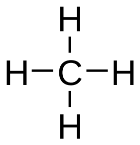
Alkanes

Alkanes are the simplest organic molecules, they only contain C and hydrogen, and only contain single bonds.

Compounds that have the *maximum* number of bonded hydrogens, are said to be *saturated*.

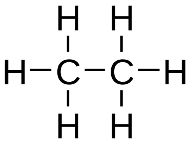
Alkanes are saturated hydrocarbons, with a general Formula: C_nH_{2n+2}

The simplest members of this group are the *n-alkanes*.



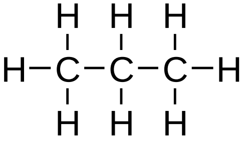
$H-\overset{H}{\underset{H}{C}}-H$

methane C_1H_4



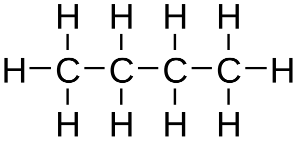
$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

ethane C_2H_6



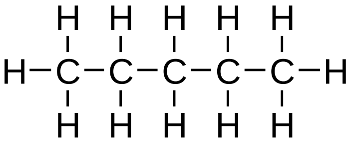
$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

propane C_3H_8



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

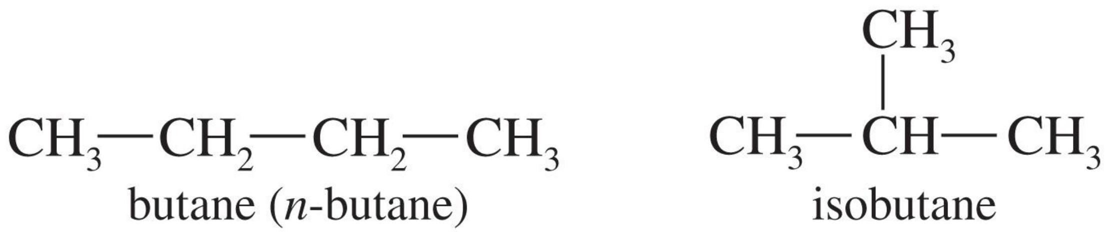
butane C_4H_{10}

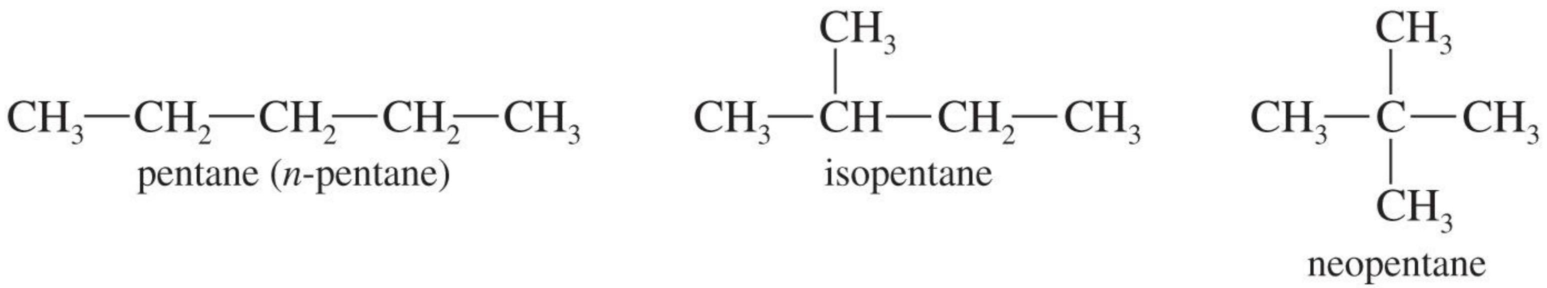


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

pentane C_5H_{12}

The n-alkanes are *straight chain* molecules, but there are also *branched* alkanes (isomers).





Any series that differs only by an increasing number of $–CH_2$- groups is known as a **Homologous series**.

The individual members are said to be **homologs** of each other.

Nomenclature of Alkanes

There are two general types of nomenclature:

trivial names (acetone, acetic acid)
IUPAC System (propanone, ethanoic acid)

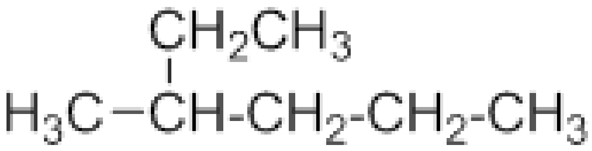
IUPAC or Systematic Names

The systematic way to (UNAMBIGUOUSLY) name all organic compounds.

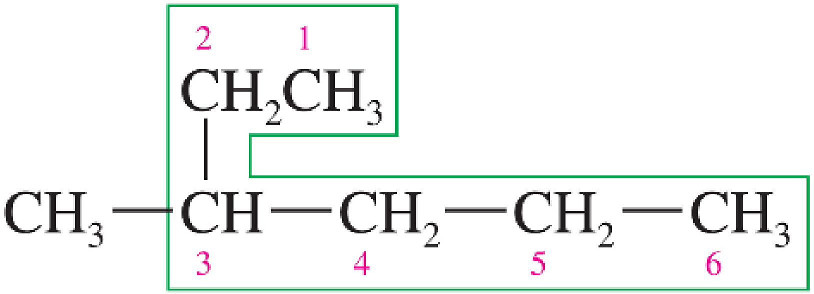
For alkanes:

(1) Find the longest continuous chain of carbon atoms. This is the *base name* of the compound.
(2) Number the *longest* chain beginning with the end *nearest* a substituent.
(3) Name the *substituent groups* attached to the longest chain as *alkyl* groups. Also state the location of each alkyl group according to its numbered carbon on the main chain.
(4) When two or more substituents are present, list them in *alphabetical order*. If two or more of the same alkyl groups are present, use the prefixes *di*-, *tri*- etc. to avoid repetition.

Examples:

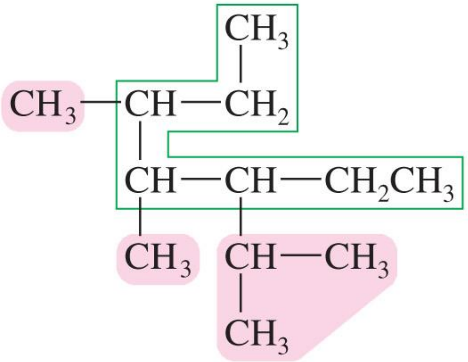


$$H_3C-\overset{\displaystyle CH_2CH_3}{\overset{|}{C}H}-CH_2-CH_2-CH_3$$



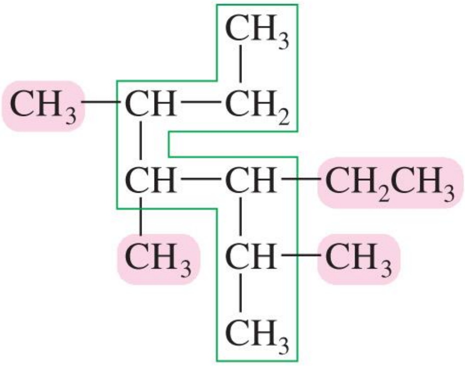
3-methyl*hexane*

If there are two chains of equal length, choose the chain that has the *highest* number of substituents.



wrong

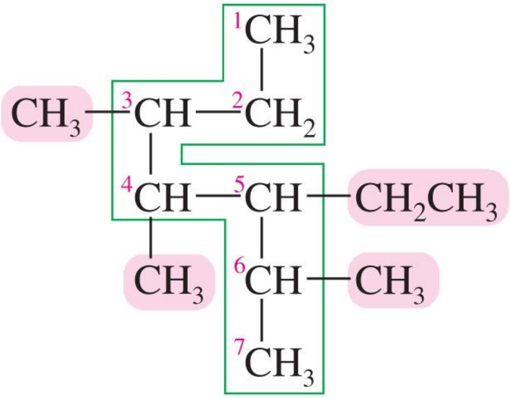
seven-carbon chain, but only three substituents



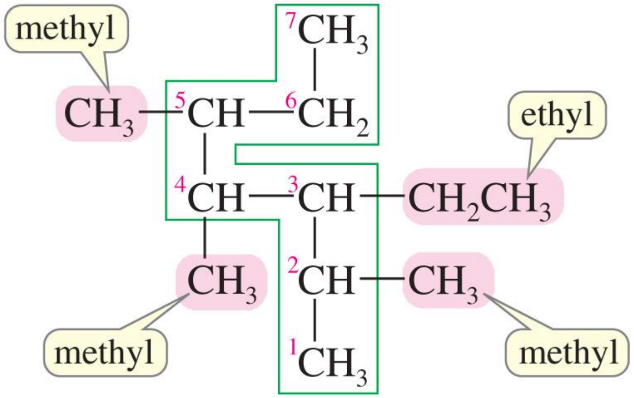
correct

seven-carbon chain, four substituents

Numbering starts at the end *nearest* a substituent so that the alkyl substituents have as *low numbers as possible*.



incorrect



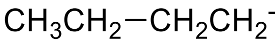
correct

3-ethyl-2,4,5-trimethylheptane

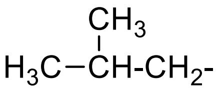
Alkyl groups are named by replacing the *–ane* suffix of the alkane name with *–yl*.

E.g.	CH_3CH_3	Ethane	CH_3CH_2-	*Ethyl* group
	$CH_3CH_2CH_3$	Propane	$CH_3CH_2CH_2$-	*Propyl* group

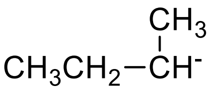
Common branched alkyl groups have trivial names:


$CH_3CH_2-CH_2CH_2^-$

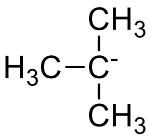
butyl


$H_3C-\overset{CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}$

isobutyl

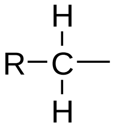

$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H^-$

sec-butyl

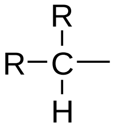

$H_3C-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{}^-$

tert-butyl
t-butyl

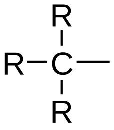
The names *sec* and *tert* are short for secondary and tertiary, referring to the degree of alkyl substitution.


$R-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-$

Primary
1^o carbon


$R-\underset{H}{\underset{|}{\overset{R}{\overset{|}{C}}}}-$

Secondary
2^o carbon


$R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-$

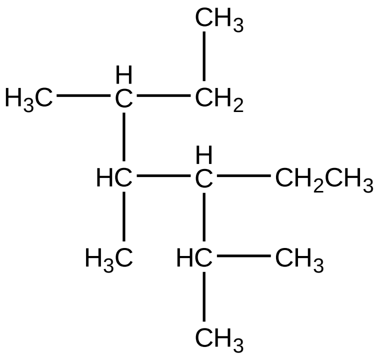
Tertiary
3^o carbon

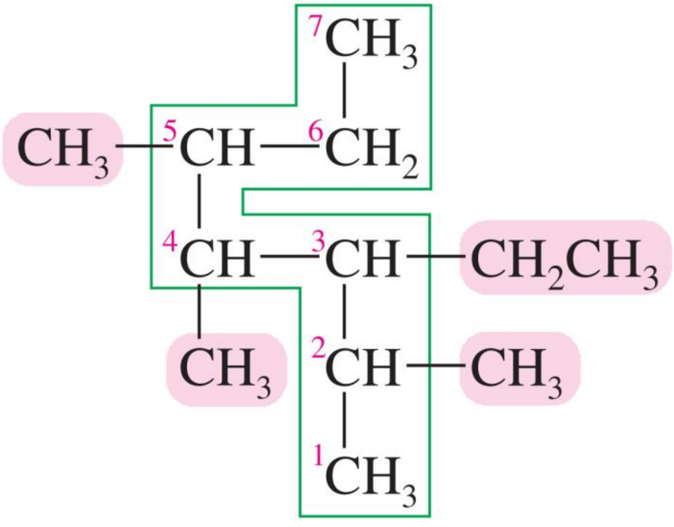
Prefixes are used when there are more than one type of alkyl substituent

Di = 2
Tri = 3
Tetra = 4
Penta = 5

The prefixes *do not count* when alphabetizing.

The below compound is 3-ethyl-2,4,5-trimethylheptane





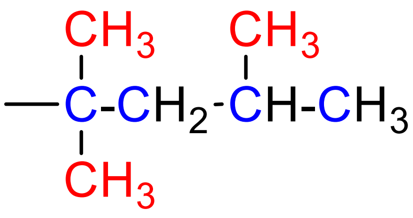
3-ethyl-2,4,5-trimethylheptane

Complex Substituents

These are named as follows:

(a) The base alkyl group is numbered starting with the carbon bonded to the main chain.

(b) The substituents are listed with the appropriate numbers, and parentheses are used to separate the substituent name.



$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$$

a (*1,1,3-trimethylbutyl*) group

Properties of Alkanes

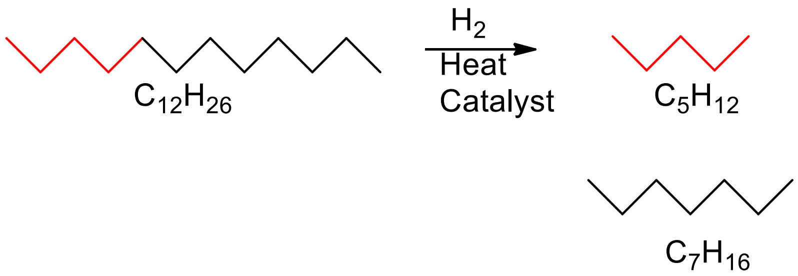
Natural gas, gasoline, oils and paraffin wax are all alkanes, and so alkanes are often used as fuels, lubricants and solvents.

Alkanes are *non-polar*, and are said to be h*ydrophobic* ('water hating') since they do not dissolve in water.

Typically the density of alkanes is around 0.7g/ml, and so when an alkane and water are mixed, they will form two separate phases, with the alkane on top. (Oil floats on water).

Reactivity of Alkanes

Shorter chain alkanes are obtained commercially by the ‘catalytic cracking’ of larger chain alkanes such as crude oil or petroleum refining.



The process of using hydrogen gas to ensure all the products are alkanes is called *hydrocracking*.

In general, alkanes are chemically unreactive, although reactions do occur under forcing conditions.

Combustion

Alkanes are converted to carbon dioxide and water at high temperatures.

$$CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

(This is why alkanes are good fuels).

Halogenation

Alkanes will react with halogens (F_2, Cl_2, Br_2, I_2) under conditions of heat or light.

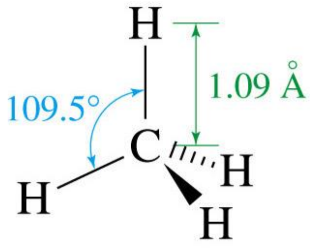
$$CH_4 + Cl_2 \longrightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$

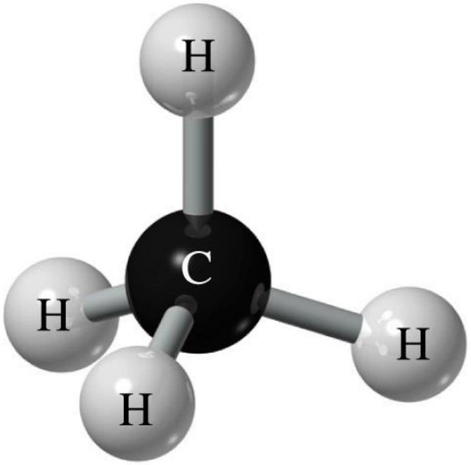
Mixtures of alkyl halides are formed.

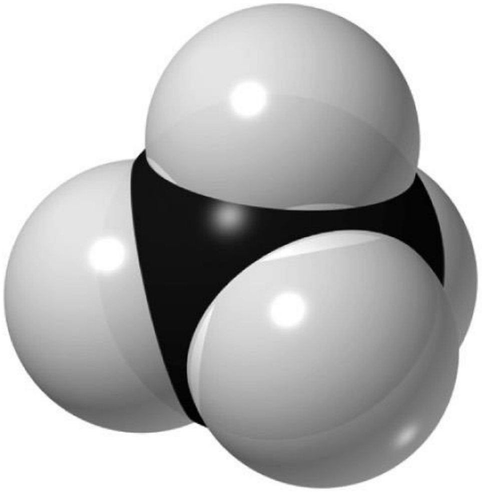
Structure and Conformation of Alkanes

Because alkanes are saturated, they exemplify sp^3 hybridized carbon, and most of the fundamental structural and conformational properties of organic molecules can be found in structures of alkanes.

E.g. Methane, CH_4, is the simplest alkane.





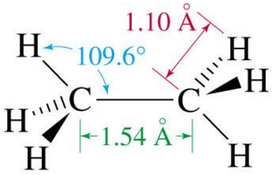


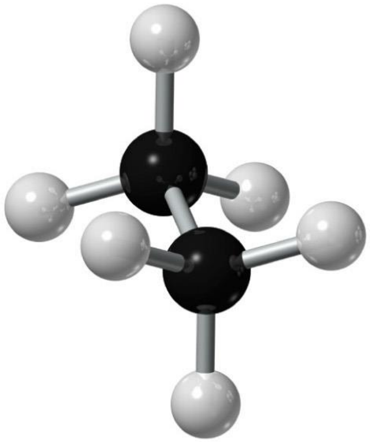
It is perfectly tetrahedral, with bond angles of 109.5°.

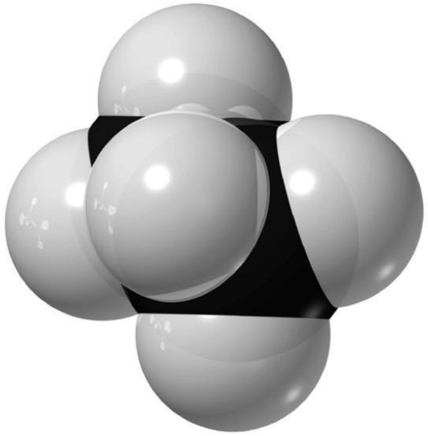
The C-H bond length is 1.09Å. (1.09×10^{-10} m).

Ethane

Ethane can be envisaged as two methyl groups joined by overlapping sp^3 orbitals forming the C-C bond.

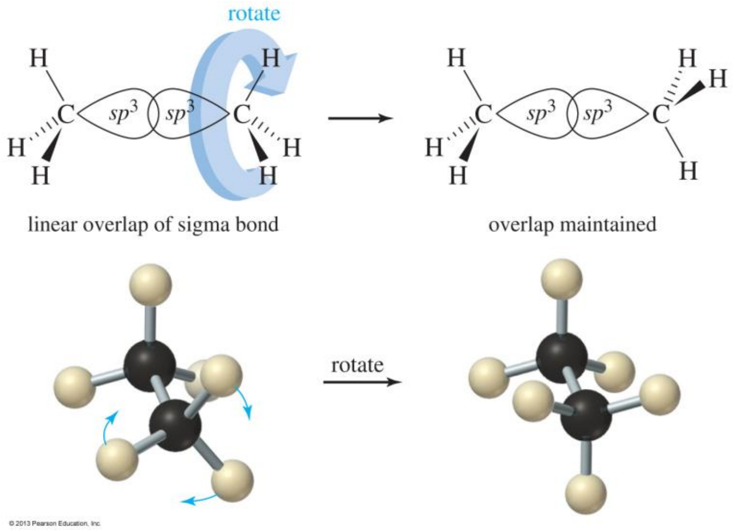






The C-C bond is 1.54Å.

As mentioned before, because of the free rotation about the C-C bond, ethane exists in many *conformations* (conformers).



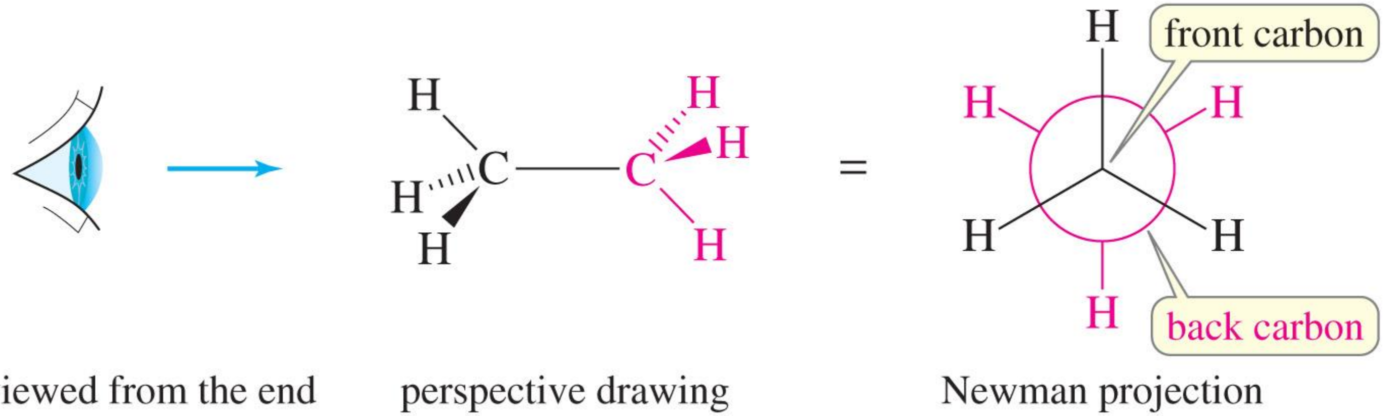
Drawing Conformations

There are three common ways of drawing conformations:

Wedges (seen before)
Newman Projections
Sawhorse Structures

Newman Projections

The molecule is drawn as if it is viewed straight down the C-C bond.



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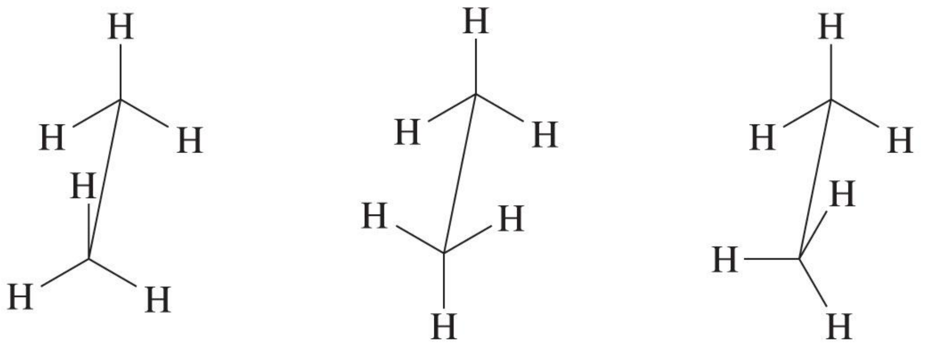
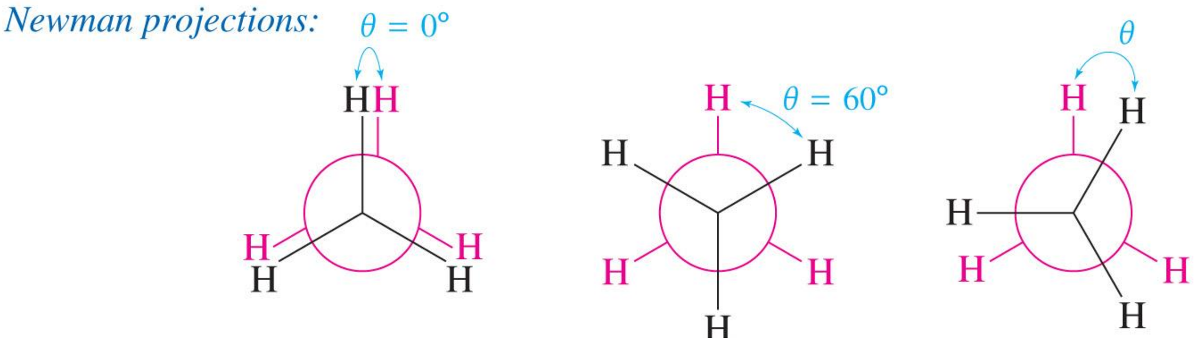
The ***front*** **carbon** is drawn with 3 bonds in a Y shape
The ***back*** **carbon** is drawn as a circle with 3 bonds pointing out from it.

Sawhorse Structures

These picture the molecule as viewed looking down on the C-C bond at an angle from above.



eclipsed, θ = 0°   staggered, θ = 60°   skew, θ = anything else



The dihedral angle, θ, is the angle between the C-H bonds on the front of a Newman projection, and those on the back.

When θ = 0° it is known as the **Eclipsed** conformation.

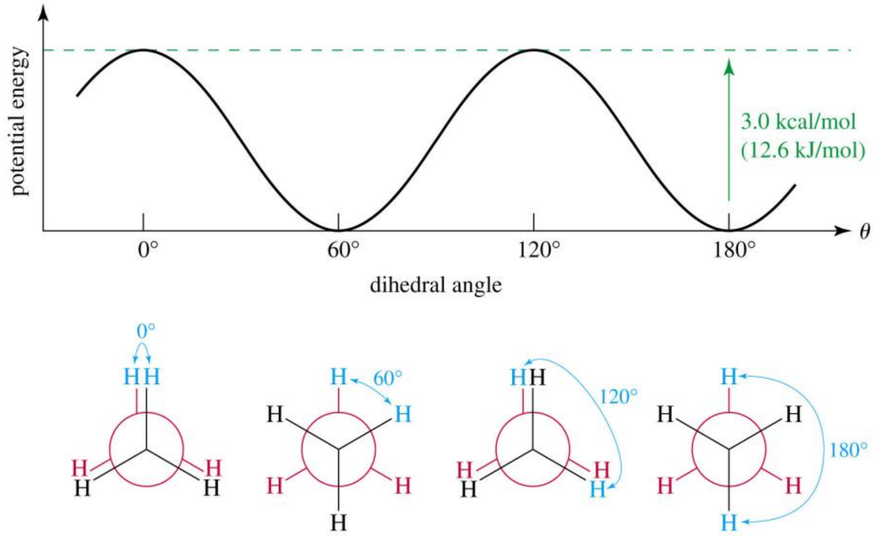
When θ = 60° it is called the **Staggered** conformation.

Any other conformation is known as a **Skew** conformation.

The energy difference between these conformations is only about 3kcal/mol (13kJ/mol). This is a *small* amount of energy, and at room temperature, molecules have enough energy to overcome this small barrier.

Therefore, a room temperature sample of ethane gas would contain *all* the different conformations – although not all in the same proportions.

The energy difference arises from *electron repulsions* between the different C-H bond electrons.

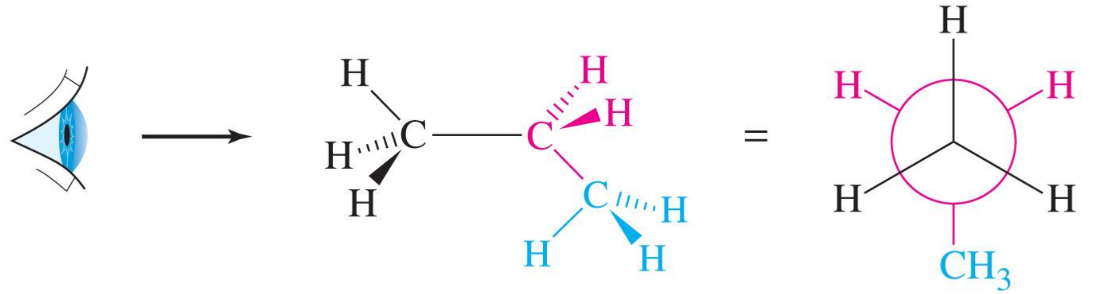


As the ethane molecule rotates through eclipsed and staggered conformations, the potential energy of the systems changes.

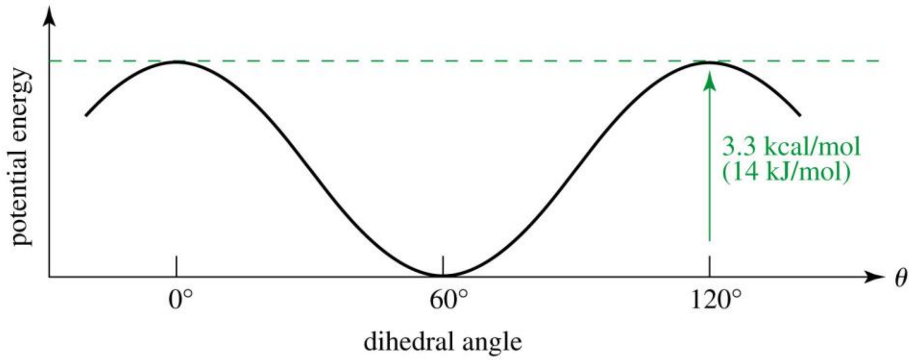
The resistance to rotation is called **torsional strain**, and the 3kcal/mol is called the **torsional energy**.

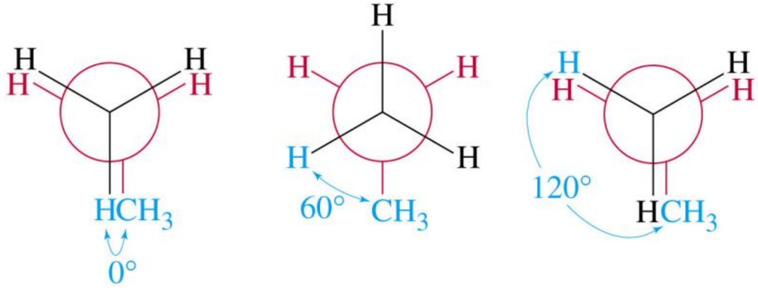
Many organic reactions depend on a molecule's conformation, and the study of this is called *conformational analysis*.

Conformations of Propane



viewed from the end perspective drawing Newman projection





The torsional energy of propane is 3.3kcal.

The increase versus ethane is because of the greater size of a methyl group than of a hydrogen.

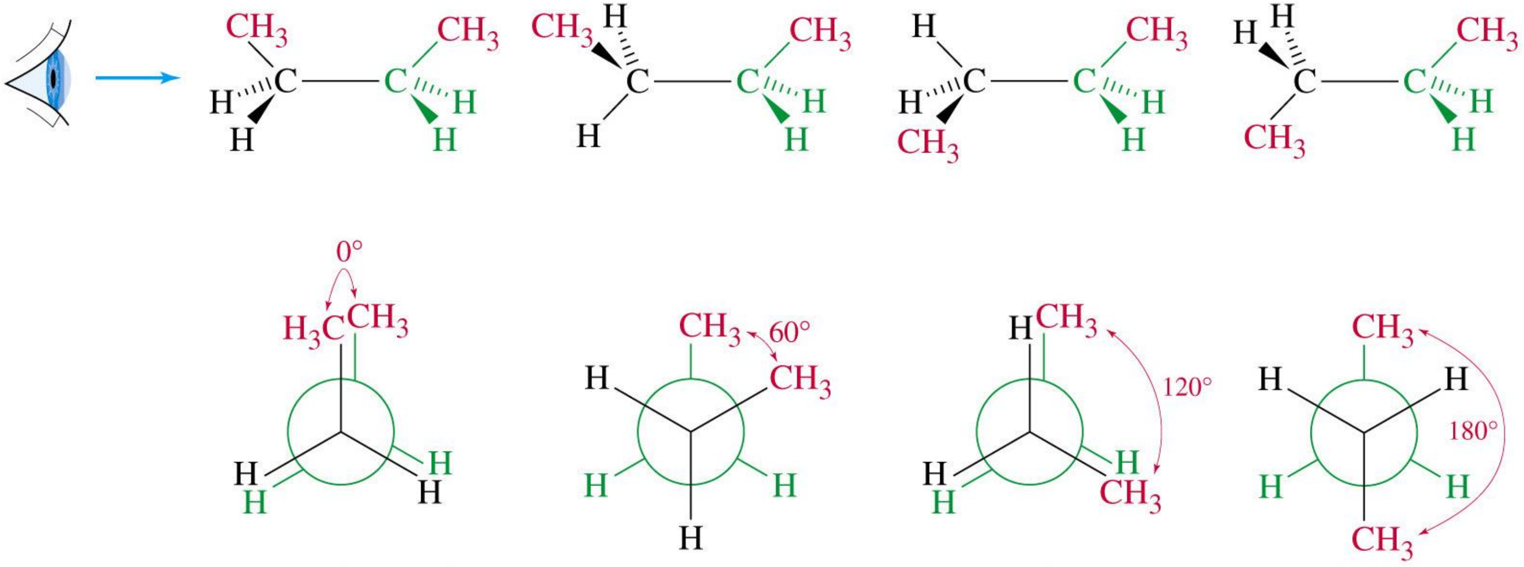
Eclipsing energy of C-H / C-H < Eclipsing energy of C-H / C-CH_3

Conformations of Butane

The more carbons in a chain, the more conformations a molecule can adopt.

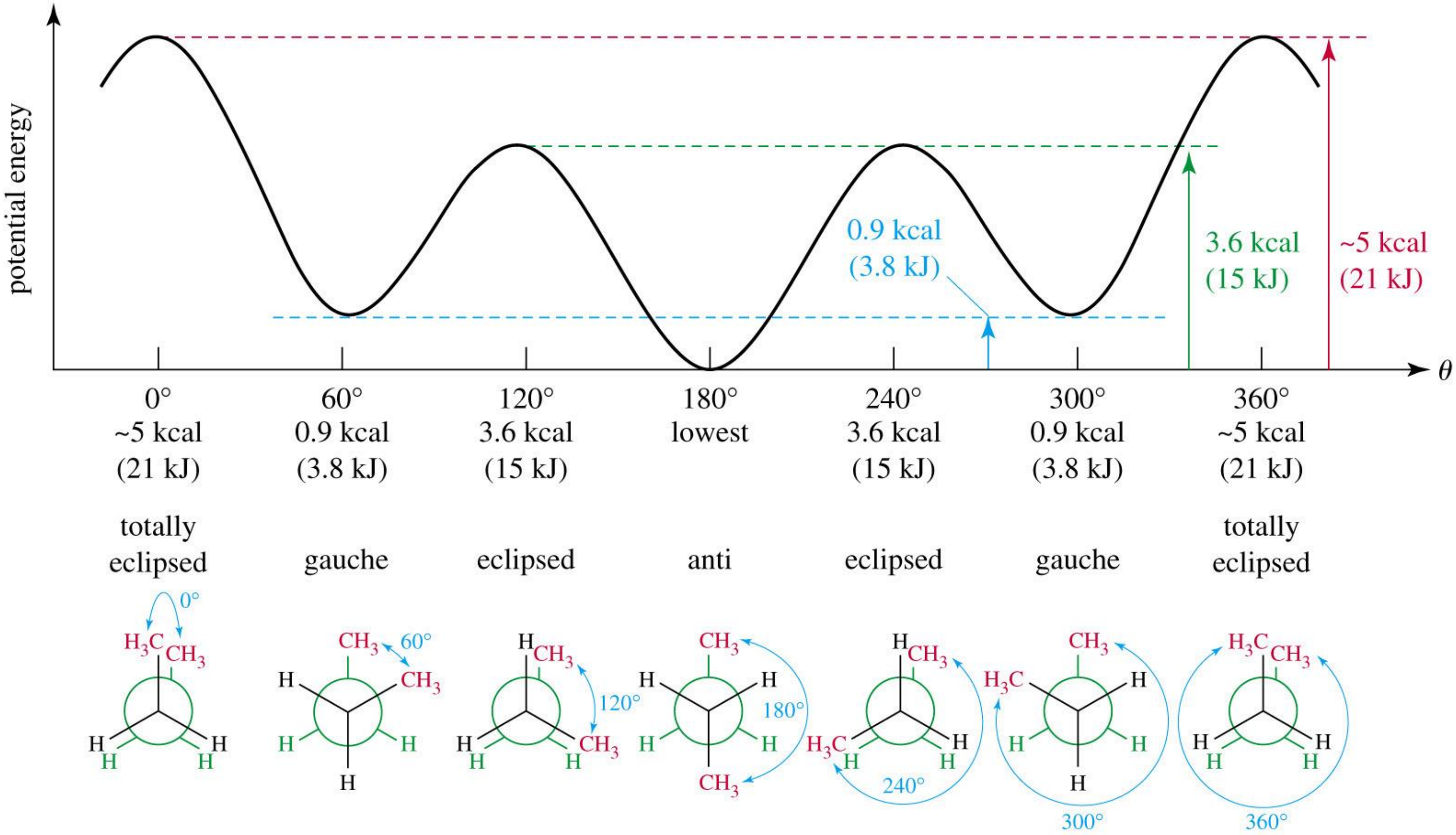
Butane can adopt four *important* conformations.

- Totally Eclipsed
- Gauche
- Eclipsed
- Anti



totally eclipsed (0°) gauche (60°) eclipsed (120°) anti (180°)

Now θ represents the angle between the two C-CH_3 bonds.

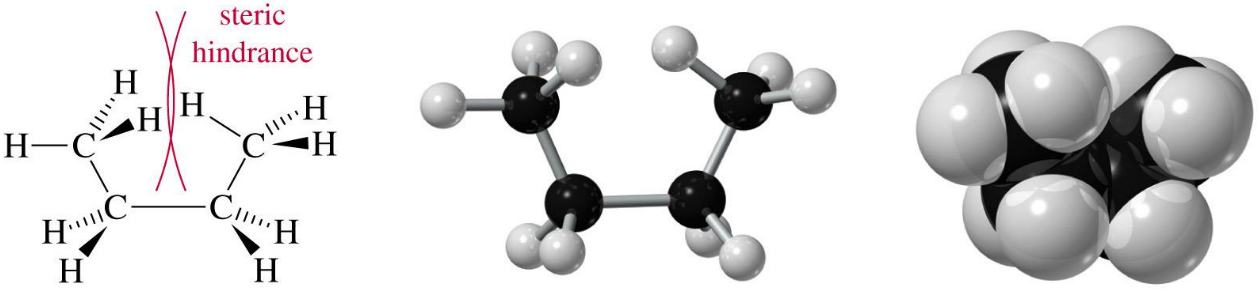


All eclipsed conformations are of *higher* energy than any of the staggered ones.

The anti conformation is of *lowest energy* since the bulky methyl groups are oriented furthest away from each other in this conformation.

Steric Hindrance

The totally eclipsed conformation of butane is 1.4kcal/mol higher in energy than the other eclipsed conformations, due to the forcing together of the methyl groups.

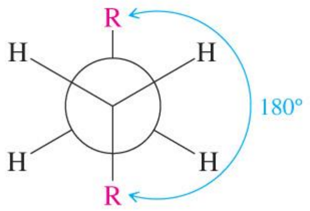


Totally eclipsed conformation of butane

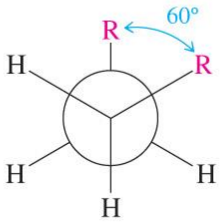
The methyl groups’ electron clouds repel each other.
The interference of bulky substituents with each other is called **steric hindrance**.

Higher Alkanes

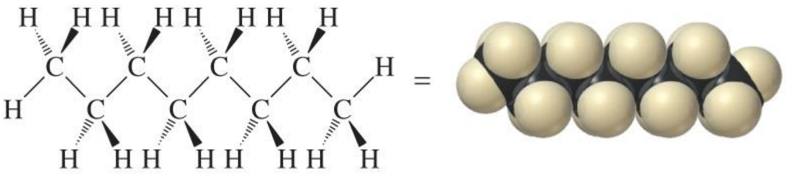
Higher alkanes behave in an analogous way to butane.
The lowest energy conformation for any straight chain alkane is having all the C-C backbone bonds oriented as anti conformations.



anti conformation



gauche conformation



octane, all anti conformation

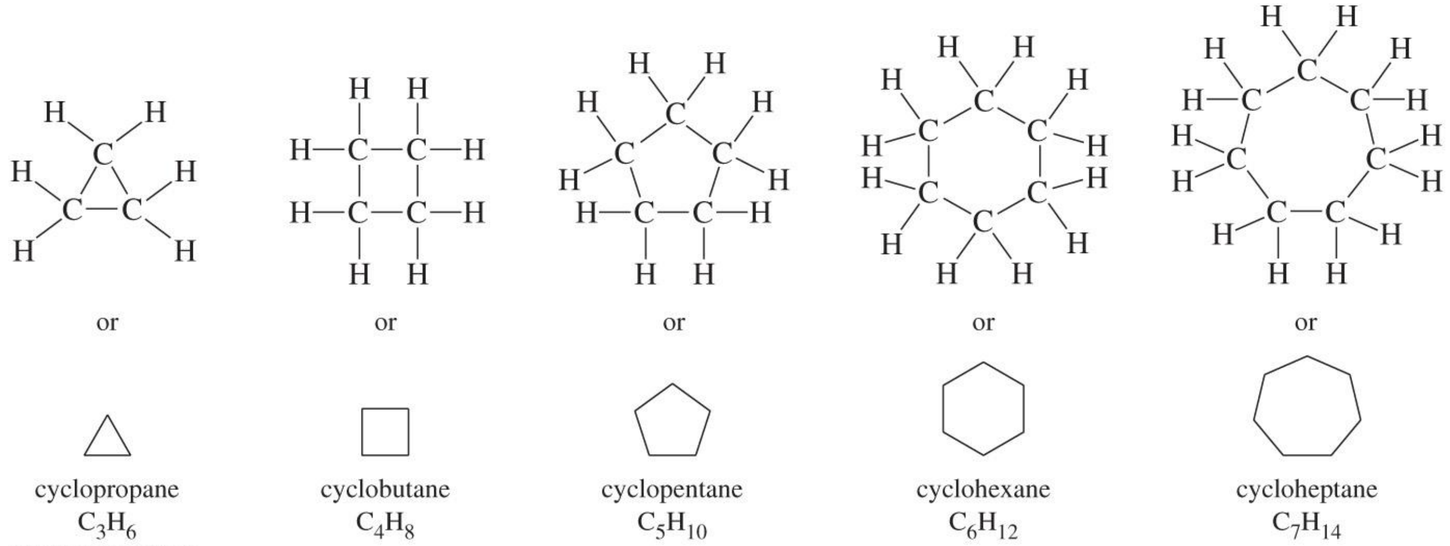
This gives a zigzag type backbone.

Cycloalkanes

In organic chemistry, many common molecules are *cyclic*.

Cycloalkanes are simply alkanes that are cyclic.

Just add *cyclo*- before their name. (The opposite of cyclic is *acyclic*).



cyclopropane C_3H_6

cyclobutane C_4H_8

cyclopentane C_5H_{10}

cyclohexane C_6H_{12}

cycloheptane C_7H_{14}

Notice the general formula for cycloalkanes is C_nH_{2n}

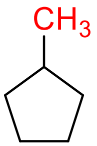
Nomenclature of Cycloalkanes

This is the same as for alkanes, although two extra rules apply.

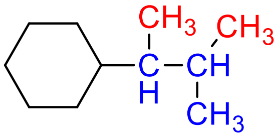
Rule A: Decide whether the *cyclic* or *acyclic* portion contains more carbons. This determines the base name. (*Alkyl*-substituted cycloalkane or *Cycloalkyl*-substituted alkane).

Rule B: Carbons are numbered to give the lowest numbers for substituted carbons.

Examples:

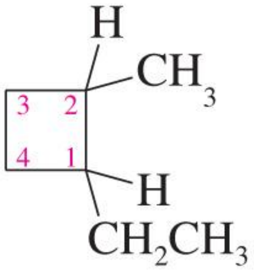


methylcyclopentane

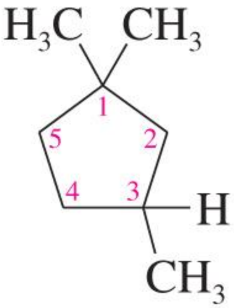


(1,2-dimethylpropyl)cyclohexane

Numbering starts at the *most* substituted carbon, and goes around in order to give the *lowest* numbers.

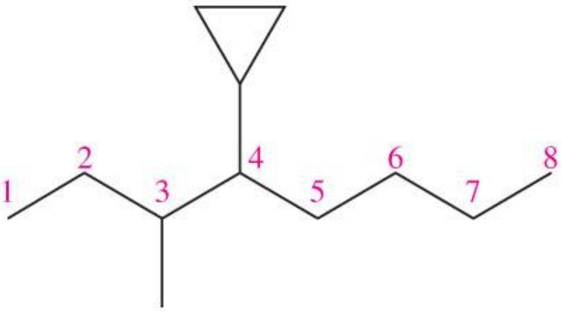


1-ethyl-2-methylcyclobutane

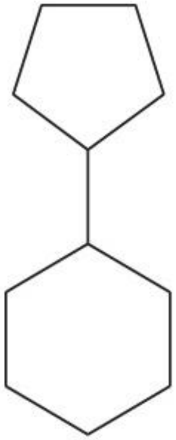


1,1,3-trimethylcyclopentane

When there are more acyclic than cyclic carbons, the cyclic part becomes a *cycloalkyl* substituent.



4-cyclopropyl-3-methyloctane



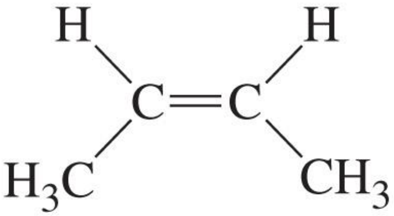
cyclopentylcyclohexane

Geometric Isomerism In Cycloalkanes

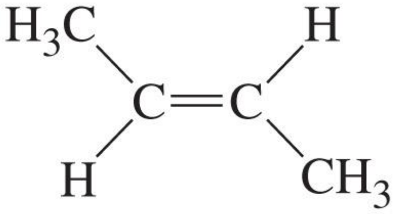
Open chain alkanes undergo free rotation about their C-C bonds.

Alkenes, with double bonds, *cannot* undergo free rotation.

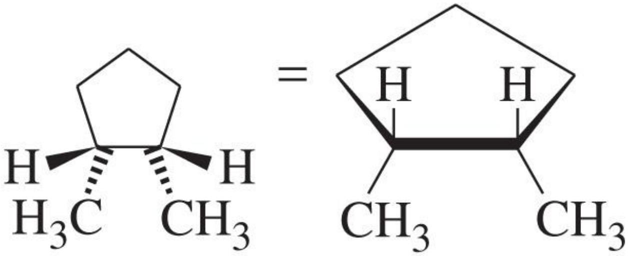
Cycloalkanes also cannot undergo free rotation.
Substituted cycloalkanes can also give rise to *cis* and *trans* isomers.



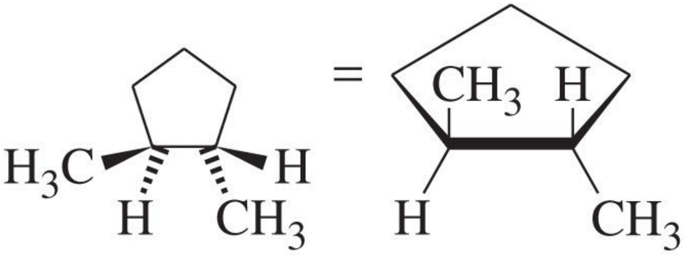
cis-but-2-ene



trans-but-2-ene



cis-1,2-dimethylcyclopentane



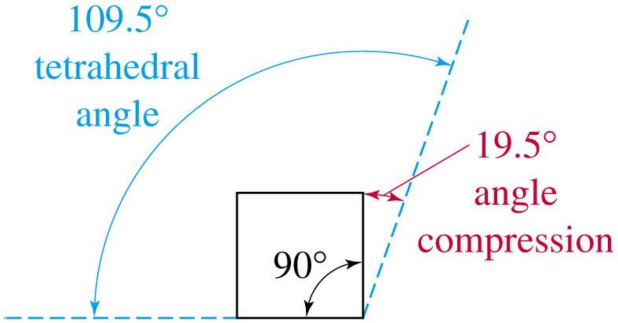
trans-1,2-dimethylcyclopentane

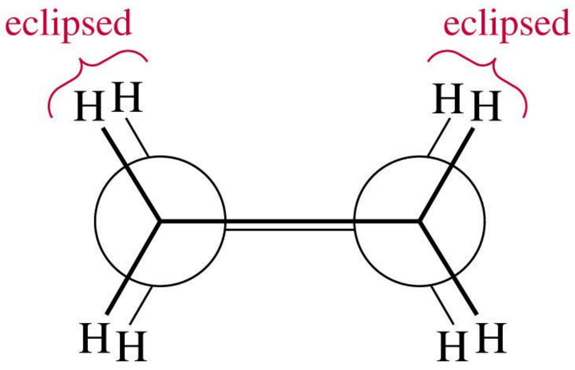
Ring Strain in Cycloalkanes

If a cycloalkane requires bond angles **different** to 109.5° then the sp^3 orbitals cannot overlap as efficiently as possible.

This gives rise to **angle strain** (Bayer strain).

Consider “planar” cyclobutane:





Newman projection
of planar cyclobutane

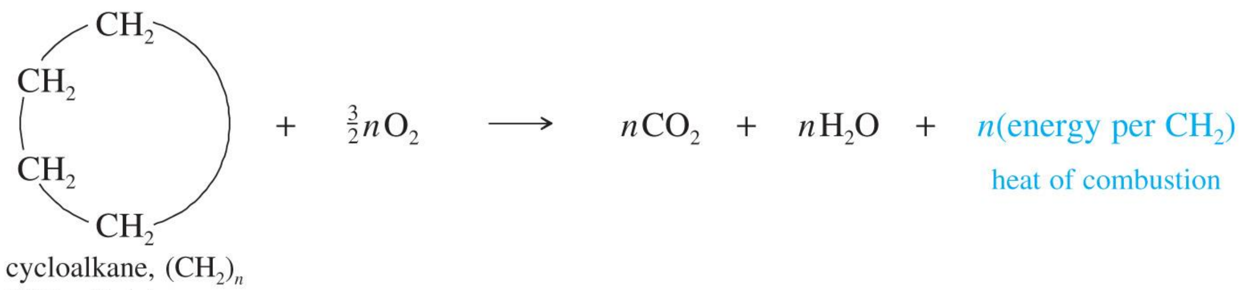
Along with the angle strain, there is also eclipsing of the hydrogens – *torsional strain*.

The combination of angle and torsional strains is called **Ring Strain**.

Calculation of Ring Strain

This is calculated through *heats of combustion*.

Already seen that alkanes can be combusted – so can cycloalkanes.



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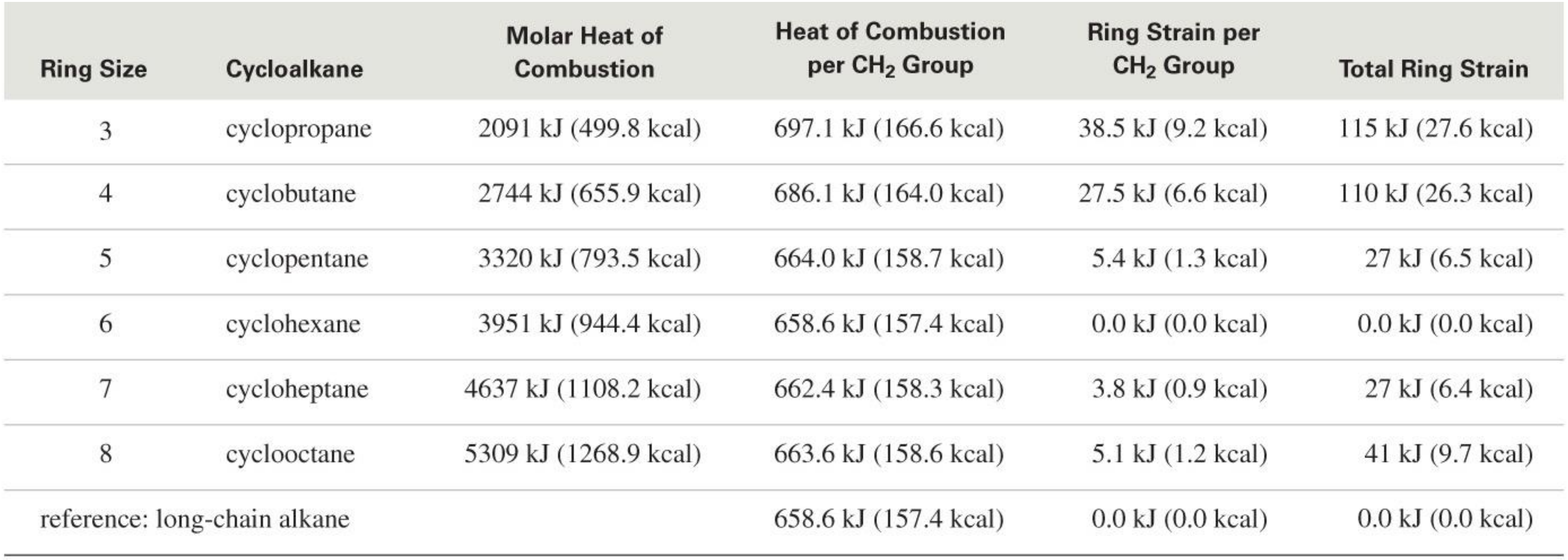
The energy released is the **heat of combustion**, and this value can be converted into useful information.



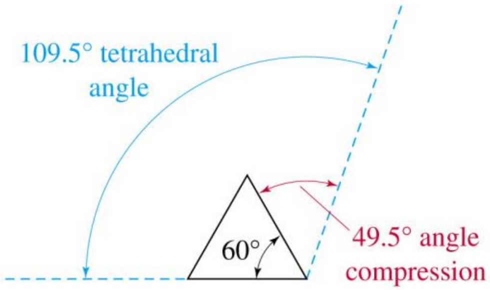
Ring Size	Cycloalkane	Molar Heat of Combustion	Heat of Combustion per CH_2 Group	Ring Strain per CH_2 Group	Total Ring Strain
3	cyclopropane	2091 kJ (499.8 kcal)	697.1 kJ (166.6 kcal)	38.5 kJ (9.2 kcal)	115 kJ (27.6 kcal)
4	cyclobutane	2744 kJ (655.9 kcal)	686.1 kJ (164.0 kcal)	27.5 kJ (6.6 kcal)	110 kJ (26.3 kcal)
5	cyclopentane	3320 kJ (793.5 kcal)	664.0 kJ (158.7 kcal)	5.4 kJ (1.3 kcal)	27 kJ (6.5 kcal)
6	cyclohexane	3951 kJ (944.4 kcal)	658.6 kJ (157.4 kcal)	0.0 kJ (0.0 kcal)	0.0 kJ (0.0 kcal)
7	cycloheptane	4637 kJ (1108.2 kcal)	662.4 kJ (158.3 kcal)	3.8 kJ (0.9 kcal)	27 kJ (6.4 kcal)
8	cyclooctane	5309 kJ (1268.9 kcal)	663.6 kJ (158.6 kcal)	5.1 kJ (1.2 kcal)	41 kJ (9.7 kcal)
reference: long-chain alkane			658.6 kJ (157.4 kcal)	0.0 kJ (0.0 kcal)	0.0 kJ (0.0 kcal)

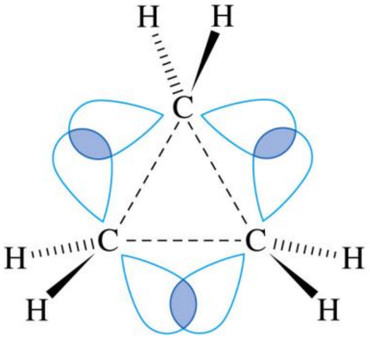
All units are per mole.

Note: Cyclopropane and cyclobutane are *highly* strained
Cyclopentane and cycloheptane have *low* ring strain
Cyclohexane has no ring strain !

Cyclopropane

Cyclopropane is the most strained cycloalkane.





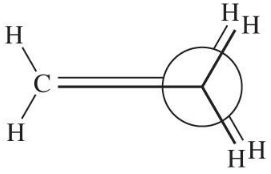
“bent bonds”
nonlinear overlap

This is due to two effects: Angle Strain
Torsional Effects

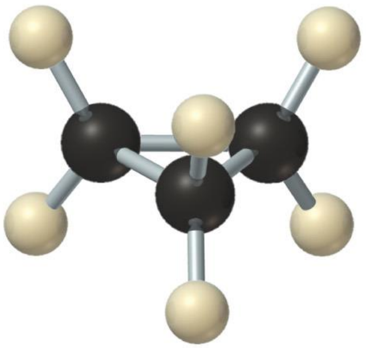
Bonding Overlap is reduced because the **enforced** 60° bond angle leads to poor overlap of the sp^3 orbitals.

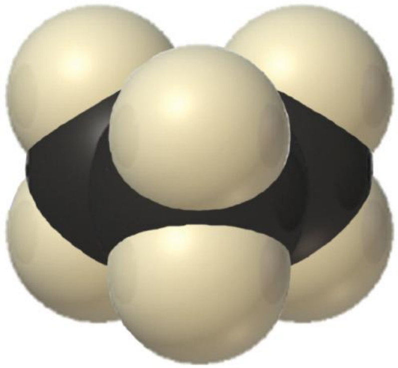
The three membered ring has to be planar, and all the C-H’s are eclipsed.

The angle strain is *larger* than the torsional effects for cyclopropane.



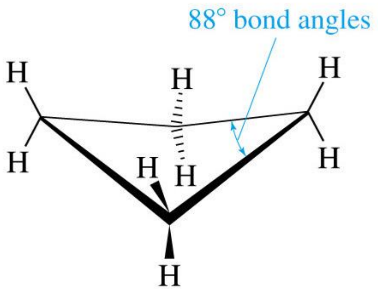
Newman projection
of cyclopropane



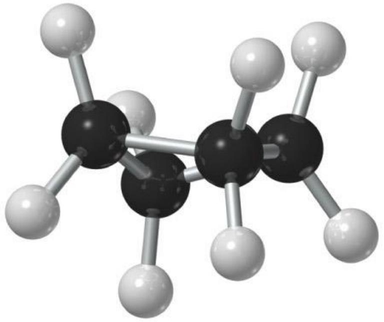


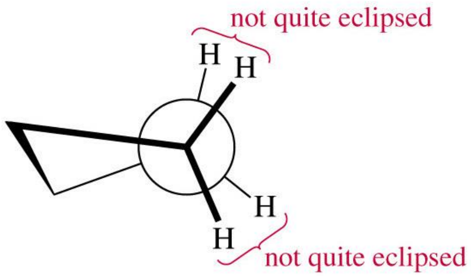
Cyclobutane

Cyclobutane is **neither** planar, **nor** a perfect square.



slightly folded conformation



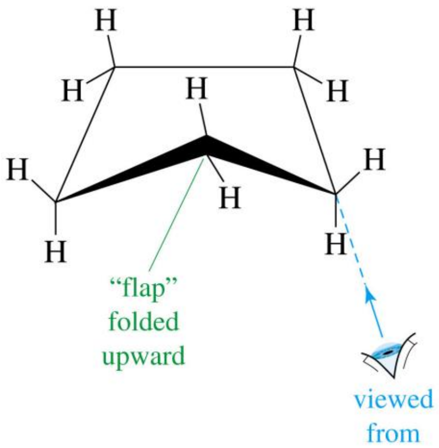


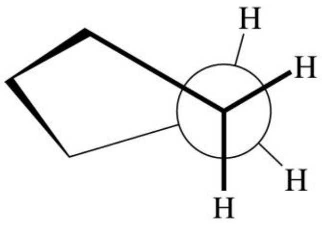
Newman projection of one bond

A planar geometry would force all the C-H bonds into eclipsing positions.

Cyclobutane actually adopts a slightly puckered conformation, with bond angles of 88°. This increases angle strain but reduces torsional strain.

Cyclopentane





Newman projection showing relief of eclipsing of bonds

Cyclopentane is not planar either, since this also would require all C-H's to be eclipsing.

The molecule adopts a puckered 'envelope' conformation, which reduces the torsional strain.

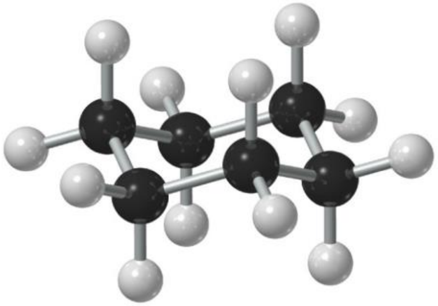
Cyclohexane

Cyclohexane is by far the most common cycloalkane in nature and also in organic chemistry.

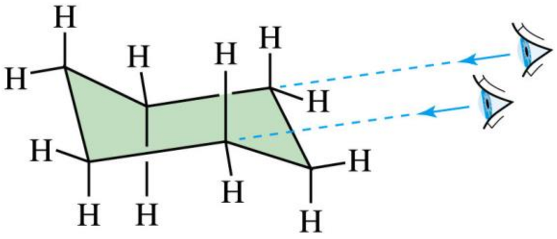
Zero ring strain implies the bond angles must be 109.5° (no angle strain) and also no eclipsing interactions between the C-H bonds (no torsional strain).

Boat and Chair Conformations

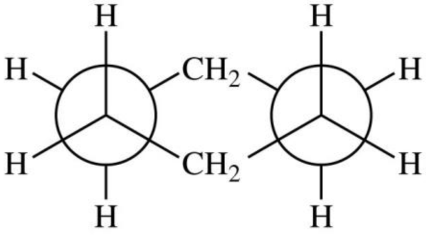
Cyclohexane adopts a puckered structure. The most stable conformation for cyclohexane is called the **chair** conformation.



chair conformation



viewed along the “seat” bonds

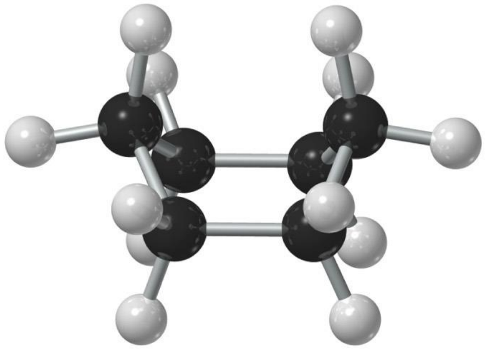


Newman projection

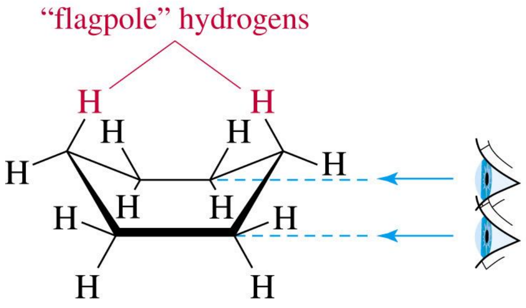
In the chair conformation, all the bond angles are 109.5° and all the C-H bonds are staggered. (Zero ring strain)

Boat Conformation

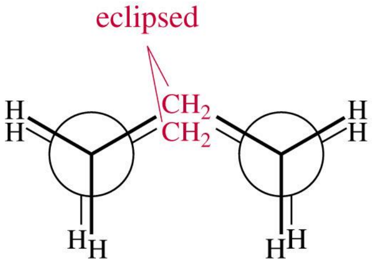
Cyclohexane can also exist in another conformation called the **boat**.



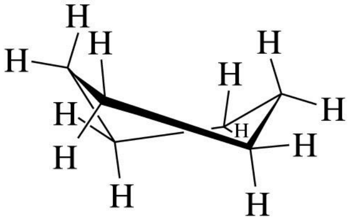
boat conformation



symmetrical boat



Newman projection

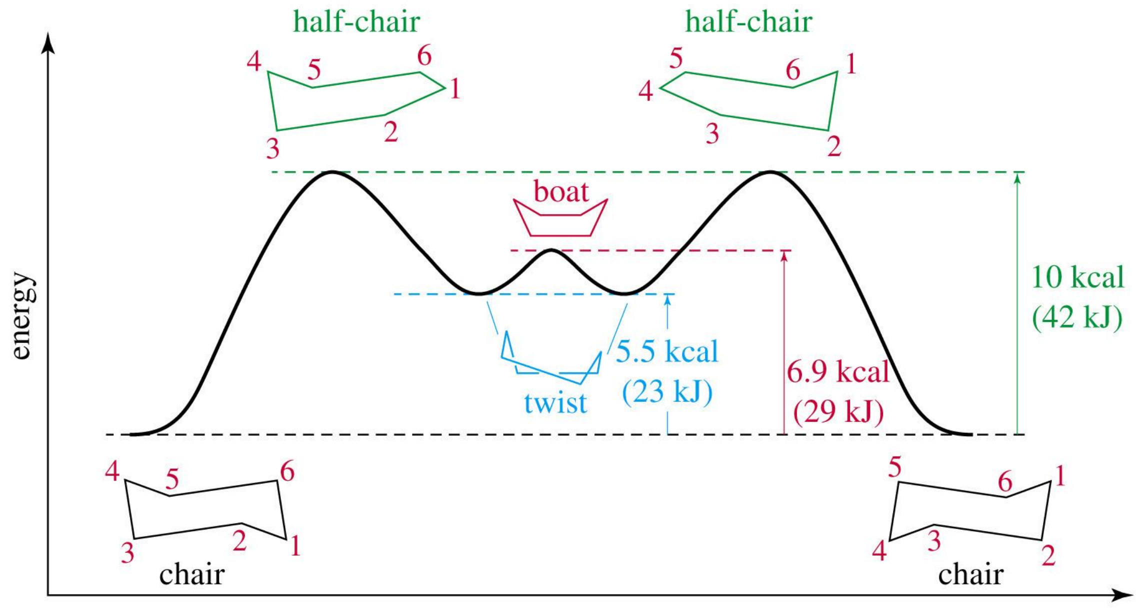


"twist" boat

The boat is just a chair with the footrest flipped up.
This also has bond angles of 109.5° and thus avoids any angle strain, *but* there is torsional strain.

The two hydrogens at the ends of the boat are in close contact, causing torsional strain. These *flagpole hydrogens* are eclipsed.

To avoid these unfavorable interactions, the boat conformation skews slightly, giving a *twist boat* conformation.

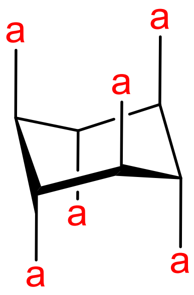


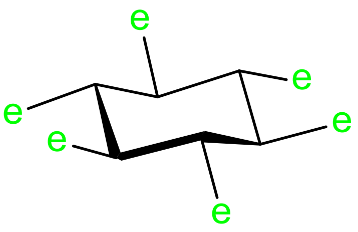
The chair is the **lowest** energy conformation, although since the energy barrier to ring flip is fairly small, there will always be some other conformations present.

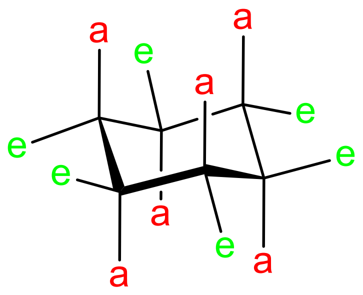
The *half chair* is the point of highest energy, and is not a stable conformation.

Axial And Equatorial Positions

If we look at an instantaneous snapshot of cyclohexane in a chair conformation, there are 2 types of C-H bond.

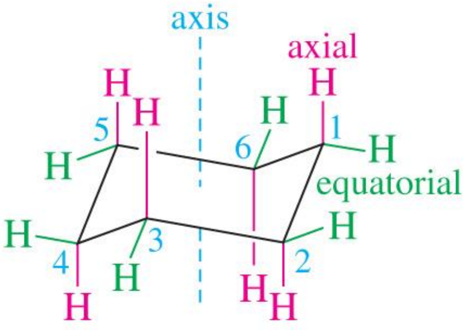


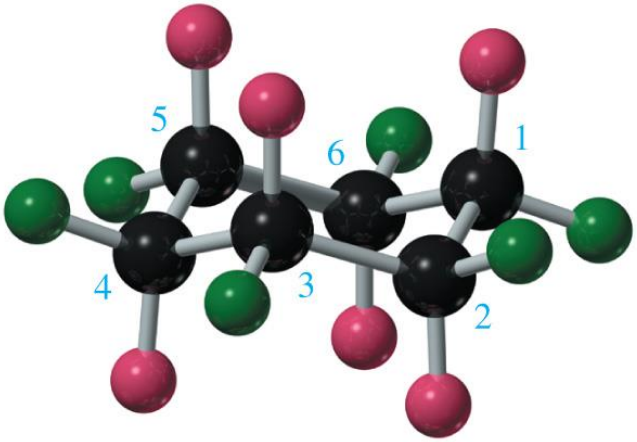




Six of the C-H bonds point straight up and down (*axial* bonds).
Six of the C-H bonds point out from the ring (*equatorial* bonds).

Notice the *alternating* pattern of the positions.

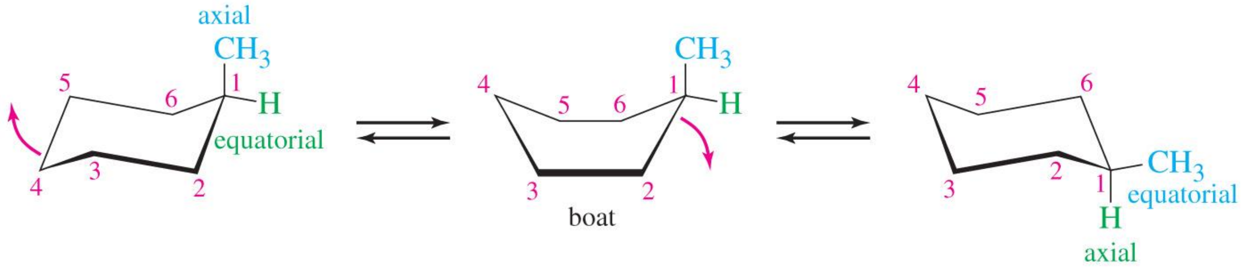




Conformations of Monosubstituted Cyclohexanes

A substituent on a cyclohexane ring can occupy either an *axial* or *equatorial* position.

Consider methylcyclohexane:



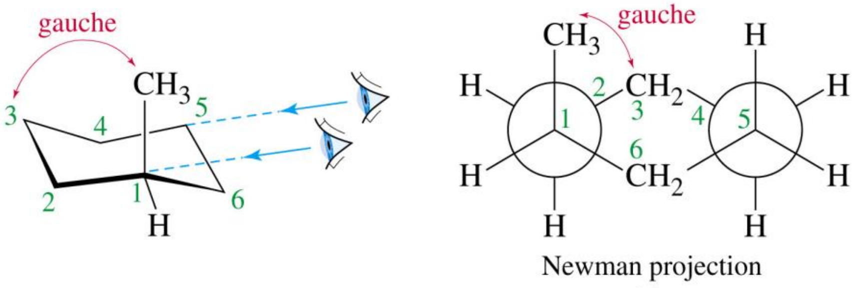
The chair conformation with the methyl *axial* can interconvert via a boat conformation into a chair conformation with the methyl *equatorial*.

The energy barrier for this is low, and this interconversion takes place rapidly at room temperature, although the conformation of lower energy predominates.

It is found that the methyl *equatorial* conformation is 1.7kcal/mol *lower* in energy than the methyl *axial* conformation.

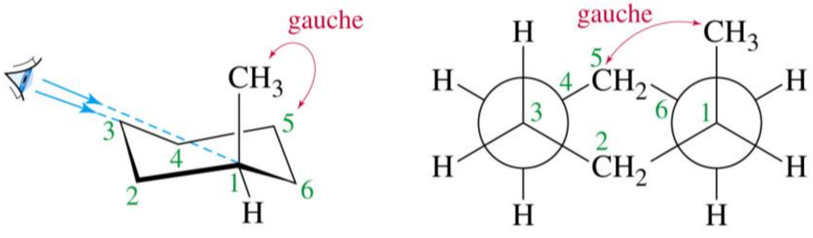
Both chair conformations are lower in energy than the boat.

When the methyl group is **axial**, it is gauche to C3 and C5.



Newman projection

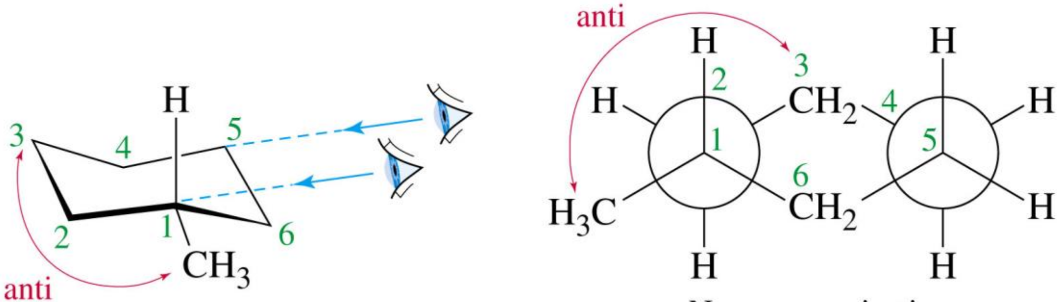
(a)



Newman projection

(b)

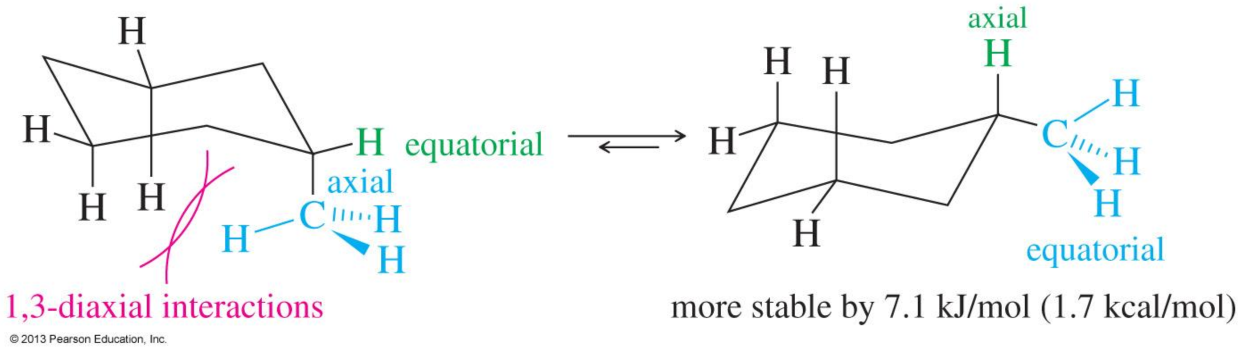
When the methyl is **equatorial**, it is anti to C3.



Newman projection

So axial methylcyclohexane has 2 gauche interactions (2 x 0.9kcal)
Equatorial methylcyclohexane has no gauche interactions.
Predict that **EQUATORIAL** is favored by 1.8kcal. (Good agreement).

This gauche interaction is also known as a **1,3 diaxial interaction**.



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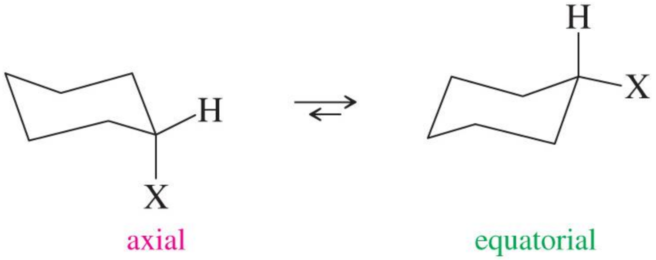
The axial substituents on C1 and C3 are close in space and their electron clouds repel one another.

Generally a *larger* substituent gives rise to a *larger* difference in energy between the axial and equatorial conformations.



	ΔG (axial–equatorial)	
X	**(kJ/mol)**	**(kcal/mol)**
—F	0.8	0.2
—CN	0.8	0.2
—Cl	2.1	0.5
—Br	2.5	0.6
—OH	4.1	1.0
—COOH	5.9	1.4
$—CH_3$	7.6	1.8
$—CH_2CH_3$	7.9	1.9
$—CH(CH_3)_2$	8.8	2.1
$—C(CH_3)_3$	23	5.4

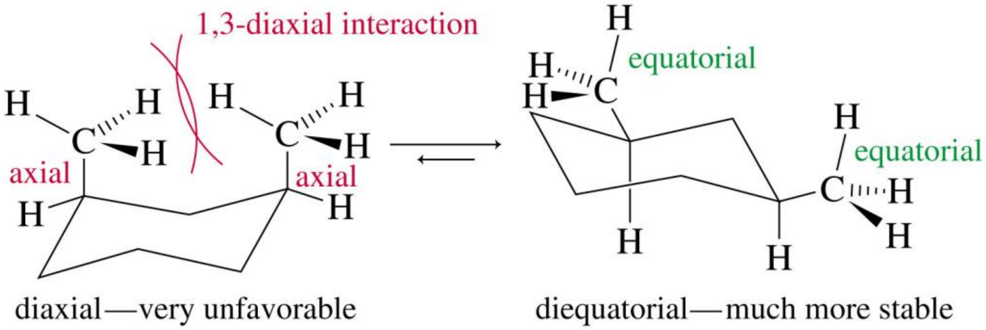
(Often t-Bu groups are used to fix cyclohexanes into single conformations).

Conformations of Disubstituted Cyclohexanes

There are severe steric interactions when there are two large groups axially oriented on C1 and C3 (or C1 and C5).

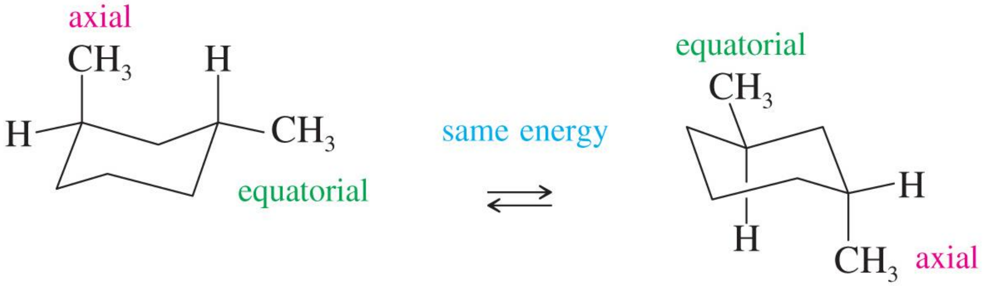
E.g. the differences between *cis* and *trans*-1,3-dimethylcyclohexanes.

Consider cis-1,3-dimethylcyclohexane:



The *diaxial* conformation has very unfavorable 1,3 diaxial interactions, and so the molecule will flip to the lower energy *diequatorial* conformation

Now, consider trans-1,3-dimethylcyclohexane:



Both conformations of trans-1,3-dimethylcyclohexane are the **same** since they both contain an axial and equatorial arrangement. (Same molecule).

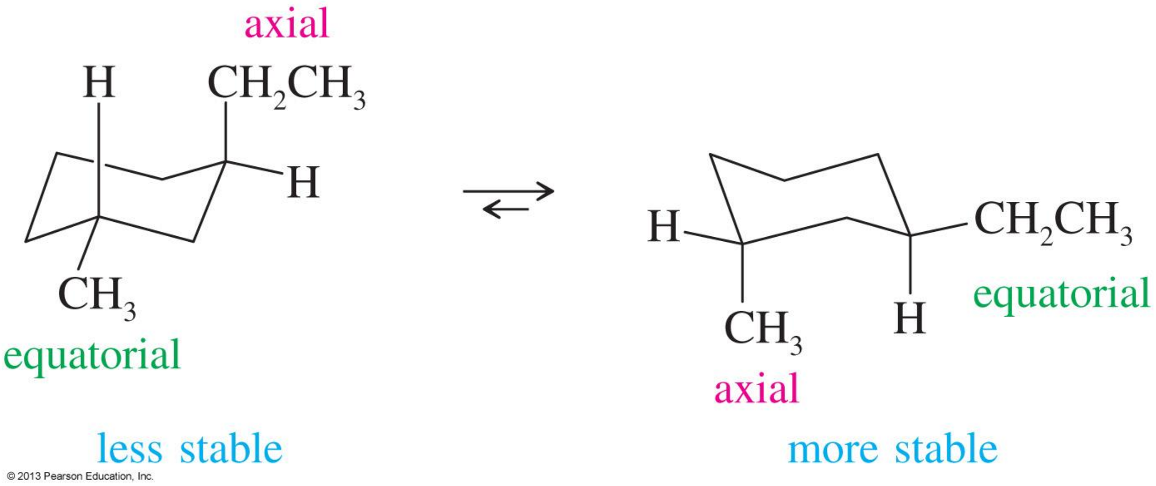
The stable conformer of cis-1,3-dimethylcyclohexane has the diequatorial conformation. The trans isomer must have one methyl group in an axial (unfavorable) position.

Therefore the cis isomer would be predicted to be *more stable* by around 1.7kcal/mol.

Substituents of Different Sizes

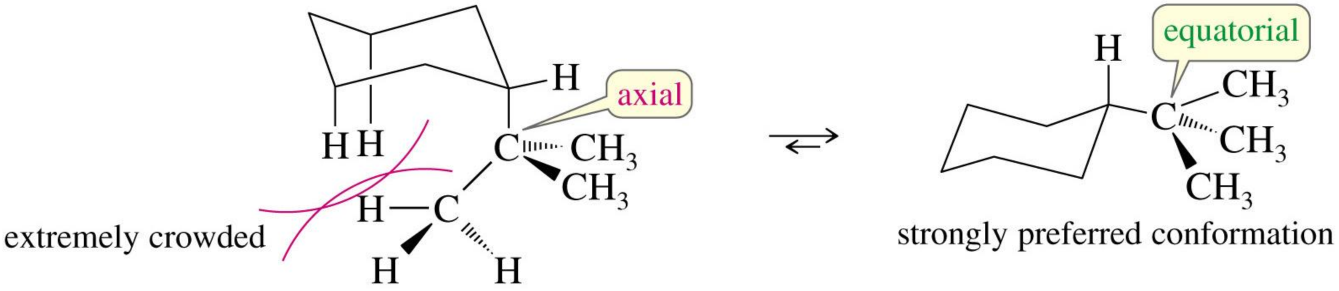
The energy difference between axial and equatorial positions is generally higher for larger (bulkier) groups.

Therefore to determine the most stable conformations for substituents of different sizes, if both cannot go equatorial, then the **larger** group goes **equatorial**, and the **smaller** goes **axial**.



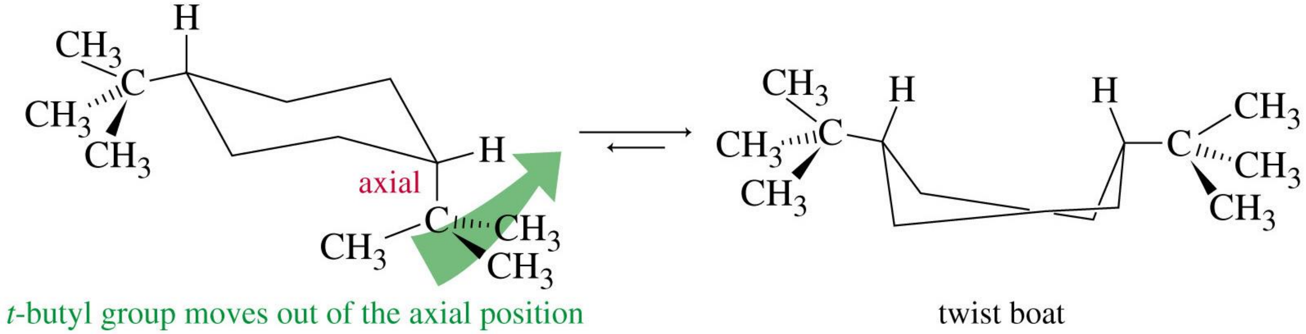
Extremely Bulky groups

As a general rule, a t-butyl group will always go equatorial because it is so bulky.



If there are two t-butyl groups in the same cyclohexane molecule, they *both* will want to go equatorial.

If they cannot, then the molecule can be forced into a twist boat conformation, which is less sterically crowded, and of lower energy.



Bicyclic Alkanes

When two or more rings are joined, the molecule is said to be *polycyclic*.
(A molecule with two joined rings is *bicyclic*, etc.)

There are 3 ways that rings can be joined:

- Fused
- Bridged
- Spirocyclic

Fused Rings

Fused rings share two *adjacent* carbon atoms and the bond between them. (These are the most common).

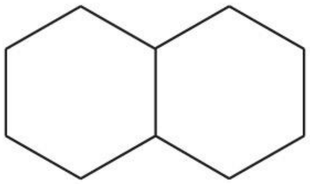
Bridged Rings

These share two *non-adjacent* carbon atoms (the bridgehead carbons) and one or more carbon atoms between them.

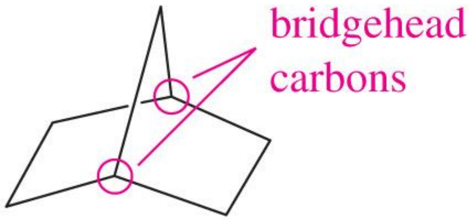
Spirocyclic Compounds

The two rings share only one carbon atom. (These are comparatively rare).

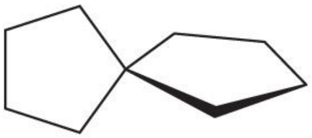
fused bicyclic



bridged bicyclic



spirocyclic

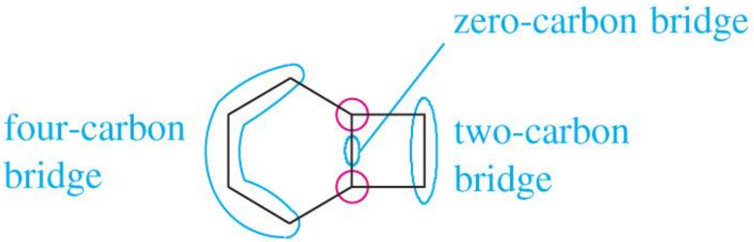


Nomenclature of Bicyclic Alkanes

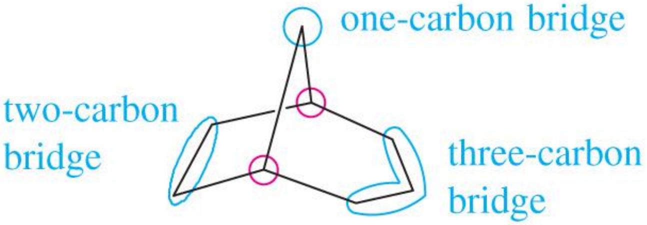
Rule 1 The name is based on the number of carbons in the ring systems.

Rule 2 This name is prefixed by bicyclo- (or spiro-), and square brackets with three (or two) numbers.

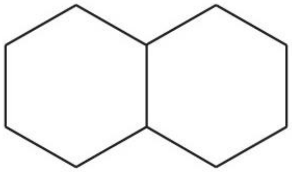
Rule 3 For fused and bridged compounds: count the carbon bridges around the shared atoms, and arrange the three numbers in decreasing order. (Spirocyclic systems only have two numbers, but the same rule applies).



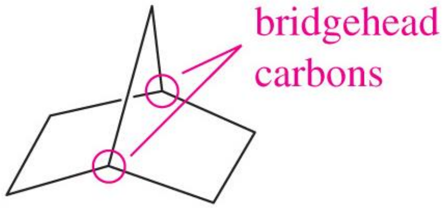
bicyclo[4.2.0]octane



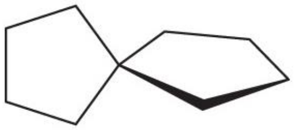
bicyclo[3.2.1]octane



bicyclo[4.4.0]decane
(decalin)



bicyclo[2.2.1]heptane
(norbornane)

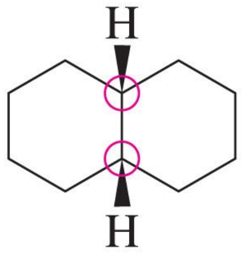


spiro[4.4]nonane

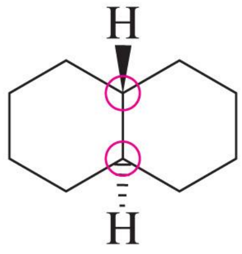
Cis and trans-Decalin

Decalin is probably the most common bicyclic alkane.

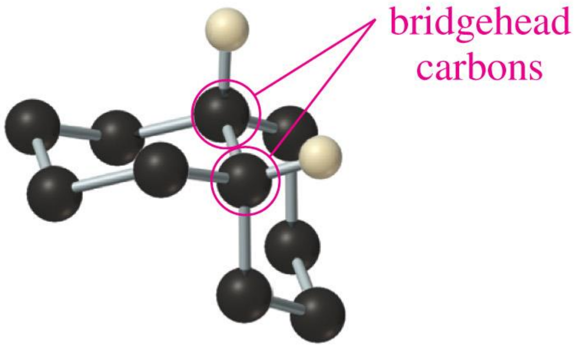
It can exist in two geometric isomers (*cis* and *trans* decalin). Both isomers have both cyclohexanes in chair conformations.



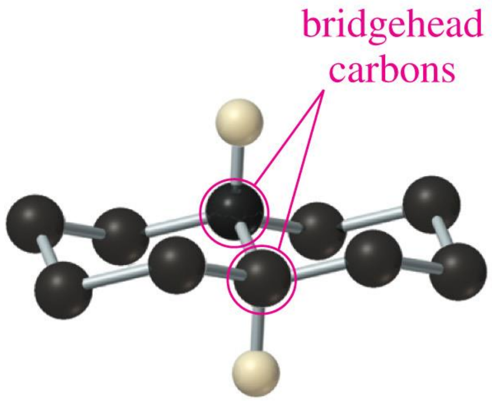
cis-decalin



trans-decalin



cis-decalin



trans-decalin

Cis-decalin has a cis ring fusion (both hydrogens up)

Trans-decalin has a trans ring fusion. (one hydrogen up, one down)

Cis-decalin is fairly flexible, whereas *trans*-decalin is quite rigid.