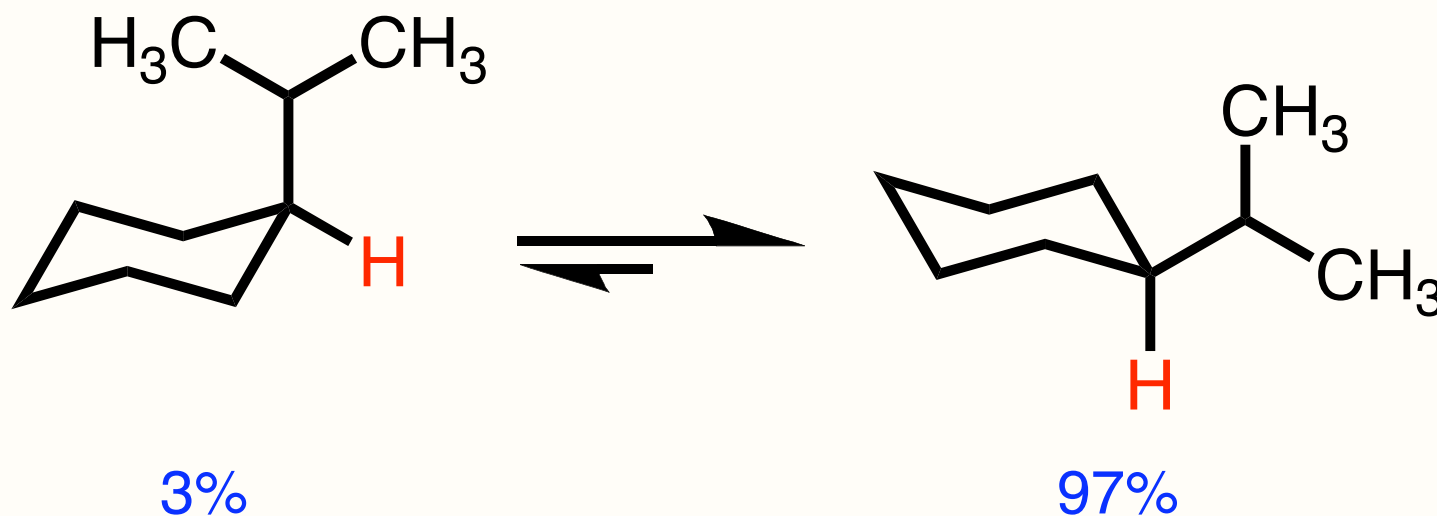
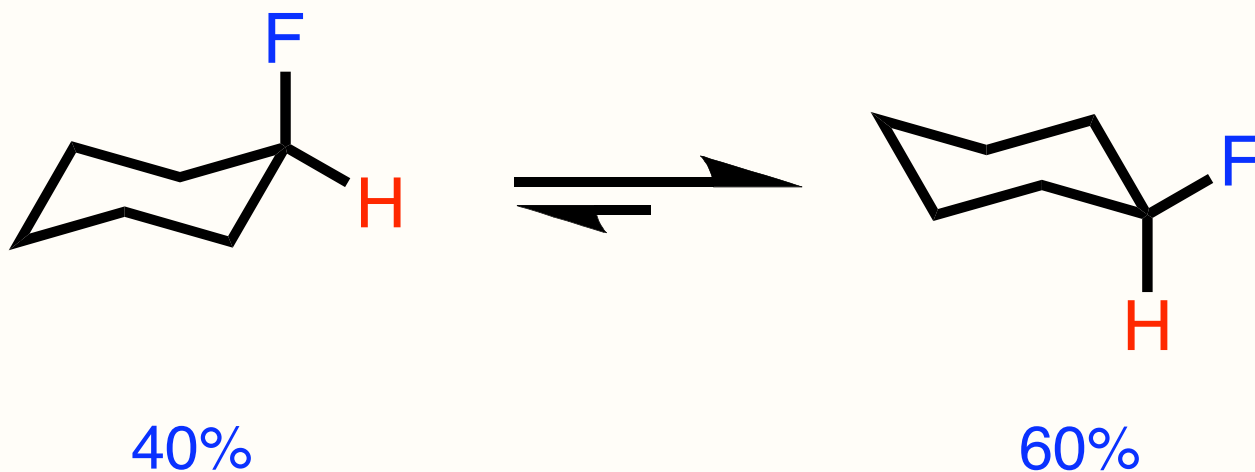
Van der Waals strain
between hydrogens of
axial CH₃ and axial
hydrogens at C-3 and C-5



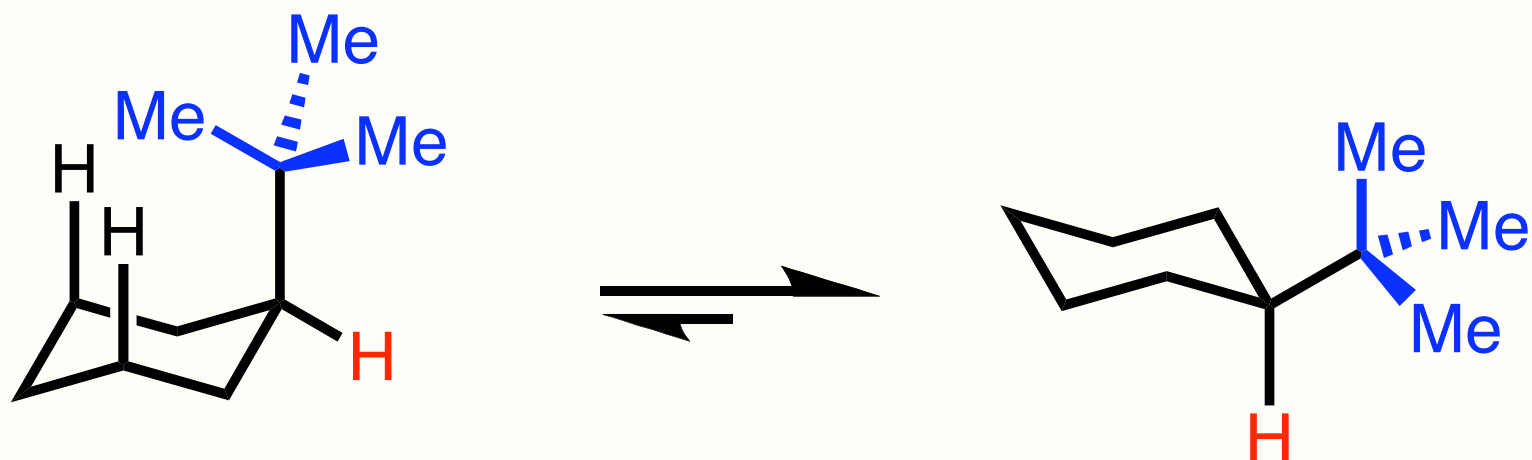
Smaller van der Waals strain
between hydrogens at C-1
and axial hydrogens
at C-3 and C-5

- these **interactions** are very similar to those found in the *syn*-periplanar and *gauche* conformations of *n*-butane

The Bigger the Group, The Bigger the Strain



tert-Butyl Group is Very "Bulky"



Less than 0.01%
(Severe 1,3-diaxial repulsions
involving *tert*-butyl group)

Greater than 99.99%
(Decreased van der Waals strain)

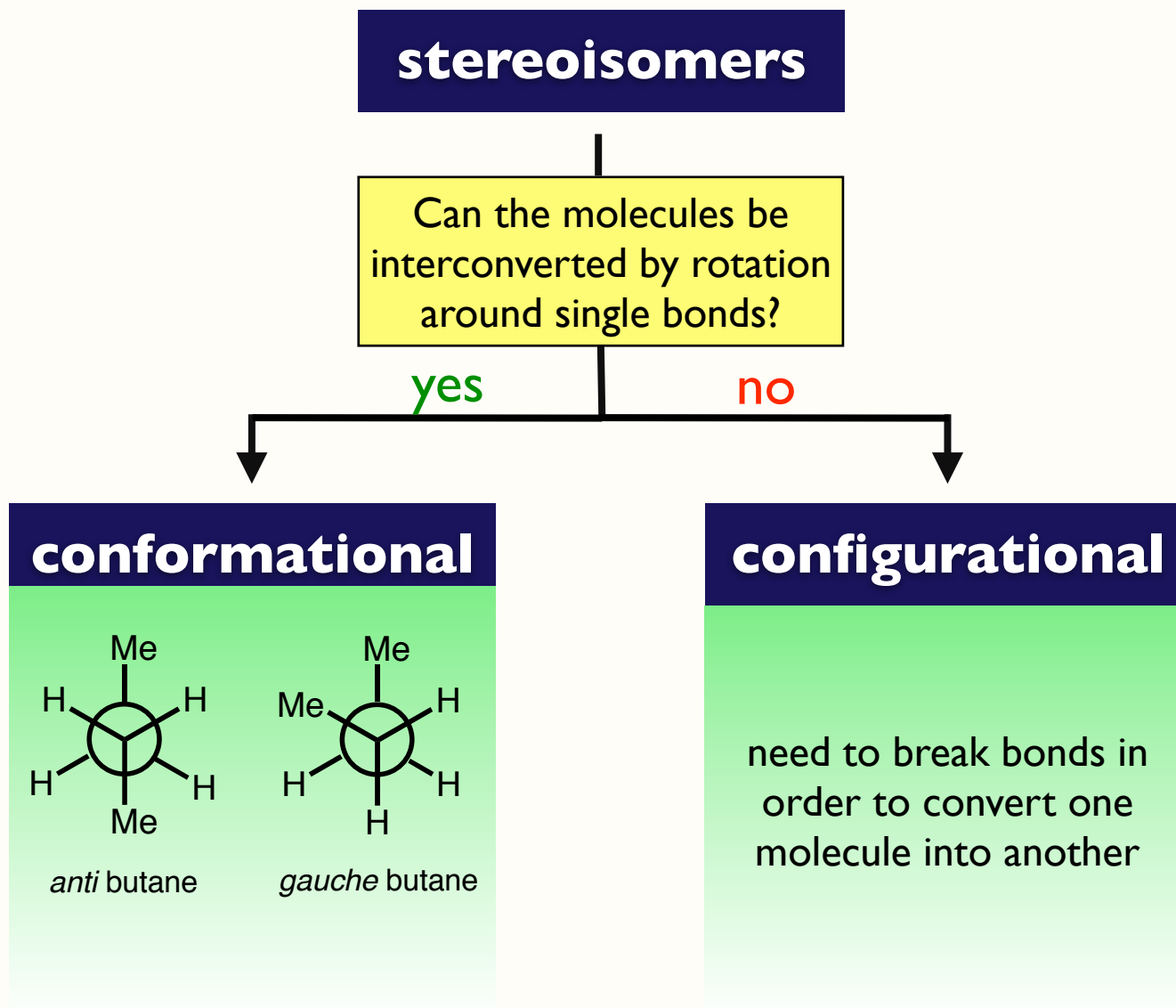
The energy difference between axial and equatorial conformers is ~20 kJ/mol and the equilibrium constant (K) is >3000. At room temperature, >99.99% of *tert*-butylcyclohexane is in the equatorial conformation.

Conformational and Configurational Stereoisomers of Disubstituted Cycloalkanes

Sections 3.11-3.12

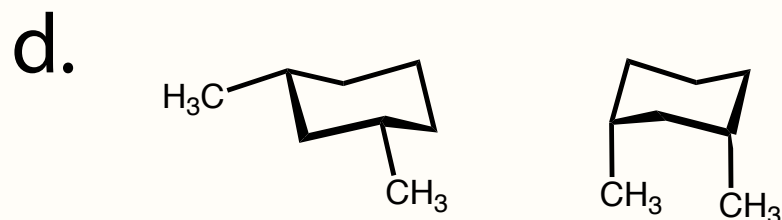
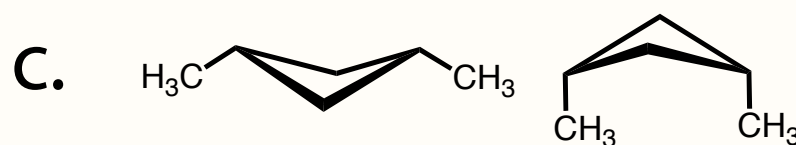
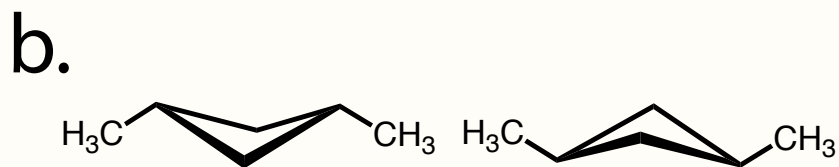
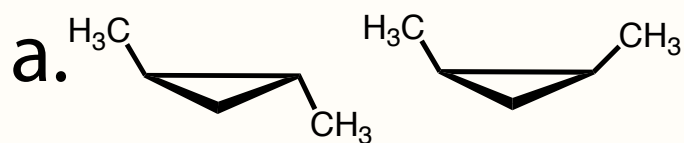
You are responsible for Sections 3.13-3.15

Reminder: Isomer Classification



Self Test Question

Determine which set of molecules are configurational stereoisomers; the remaining three sets are either conformational isomers or identical.



A. a

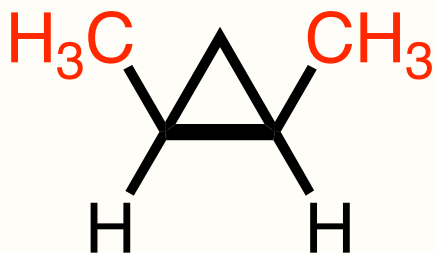
B. b

C. c

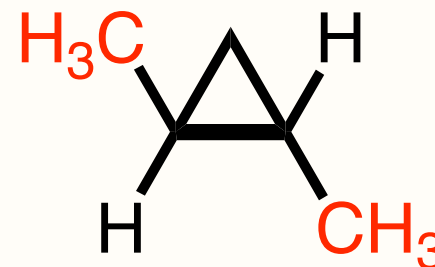
D. d

Configuration isomers differ from conformational isomers in that they can only be interconverted through bond breaking processes. **The answer is A.** Pairs C and D are conformational stereoisomers (conformers) of one another. Pair B are identical.

Configurational Stereoisomers of 1,2-Dimethylcyclopropane



cis-1,2-Dimethylcyclopropane

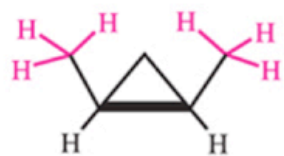


trans-1,2-Dimethylcyclopropane

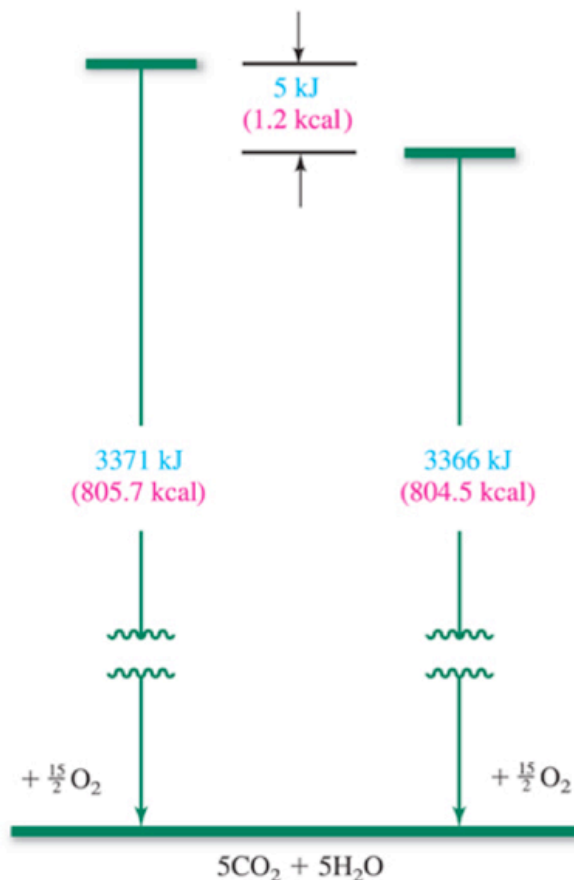
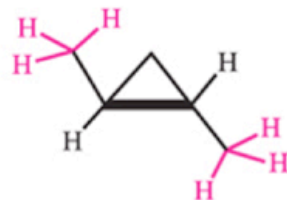
- no conformational isomers of cyclopropane since there is no rotation around C-C bonds in the ring
- *cis* = groups on the same side (plane) of ring
- *trans* = groups on the opposite side (plane) of ring
- configurational stereoisomers = must break bonds to interconvert

Relative Stabilities of Configurational Isomers Measured by Heat of Combustion -

cis-1,2-Dimethylcyclopropane

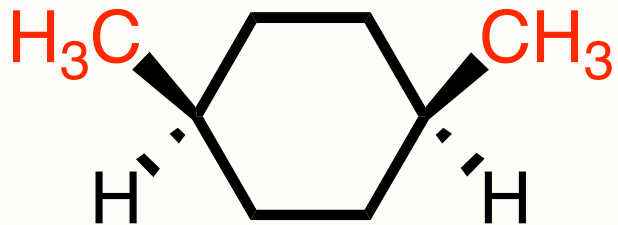


trans-1,2-Dimethylcyclopropane



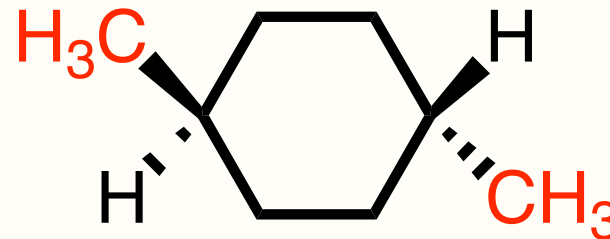
cis configuration =
methyl groups closer =
greater steric strain =
higher energy =
more heat released upon
combustion =
higher heat of combustion

Configurational Stereoisomers of 1,4-Dimethylcyclohexane



cis-1,4-Dimethylcyclohexane

higher energy
(less stable)



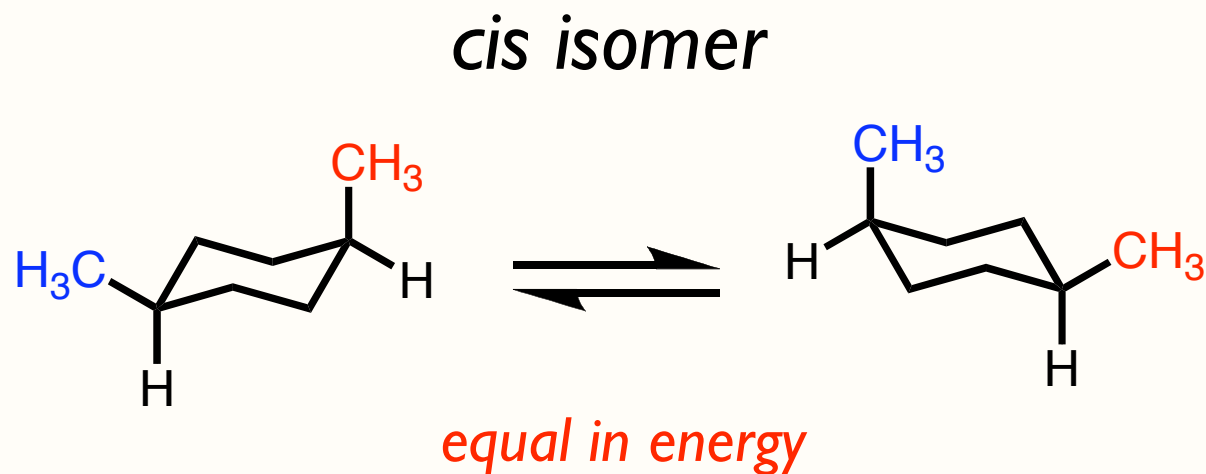
trans-1,4-Dimethylcyclohexane

lower energy
(more stable)

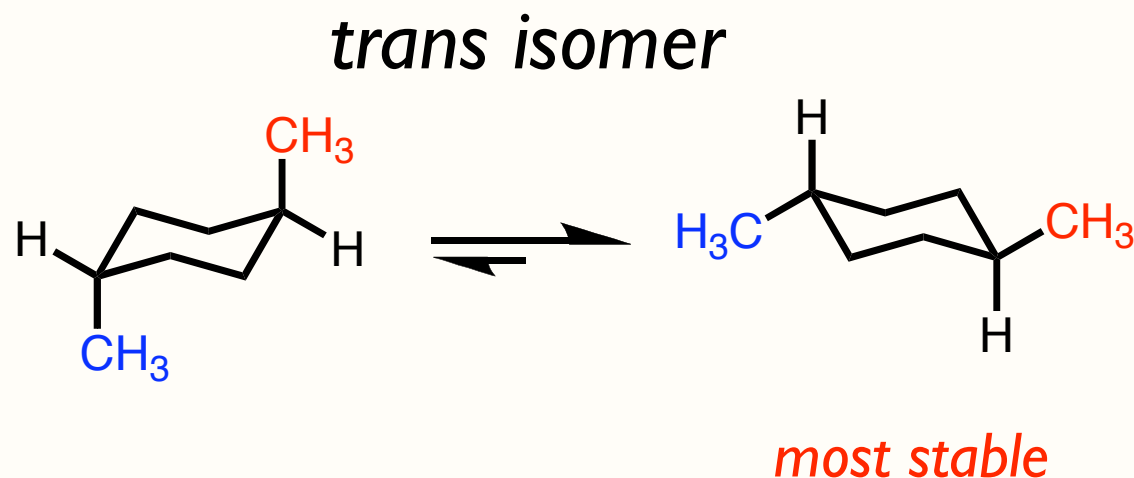
- *trans* is more stable in 1,4 configuration
- but not because of steric strain: methyl groups are too far apart to crowd each other

Conformational Analysis of *Cis*- and *Trans*-1,4-dimethylcyclohexane

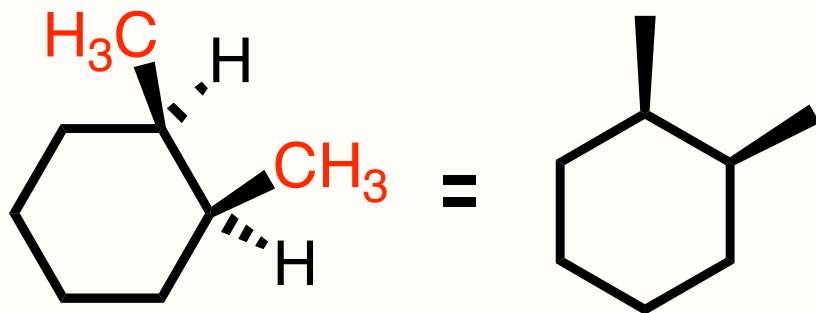
- two equivalent conformations
- each has one axial methyl groups and one equatorial methyl group



- more groups equatorial = more stable
- overall, *trans* is more stable than *cis* because it can adopt conformation with all groups equatorial

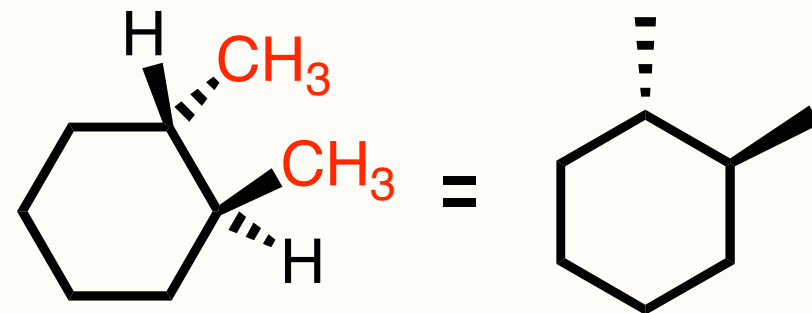


Configurational Stereoisomers of 1,2-Dimethylcyclohexane



cis-1,2-dimethylcyclohexane

higher energy
(less stable)



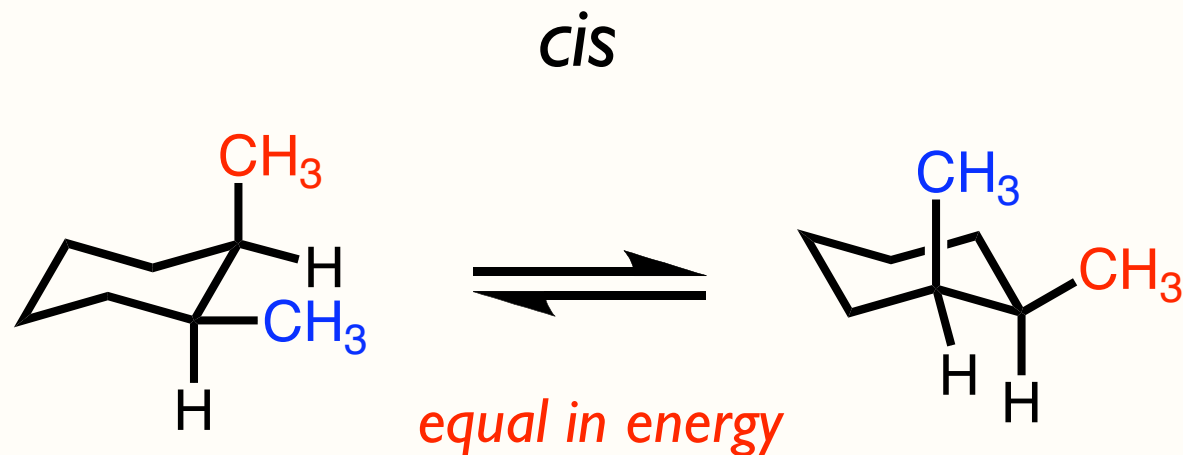
trans-1,2-dimethylcyclohexane

lower energy
(more stable)

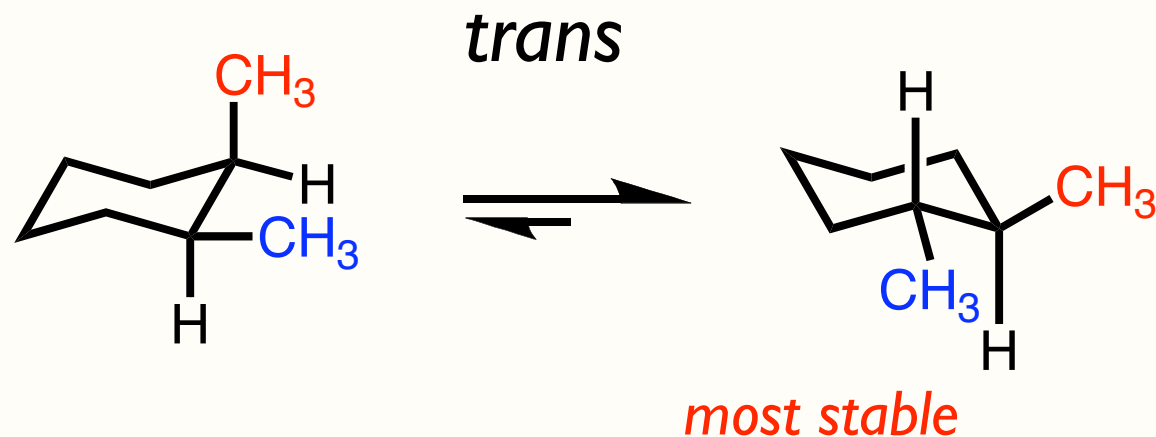
- *trans* is also more stable in 1,2 configuration
- *trans* can adopt conformation with both methyl groups equatorial

Conformational Analysis of *Cis*- and *Trans*-1,2-dimethylcyclohexane

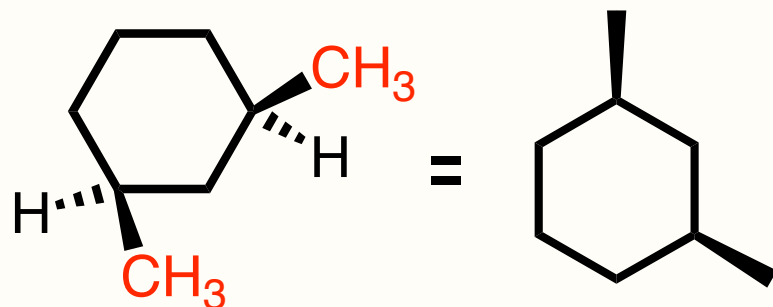
- two equivalent conformations
- each has one axial methyl groups and one equatorial methyl group



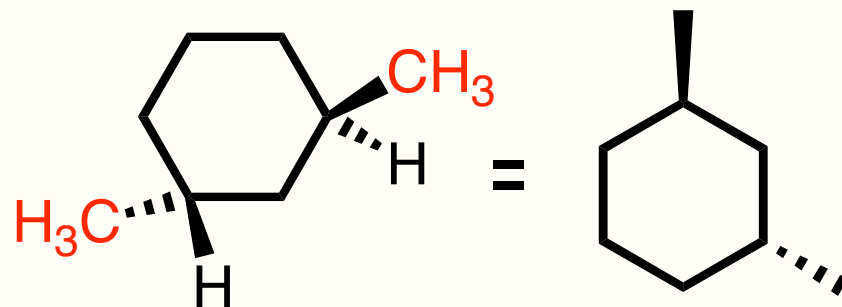
- more groups equatorial = more stable
- overall, *trans* is more stable than *cis* because it can adopt conformation with all groups equatorial



Configurational Stereoisomers of 1,3-Dimethylcyclohexane



cis-1,3-dimethylcyclohexane



trans-1,3-dimethylcyclohexane

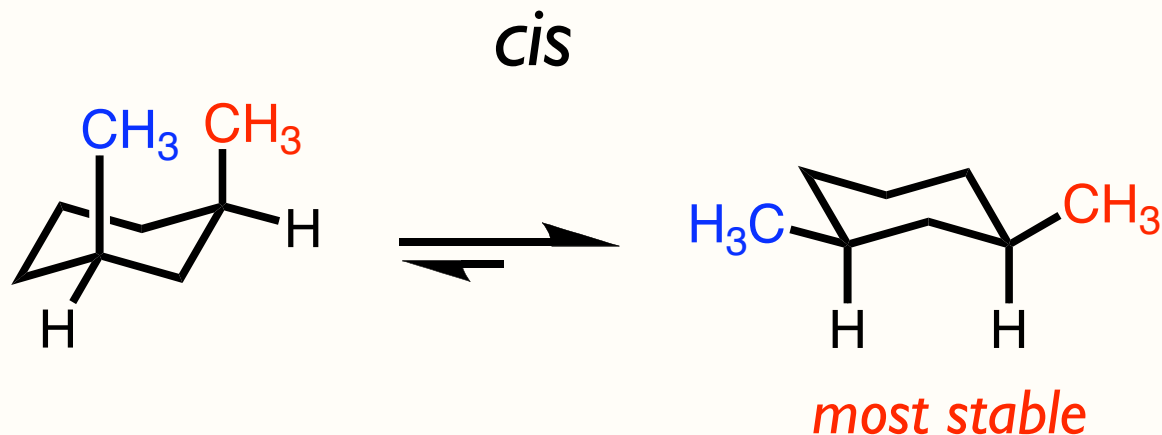
lower energy
(more stable)

higher energy
(less stable)

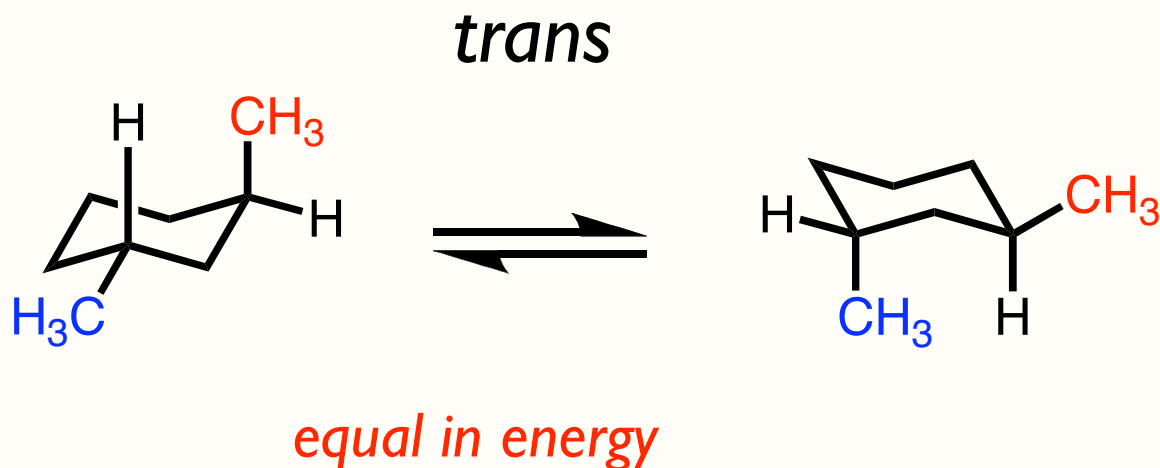
- unlike 1,2 and 1,4-disubstituted rings, *cis*-1,3 is most stable
- *only cis* can adopt a conformation with both methyl groups in equatorial positions

Conformational Analysis of *Cis*- and *Trans*-1,3-dimethylcyclohexane

- two axial groups is much higher in energy than two equatorial groups
- in this case, *cis* is the configuration with the conformation with most equatorial groups

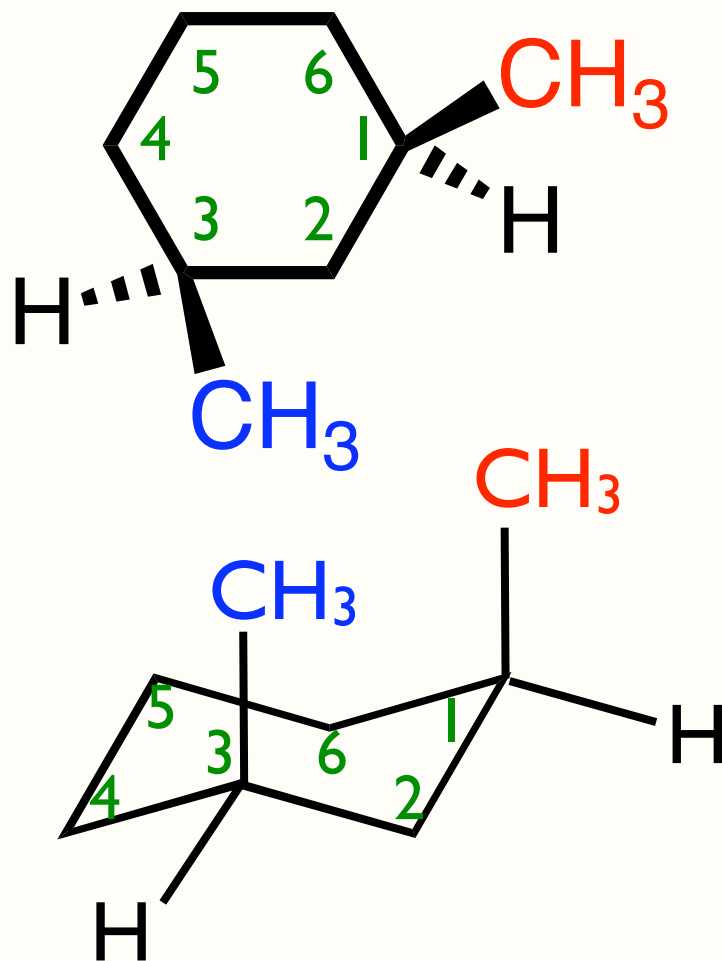


- two equivalent energy conformations for *trans*
- each has one axial and one equatorial methyl group



Converting Wedge & Dash Drawings of Cyclohexane to Chair-Conformations

While wedge & dash drawings are convenient, they give little information about conformational relationships.

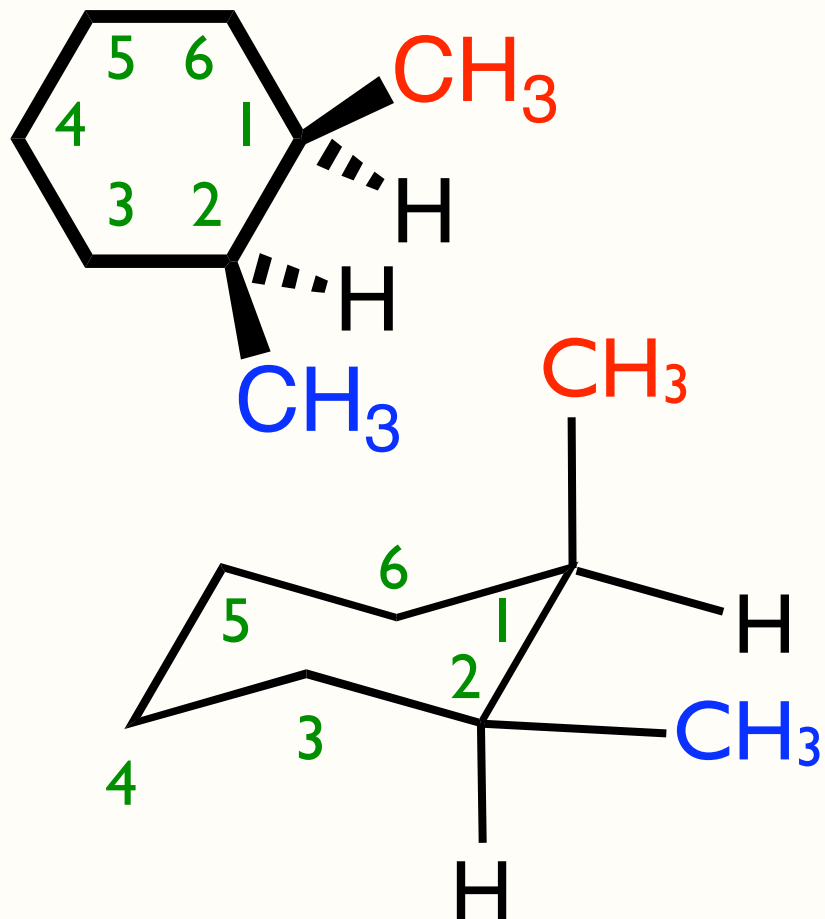


Steps

1. Number the wedge & dash drawing.
2. Draw a chair-cyclohexane skeleton.
3. Number the chair skeleton.
4. Draw axial and equatorial positions on the skeleton where substituents will go.
5. Place the first substituent in either position.
6. Place second substituent *cis* or *trans* relative to the first.

A Trickier Example

While wedge & dash drawings are convenient, they give little information about conformational relationships.

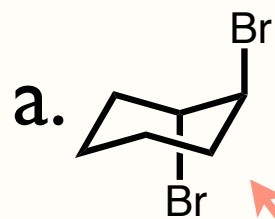
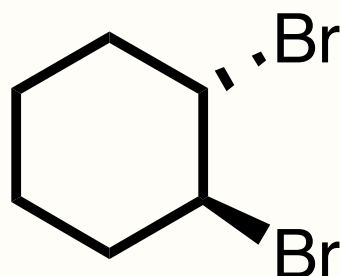


Steps

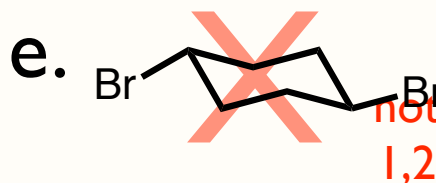
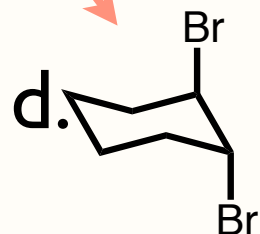
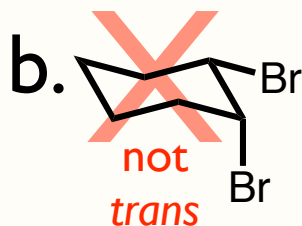
1. Number the wedge & dash drawing.
2. Draw a chair-cyclohexane skeleton.
3. Number the chair skeleton.
4. Draw axial and equatorial positions on the skeleton where substituents will go.
5. Place the first substituent in either position.
6. Place second substituent *cis* or *trans* relative to the first.

Self Test Question

Which is the most stable conformation of *trans*-1,2-dibromocyclohexane?



identical



A. a

B. b

C. c

D. d

E. e

The answer is C. Compound E is not *trans*-1,2-dibromocyclohexane but *trans*-1,4-dibromocyclohexane, a structural isomer. Structure B is *cis*-1,2-dibromocyclohexane, a configurational isomer. *trans*-1,2-Dibromocyclohexane is therefore represented by conformers A, D and C. Conformers A and D are identical and higher in energy than C since they have two substituents in the axial position while C has two groups in equatorial positions.

Next Lecture...

Chapter 4: Sections 4.1-4.10