

## Hydrocarbons

Organic structures that contain only carbon and hydrogen

saturated - a compound is termed “saturated” if it has the maximum hybridization ( $sp^3$ )  
at each carbon

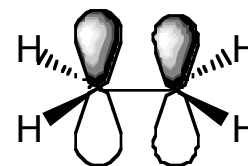
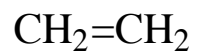
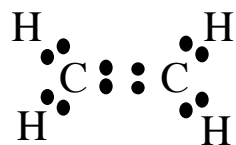
therefore: no double or triple bonds

a saturated carbon species is termed an ALKANE



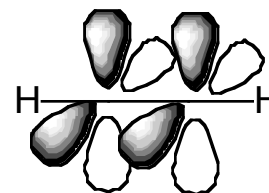
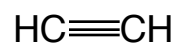
the compound has a root name indicating the number of carbons and the -ane suffix

an ALKENE has a carbon-carbon double bond



all three structures represent ethylene (or ethene)

an ALKYNE has a carbon-carbon triple bond



all three structures represent acetylene (or ethyne)

## Straight Chain Alkanes

the alkanes are named according to the number of carbon atoms

ends with -ane suffix

root name	# of carbons (n) $\text{H}-(\text{CH}_2)_n-\text{H}$
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

all alkanes have the empirical formula  $\text{C}_n\text{H}_{(2n+2)}$

## IUPAC Nomenclature

naming of carbon chains containing branches (non-straight chain)

- find the longest continuous carbon chain in the structure

this determines the root name

- any carbon not on this continuous chain is a substituent (appendage)

- number the main chain starting from the end closest to a substituent

- the substituents are still named according to the number of carbons

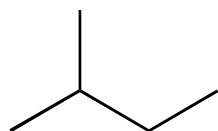
the suffix of the appendages is now -yl instead of -ane

-CH<sub>3</sub>            methyl

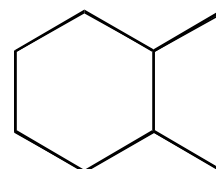
-CH<sub>2</sub>CH<sub>3</sub>       ethyl

- place all substituent names before the root name in alphabetical order

- the substituent must be numbered to indicate the point of attachment to the main chain
- group multiple substituents of the same kind together and label di- tri-, etc.
  - when alphabetizing, the prefixes di-, tri-, n-, t- are ignored  
(the only prefix used for alphabetizing is iso-, explained in common names)
- with a ring compound the number of carbons in the ring determines root name with cyclo- prefix



2-methylbutane



1,2-dimethylcyclohexane

- halogens are named as substituents,  
e.g. fluoro- chloro- bromo- or iodo-

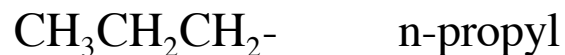
## Common Names

many alkyl substituents have common names

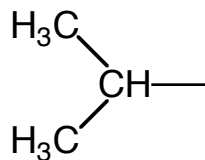
examples: consider propyl

there are two ways an alkyl appendage with three carbons can be attached

any straight chain appendage has the n- prefix



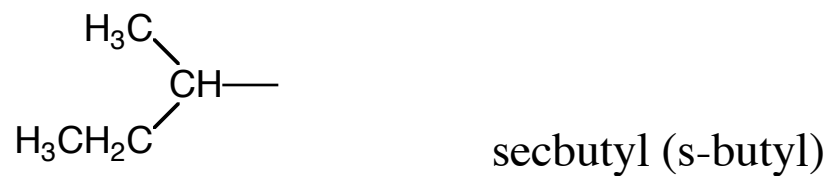
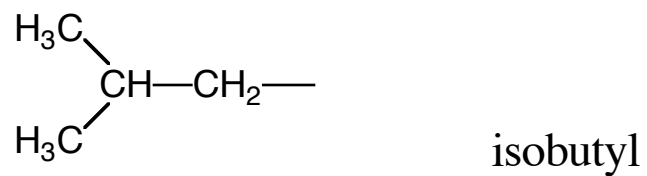
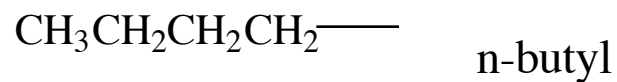
this distinguishes the straight chain compound from the other isomer



isopropyl (1-methylethyl)

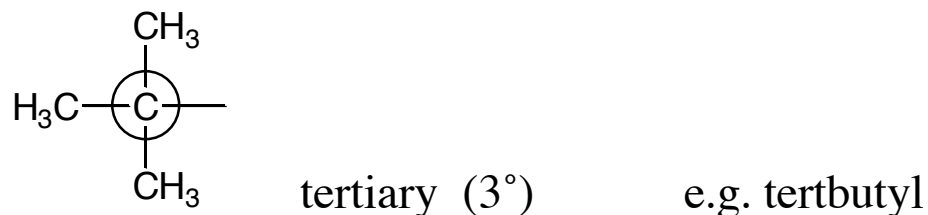
as the alkyl chain gets larger more possibilities exist

consider butane:



the sec- and tert- prefixes for common names are based upon the degree of substitution at the bonded carbon site

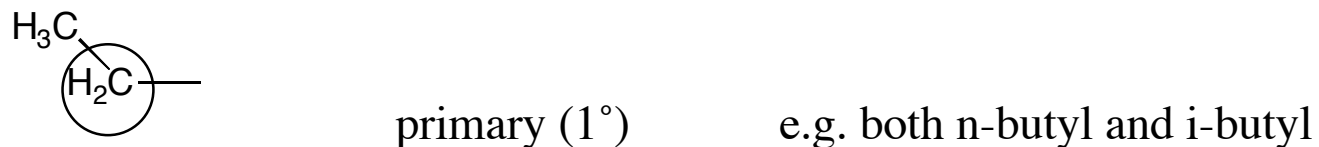
if a carbon substituent is bonded to three other carbon atoms it is called a tertiary carbon



if a carbon substituent is bonded to two other carbon atoms it is a secondary carbon

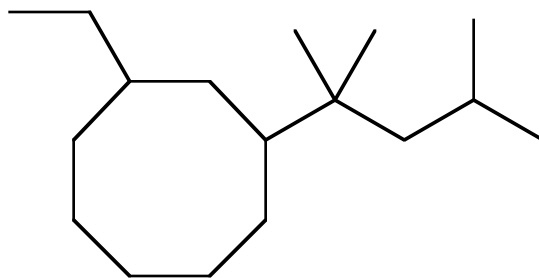


if a carbon substituent is bonded to only one other carbon atom it is a primary carbon



## Complex Alkyl Groups

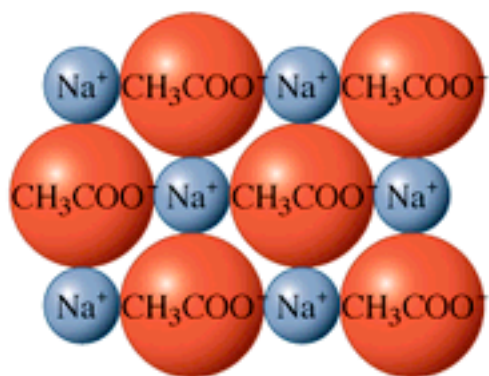
for even more complicated alkyl substituents the structure is named according to the IUPAC rules and the whole appendage is placed in parenthesis



1-ethyl-3-(1,1,3-trimethylbutyl)cyclooctane

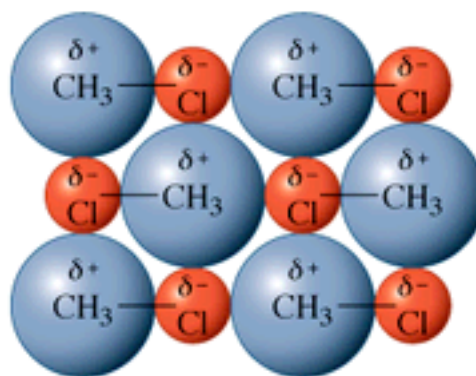
## Attractive Forces in Alkanes

- type of electron correlation between molecules determine the physical properties



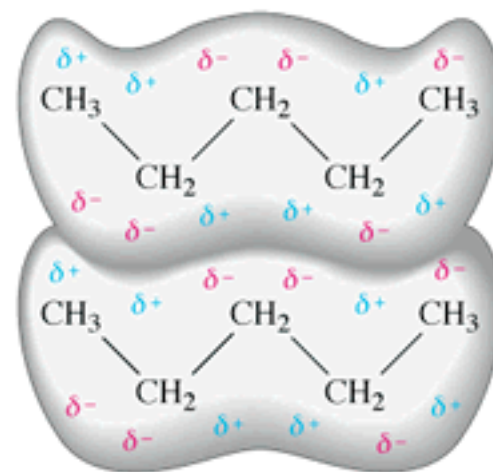
A

coulombic attraction



B

dipole-dipole



C

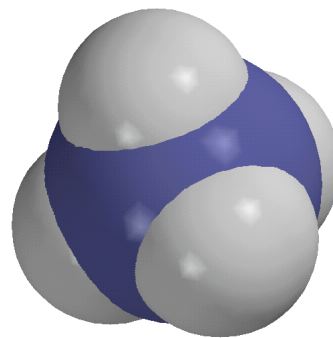
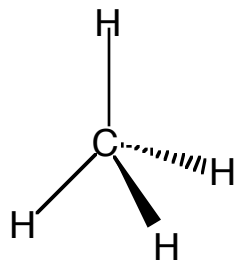
van der Waals forces  
(London dispersion)

## Conformational Analysis of Alkanes

- physical properties of molecules are determined by intermolecular forces  
(forces between molecules)
- the internal structure of a given molecule can affect the energy due to sterics  
(intramolecular interactions)

conformer: different arrangements in space resulting from rotation of  $\sigma$  bonds

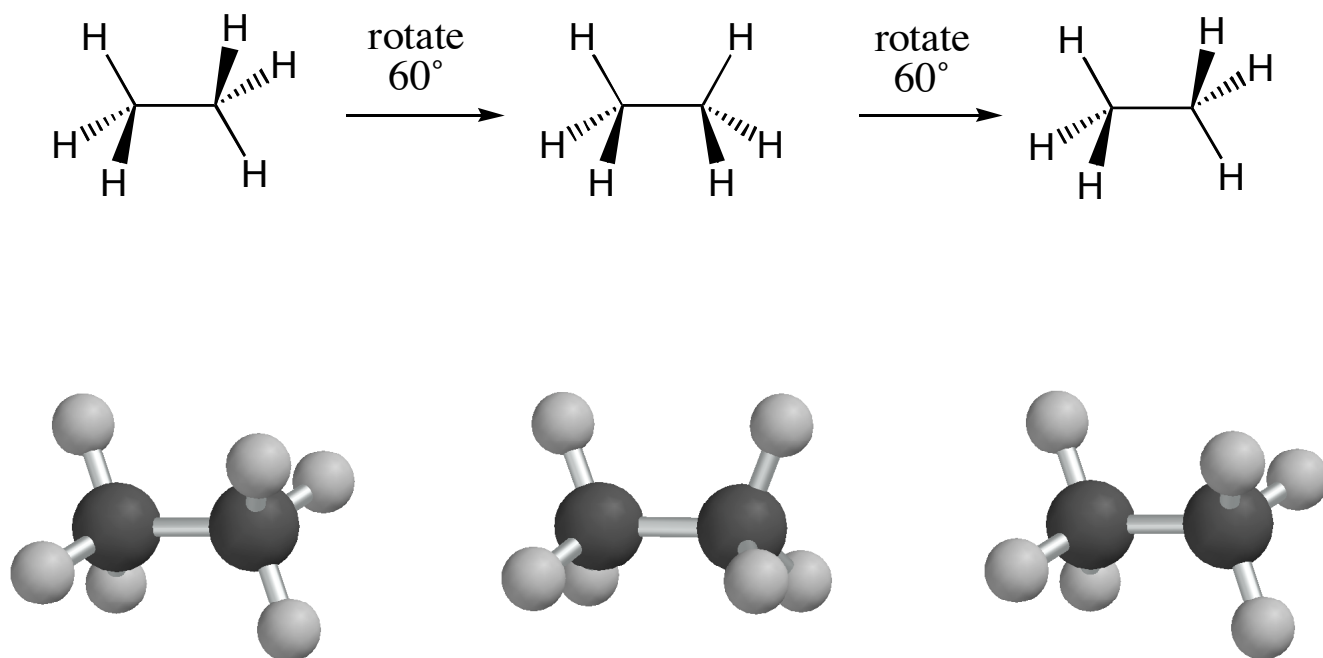
consider methane:



no conformations possible; methane has a given energy value  
(any rotation about the equivalent C-H  $\sigma$  bonds yields the same structure in 3-D)

\*this is not the case with any higher hydrocarbon homologue

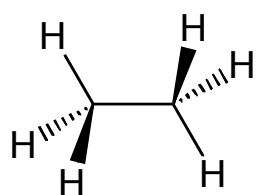
## Conformational Analysis of Ethane



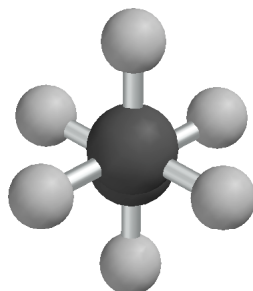
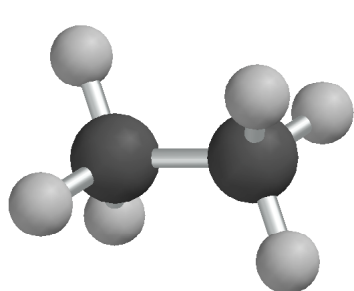
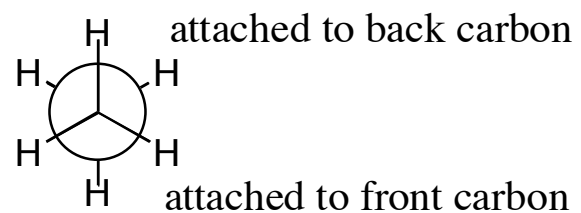
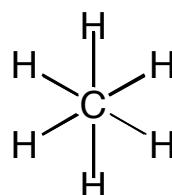
\*these structures do not have the same energy

# Newman Projections

- convenient way to view conformational analysis

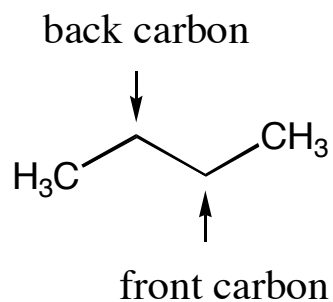


change  
view  
→

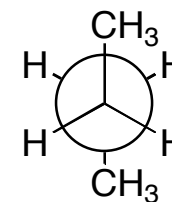


## To Draw Newman Projections

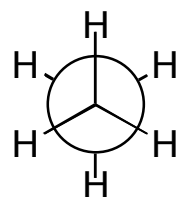
- determine what bond is being considered
- determine which atom is front atom of bond and which is back atom of bond
  - the substituents attached to the front atom are drawn to a point, the substituents attached to the back atom are drawn to a circle
  - the relative angles and orientation of the substituents are maintained



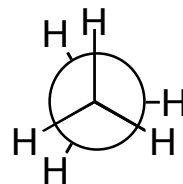
attached to front carbon: methyl group, 2 hydrogens  
attached to back carbon: methyl group, 2 hydrogens



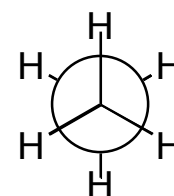
## Newman projections of ethane conformations



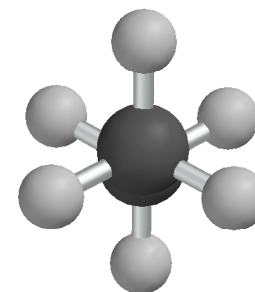
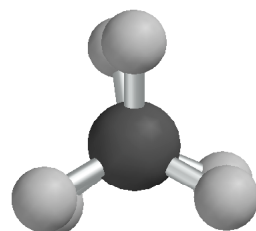
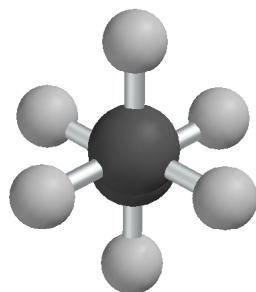
staggered



eclipsed



staggered

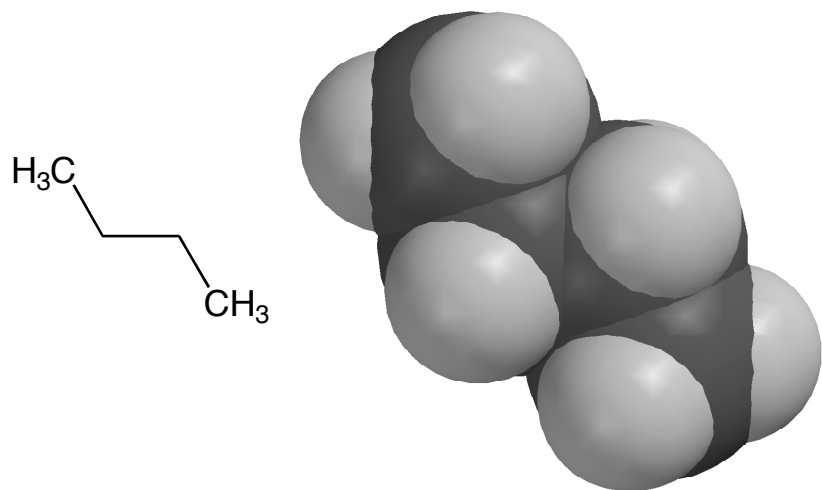


Newman projections demonstrate energetic and spatial interactions of conformers

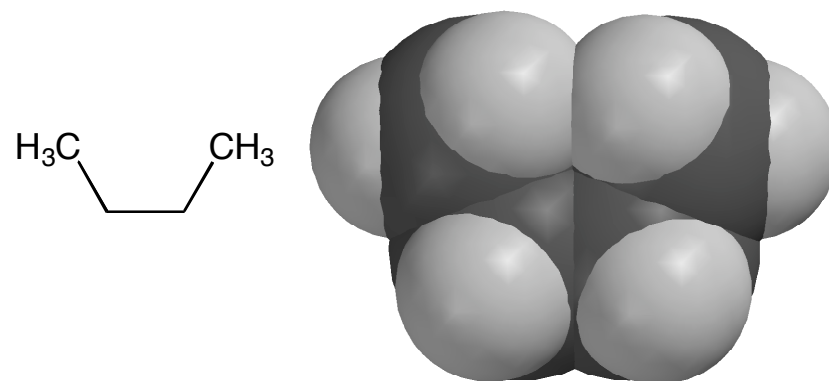
## Eclipsed Conformations are Higher in Energy

Mainly due to sterics

Consider the space filling area of the atoms

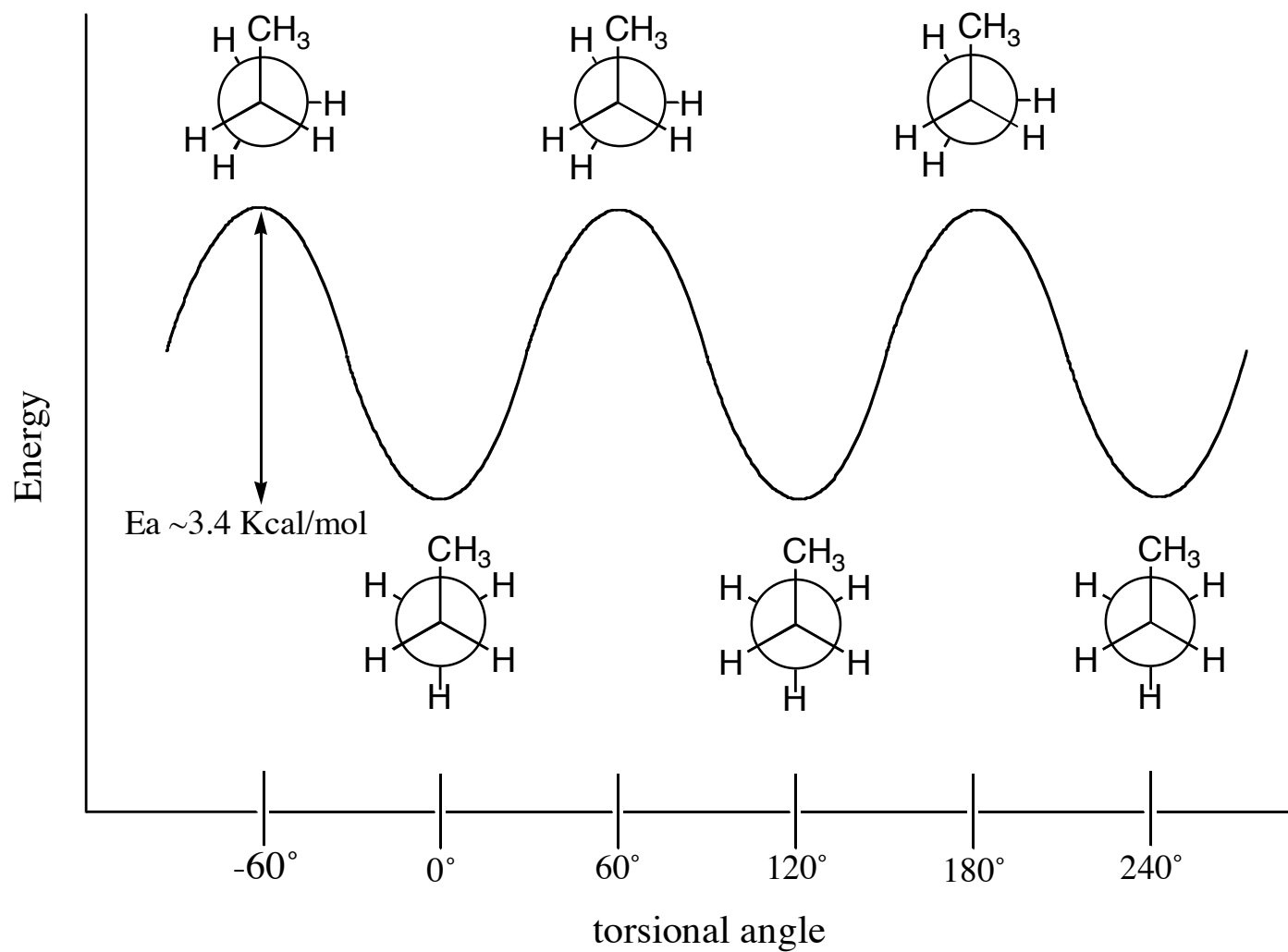


staggered



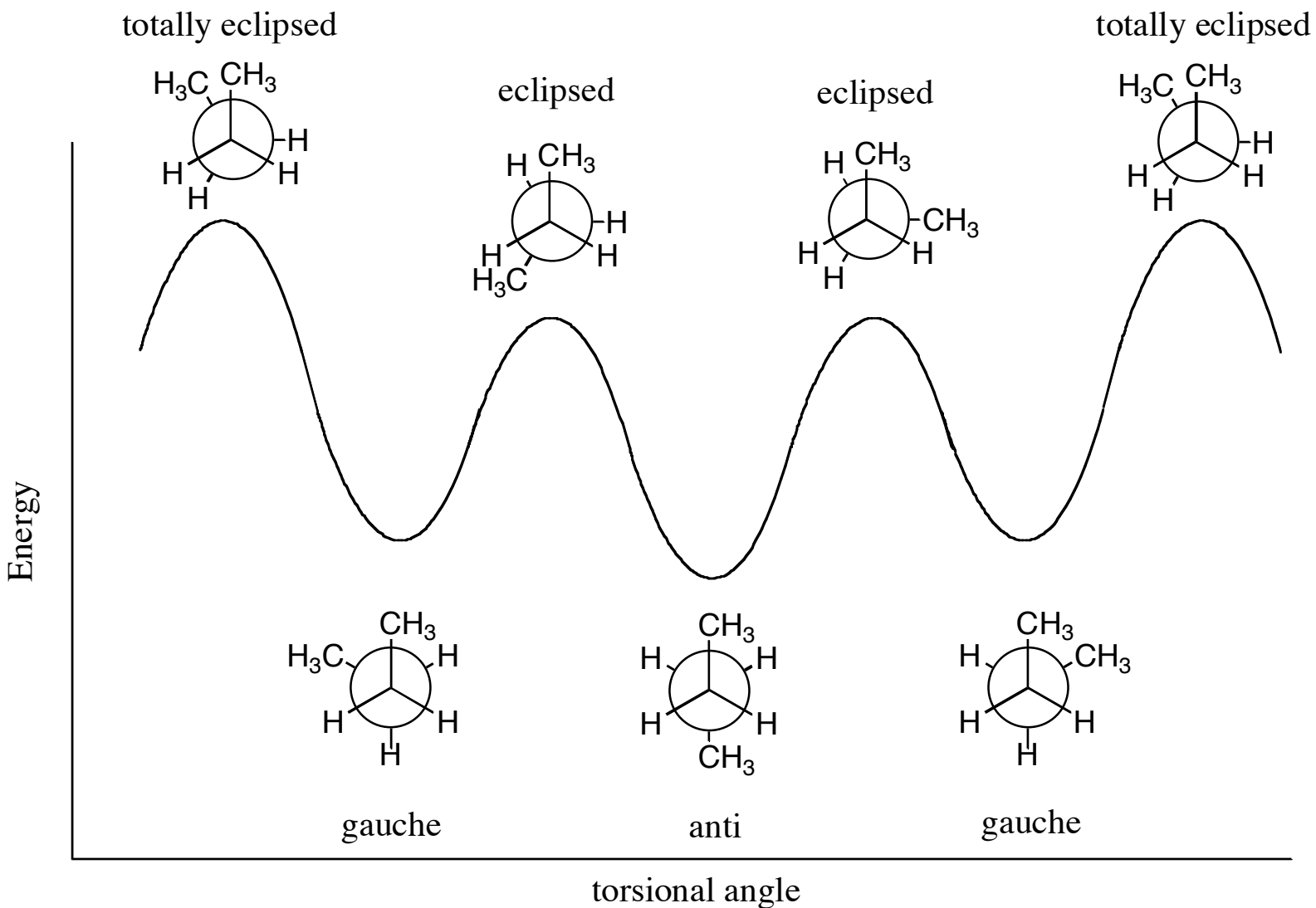
eclipsed

# Conformational Energy Diagram for Propane



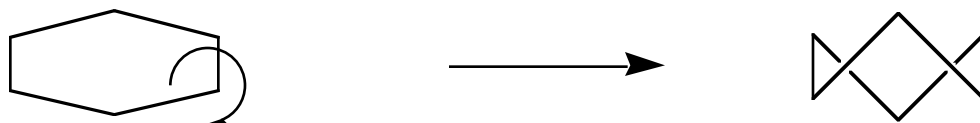
## Different Types of Interactions Arise with Larger Carbon Structures

Consider n-Butane viewing down C<sub>2</sub>-C<sub>3</sub> carbon-carbon bond



## Formation of Rings (Cycloalkanes)

due to the ring the  $\sigma$  bonds cannot rotate to any angle



do not have the same conformational analysis as other alkanes

therefore rings adopt a certain preferred geometry

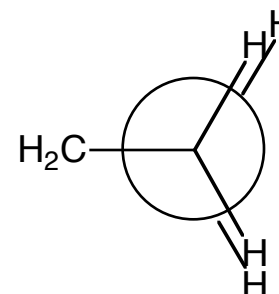
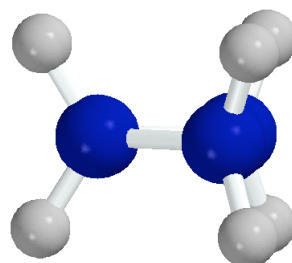
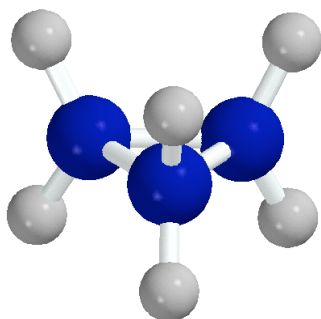
## Ring Strain of Simple Cycloalkanes

ring size	cycloalkane	total ring strain Kcal/mol	ring strain per CH <sub>2</sub> Kcal/mol
3	cyclopropane	27.6	9.2
4	cyclobutane	26.4	6.6
5	cyclopentane	6.5	1.3
6	cyclohexane	0	0
7	cycloheptane	6.3	0.9
8	cyclooctane	9.6	1.2

small rings have large strain

cyclohexane has least amount of strain

## Geometry of Cyclopropane



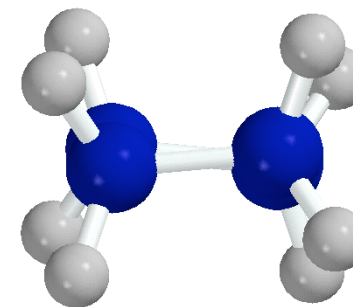
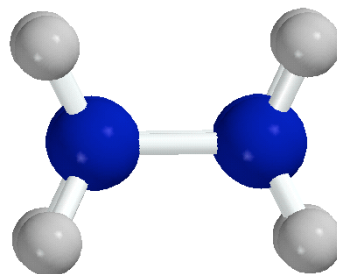
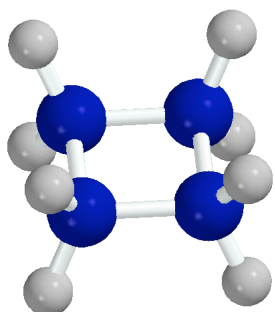
All three carbon atoms must be coplanar

this geometry causes strain due to both small bond angles and torsional strain

## Geometry of Cyclobutane

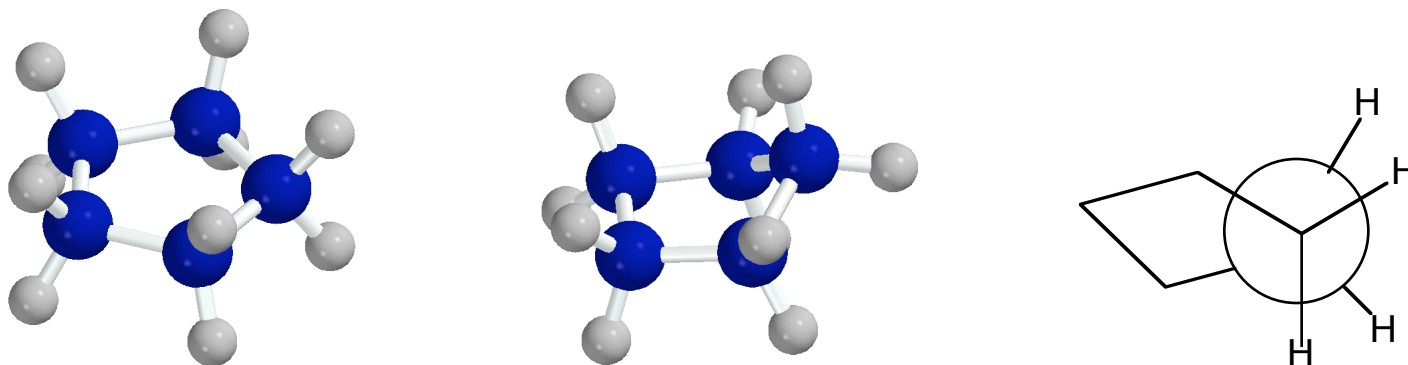
structure if constrained to plane

actual structure



cyclobutane adopts a “puckered” conformation in order to lower torsional strain  
still have high bond angle strain

## Geometry of Cyclopentane



the ring forms a preferred geometry to lower torsional strain

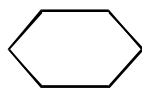


the form is called the “envelope” due to its similarity to a mailing envelope  
still though has both angle strain and torsional strain

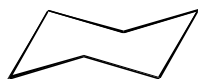
## Geometry of Cyclohexane

cyclohexane has little ring strain

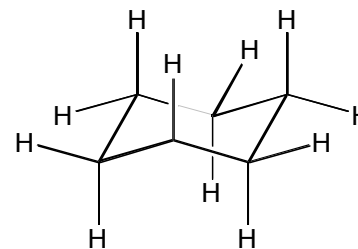
the reason is the ability of the ring to form a stable conformation



planar cyclohexane  
bad bond angles

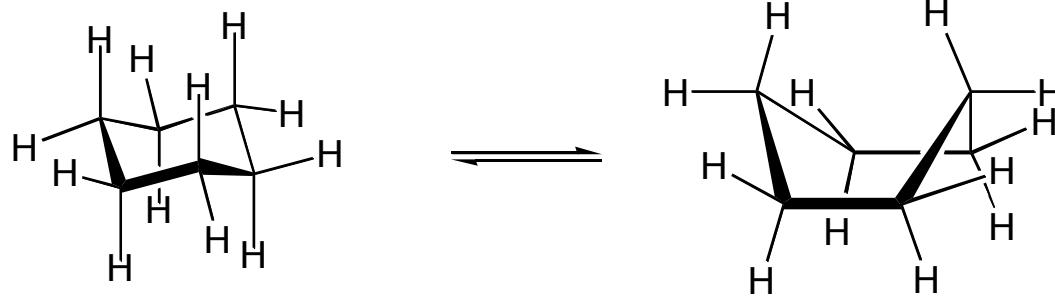


chair cyclohexane  
near perfect  $sp^3$   
bond angles

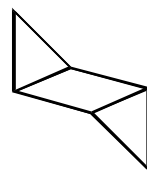
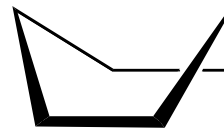


chair with substituents

## Reason for the Names of Various Conformers of Cyclohexane



remove hydrogens



"chair"

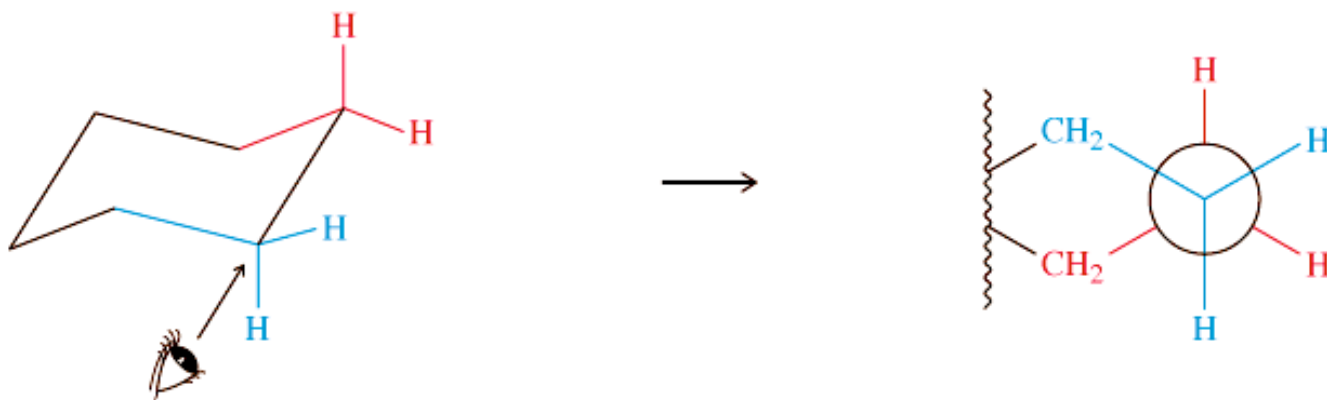
stylized renderings



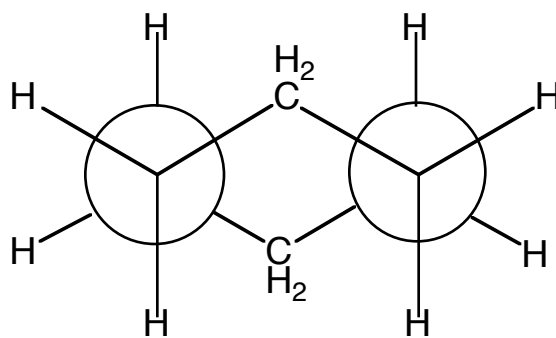
"boat"

## Newman Projection

the lack of torsional strain can be seen in a Newman projection

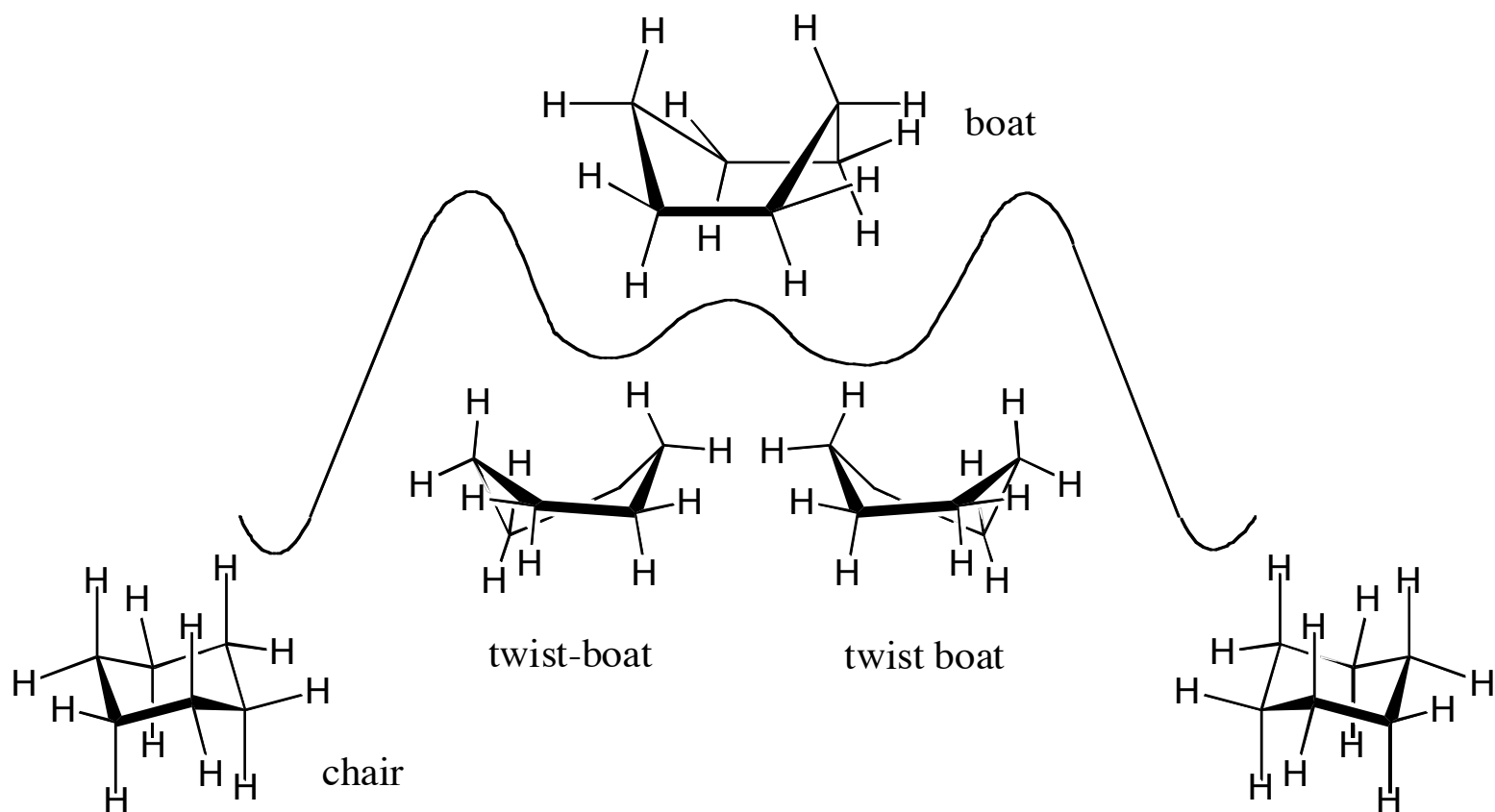


nearly perfect staggered alignment



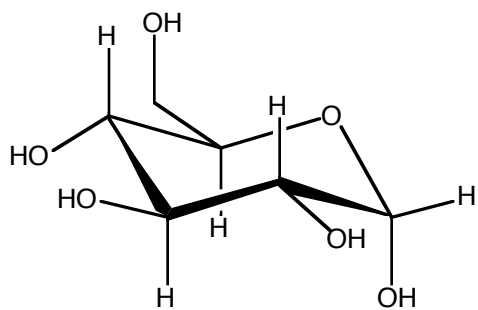
still have some gauche interactions, but energy is low for this conformation

## Chair-Chair Interconversion with Cyclohexane

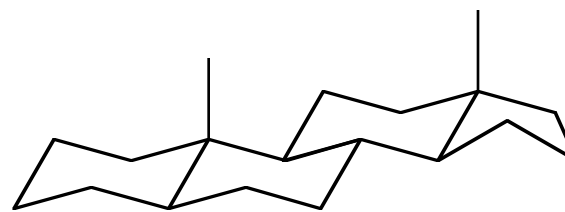


key point - there are two distinct chair conformations for a cyclohexane which can interconvert

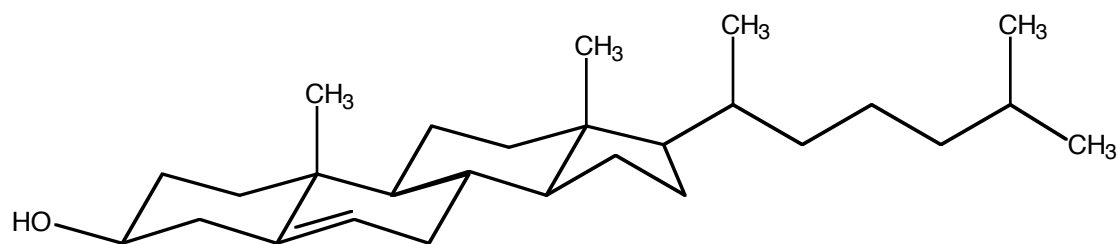
## Types of 6-Membered Rings in Biological Applications



D-glucose



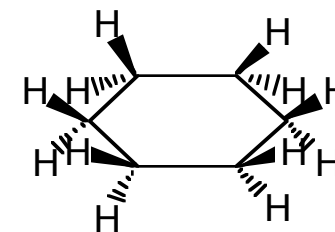
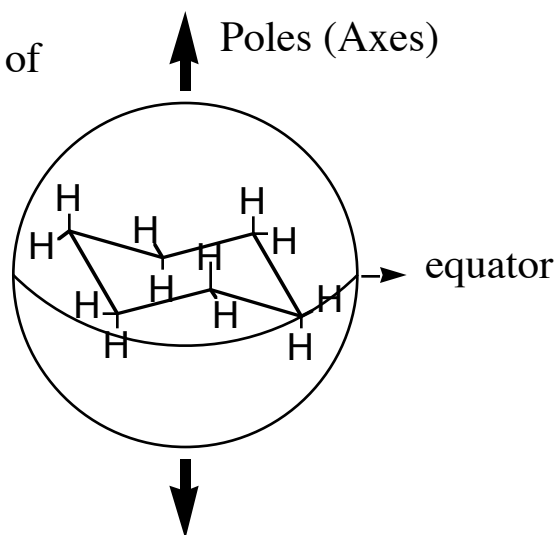
steroid ring junction



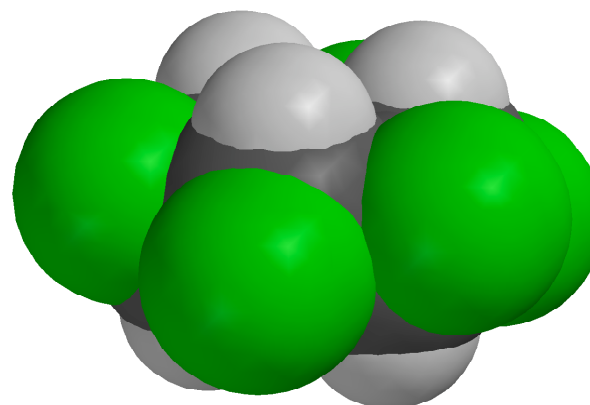
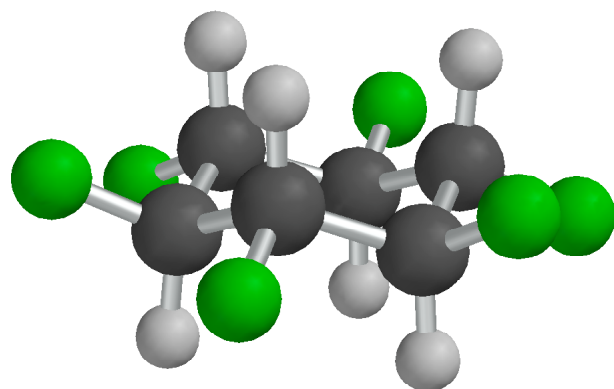
cholesterol

## In a Chair Conformation there are Two Types of Positions

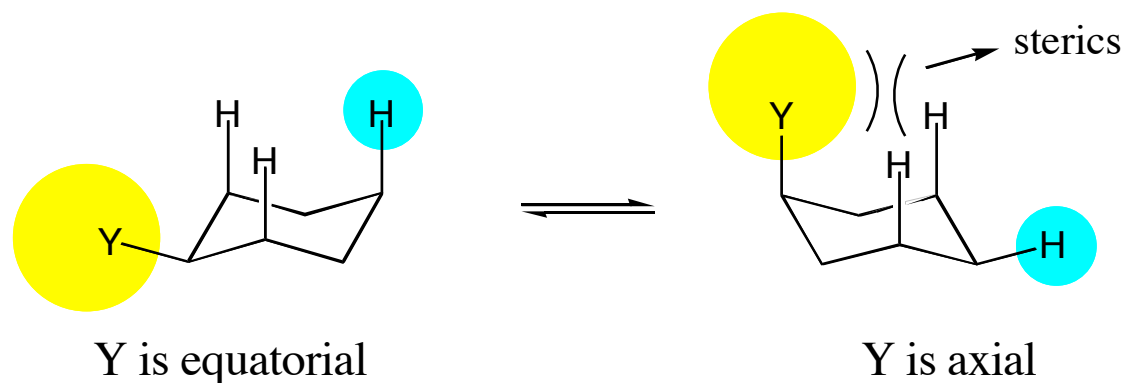
there are two distinct types of hydrogens in the chair conformation:  
axial and equatorial



in a flat conformation  
there is only one type  
of hydrogen



## The Axial and Equatorial Positions have Different Spatial Requirements

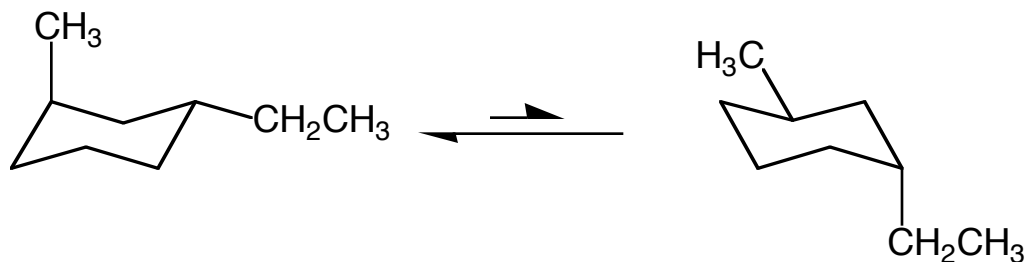


the bigger Y substituent has more steric interactions in an axial position than equatorial

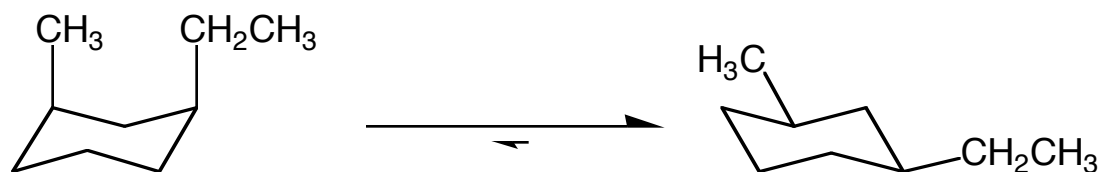
the chair conformation which has the Y group equatorial is therefore more stable

## A Substituent would Prefer to be in an Equatorial Position

if there are two substituents they will compete for the equatorial position



ethyl is bigger than methyl so this trans-cyclohexane would prefer left conformer

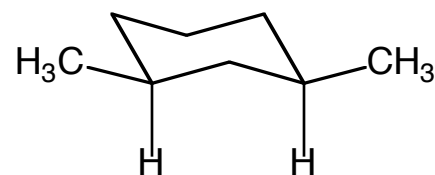
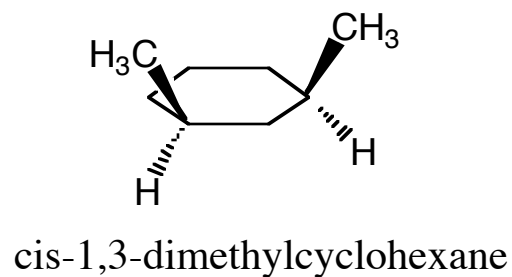


if both substituents can be in the equatorial position

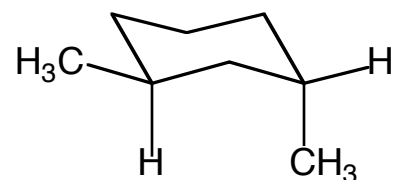
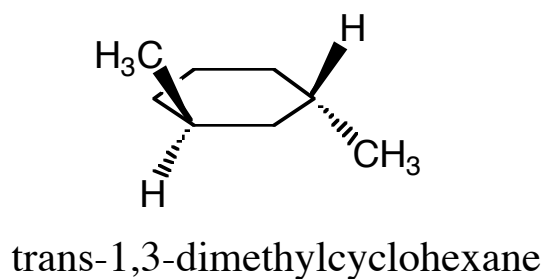
this conformer will be heavily favored

## Don't Confuse Equatorial/Axial with cis/trans

cis/trans ring junction refers to whether both substituents are on the same side or opposite sides of the ring



both methyls equatorial



one methyl equatorial,  
one methyl axial