Alkanes · Introduction to 3D Structures

• Alkanes are hydrocarbons, i.e. organic molecules that contain only carbon (C) and hydrogen (H) atoms.
• Alkanes are unsaturated (have no double/triple bonds), but may have rings.
• Alkanes are generally unreactive and form the "backbone" skeleton of most organic molecules.

1 Basic Organic Nomenclature

Two kinds:
• Common or trivial names
• IUPAC (International Union of Pure and Applied Chemists!), systematic naming system.

1.1 Basic IUPAC Rules

1) Find the longest (main) chain with the maximum number of substituents.
2) Number to give first substituent lowest number (then next lowest etc.): **look for first point of difference**, and **only** IF all other things are equal, number them alphabetically (but **only if all else** is equal).
3) name substituents as "alkyl".
4) multiple substituents use the di-, tri-, tetra- etc. prefixes.
5) substituents ordered alphabetically in the final name.
• **ignore di-, tri-, (unless part of complex substituent!)** and also **sec-** and **tert-** and **other prefixes** that **are hyphenated** when part of a name.
• **Do not ignore iso- and cyclo-** (because these are n**ot hyphenated when part of a name).**
6) **Complex substituents** are numbered so that the **#1 carbon as the one that is attached to the main chain.**
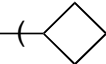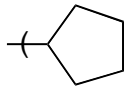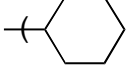
Example:
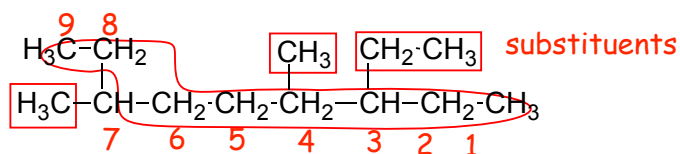
1) longest chain = 9, therefore a substituted nonane
2) start numbering from right, gives lowest numbers for substituents
3) 2 methyl substituents, one ethyl substituent
4) dimethyl and ethyl substituents

3-ethyl-4,7-dimethylnonane

dashes between numbers and names, commas between numbers!!

1.2 Nomenclature Terms You Are REQUIRED to Know

methane	CH_4	$-CH_3$	methyl	-Me		
ethane	C_2H_6	$-CH_2CH_3$	ethyl	-Et		
propane	C_3H_8	$-CH_2CH_2CH_3$	propyl	-Pr		cyclopropyl
		$-CH \begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}$	isopropyl	-i-Pr		
butane	C_4H_{10}	$-CH_2CH_2CH_2CH_3$	butyl	-Bu		cyclobutyl
		$-CH \begin{smallmatrix} CH_2CH_3 \\ CH_3 \end{smallmatrix}$	sec-butyl	-sec-Bu		
		$-CH_2CH \begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}$	isobutyl	-i-Bu		

$$
\begin{array}{c}
CH_3 \\
| \\
-C-CH_3 \\
| \\
CH_3
\end{array}
\qquad \text{tert-butyl} \qquad \text{-t-Bu}
$$

pentane	C_5H_{12}	$-(CH_2)_4CH_3$		cyclopentyl
hexane	C_6H_{14}	$-(CH_2)_5CH_3$		cyclohexyl
heptane	C_7H_{16}	$-(CH_2)_6CH_3$		as above
octane	C_8H_{18}	$-(CH_2)_7CH_3$		as above
nonane	C_9H_{20}	$-(CH_2)_8CH_3$		as above
decane	$C_{10}H_{22}$	$-(CH_2)_9CH_3$		as above
undecane	$C_{11}H_{24}$	$-(CH_2)_{10}CH_3$		as above
dodecane	$C_{12}H_{26}$	$-(CH_2)_{11}CH_3$		as above

Some other substituents that you are also required to know……..

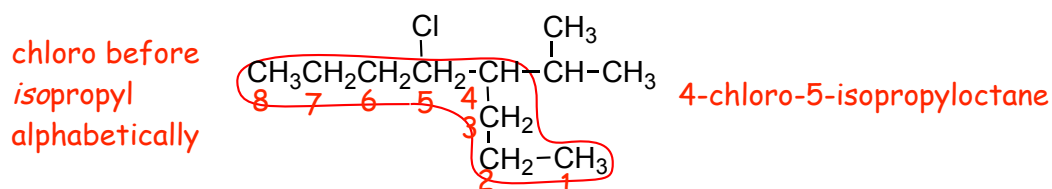-F   fluoro   -Br   bromo   benzene ring as a substituent   phenyl (-Ph)

-Cl   chloro   -I   iodo
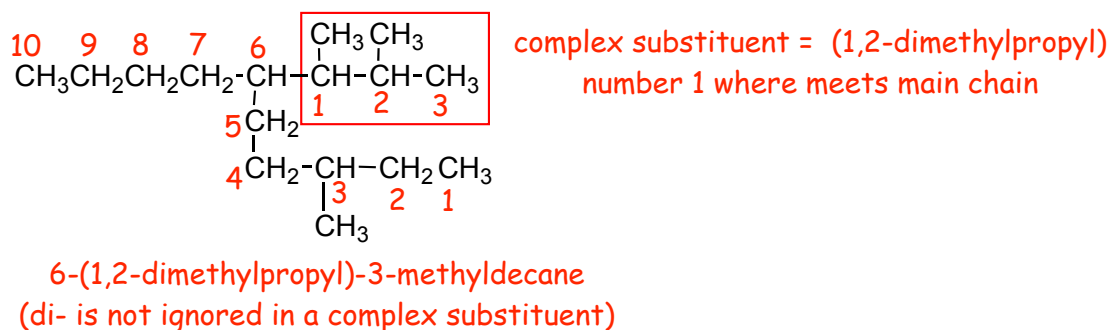
• The halogens are straightforward.
• When the aromatic benzene ring is a substituent it is a phenyl substituent (-Ph).

Example:

chloro before *iso*propyl alphabetically

$$CH_3CH_2CH_2CH_2-\underset{4}{CH}-\underset{}{CH}-CH_3$$
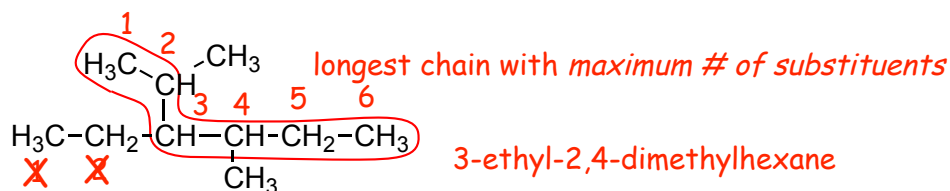
4-chloro-5-isopropyloctane

• **Here**, the substituents get the same numbers numbering from **either end**, 4 and 5. In this case then the substituents are numbered alphabetically, and because chloro- comes before isopropyl alphabetically then we have 4-chloro and 5-isopropy.
• We **only** number substituents alphabetically when **all else is equal**, which is rare!

Example:

complex substituent = (1,2-dimethylpropyl)
number 1 where meets main chain

6-(1,2-dimethylpropyl)-3-methyldecane
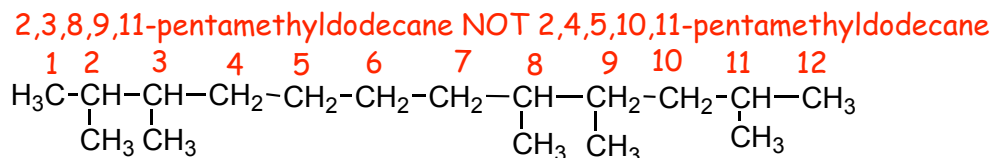(di- is not ignored in a complex substituent)

• The longest chain has **10** carbons, therefore it is a **decane**.
• There is a methyl substituent in the #3-position.
• There is a complex substituent in the #6-position, this substituent is named according to IUPAC rules.
• **Complex substituents** are **always numbered so that the #1 carbon is the one that is attached to the main chain** (the numbering isn't to give the substituents the lowest number in this case), number this way even if this does not generate the longest possible chain
• **Note that the "di" in the complex substituent is not ignored alphabetically (di is ignored alphabetically in all other cases!).**

Alkanes : page 2

Example

H₃C—CH / CH₃ ... longest chain with *maximum # of substituents*

3-ethyl-2,4-dimethylhexane

• When there are **two** possible longest chains, as in this case, choose the one that is **most branched**, i.e., has the largest number of substituents.
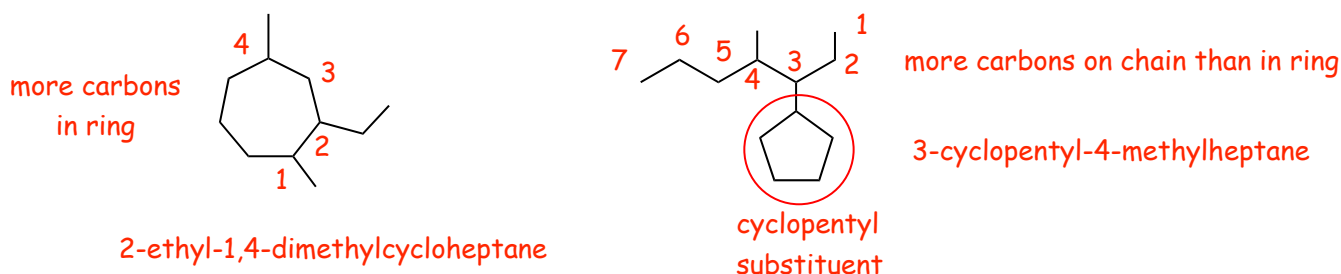
Example

2,3,8,9,11-pentamethyldodecane NOT 2,4,5,10,11-pentamethyldodecane

$$\underset{1}{H_3C}-\underset{2}{CH}-\underset{3}{CH}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_2}-\underset{8}{CH}-\underset{9}{CH_2}-\underset{10}{CH_2}-\underset{11}{CH}-\underset{12}{CH_3}$$

with CH_3 groups at positions as shown

• look for **the first point of difference**, in this case the number of the second substituent
• Therefore, number starting at the left-hand end (2,3,8,9,11), even though numbering form the right (2,4,5,10,11) would "add up" to a smaller number
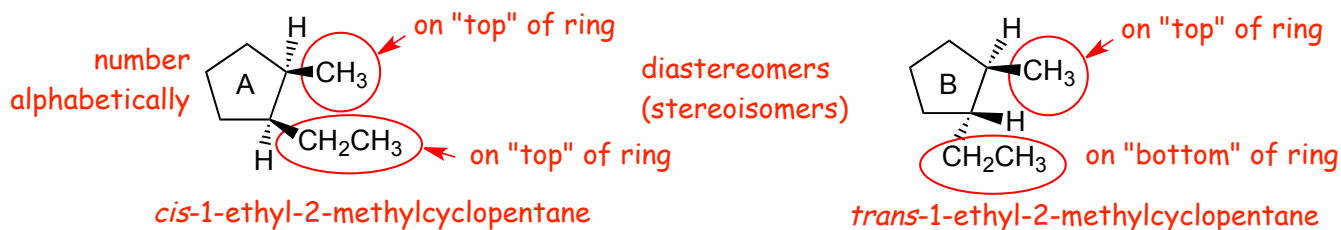
1.3 Cyclic Alkanes
• The rules are the **same**, find the longest chain, if it is in a ring, then the main chain becomes a **cyclo**alkane.

more carbons in ring

more carbons on chain than in ring

3-cyclopentyl-4-methylheptane

cyclopentyl substituent

2-ethyl-1,4-dimethylcycloheptane

• If the longest chain is **not** in the ring, then the ring is the substituent (example on the right, above).
• We need to decide whether the longest chain is not in a ring, or in a ring, we don't look for a longest chain that includes both atoms in a chain and also outside a chain, the numbering wouldn't work well if we tried to do that!
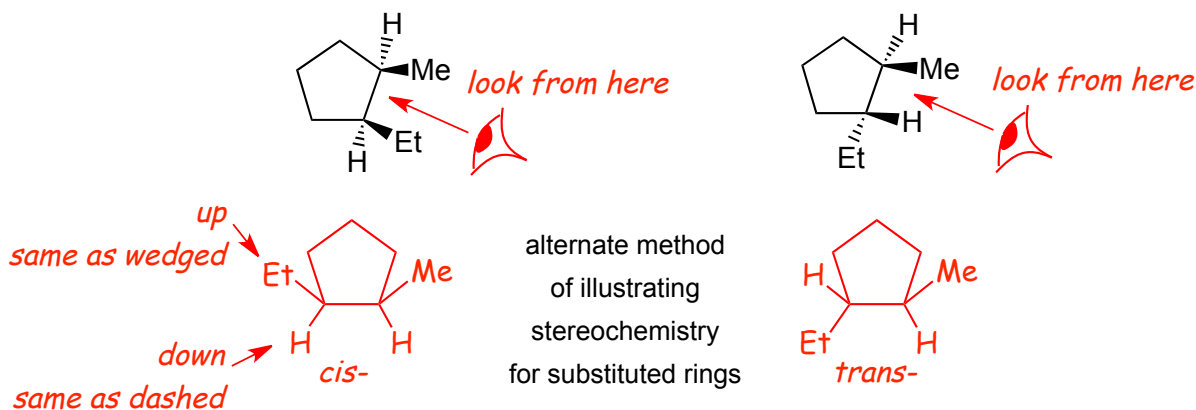
1.4 Stereoisomers of Cyclic Alkanes
• Remember, a wedged bond means pointing "up" and a dashed bond means pointing "down".

number alphabetically

on "top" of ring

diastereomers (stereoisomers)

on "top" of ring

on "top" of ring

on "bottom" of ring

cis-1-ethyl-2-methylcyclopentane

trans-1-ethyl-2-methylcyclopentane

• In A, the methyl and ethyl groups both point "up", both are both on the same "side" of the cyclopentane ring (both on "top"), this is a *cis*-isomer.
• In B, the methyl group points "up" and the ethyl group points "down", they are on opposite sides of the cyclopentane ring (one on "top" the other on the "bottom", this is a *trans*-isomer
• They differ in the way that the atoms point in space, they are a pair of **stereoisomers** (diastereomers).
• **Note**, in the structure on the left the substituents were numbered **alphabetically** (ethyl before methyl) **only** because in this case **everything else was equal**, the substituents would have been 1 and 2 whichever way we numbered.

Alternate Method for Drawing Ring Structures to Illustrate Stereochemistry

look from here

look from here

up
same as wedged

down
same as dashed
cis-

alternate method
of illustrating
stereochemistry
for substituted rings

trans-

• "Looking" from the side indicated by the eyeball clearly indicates which substituents are on "top" of the ring and which are on the "bottom".
• This alternate drawing method of representing stereochemistry on rings uses bonds that point up or down, to represent dashed/wedged bonds, assuming that you are looking at the structure towards the relevant bond.

2 Conformations of Alkanes

• A conformation is the arrangement of the atoms of a structure in space that can move as a result of rotation around a single covalent bond.
• Conformations represents the different shapes that a structure has as a result of rotations around single bonds.
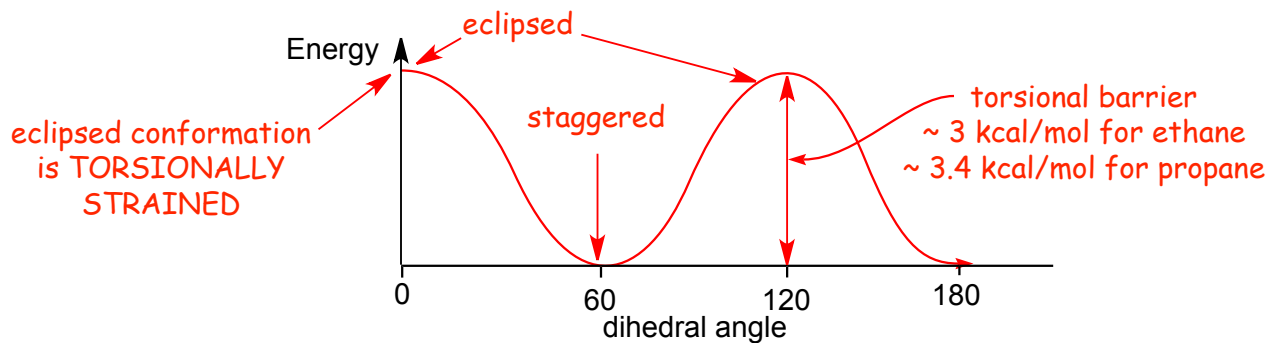
2.1 Acyclic Alkanes

Methane: Tetrahedral by VSEPR *(remember: VSEPR minimizes the total energy of the electrons)*

$109°$ or... $109°$ or... $109°$ etc.
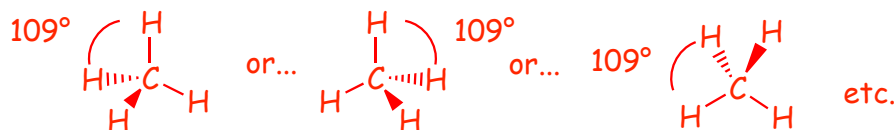
• Drawing the tetrahedral geometry in different orientations, but all have TWO plain and one wedged and one dashed bond.
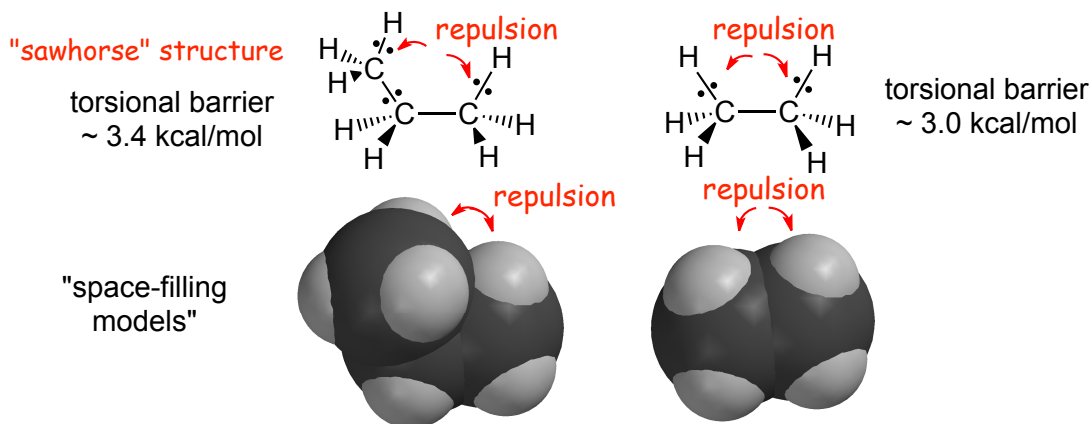
Ethane - Is conformationally "mobile", meaning that rotation around the single C-C bond is energetically facile and rapid. Below are shown two "3D" structures, using wedged/dashed bond formalism (also sometimes known as "sawhorse" structures) that illustrate the molecular geometry.
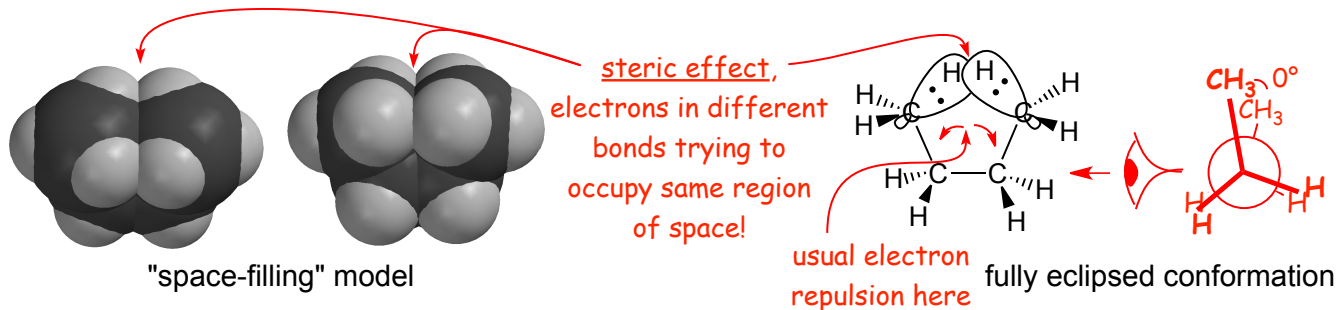

"sawhorse" structure

no change in C–C
bonding upon
rotation

back + top

rotation

front + bottom

$60°$ dihedral angle

staggered conformation

Newman
Projection

repulsion raises the
electron energy
THREE
C-H/C-H repulsions

repulsion

$0°$

eclipsed
conformation

Energy vs. dihedral angle diagram with labels: eclipsed, staggered, eclipsed conformation is TORSIONALLY STRAINED, torsional barrier ~ 3 kcal/mol for ethane ~ 3.4 kcal/mol for propane. Axis marks: 0, 60, 120, 180, dihedral angle.

• The eclipsed conformation is higher in energy due to **torsional strain**.

Propane versus Ethane

"sawhorse" structure
torsional barrier ~ 3.4 kcal/mol
repulsion
repulsion
torsional barrier ~ 3.0 kcal/mol

"space-filling models"
repulsion
repulsion

• –H vs. -CH3. results in more repulsion in the eclipsed conformation in propane compared to ethane.
• Propane has slightly more torsional **strain** energy than ethane.

Butane

"space-filling" model

steric effect, electrons in different bonds trying to occupy same region of space!

usual electron repulsion here

fully eclipsed conformation

CH_3 0°
CH_3

• **Two** unfavorable interactions in the fully eclipsed conformation of butane that contribute to torsional strain,
1) an electron repulsion effect, and 2) a steric effect.
• A steric effect is the increase in electron energy that occurs when two sets of electrons attempt to occupy the same region of space.
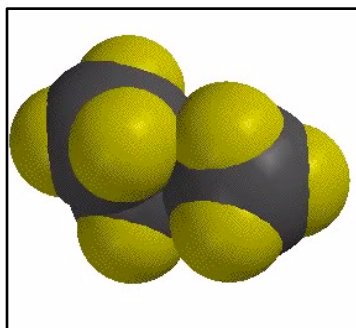

Visualize the Difference Between Electron Repulsion and the Steric Effect

Energy vs –CH₃/–CH₃ dihedral angle diagram:

totally eclipsed — H₃C CH₃ / H H / H

gauche — CH₃ CH₃ / H H / H

eclipsed — H CH₃ / H H / CH₃

anti — CH₃ / H H / H H / CH₃

maximum TORSIONAL STRAIN in totally eclipsed conformation

~ 4.6 kcal/mol

~ 0.9 kcal/mol

~ 3.8 kcal/mol

x-axis: 0   60   120   180

–CH₃/–CH₃ dihedral angle
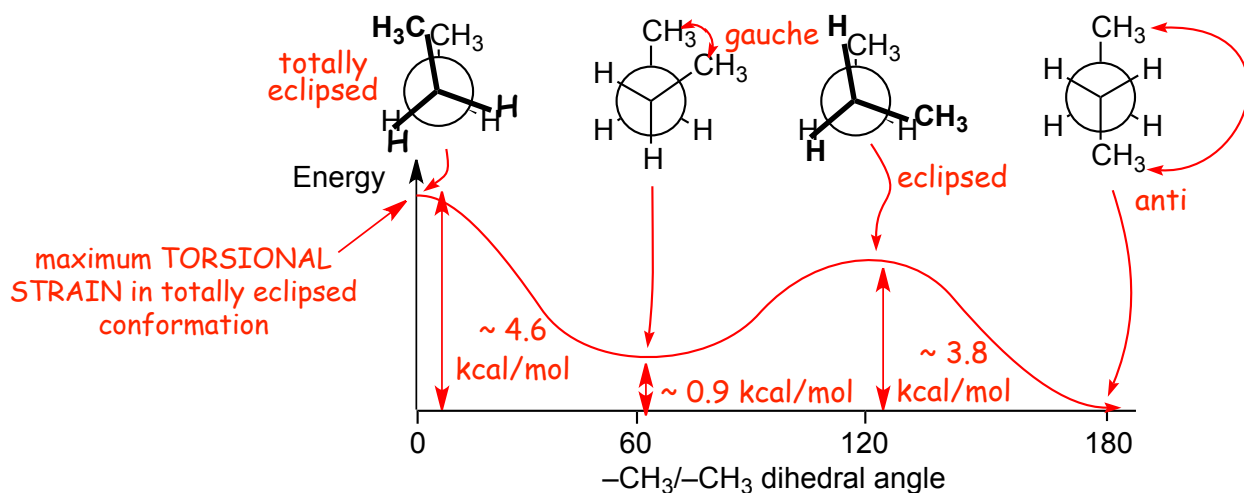
• Although we identify and give special names to some of the conformations at energy minima and maxima, don't forget that there are actually an **infinite** number of conformations, and that at room temperature, butane will explore all of them pretty rapidly, although it **will** spend more time in the conformations at the energy minima.

Alkane Chains

$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$
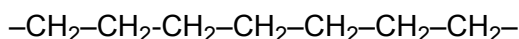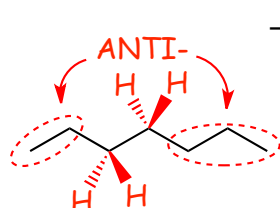
ANTI-

*all of the large alkyl groups are ANTI-
at each C-C bond in the "zig-zag"*

• When we draw alkyl chains in the usual "zig-zag" way, we are doing more than just indicating the positions of the carbon atoms, we are drawing the chain in such a way that ALL of the large alkyl groups are ANTI-with respect to each other for all of the C-C bonds in the chain, i.e. we are drawing the lowest energy conformation, the **all anti** conformation.

Example Problem: Draw a 3-D sawhorse structure AND Newman projection for the lowest energy conformation for internal rotation around the C2-C3 bond in 3-methylpentane, looking from C2 to C3
• The Newman projection "looks" down the relevant bond:

unavoidable gauche interaction

largest groups anti
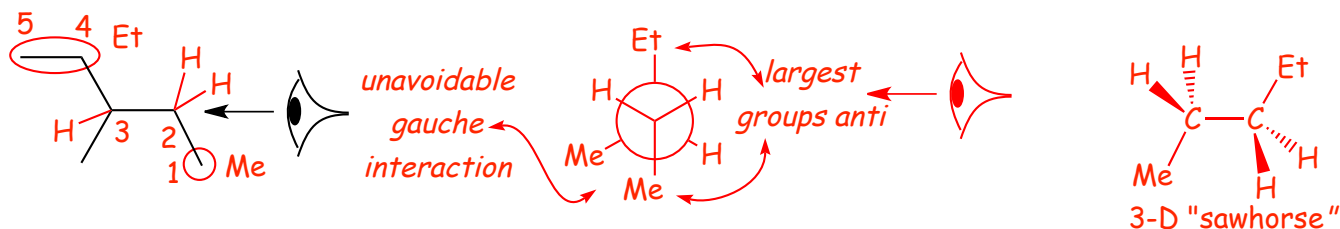
3-D "sawhorse"

• The 3-D sawhorse structure "looks" at the relevant bond from the side


OR (rotate a little)   but NOT
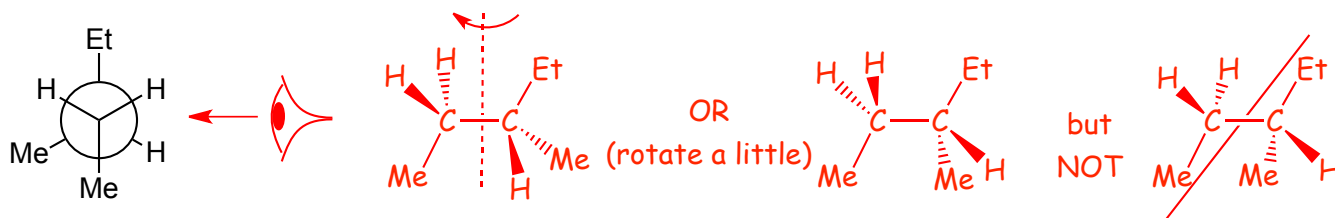
• Either of the first two structures are good, they just have a slightly different perspective, the left hand one is tilted a little to the "right", the one in the middle is tilted a little to the "left", so that the atoms behind can be seen, the structure to the far right does not have reasonable perspective, the wedged/dashed bonds do not make sense.

Example Problem: draw a Newman projection and 3-D sawhorse structure for the lowest energy conformation for internal rotation around the C3-C4 bond in 2,3,4,4-tetramethylhexane
• **First** convert the IUPAC name into a line-angle structure…..
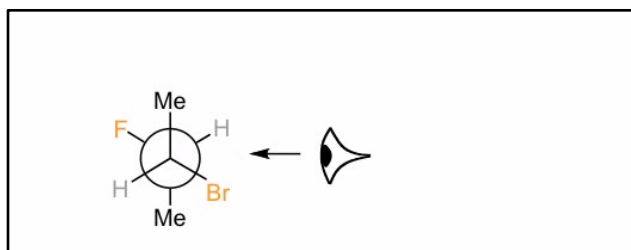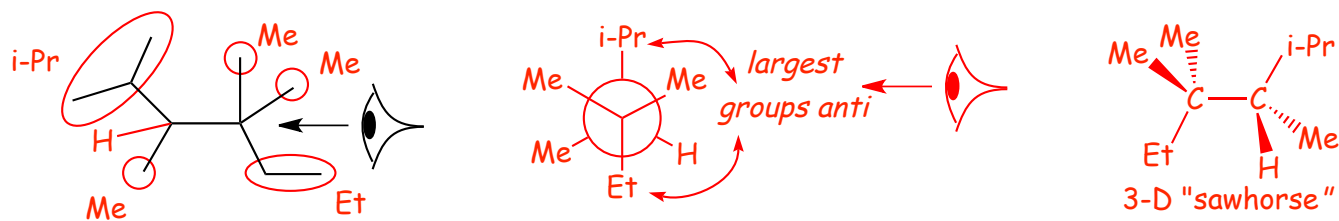
Visualize Drawing a 3-D/Sawhorse Structure from a Newman Projection (and how to get the perspective correct)
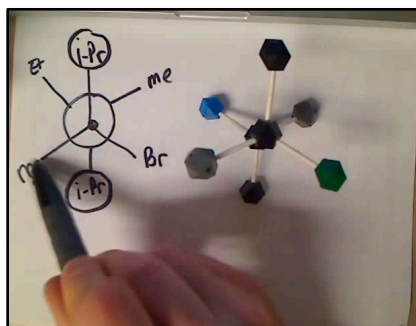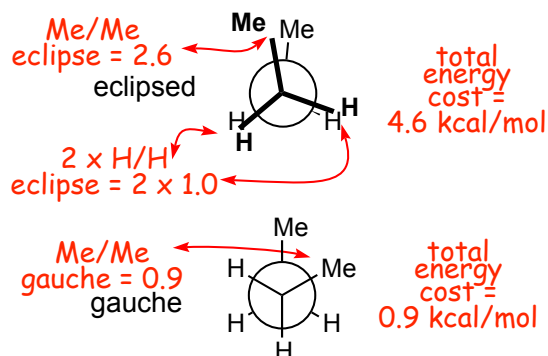

Visualize Drawing and/Sawhorse Structure from a Newman Projection Using a Model Kit (and how to get the perspective correct)

2.2 Conformational Energy Barriers

The energy increases associated with electron repulsion and steric effects in alkane conformations can be quantified (see table). You should **not** memorize these numbers.

Example Problem: Give the energy required to attain the fully eclipsed and gauche conformations of butane

Me/Me eclipse = 2.6
eclipsed
2 x H/H eclipse = 2 x 1.0
total energy cost = 4.6 kcal/mol

Me/Me gauche = 0.9
gauche
total energy cost = 0.9 kcal/mol

• agrees with energy diagrams above

ECLIPSING Interactions	Energy kcal/mol	GAUCHE Interactions	Energy kcal/mol
H / H	~1.0	Me / Me	~0.9
H / Me	~1.4	Et / Me	~0.95
Me / Me	~2.6	i-Pr / Me	~1.1
		t-Bu / Me	~2.7

2.3 Cyclic Alkanes

Example: Cyclopropane

orbital overlap is poor for sp³ angle of ~ 109°

60° NOT ~ 109°

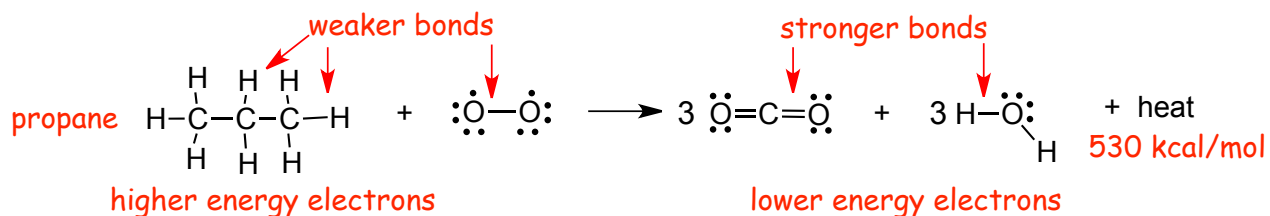*ALL eclipsing interactions*
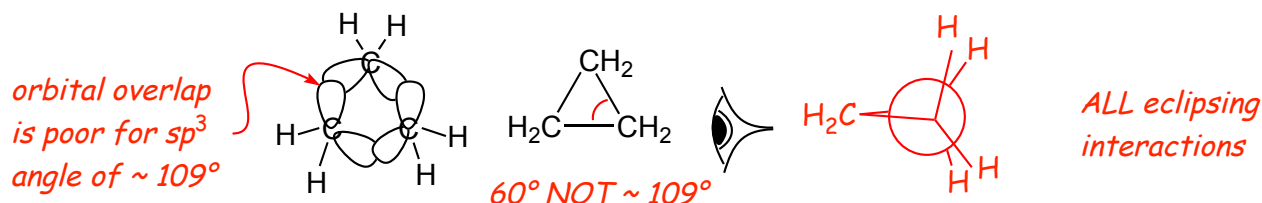
• Cyclopropane has considerable **strain energy**, due to:
1) eclipsing interactions (see Newman projection)
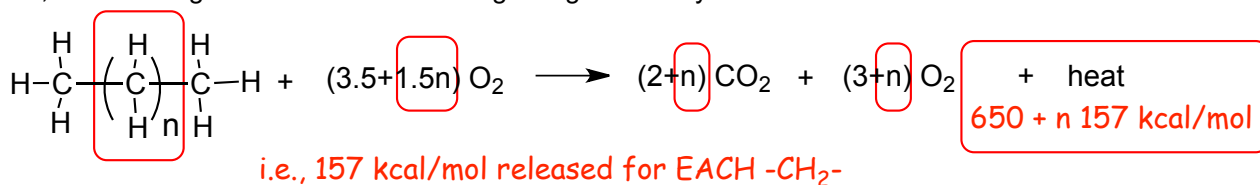2) weak bonds (high energy electrons) due to poor overlap of A.O.s

Measuring strain energy using combustion analysis: Alkanes (e.g. propane) burn according to the following:
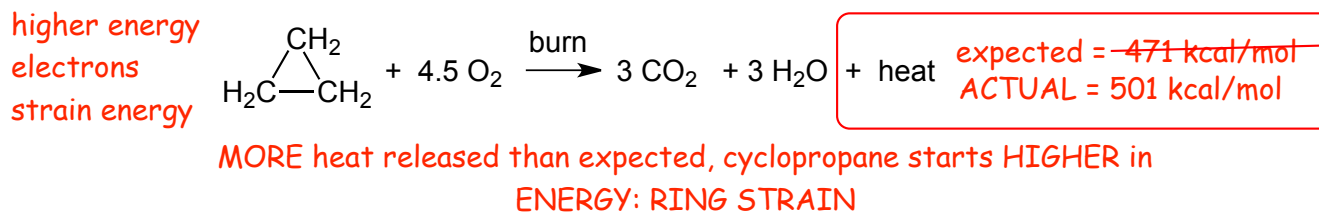
$$propane + 5\ O_2 \xrightarrow{burn} 3\ CO_2 + 4\ H_2O + heat$$

measure the heat
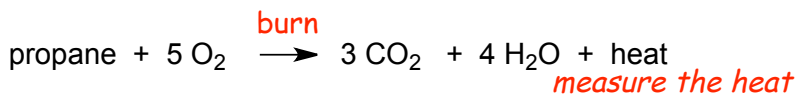
• The heat energy comes from the energy of the electrons in the C-H and C-C bonds of a hydrocarbon and the oxygen, for example, propane:

weaker bonds   *stronger bonds*

propane $H-C-C-C-H$ + $:\ddot{O}-\ddot{O}: \longrightarrow$ 3 $\ddot{O}=C=\ddot{O}$ + 3 $H-\ddot{O}:$ + heat

higher energy electrons   *lower energy electrons*   530 kcal/mol

• The C=O and O-H bonds in the carbon dioxide and water are stronger that the C-H, C-C and O-O bonds in the propane and oxygen, stronger bonds mean lower energy electrons, the electrons "go" from higher energy to lower energy upon burning, this electron energy is released in the form of heat (and light).
• The amount of heat that is released upon burning a hydrocarbon depends upon the number of C-C and C-H bonds, and so the generic formula for burning straight chain hydrocarbons is:
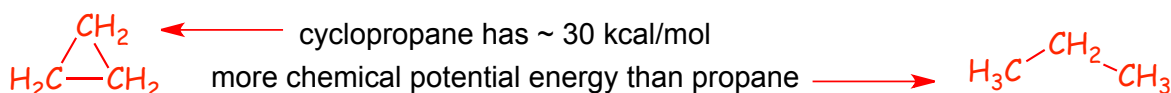
$$H-C-(C)_n-C-H + (3.5+1.5n)\ O_2 \longrightarrow (2+n)\ CO_2 + (3+n)\ O_2 + heat$$

650 + n 157 kcal/mol

i.e., 157 kcal/mol released for EACH -CH₂-

• Thus 3 x 157 = 471 kcal/mol would be expected be released for burning cyclopropane on this basis.

higher energy electrons strain energy

$$cyclopropane + 4.5\ O_2 \xrightarrow{burn} 3\ CO_2 + 3\ H_2O + heat$$

expected = ~~471 kcal/mol~~
ACTUAL = 501 kcal/mol

*MORE heat released than expected, cyclopropane starts HIGHER in ENERGY: RING STRAIN*

• **More** energy is released than expected due to the **strain energy** in the cyclopropane.
• The **more strain energy** molecule "has", the **more heat is released** upon burning:

ring strain ~ 501 - 471 ~ 30 kcal/mol, thus:

cyclopropane has ~ 30 kcal/mol more chemical potential energy than propane $\longrightarrow$ $H_3C-CH_2-CH_3$

Strain Energies as a Function of Ring Size for Cycloalkanes

| angle (assume flat)	cycloalkane	# of eclipsing interactions	strain energy kcal/mol
60	△	3	27.3
90	□	4	26.5
108 (almost 109!)	⬠	5	6.2
120	⬡	6	0 !!!
128	⬣	7	6.2

How do we explain the trends in strain energy in the table? **Quite simply, the rings are not flat!**

Cyclobutane

twists to reduce eclipsing interactions
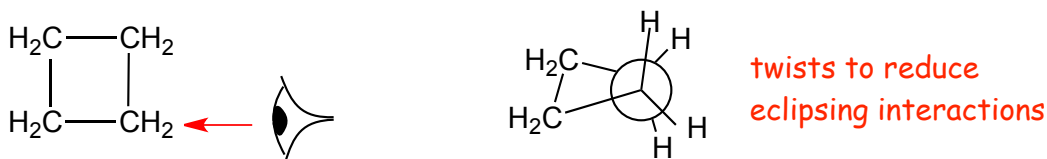
• The ring "puckers" (twists) to decrease eclipsing, however, there are still 4 eclipsing interactions.
• The overall ring strain for cyclobutane is similar to that for cyclopropane.

Cyclopentane - Adopts "envelope" structure:

"envelope" conformation further twisted to reduce the eclipsing interactions
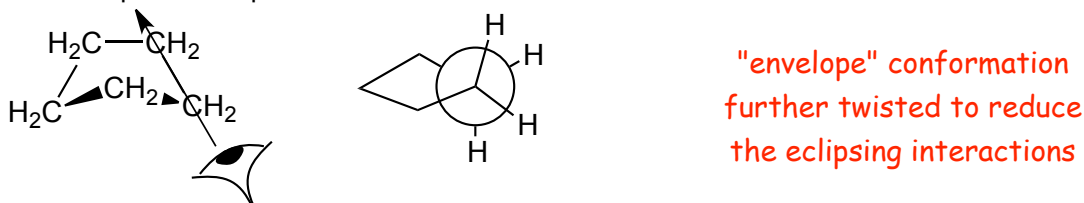
• The 5 eclipsing interactions are now small as a result of twisting into an "envelope" conformation, which is almost a staggered conformation (but not quite!).
• The envelope "migrates" around the ring, i.e. the carbon that "points up" rapidly changes position around the ring.

2.4 Cyclohexanes
• **Cyclohexane has zero ring strain (minimal total electron energy!)**
• The lowest energy conformation is the "chair".

these 2 carbons behind the page

● in plane of page

all bond angles ~109°
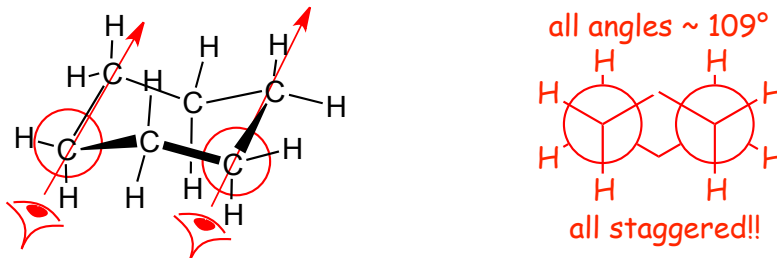all staggered conformation

these 2 carbons in front of page
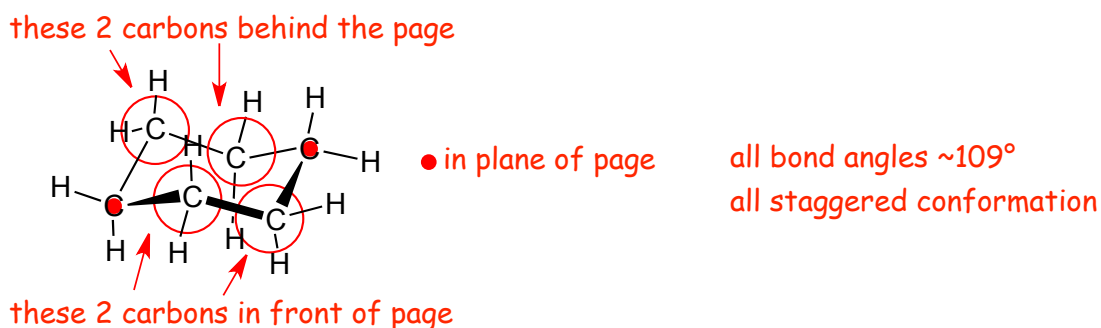
• As the chair is drawn, 2 carbons are **behind** the plane of the paper, 2 are **in** the plane of the paper, and 2 are **in front** of the plane of the paper.

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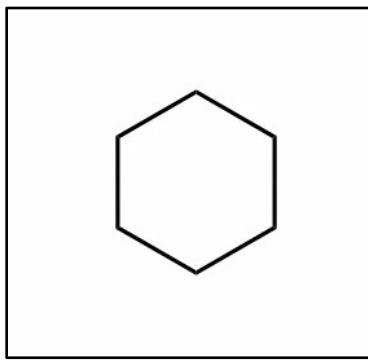
Visualize the Cyclohexane Chair

• The chair is **completely staggered** (it has zero eclipsing interactions).

all angles ~ 109°

all staggered!!

• The chair has all bond angles ~109·, AND, it is completely staggered, which accounts for the zero-ring strain, in turn this accounts for the very high frequency cyclohexanes and related 6-membered rings are encountered in nature.
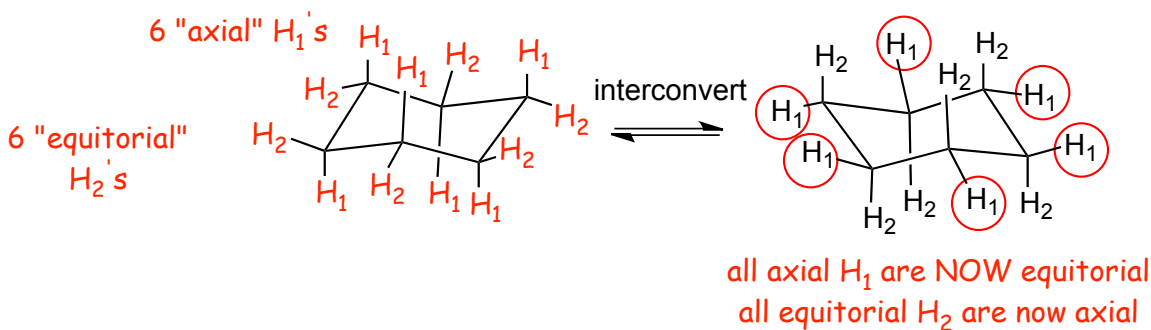• Another conformation is the boat:

all angles ~ 109°
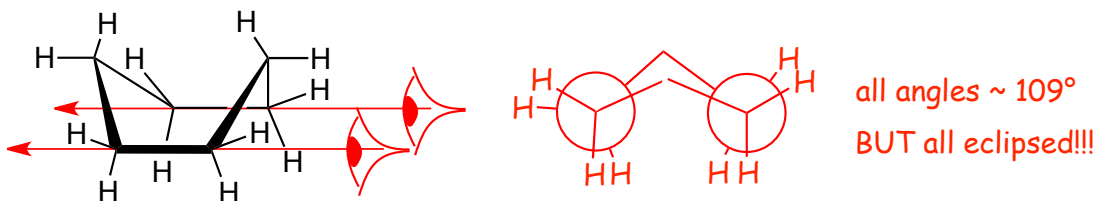
BUT all eclipsed!!!

• The boat does have all bonds angles ~109°, **but**, it has almost all eclipsing interactions, and so it is a **high-energy** conformation.

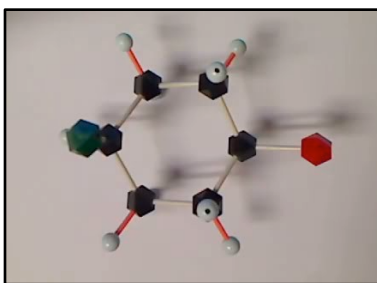**Energetics of Interconversion of Chair Conformations**

chair

boat

other chair

Energy

twist boat

twist boat

~10.8 kcal/mol

"reaction" coordinate
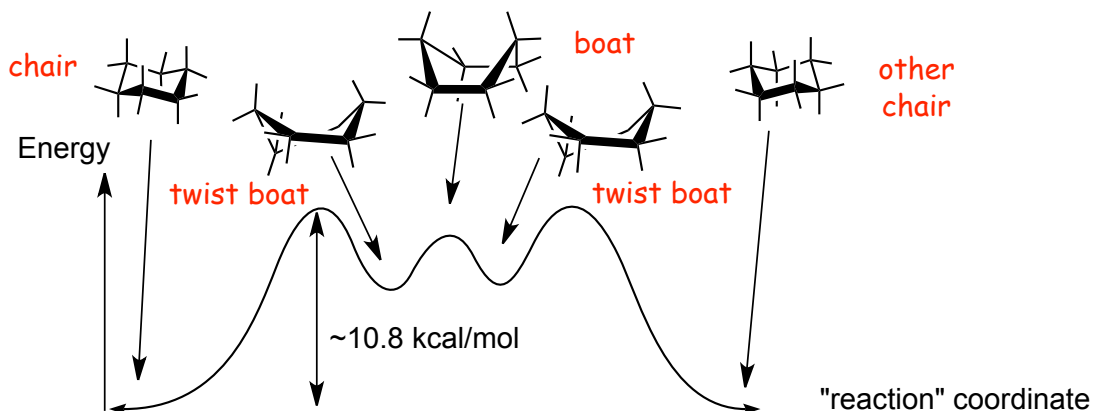
• Barrier to interconverting one chair to another ~ 10.8 kcal/mol.
• Takes ca. 65 microseconds at room temperature.
• Even though this is still fast, it is a LOT slower than rotation around a single C-C bond in, for example, CH_3–CH_3.

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6 "axial" H₁'s

6 "equitorial" H₂'s

interconvert

all axial H₁ are NOW equitorial
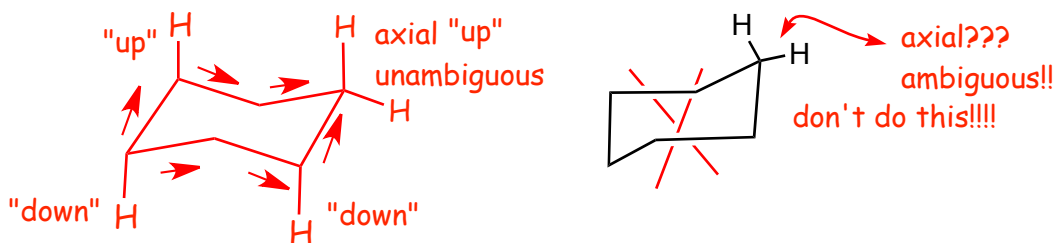all equitorial H₂ are now axial

• Interconversion between chairs converts ALL axial H's to equitorial and *vice versa*.
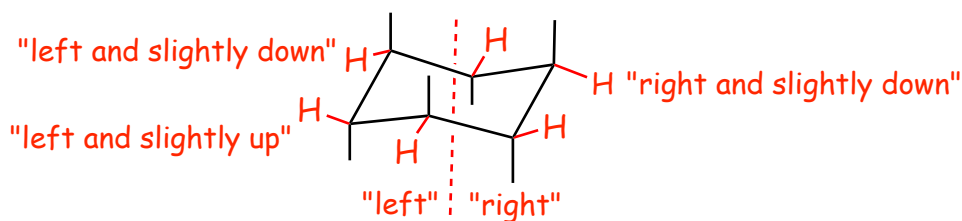

Visualize the Chair-to-Chair Interconversion Using the HGS Model Kit

Drawing Chair Conformations
• A properly drawn chair consists of three parallel lines, don't draw a chair as shown below.
• the **AXIAL BONDS** should all be straight UP on carbons that "point up", and straight DOWN on "down" carbons.

"up"   H   H   axial "up"
                  unambiguous

"down" H   H   "down"

H   H   axial???
          ambiguous!!
          don't do this!!!!

• The equitorials on the "left" point left, on the "right" point right.
• The **equatorial bonds** go "slightly down" on carbons where the axials are "up", and "slightly up" on carbons where the axials are "down".

"left and slightly down" H   H
"left and slightly up" H   H "right and slightly down"
          H
          "left"   "right"   H

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2.5 Monosubstituted Cyclohexanes

• It costs **energy** to have a substituent in the axial position compared to the equitorial position.

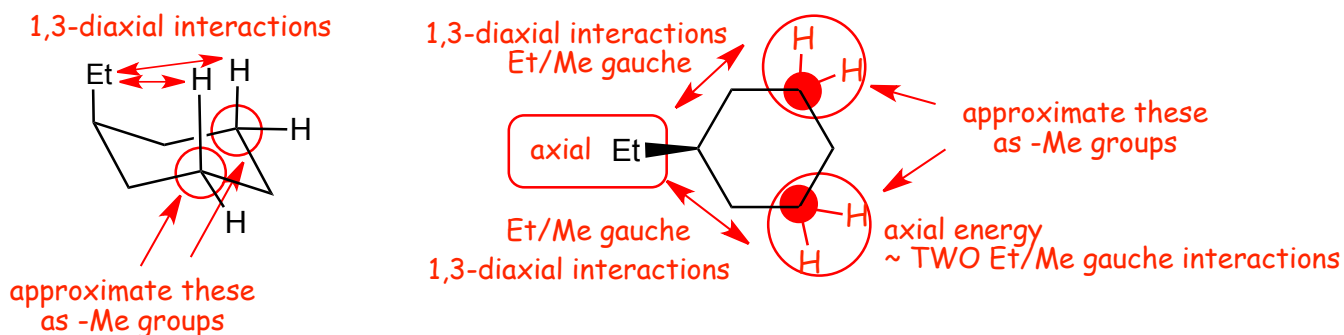**Example:** Ethylcyclohexane

TWO gauche interactions   NO gauche interactions
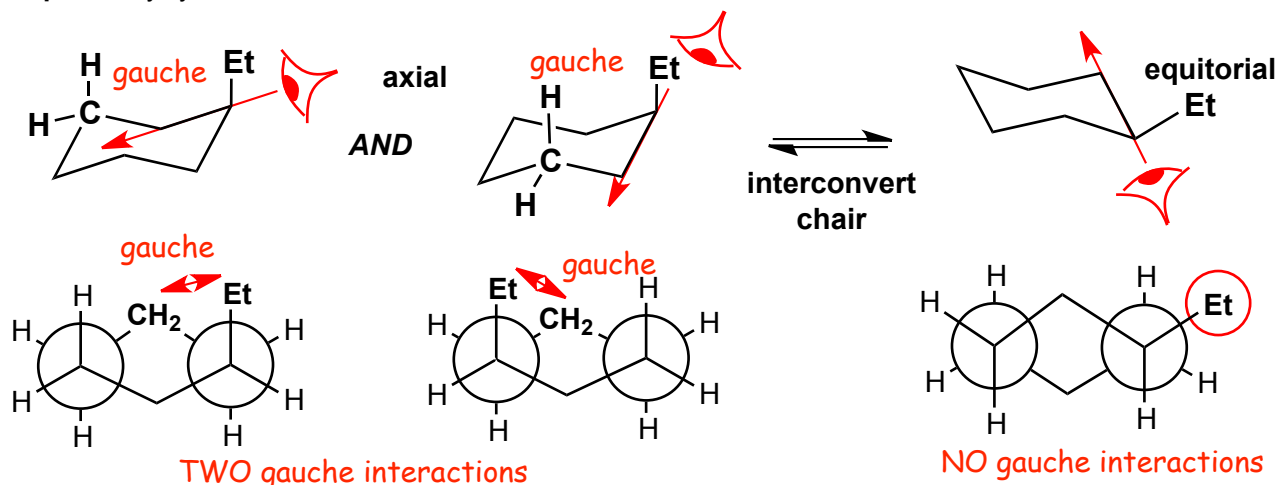
• **Two gauche interactions in the axial conformation**, zero gauche interactions in the equatorial conformation, **thus** the **axial** is **higher** in **energy.**

Take Another look at this…
• **Two 1,3-diaxial interactions:** which is another way of saying **two gauche interactions.**

• **Gauche** interactions in cyclohexanes are **also referred to as "1,3-diaxial interactions"**, since the arise as a result of electron **repulsion** between the electrons in the bonds of the **axial** substituent (ethyl here) and those in the **axial** C-H bonds on the "3rd carbons" from the substituent.
• the energy is roughly **two** Ethyl/Methyl gauche interactions.
 • We **approximate** the #3 cyclohexane ring carbons as methyl groups.
• The energy of a substituent in the **axial** position is roughly 2 x a Substituent/-Me gauche interaction.

Approximate the axial interaction to an R/Me gauche interaction, then can calculate the energy "cost"
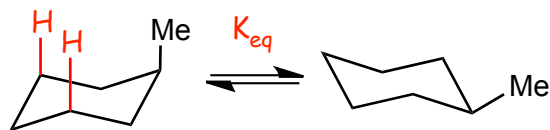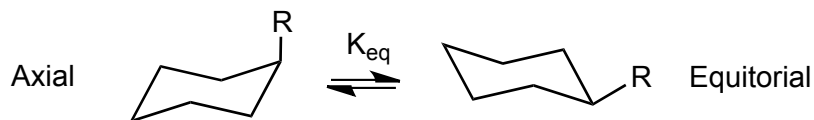

2 x Me/Me gauche = 2 x 0.9 = 1.8 kcal/mol

E(axial) - E(equitorial) ~ – 1.8 kcal/mol

$K_{eq} = e^{-\Delta E/RT}$ $K_{eq} = e^{1800/600} = 20$

therefore at equilibrium, ~ 5% axial and ~ 95% equitorial

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Axial/Equitorial Equilibria for Monosubstituted Cyclohexanes

| R	R/Me gauche	ΔE = 2 R/Me gauche	K_{eq}	% Equitorial	% Axial
–Me	~0.9	1.8	20	~95%	~5%
–Et	~0.95	1.9	24	~96%	~4%
–i-Pr	~1.1	2.2	39	~97.5%	~2.5%
–t-Bu	~2.7	5.4	8100	~99.99%	~0.01%

• t-Butylcyclohexane essentially "locked" into the equitorial conformation.

2.6 Disubstituted and Polysubstituted Cyclohexanes
### *cis-* and *trans*-isomers
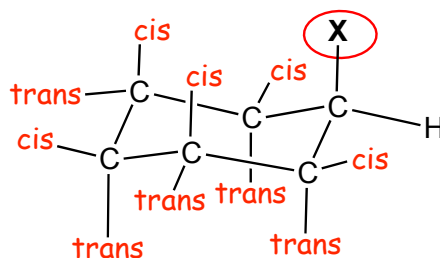
 • With respect to the substituent X, which is "up", axial and equatorial substituents that are also "up" and cis-, axials and equitorials that are "down" are trans-
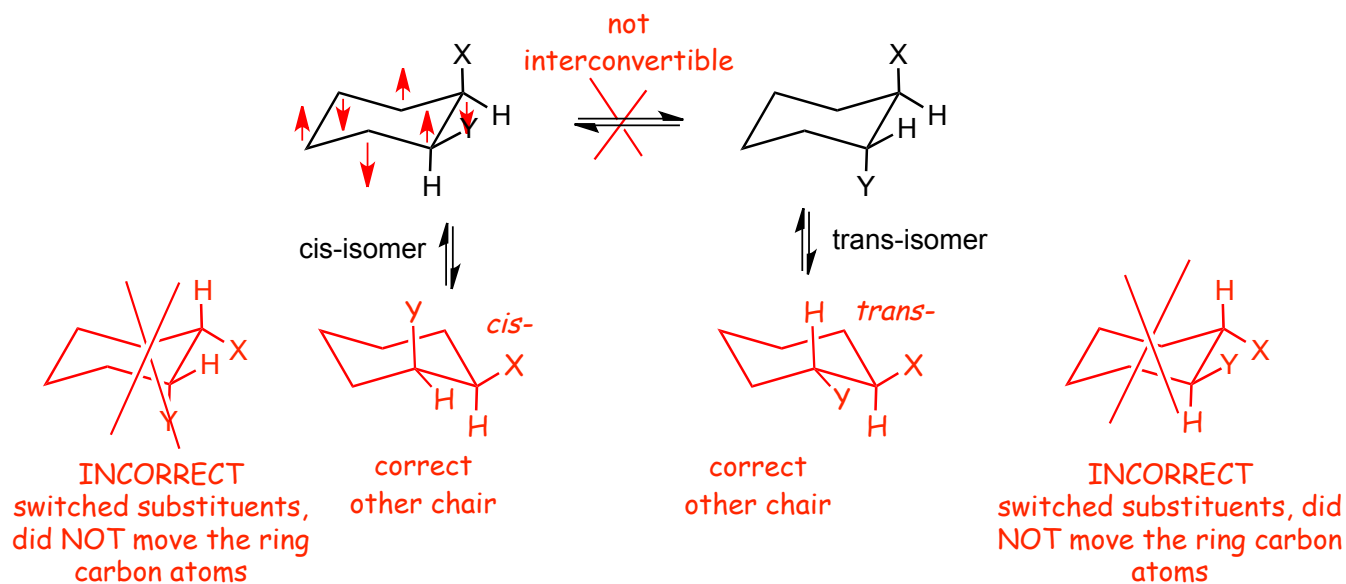

• Cis- and trans- isomers are **not** interconvertible, however, **each** has two chair conformations.

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• When drawing other chair, it is **very important** to **both** make all axials equatorial and vice versa, **and** to interchange the positions of the carbon atoms. If you ONLY interchange the axials and equitorials without also changing the carbons, you will usually make a **stereoisomer**, i.e. a different structure
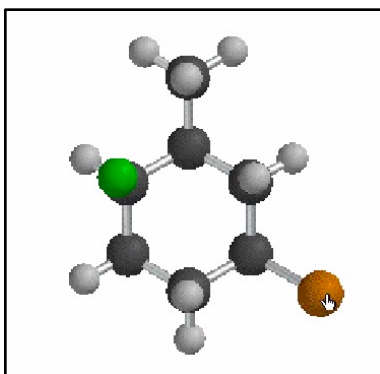

Visualize Drawing Correct Chair Conformations for Substituted Cyclohexanes

Example Problem: Identify lowest energy conformation of *cis*-1-chloro-4-t-butylcyclohexane


larger t-Bu group equitorial, lower energy
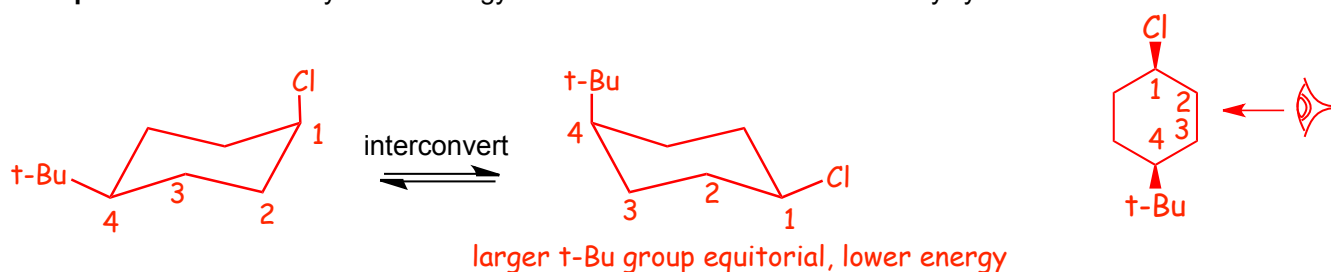
• Note that the assignment of the numbers to the carbons in the ring in the line-angle structure is arbitrary, #1 doesn't have to be at the top, but it is often convenient to put #1 at either the "top" or "bottom" positions.
• Note **also** that having carbon #1 on the "right" in the chairs is also arbitrary, but it is often convenient to do so (but not required!).
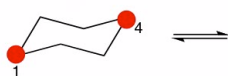
Example Problem: Identify the lowest energy conformation of the *trans*-1-isopropyl-3-methylcyclohexane structure provided….

lower energy, larger
i-Pr equitorial
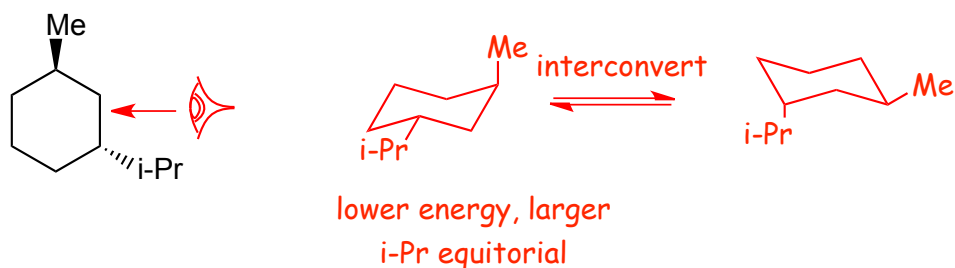
**Important**, do not make the mistake of drawing the wrong enantiomer:

NOT the same!!
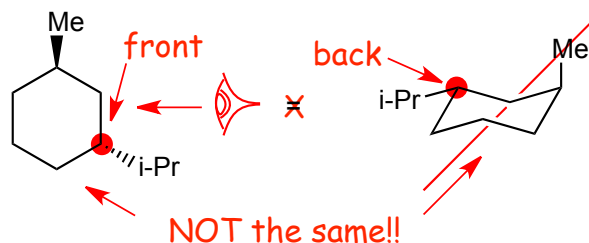
• Changing the carbons that the substituents are attached to, especially "front" to "back" will often generate make a **stereoisomer**, i.e. a different structure.

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Visualize Chair-to-Chair Interconversions and Avoiding Common Misconceptions
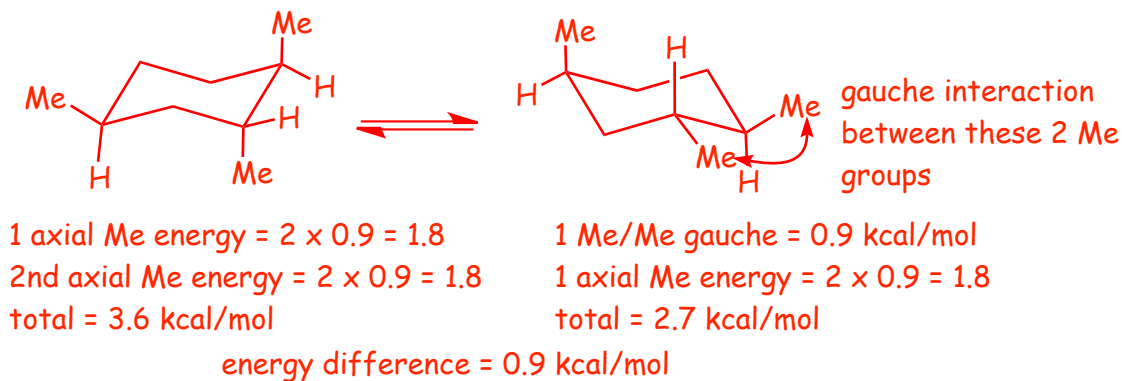
Example Problem: Determine the energy difference between the lowest and highest energy conformations of the following structure (quantitative, not just qualitative).
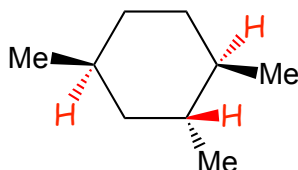
• We will need the table of gauche interactions that we used earlier.

ECLIPSING Interactions	Energy kcal/mol	GAUCHE Interactions	Energy kcal/mol
H / H	~1.0	Me / Me	~0.9
H / Me	~1.4	Et / Me	~0.95
Me / Me	~2.6	i-Pr / Me	~1.1
		t-Bu / Me	~2.7

• Remember, the energy associated with 1 axial interaction is equal to 2 gauche interactions.

gauche interaction between these 2 Me groups

1 axial Me energy = 2 x 0.9 = 1.8
2nd axial Me energy = 2 x 0.9 = 1.8
total = 3.6 kcal/mol

1 Me/Me gauche = 0.9 kcal/mol
1 axial Me energy = 2 x 0.9 = 1.8
total = 2.7 kcal/mol

energy difference = 0.9 kcal/mol

• Here we see **another** form of "hidden" gauche interaction between the two -Me substituents when they are adjacent and both equatorial (also fairly easy to see in a molecular model).

gauche interaction between these 2 Me groups