Chapter 4:
Organic Compounds

Part 3: Substituted Cycloalkanes

Cycloalkanes: Ring Strain

Angle strain results when carbon bond angles deviate from the ideal 109.5° bond angle

good overlap

poor overlap

Cyclopropane

60

Cyclobutane

90

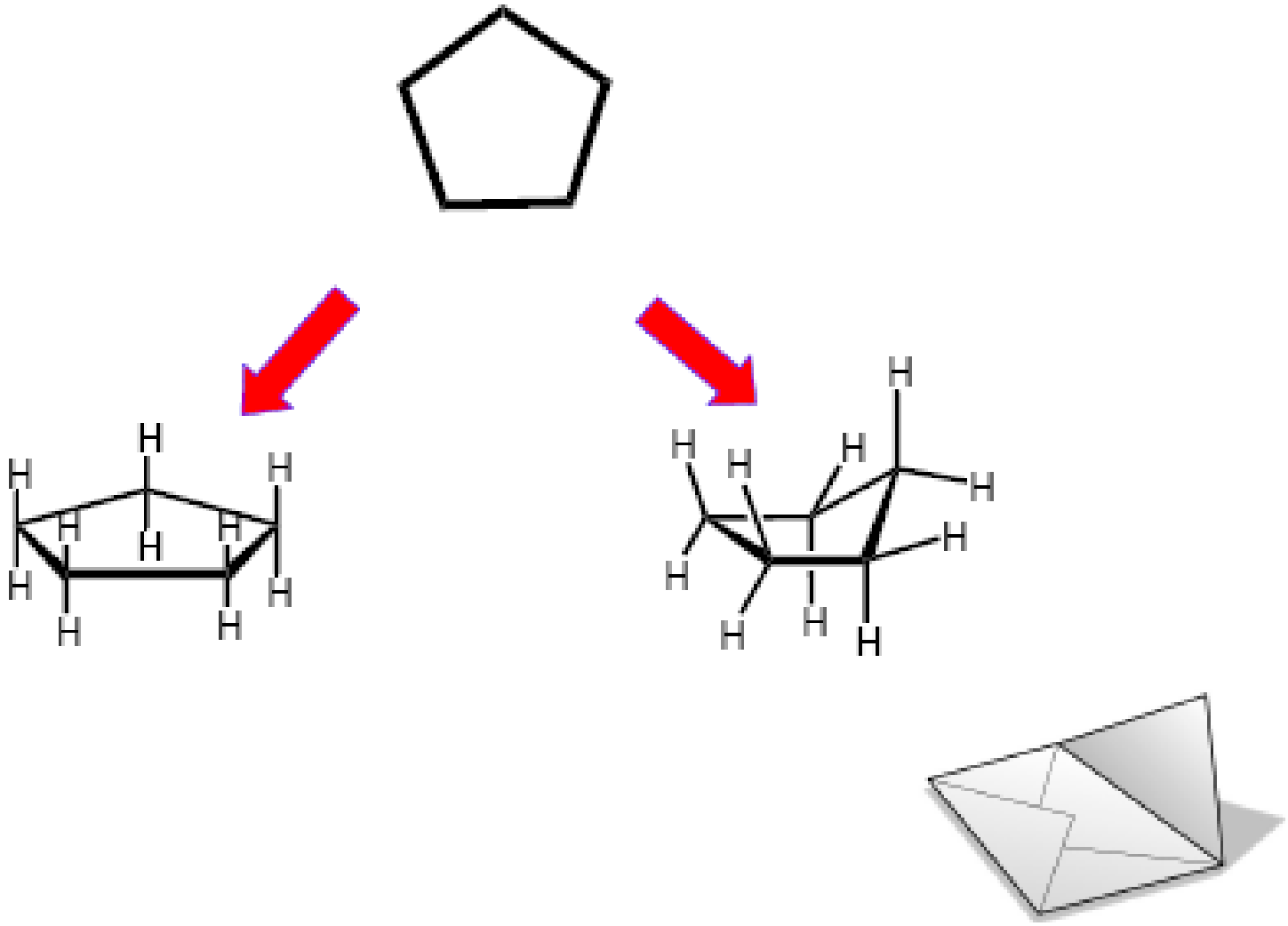
Cyclopentane

108

Cyclohexane

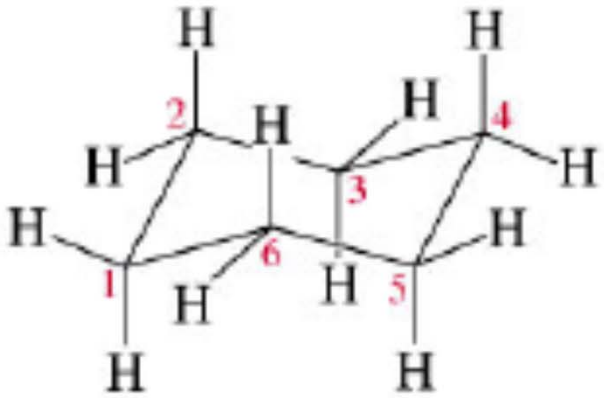
120

Cyclopentane



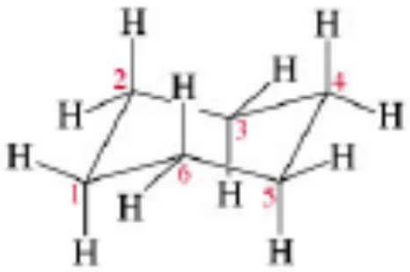
Cyclohexane

- The most important cyclic alkane and found throughout nature (i.e. similar to structural units in sugars).
- MCAT's love cyclohexanes
- Understand terminology: axial, equitorial, cis, trans, and geminal

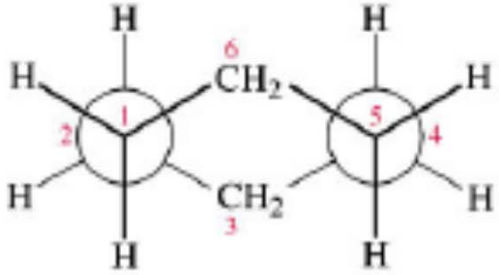


Substituents on the same carbon are called geminal

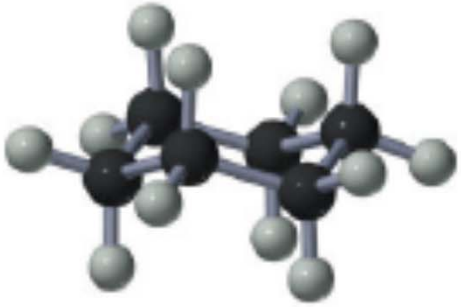
Drawing Cyclohexane



chair conformer of cyclohexane



Newman projection of the chair conformer

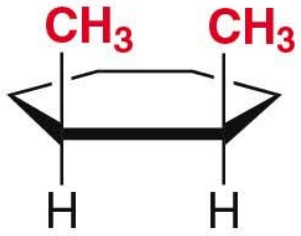


ball-and-stick model of the chair conformer of cyclohexane

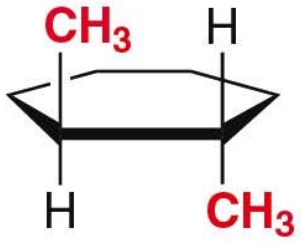
The chair conformation of cyclohexane is free of ring strain, because the carbons are closer to tetrahedral.

Cis-trans Isomerism

- These two structures are NOT constitutional isomers. WHY?



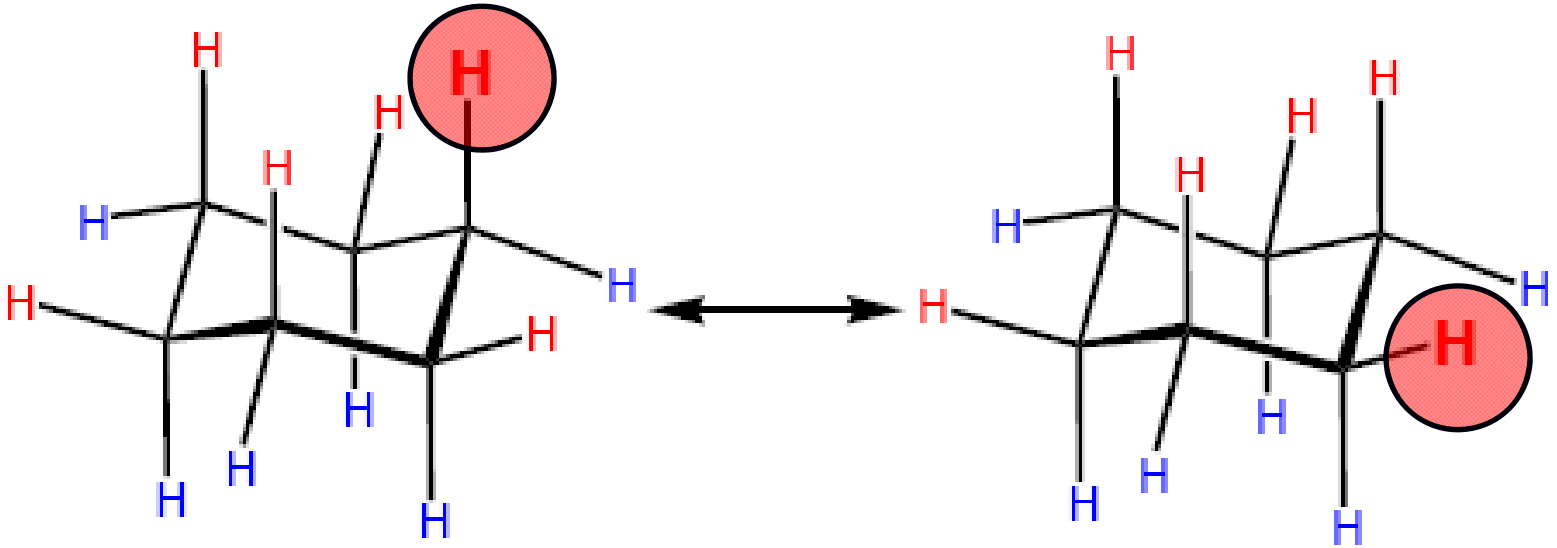
cis-1,2-Dimethylcyclohexane



trans-1,2-Dimethylcyclohexane

- They are STEREOISOMERS. HOW?

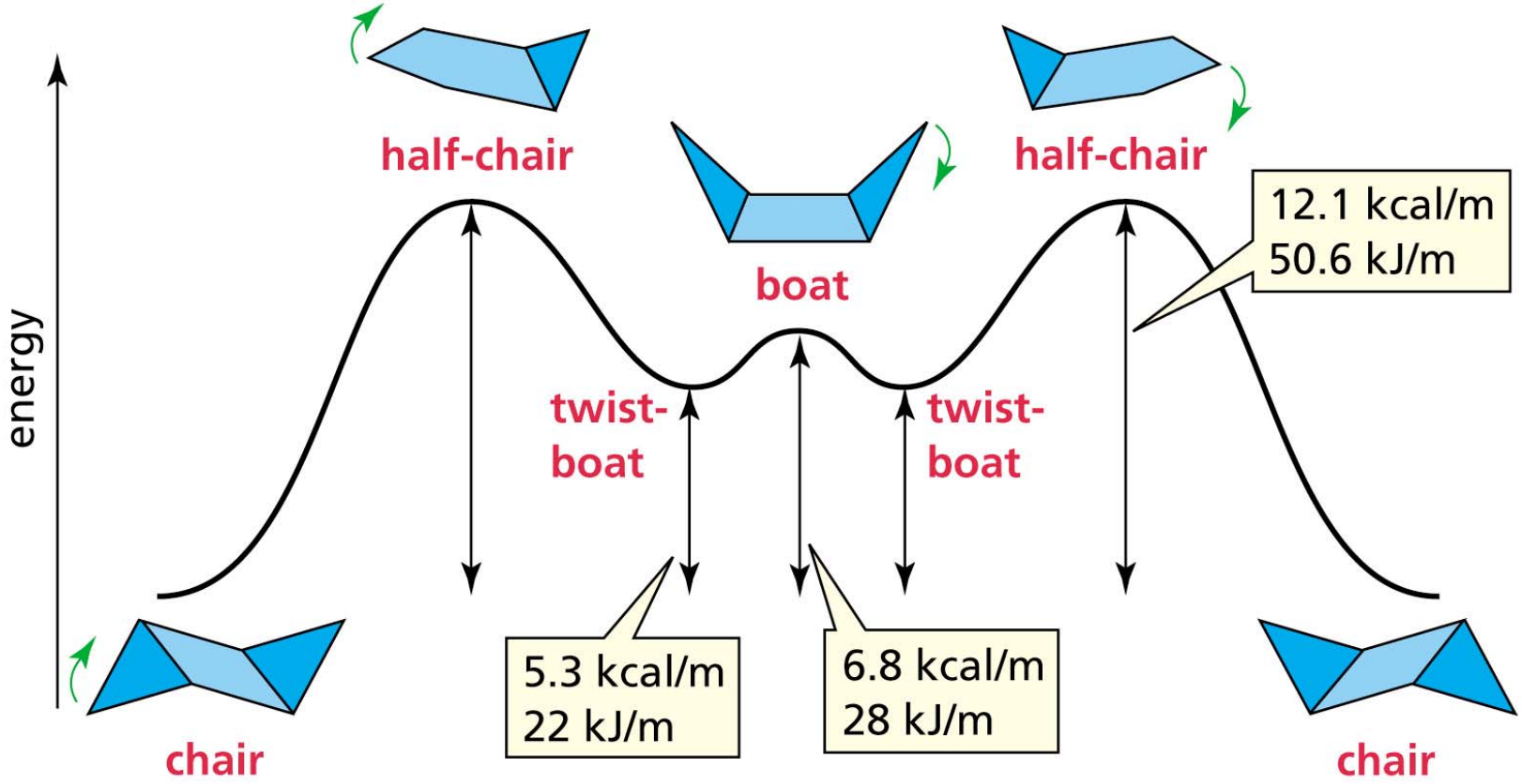
Ring Flipping in Cyclohexane



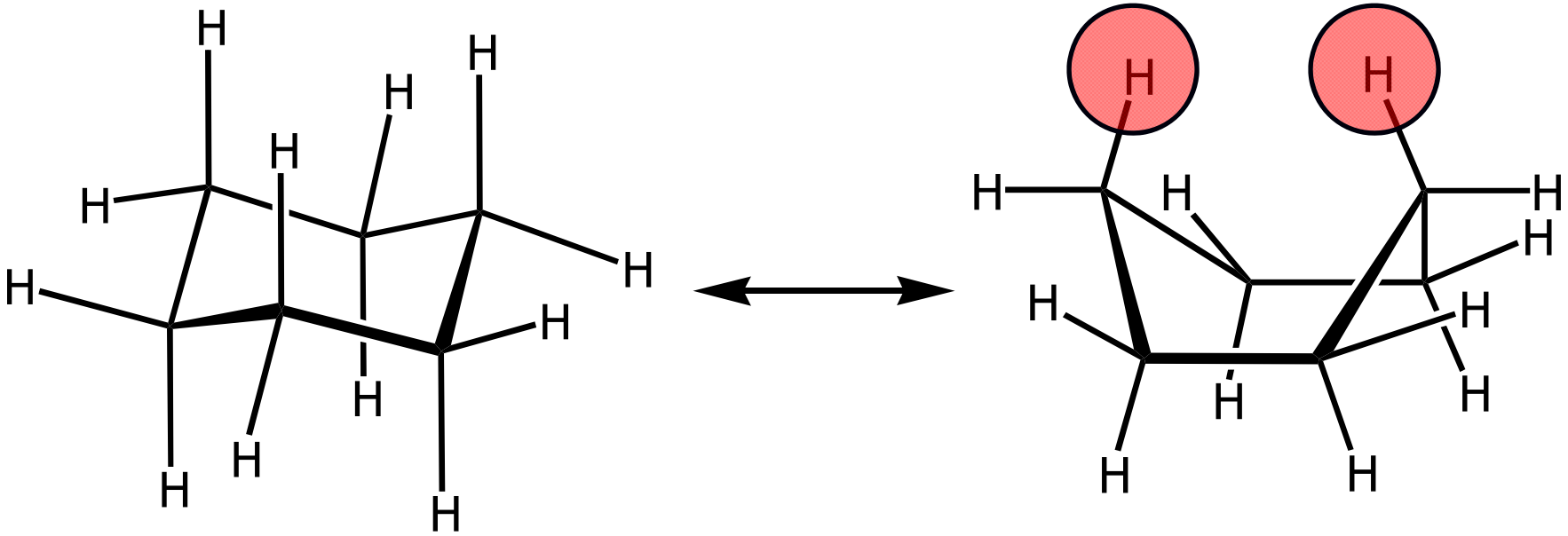
CIS – substitutents on the same side

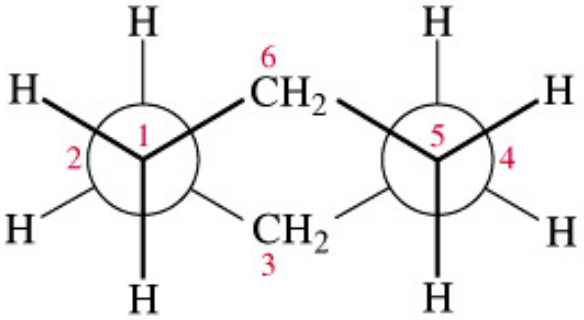
TRANS – substitutents on opposite sides

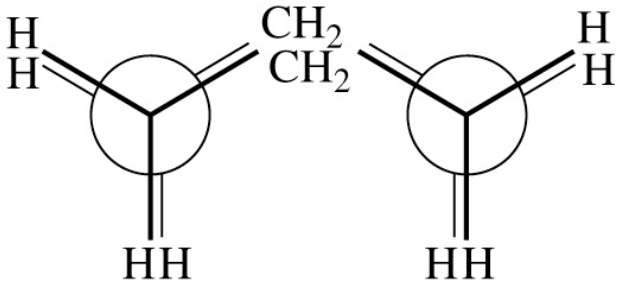
Conformations of Cyclohexane



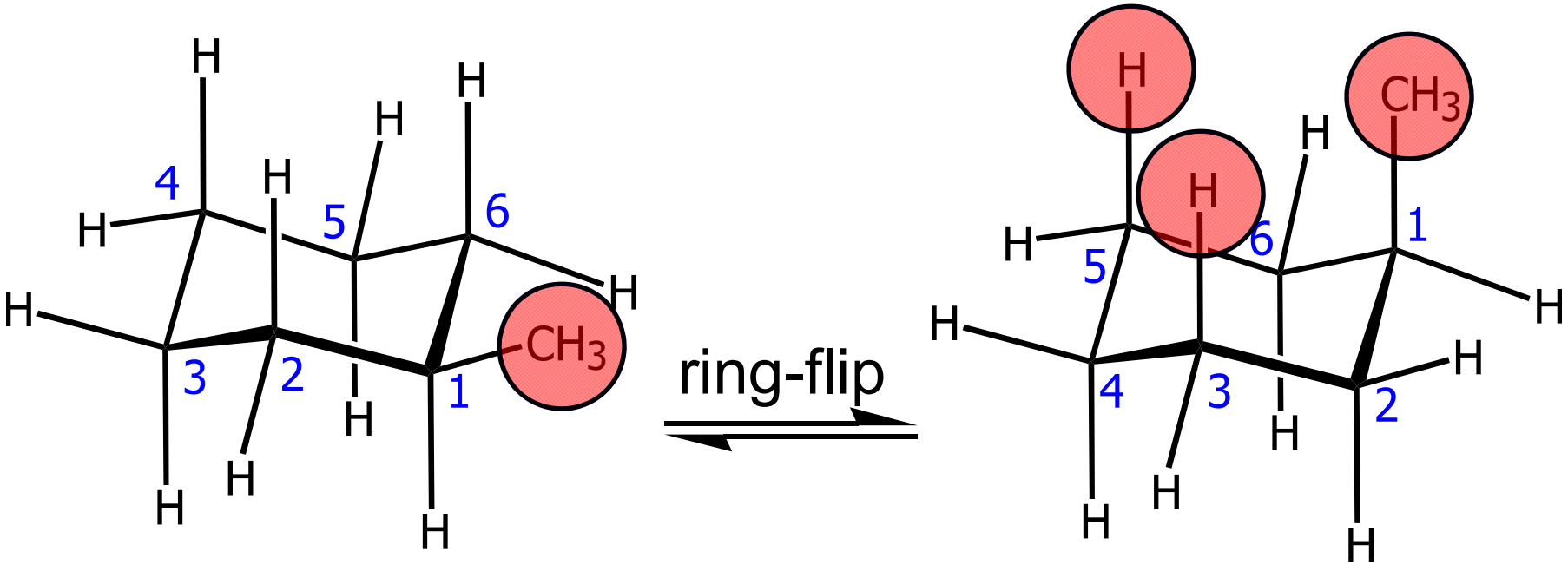
Ring Flipping in Cyclohexane







Conformations of Monosubstituted Cyclohexanes

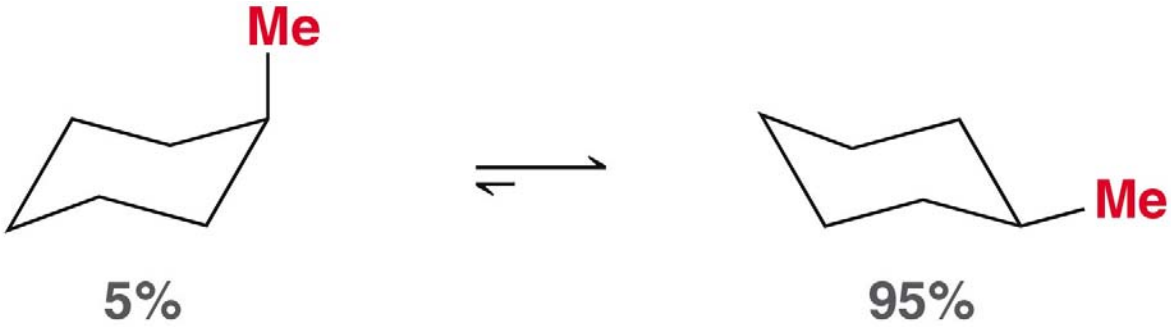


equitorial

axial

Monosubstituted Cyclohexane

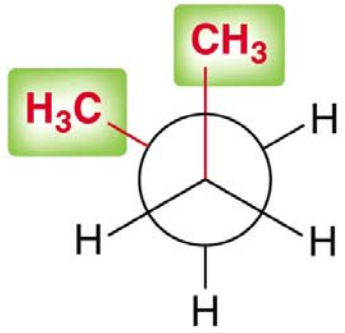
- Flipping a chair is not like flipping a pancake. Flipping a chair is the result of C–C single bonds rotating ONLY.



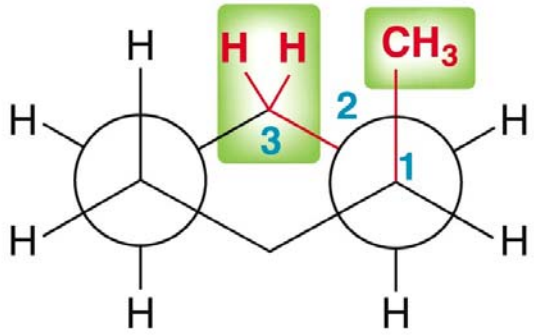
- If both versions of the CHAIR were equally stable, you would have a 50/50 mixture of axial/equatorial.
- Why does the equatorial chair dominate the equilibrium?
- The axial substituent causes additional steric strain.

Monosubstituted Cyclohexane

- 1,3-diaxial interactions are equivalent to gauche interactions

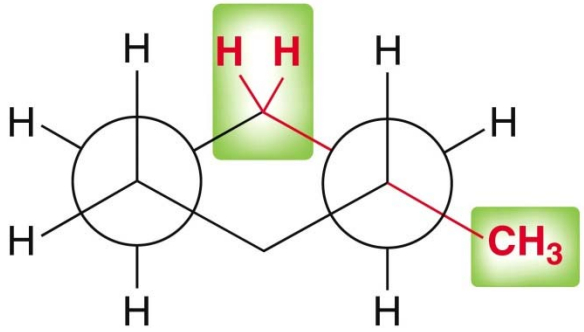


Gauche interaction



1,3-Diaxial interaction

- When the substituent is in the equatorial position, it is equivalent to an anti interaction.



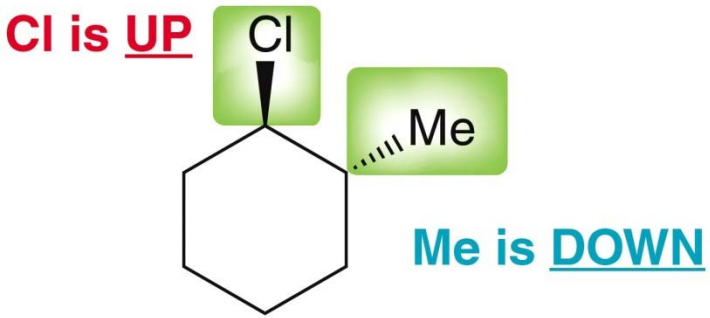
Monosubstituted Cyclohexane

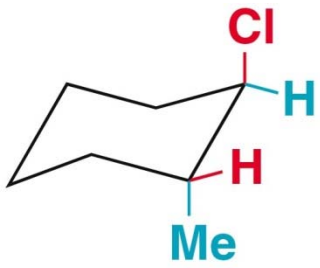
- Larger groups will cause more steric crowding in the axial position. Consider Table 4.8.

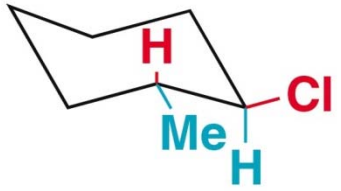
SUBSTITUENT	STERIC HINDRANCE FROM 1,3-DIAXIAL INTERACTIONS (KJ/MOL)	AXIAL-EQUATORIAL RATIO (AT EQUILIBRIUM)
—Cl	2.0	70 : 30
—OH	4.2	83 : 17
—CH_3	7.6	95 : 5
—CH_2CH_3	8.0	96 : 4
—$CH(CH_3)_2$	9.2	97 : 3
—$C(CH_3)_3$	22.8	9999 : 1

Disubstituted Cyclohexane

- When multiple substituents are present, the positioning of the groups on the chair must be shown by using solid or dashed wedges or by showing the groups in either axial or equatorial positions.

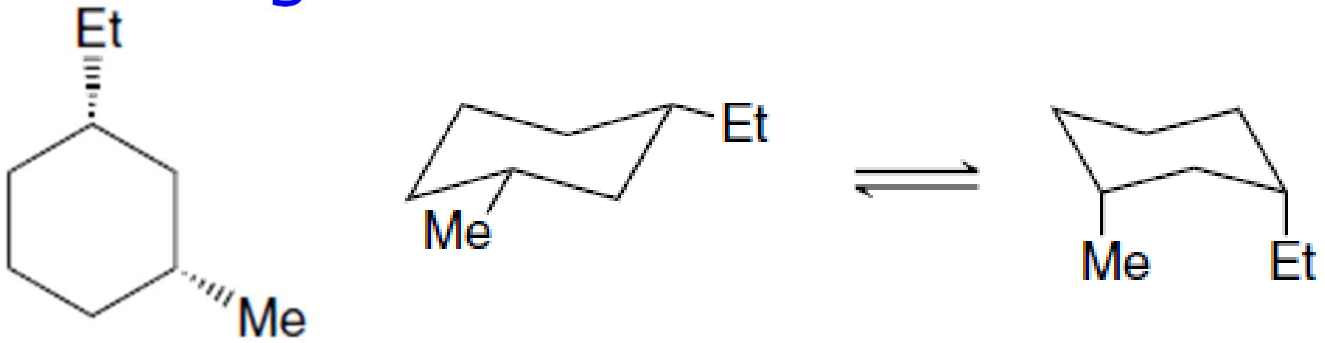




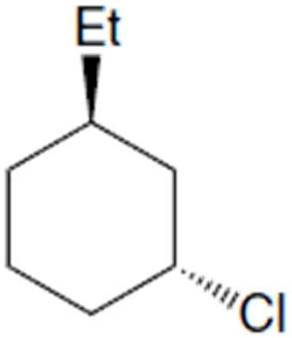


Disubstituted Cyclohexane

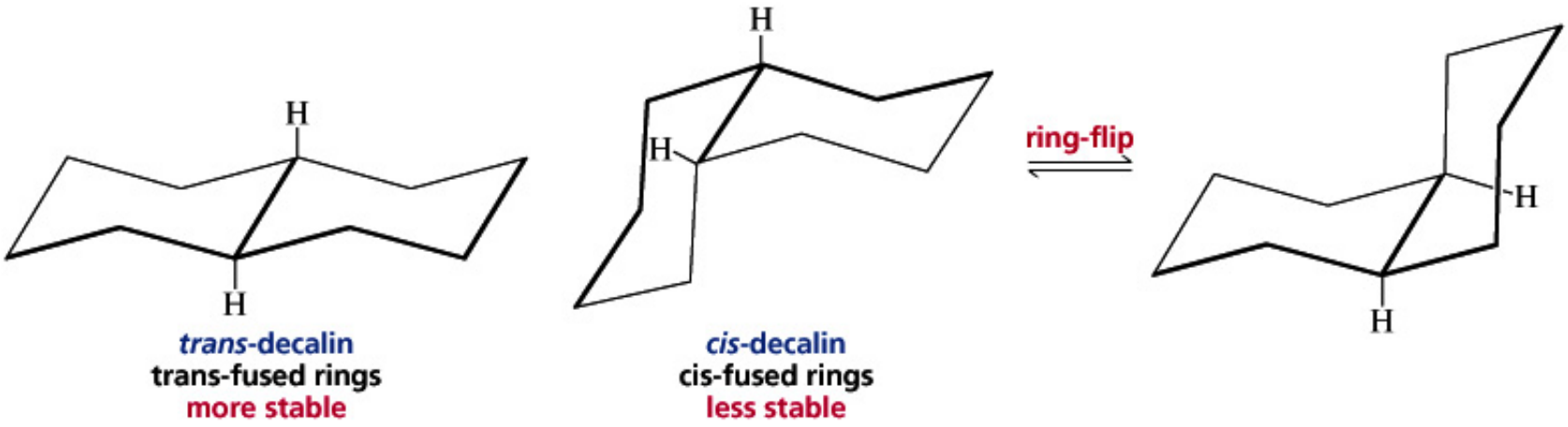
- Consider both chair conformations for the following molecule.



- Which would you expect to be more stable? WHY?
- Do the same analysis for this molecule.



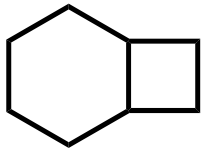
Fused Rings



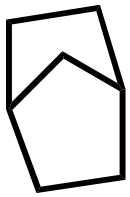
Trans-fused cyclohexane is more stable than cis-fused

And this is not on the exam…..

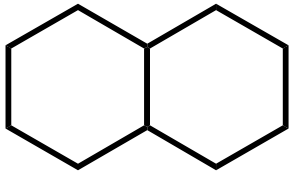
Bicyclic Ring Systems



Bicyclo[4.2.0]octane



Bicyclo[2.2.1]heptane



Bicyclo[4.4.0]decane

Naming Bycylic Ring Systems

1. Count total number of carbons.
2. Largest ring, next largest & smallest give us the numbering. This is put in brackets.
3. Put together name with the bicyclo- prefix.
4. *This is not on the exam either.*

spiro[4.4]nonane

For Next Time….

- Monday Finish Chapter 4 (if we haven't)
  - Chapter 5 (5.1-5.4)
  - BRING YOUR MODEL SET!
- Wednesday Exam #1 (Chapters 1-4)
- Homework Problems Chapter 4
- #1, 6, 10, 19, 25, 28, 36, 43, 48, 51,52, 63