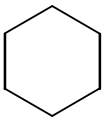
Cycloalkanes

· **Cyclic saturated alkanes, general formula C_nH_{2n}**
· **Named by adding the prefix cyclo to the corresponding acyclic alkane name.**

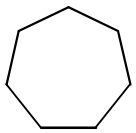
cyclopropane
C_3H_6

cyclobutane
C_4H_8

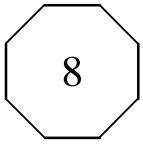
cyclopentane
C_5H_{10}



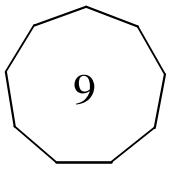
cyclohexane
C_6H_{12}



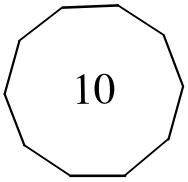
cycloheptane
C_7H_{14}



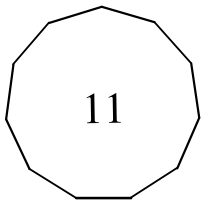
cyclooctane
C_8H_{16}



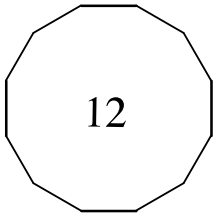
cyclononane
C_9H_{18}



cyclodecane
$C_{10}H_{20}$



cycloundecane
$C_{11}H_{22}$



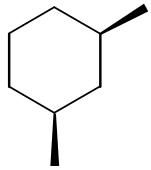
cyclododecane
$C_{12}H_{24}$

· **Rings have very limited conformational freedom compared to their acyclic counterparts.**

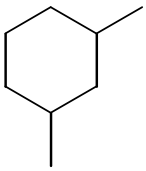
Naming Cycloalkanes

stereochemistry — **number(s)-substituent(s)** — **parent ring**

example

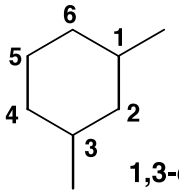


1. Find the parent.



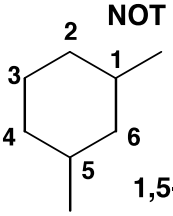
cyclohexane

2. Locate and number the substituents.



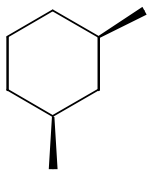
1,3-dimethyl

NOT



1,5-dimethyl

3. Add the stereochemistry.



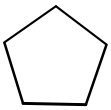
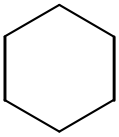
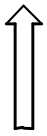
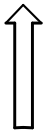
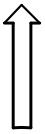
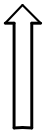
***cis*-1,3-dimethyl-cyclohexane**

⇧
Full name

Remember that cycloalkane *cis*- and *trans*-isomers don't interconvert- they are CONFIGURATIONAL isomers.

Cycloalkanes and *angle strain*

angle strain =	the strain induced in a molecule when a bond angle deviates from the ideal value

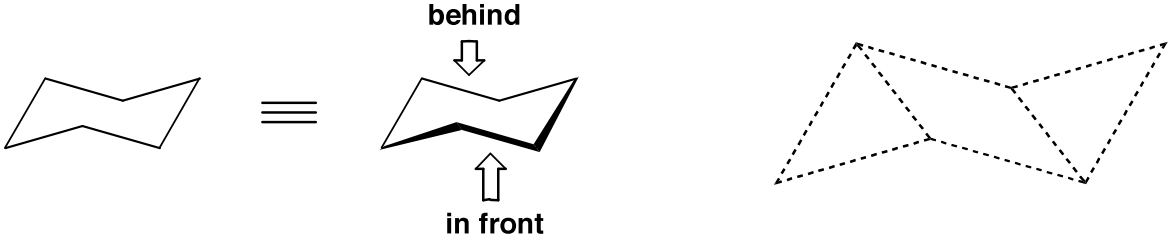
cyclopropane C_3H_6	cyclobutane C_4H_8	cyclopentane C_5H_{10}	cyclohexane C_6H_{12}
			
			
60° C-C-C bond angle?	90° C-C-C bond angle?	108° C-C-C bond angle?	120° C-C-C bond angle?

The ideal (unstrained) bond angle in sp^3 hybridised C is 109° !

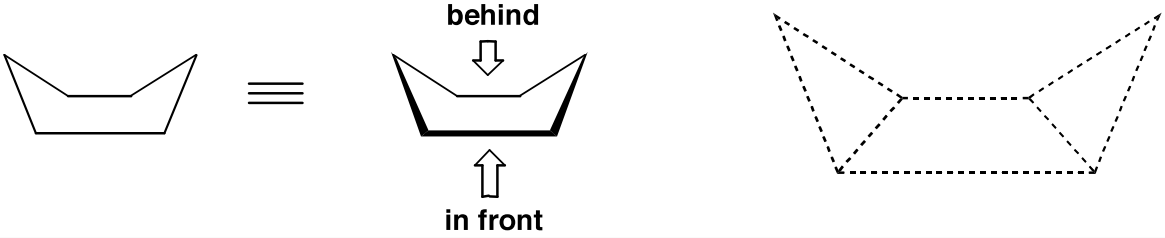
49° of angle strain?	29° of angle strain?	1° of angle strain?	11° of angle strain?

Conformations of Cyclohexane: how to draw and interpret the line diagrams

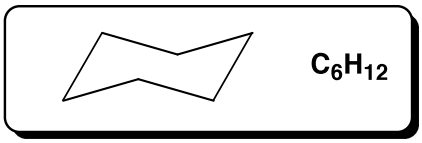
The "CHAIR" conformation



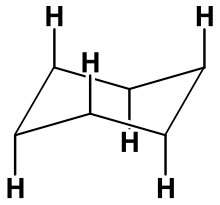
The "BOAT" conformation



Drawing the CHAIR conformation of cyclohexane: incorporating the hydrogens

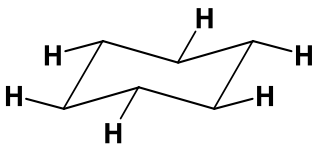


The chair conformation of cyclohexane has two different types of hydrogen: "axial" and "equatorial". All axial H's are equivalent. All equatorial H's are equivalent.



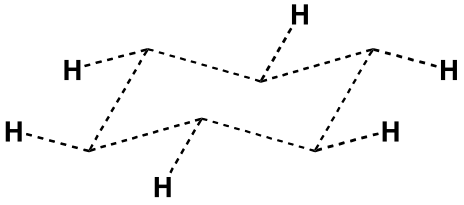
"axial" hydrogens

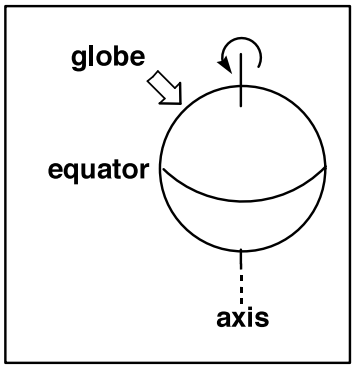
- point vertically up and vertically down
- alternate between vertically up and down
- down when ring puckering points down
- up when ring puckering points up



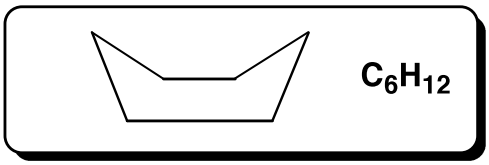
"equatorial" hydrogens

- point out at angles from the "equator"
- alternate between angled up and down
- C-H bond parallel to C-C bonds one bond away:





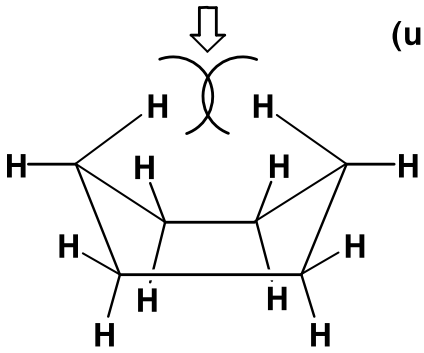
Drawing the BOAT conformation of cyclohexane: incorporating the hydrogens



The boat conformation of cyclohexane has *four* different types of hydrogens.

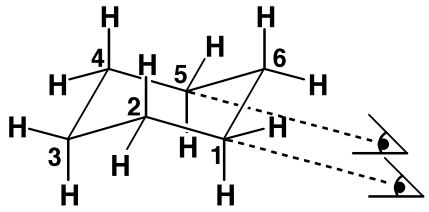
flagpole interaction: H's trying to occupy same space

(unfavourable steric strain)

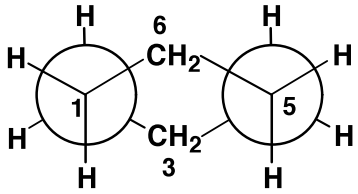


Drawing Newman projections of chair and boat cyclohexane

perspective line diagram:



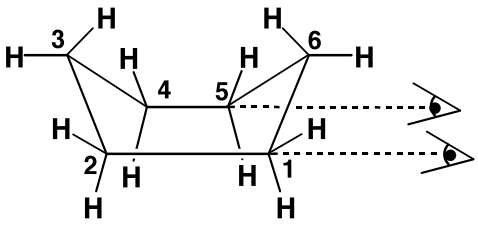
Newman projection (viewing as indicted):



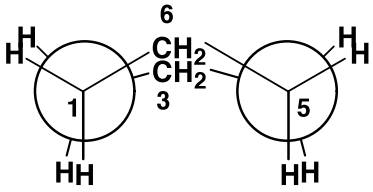
(2 and 4 obscured)

note staggered arrangement

perspective line diagram:



Newman projection (viewing as indicted):



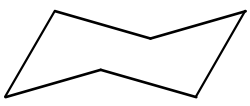
(2 and 4 obscured)

note eclipsed arrangement

Chair and boat conformations of cyclohexane: stabilities

- cyclohexane is not flat but puckered (to avoid angle strain)
- chair conformation of cyclohexane is lower energy than boat:

CHAIR

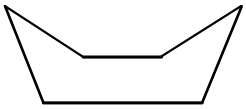


no angle strain

no torsional strain

no steric strain

BOAT



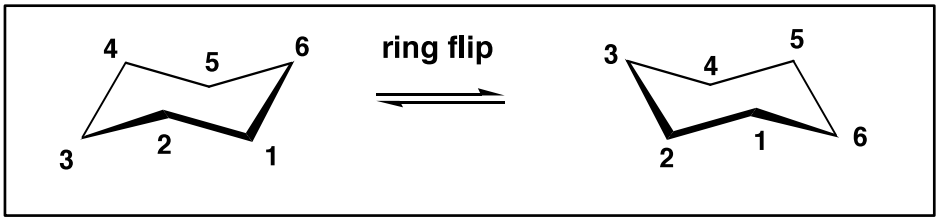
no angle strain

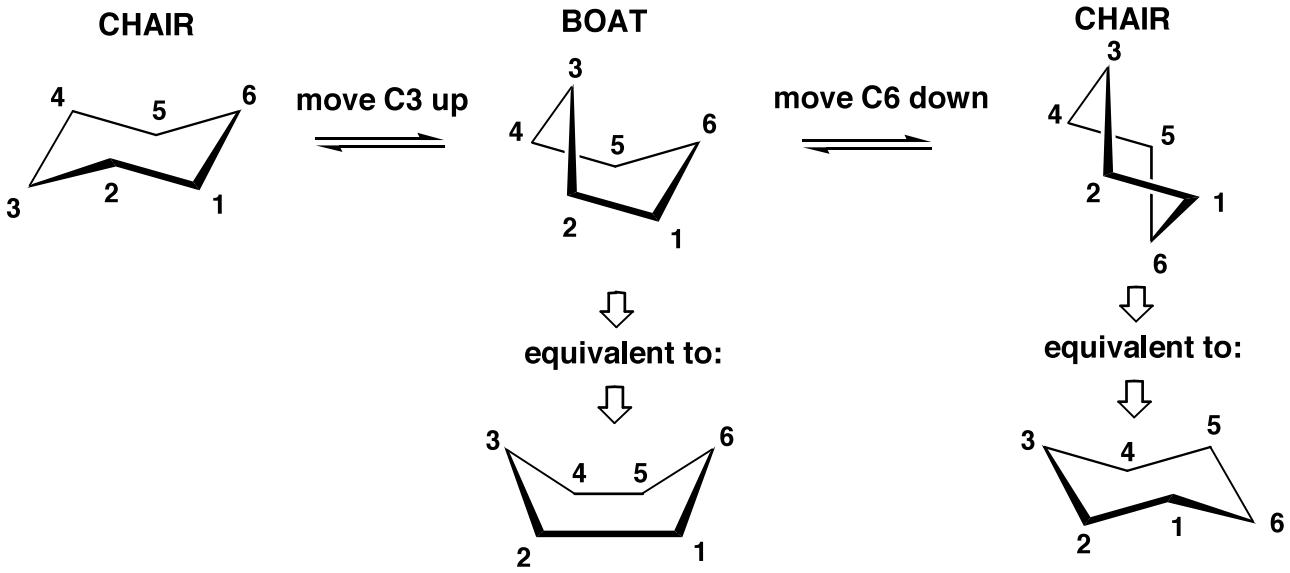
torsional strain

steric strain

- boat is 24 kJ/mol higher in energy than chair!

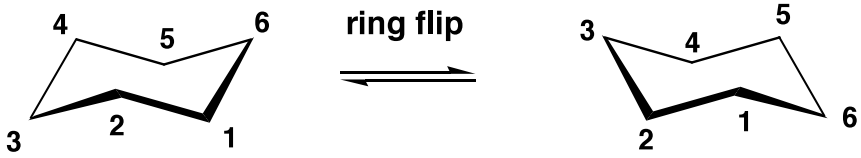
Interconverting conformations of cyclohexane: RING "FLIPPING"

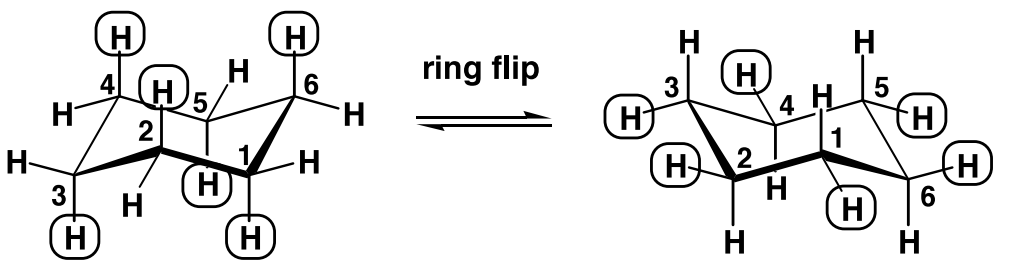




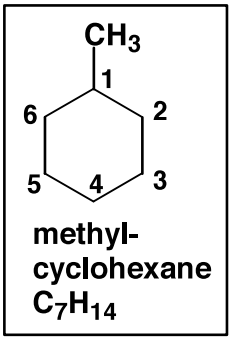
Consequences of ring flipping

- axial and equatorial substituents (hydrogens) interchange!



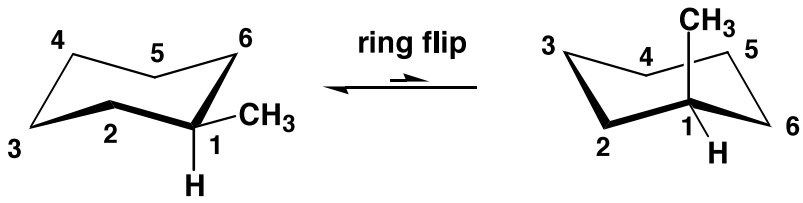


Monosubstituted cyclohexanes



methyl-cyclohexane
C_7H_{14}

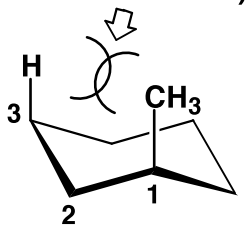
- Consider methylcyclohexane: what is the preferred conformation?
- The chair! But which one? Note that the CH_3 at C1 can be axial or equatorial (ie. there are two possible chair conformations for every substituted cyclohexane).



CHAIR (CH_3 equatorial) preferred

CHAIR (CH_3 axial)

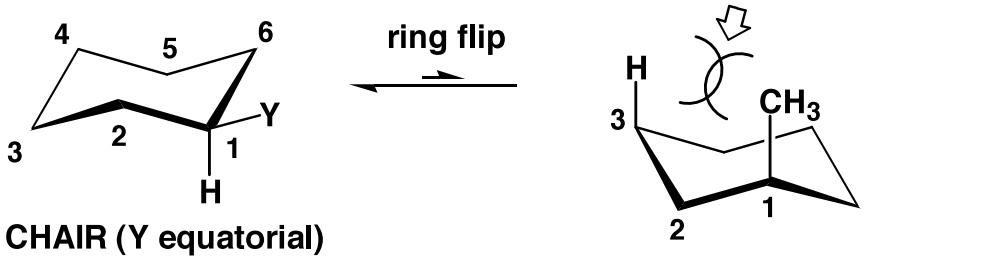
1,3-diaxial strain (steric strain: cost = 3.8 kJ/mol)



Remember:
- *Chair conformation always preferred over boat conformation.*
- *Axial and equatorial positions interchange on ring flip, but not up or down orientations.*
- *Larger substituents always prefer equatorial position.*

Monosubstituted cyclohexanes

1,3-diaxial strain



CHAIR (Y equatorial) preferred

CHAIR (Y axial)

Y	1,3-diaxial strain (kJ/mol)
CH_3	3.8
CH_2CH_3	4.0
$CH(CH_3)_2$	4.6
$C(CH_3)_3$	11.4