Alkanes, Cycloalkanes and Bicycloalkanes. Nomenclature, Structural Isomerism and Conformational Theory.

Functional Groups

More generally, specific groups of atoms are called “functional groups” and these groups do show characteristic chemical behaviour. Most of these FGs either have polar bonds or π bonds or both. We use functional groups to classify chemicals.

Functional Groups

Class Name	Functional Group	Example
Alkanes	None	Methane
Alkenes	C=C double bond	Ethane
Alkines	C≡C triple bond	Acetylene
Nitriles	-CN cyano g.	Acetonitrile
Alkohols	-OH hydroxyl g.	Ethanol
Ethers	-OR alkoxide g.	Dimethylether
Amines	$-NH_2$ amino g.	Ethylamine
Imines	=NR	Formimine
Ketones	-C(O)- carbonyl	Dimethylketone
Aldehydes	-C(O)H carbonyl	Acetaldehyde
Acids	-C(O)OH carboxyl	Acetic acid
Esters	-C(O)OR	Methylacetate
Amide	-C(O)NH-	Formamide
Anhydride	-C(O)-O-C(O)-	Acetic anhydride

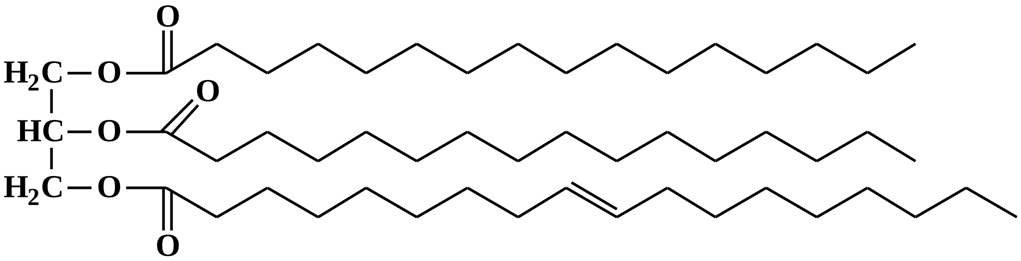
Hydrocarbons - Definitions

Hydrocarbon: A compound that contains only C and H. Hydrocarbons are classified as **saturated** or **unsaturated**. Saturated hydrocarbons have the maximally possible number of hydrogens - they are saturated with hydrogens.

Alkanes C_nH_{2n+2} (methane, ethane, propane, butane, ...)
Alkenes C_nH_{2n} (ethene, propene, butene, …)
Alkines C_nH_{2n-2} (ethine, propine, butine, …)

We use the term terms **aliphatic** and **aromatic** for all of those molecules without and with aromatic rings, respectively. The alkanes are the simplest molecules of the aliphatic type. The term aliphatic means “fat”. Originally this name was given to glycerin esters (which are fat). More generally speaking, all molecules that contain long alkyl chains are much like fats:

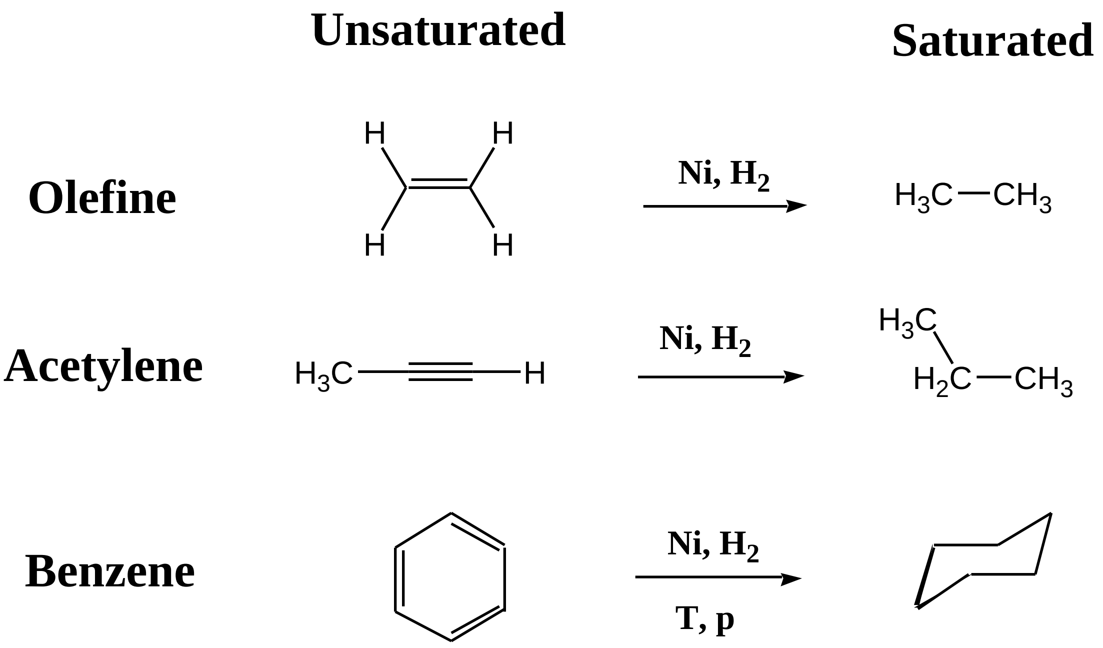
(a) insoluble in water (hydrophobic)
(b) less dense than water (about 0.7 g/ml)



animal fat

Test for Unsaturation

Unsaturated hydrocarbons do contain multiple bonds (double and/or triple bonds). The multiple bonds are functional groups with a high reactivity toward addition of H_2 (**hydrogenation**). Breaking a π bond and the H_2 bond requires less energy than is gained by the formation of two CH σ bonds. So the addition is energetically favorable. Yet it does not occur spontaneously. Need for “activation energy”. Usually we add H_2 in the presence of the **catalyst Ni**. Ni dissolves H_2 as H atoms and those atoms are very reactive.



Double Bond Equivalents: Ring or Unsaturation?

Formulas that show the relation between the number of Cs and the Hs for alkanes, alkenes, and alkines. They are:

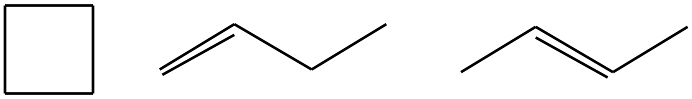
Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkines	C_nH_{2n-2}
Cycloalkanes	C_nH_{2n}
Cycloalkenes	C_nH_{2n-2}
Cycloalkines	C_nH_{2n-4}

For each ring formation from a chain molecule we need to take away one H at each end. Thus, for each ring the number of Hs will be reduced by 2. The formulas for the cyclic hydrocarbons follow easily as given. If there are two rings, subtract another 2 Hs and so on.

Hence, **chain alkenes** and **ring alkanes** have the same formula. In the general formula an unsaturation or a ring have the same consequence. We use the term **double bond equivalent** to indicate how many rings and/or unsaturations there are. Let’s look at an example.

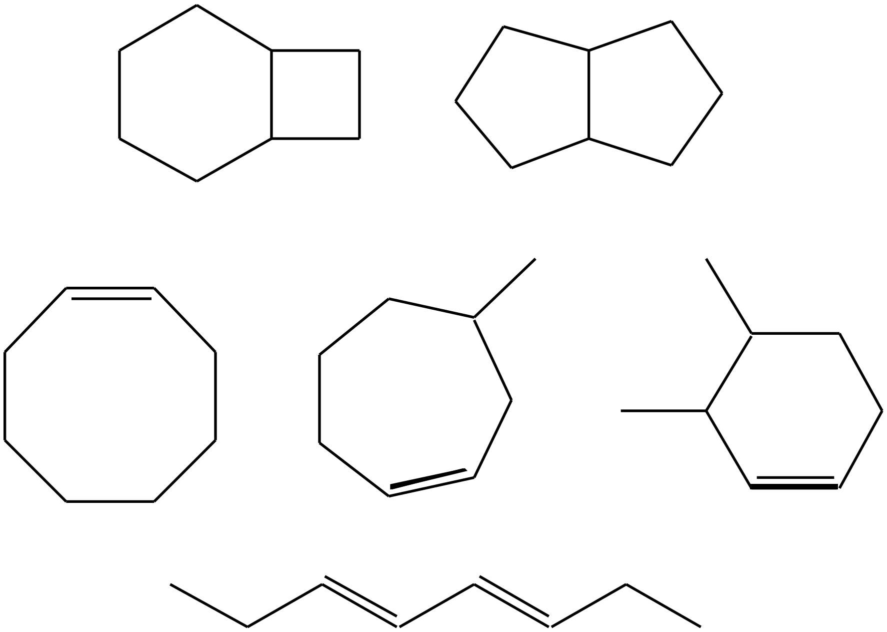
Example 1: C_4H_8.

There are n=4 Cs. If this were a acyclic alkane, then it would have 2n+2 or 10 Hs. It doesn't; 2 Hs are missing. The double bond equivalent of 2 Hs is one. Therefore C_4H_8 is either unsaturated or it is a ring. Voila:



Example 2: C_8H_{14}.

N=8, Alkane would be C_8H_{18}. 4 Hs missing; 2 DBEs. Thus, this compound has either two rings, or one ring and a double bond, or two double bonds, or one triple bond.

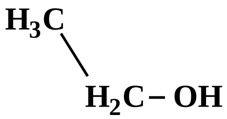


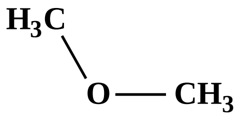
Structural Isomers

Isomers are different compounds with the same molecular formula.

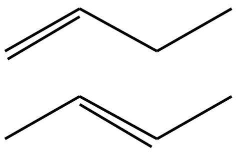
Structural isomers are isomers that have different connectivities between the atoms in the molecules. Structural isomers can be very different with regard to their chemical and physical properties.

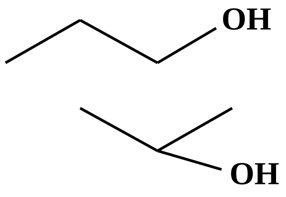
Example 1: Ethanol *versus* Dimethylether; C_2H_6O.
Different functional group; alcohol (-OH) or ether (-O-).
Ethanol can form H bonds and its bp is rather high (78.5°C) compared to that of ether (-23.6°C).





Example 2: Butenes and Propanols.
Different position of a functional group.

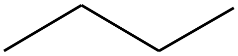




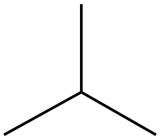
Example 3: Butanes; C_4H_{10}.

The chains of n-butane can align for optimal vdW attraction; the bp is higher (-0.5°C) that that of the branched *iso*-butane (bp = -12°C).

Butane

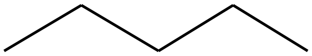


Isobutane

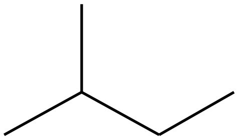


Example 4: Pentanes; C_5H_{12}.

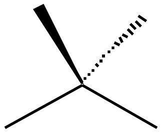
Pentane



Isopentane



Neopentane

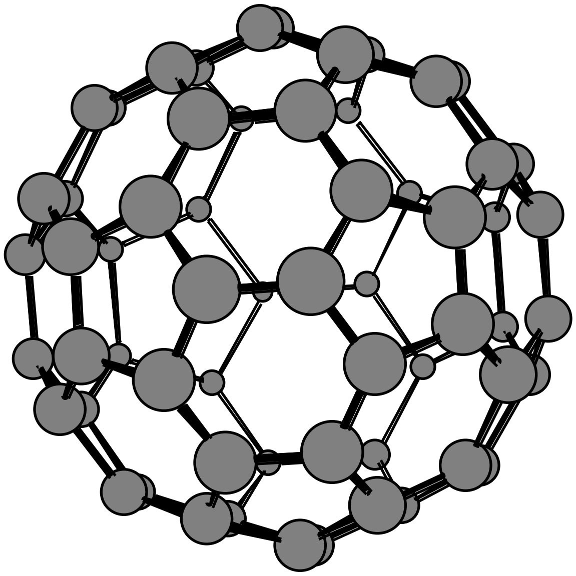


History of Organic Nomenclature

Trivial names are common. This is a pain for the beginning student who would rather have a good systematic nomenclature. Yet, as you become experienced chemists you will like the trivial names for the brevity!

Systematic nomenclature was developed by IUPAC — the International Union of Pure and Applied Chemistry.

Here is a little example to make the point about trivial names: “Buckminster Fullerene” named after the architect Buckminster Fuller - famous for his geodesic domes. Try to name this C_{60} molecule systematically! This is one of the most exciting molecule of recent years. Note the 5-rings with the 6-rings around them. Won the Nobel price in 1996.



Survey of Organic Nomenclature

Alkanes all end on the ending *-ane.* The number of Cs is given by the prefix. After the first few alkanes the nomenclature becomes systematic in that the number of the Cs becomes part of the name. For the **homologues** series — next follows by insertion of one CH_2 group — of the alkanes we get:

n	C_2H_{2n+2}	Name	Side Chain
1	CH_4	Methane	Methyl-
2	C_2H_6	Ethane	Ethyl-
3	C_3H_8	Propane	Propyl-
4	C_4H_{10}	Butane	Butyl-
5	C_5H_{12}	Pentane	Pentyl-
6	C_6H_{14}	Hexane	Hexyl-
7	C_7H_{16}	Heptane	Heptyl-
8	C_8H_{18}	Octane	Octyl-
9	C_9H_{20}	Nonane	Nonyl-
10	$C_{10}H_{22}$	Decane	Decyl-

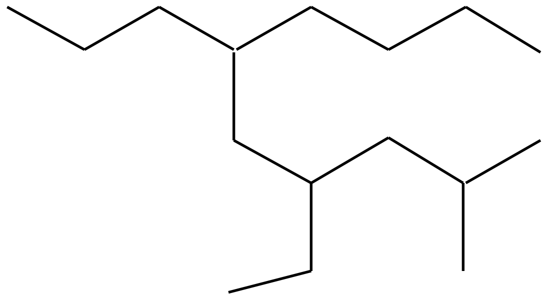
Side Chains

For branched systems we follow these rules to determine the systematic name of the molecule:

(1) Search for the longest chain. (No need for straight line)
(2) Search for all functional groups.
(3) Identify side chains and their location. Alphabetical order.
(4) Smallest sum of side chain location numbers.

Items (1) and (2) determine the name of the compound and the side chains are given in front of that name.

Example 1: Get the longest chain right. Get the numbering right.

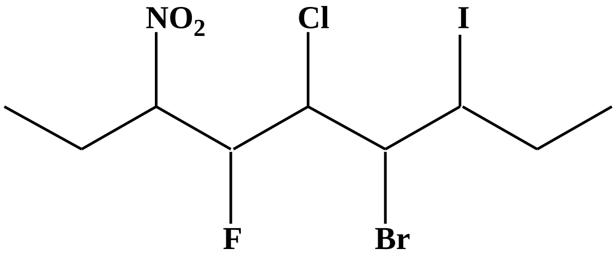


It is a decane!
It is 4-ethyl-2-methyl-6-propyldecane.

Example 2: Functional groups.

There are several ways of doing this. For now, let's give the compound the name of the basic alkane and then add the functional group just like a side chain. We always take the name of the functional group, remove the ending, and add the ending "o".

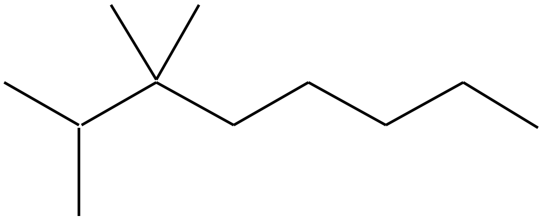
For chlorine: Replace the "ine" with "o"; chloro.



6-bromo-5-chloro-4-fluoro-7-iodo-3-nitro-nonane

Example 3: Multiple side chains of the same type.

Use prefix di, tri, tetra, penta, hexa ....

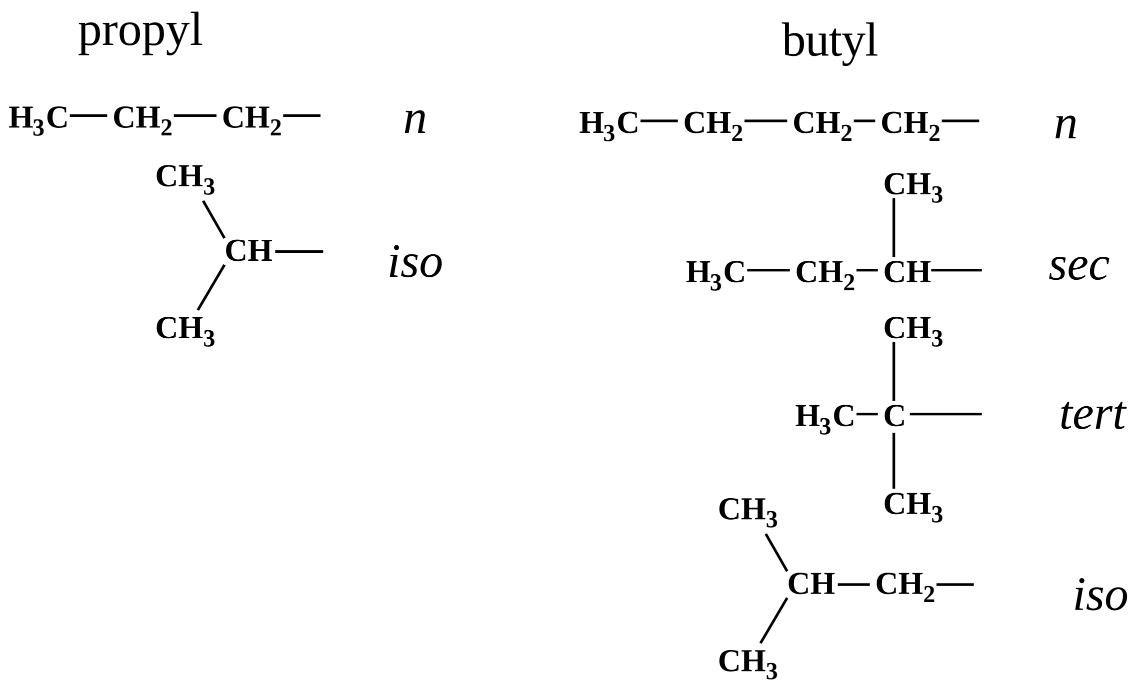


2,3,3-trimethyl-octane

Names for Alkyl Side Chains

The side chain names of straight chain alkyl groups are listed above — take the name of the alkane without the ending -ane and add the ending -yl.

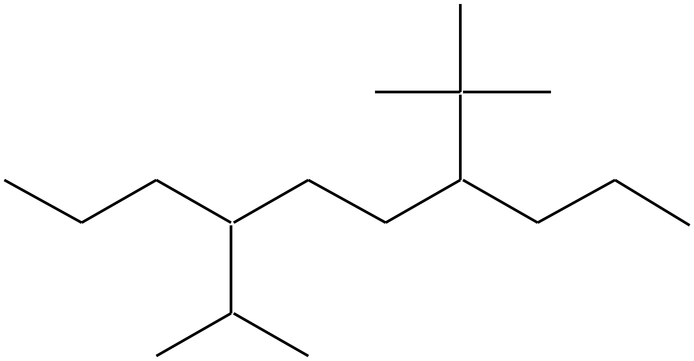
Remember these branched side chains:



Degree of Substitution. Primary, secondary, tertiary, and quaternary carbon atoms, respectively, are denoted 1°, 2°, 3°, and 4°, respectively,and they denote carbon atoms that one, two, three, or four more carbon atoms attached, respectively.

Hydrogens are said to be primary, secondary, or tertiary depending on the number of carbon atoms — 1, 2, or 3 — attached to the carbon that carries that H.

Example: Branched side chains.



4-*iso*-propyl-7-*tert.*-butyl-decane
7-*iso*-propyl-4-*tert.*-butyl-decane

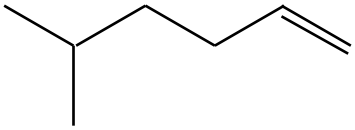
4-*iso*-propyl-7-*tert.*-butyl-decane aka
4-(2-methylethyl)-7-(2,2-dimethylethyl)decane

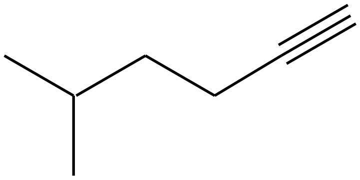
Alkenes and Alkines

The endings are -ene for the alkenes (double bond) and the ending is -ine (or -yne as in the book) for the alkines (alkynes) with their triple bonds.

Structural isomers associated with the location of the unsaturation are indicated by the number of that C atom after which the multiple bond occurs. This number comes right in front of the name of the skeleton and after the side chains.

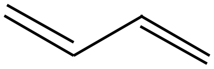
Example: 5-Methyl-1-hexyne or 5-Methyl-1-hexine.

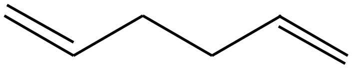




If a molecule contains two double bonds the we call it **diene** and it there are three double bonds then we call it a **triene** and so on. In these cases we give the location numbers separated by (a) comma(s). Note that we add an “a” to avoid pronounciation problems. Also note that if these numbers always differ by 2, then the molecule is conjugated.

Example: 1,3-butadiene and 1,5-hexadiene.

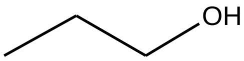


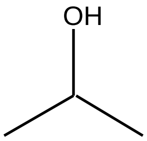


Alcohols

The final “e” is changed to “ol”. The location of the functional group is handled just like with the multiple bonds.

Example: Propanol and 2-Propanol.

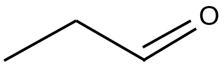


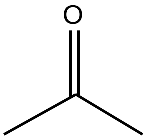


Aldehydes and Ketones

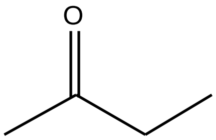
The final “e” is replaced by “al” for aldehydes and by “one” for ketones. For ketones, a very common way of naming them gives the names of both alkyl groups followed by “ketone”.

Example 1: Propanal and Propanone.





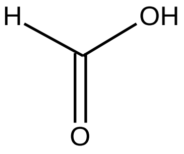
Example 2: Methylethylketone.

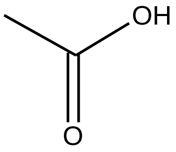


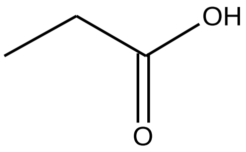
Carboxylic Acids

The ending “e” is replaced by “oic acid”. Trivial names are common for the acids.

Examples: Ethanoic acid is acetic acid; Methanoic acid is formic acid, Propanoic acid is propionic acid and so on.



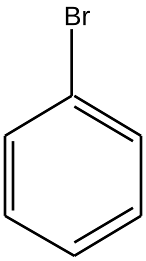


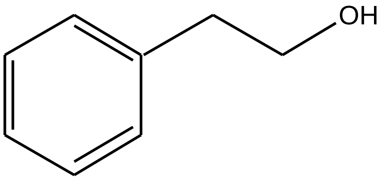


Aromatic Compounds

There are two ways. Either we consider the molecule as an “aromatic compound” and treat the rest as a substituent or we treat the benzene as a substituent. Benzene as a substituent has the name **phenyl**. If the side chain has a functional group, then we usually go with the latter option.

Examples: Bromobenzene and 2-Phenylethanol.





Conflicts in Numbering

If there are several functional groups in the molecule then we have a conflict regarding the selection of an ending. Suppose there are a carbonyl group (aldehyde) and a hydroxyl group present. “al” or “ol”? To remedy this situation, the various **functional groups are assigned different priorities**.

For the heteroatom containing groups, the basic (rough) rule is: “The higher the oxidation state, the higher the priority.”

alkyl, phenyl, X < ines < enes < amine < ol < A/K < acid derivatives.

Conformational Theory of Acyclic Compounds

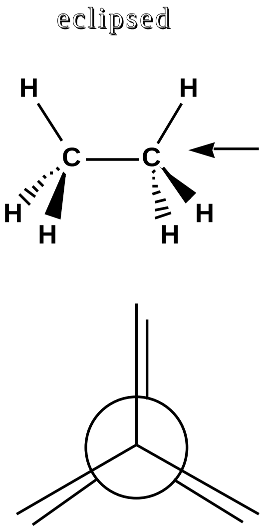
Alkanes contain CC σ bonds. The name "σ bond" was given to these bonds, because the overlap between the C sp^3 orbitals does not depend on the relative positions of the methyl groups *to a first approximation.* The rotation around the CC bond in ethane requires indeed very little energy — but not zero energy. Certain arrangements are preferred. The relative orientation of the methyl groups are called **conformations** and those structures that are local minima are called **conformers**.

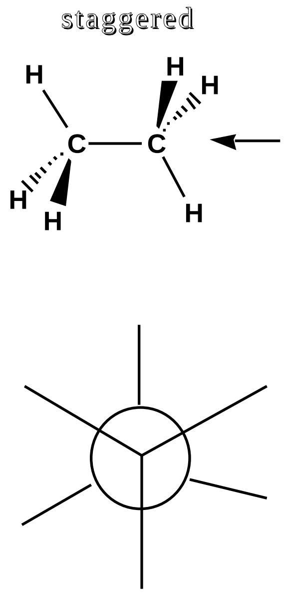
We'll be talking about rotations about CC single bonds and we need a nice way of illustrating the relative orientations. We can do this in several ways using

(a) 3-dimensional formulas
(b) using perspective drawings
(c) with Newman projections

Ethane Conformations

Examples are shown for the ***staggered*** and for the ***eclipsed*** conformations of ethane. *Eclipsed* refers to structures in which the H-C-C-H are in the same plane and *cis* with each other; *staggered* refers to structures in which the Hs of H-C-C-H avoid each other as much as possible. Anything other is called ***skew***.





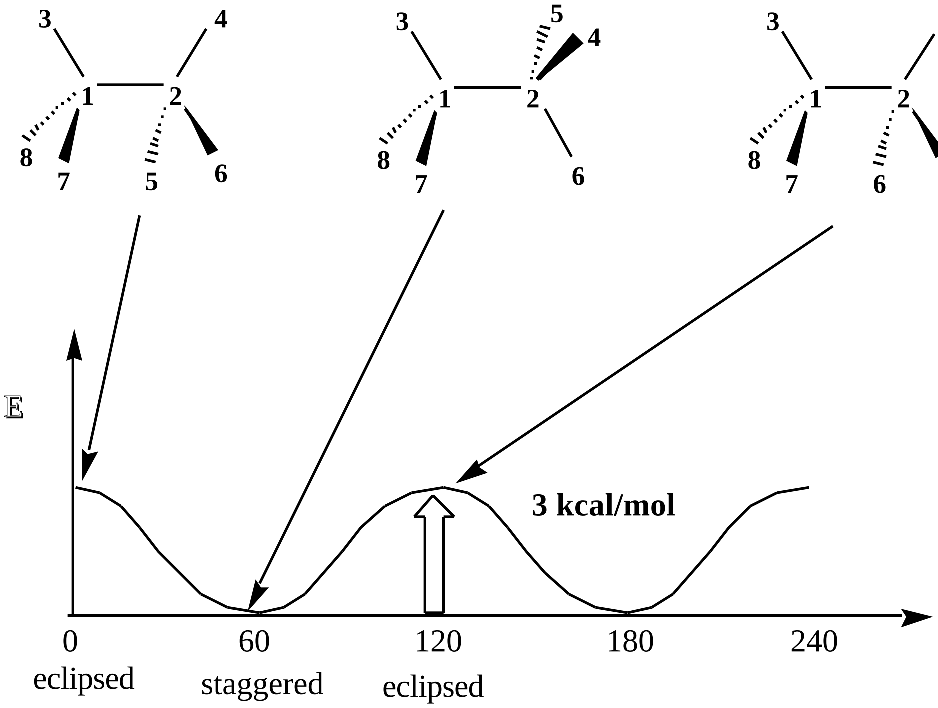
Newman Projections

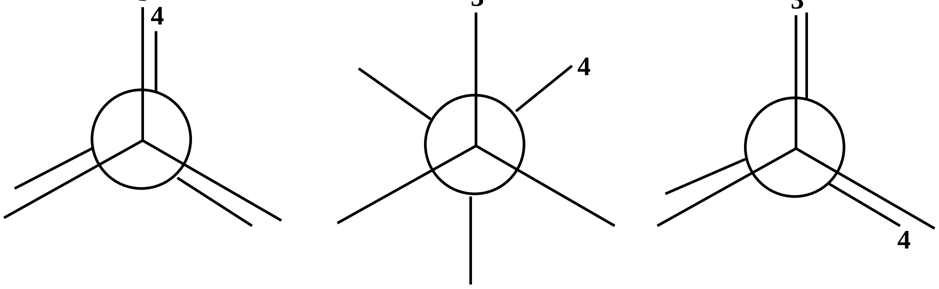
Perspective drawings that show the conformations along a bond as seen in the direction of the bond. Note the observer in the above pictures. Two rules: (1) The proximate (to the observer) C is indicated by a point to which the substituents are attached. (2) The far C is indicated as a circle from which the substituent bonds emerge.

Rotational Energy Profiles

The Newman projections are well suited to investigate *rotational barriers*. Rotational energy profiles show the energy as a function of the dihedral angle between the two groups attached *via* the single bond. Two examples: Ethane and Butane. For the latter we examine the central bond only.

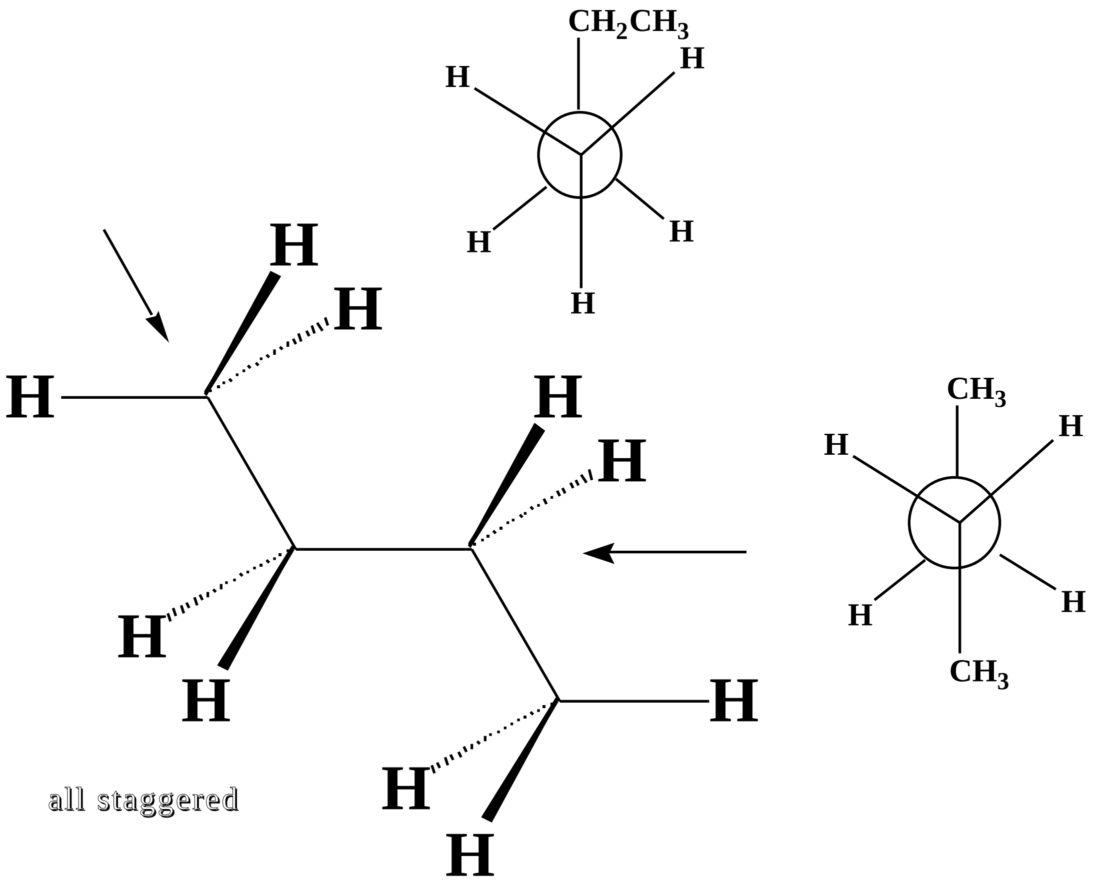
Example 1: Ethane. Let’s keep track of H3 and H4.





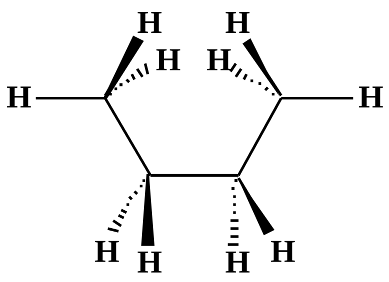
Example 2: Butane

Obviously, if there are several σ bonds in a molecule, then we might have to draw different Newman projections for *each* of the bonds that allows for different conformations. Let's look at the central and at the terminal bonds in butane as an example.



The second example will illustrate that there can be *several* structures with *staggered* conformations. These will have different energies and they will all be more stable then the *eclipsed* structures. *Trans* and *gauche* are local minima (both *staggered*) but *cis* is not a minimum (*eclipsed*). Note the new term "*gauche*" (French for left).

Example 2: Butane (central bond)



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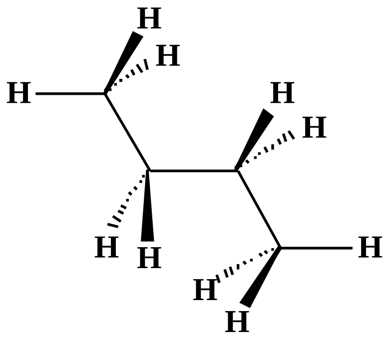

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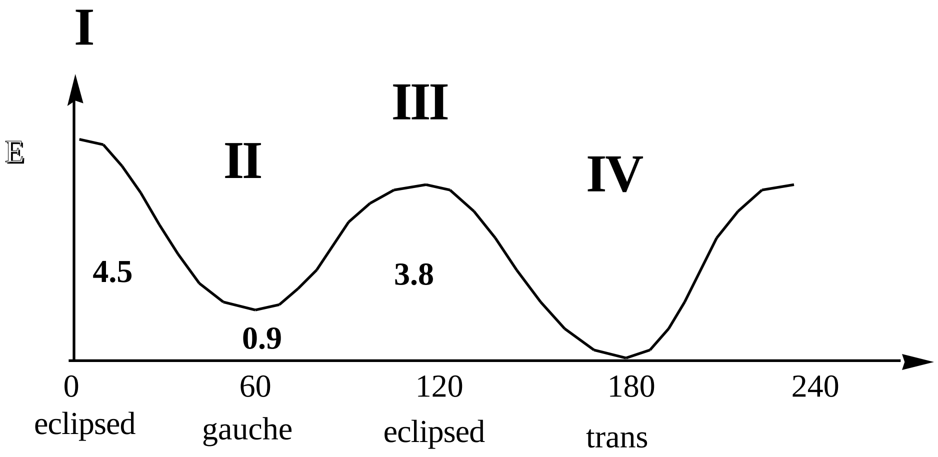

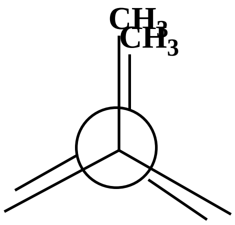

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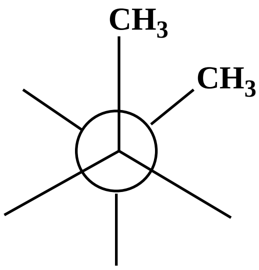

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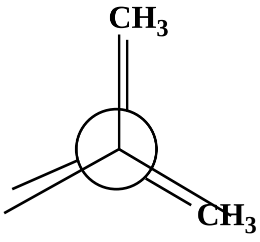

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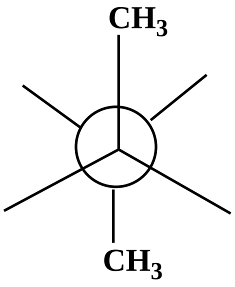


IV

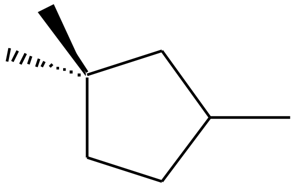
Problem

Draw the Newman projections and perspective drawings for all of the local minimum conformations of (a) 1-bromo-2-chloroethane and for (b) 3-hydroxypropanoic acid (consider both the CC bond and the CO bond of the hydroxy group). Give schematic representations of the rotational energy profiles. Clearly indicate what is *cis*, *trans*, and *gauche*, and what is *staggered* and *eclipsed*! Estimate the barriers (a good understanding of trend is half the solution).

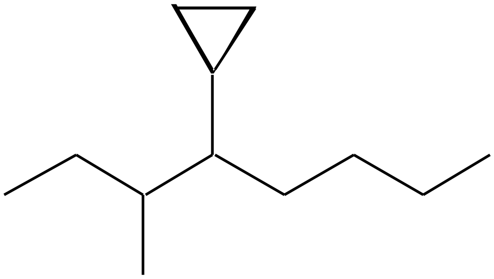
Nomenclature of Cycloalkanes

If an alkane contains a ring that is larger than the longest non-ring chain, the we call the alkane a cycloalkanes. If a small ring is attached to a larger non-ring, then you name the alkane in the usual fashion and add the "cycloalkyl" as a substituent.

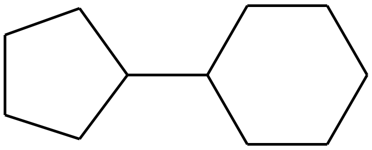
Example 1: 1,1,3-trimethylcyclopentane



Example 2: 4-cyclopropyl-3-methyloctane



Example 3: Cyclopentylcyclohexane



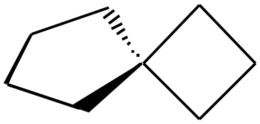
Types and Nomenclature of Bicyclic Systems

Spiro-bicyclic: Two rings share one atom.
Fused-bicyclic: Two rings share two bonded atoms.
Bridged-bicyclic: Two rings share two non-bonded atoms (they are called the bridgehead carbons).

Spiro[n.m]alkane

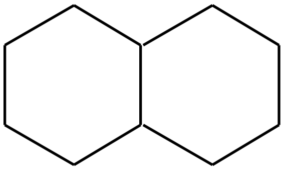
Spiro-bicyclic compounds are named according the number of C-atoms in both rings combined. The numbers "n" and "m" in [n.m] reflect how many atoms are in each bridge.

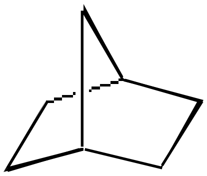
<u>Example:</u> Spiro[4.3]octane



Bicyclo[n.m.l]alkane

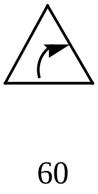
Fused and bicyclic systems are named alike. They are named according the number of C-atoms in both rings combined. The numbers "n","m" and "l" in [n.m.l] reflect how many atoms are in each bridge. For fused systems, one has [n.m.0].
<u>Examples:</u> Decaline or bicyclo[4.4.0]decane and Norbornane or bicyclo[2.2.1]heptane

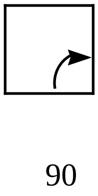


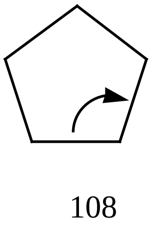


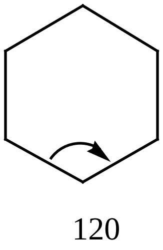
Structure of Cycloalkanes

In cycloalkanes each C-atom would have an sp^3 hybridization. That is, the angles at C should all be 109.5°. With small rings, this leads to the following apparent dilemma:







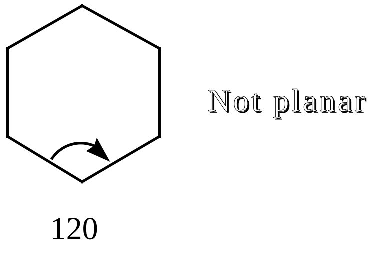


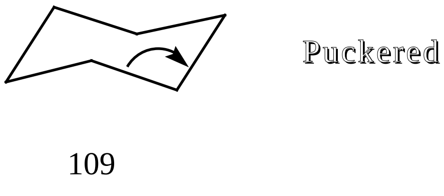
The geometric angles in the cyclopropane and cyclobutane are much **smaller** and the angles in the planar cyclohexane are much **larger**. Cyclopentane happens to be just about right.

Ring Puckering

The large rings are in fact **not planar**. Instead they are **puckered** and this ring pucker reduces the angles down to values that are consistent with the sp^3 hybridization.

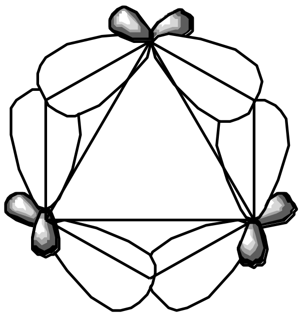
<u>Example:</u> Cyclohexane.





Bent Bonds

With the small rings the dilemma persists. If we do assume that the C-atoms are sp^3 hybridized, then we have to conclude that the bonds are bent in the fashion shown below. Such bent bonds are entirely possible. But let’s see what the consequence is for the overlap. The overlap in bent bonds is smaller than in the regular linear bonds. Thus, the bonds are weaker! We do see indeed weaker bonds in the chemistry of cyclopropane. They are quite reactive and many reactions are known that open up the ring.



Ring Strain

If the bonds in the small rings are indeed weaker, then we should see some manifestation in experiments. Let's look at the heats of combustion of these cyclic alkanes. This was first done by **Adolf Baeyer**, a German. He thought that all rings were planar. Of course, later with the development of structure determination methods it turned out that the larger rings are puckered. Yet, for the small rings he was right and for the large rings he was not totally wrong. The large rings are "strained in some way" but not because they are planar (which they are not) but because of **angle**, **torsional**, and **steric** strain (explain with C_3H_6). He argued that the small rings should be destabilized by "ring strain" and measured the heats of combustion to show that.

Heats of Combustion: Measurement of Ring Strain

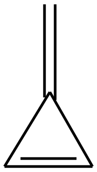
Cyclopropane + 4.5 O_2 ---> 3 CO_2 + 3 water $\Delta H(3)$
Cyclohexane + 4.5 O_2 ---> 3 CO_2 + 3 water $\Delta H(6)$

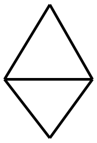
Molecules with strained rings contain more energy. If these rings are destroyed, then more energy is released. Hence, $-\Delta H(3)/3$ can be expected to larger than $-\Delta H(6)/6$. That is the case and these differences are used to quantify ring strain.

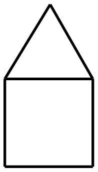
Heats of Combustion and Ring Strain

Molecule	-ΔH	-ΔH /CH_2	Strain /CH_2	Strain Total
cyclopropane	499.8	166.6	9.2	27.6
cyclobutane	655.9	164.0	6.6	26.4
cyclopentane	793.5	158.7	1.3	6.5
cyclohexane	944.5	157.4	0.0	0.0
cycloheptane	1108	158.3		6.3
cyclooctane	1269	158.6		9.6
cyclononane	1429	158.8		12.8
cyclotetradecane C_{14}	2204	157.4		0.0
methylenecyclopropene				40.9
Bicyclo[1.1.0]butane				67.0
bicyclo[2.1.0]pentane				55.3

The table shows the heats of combustion and the amount per methylene group. Arbitrarily, we set the "strain of cyclohexane" to be zero. So, this is a **relative scale**. The heats of combustion are larger for the other rings; those rings were less stable. Column 4 tells by what amount for each methylene group and column 5 contains the total strain energy. Some fancy strained rings also are included.



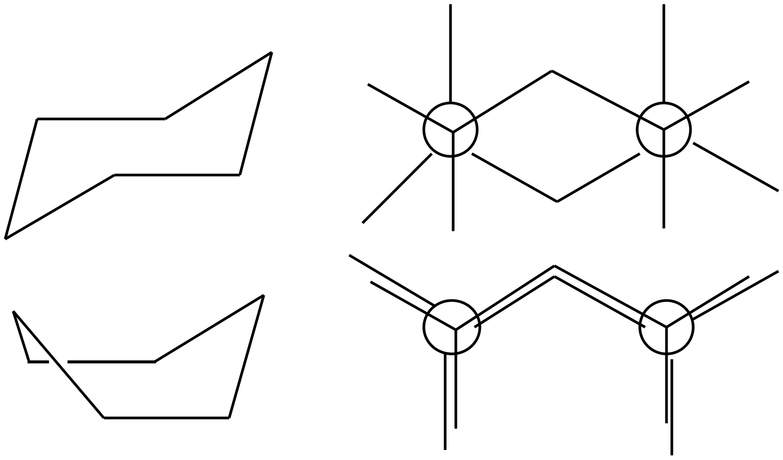




Conformers of Cyclohexane

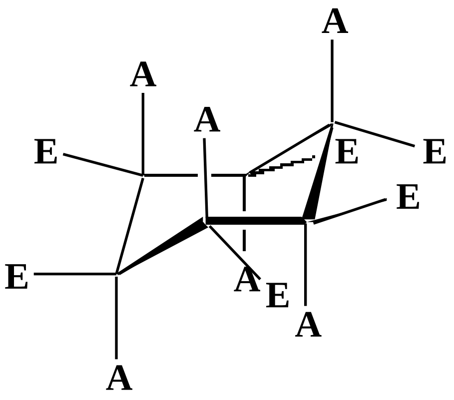
There are four types of conformations (chair, boat, twist-boat, half-chair) that are relevant. We'll focus mostly on the chair and boat forms. Models of these are shown below.

Note (a) the all *staggered* arrangement in the chair form and (b) the *eclipsing* interactions along two C-C bonds in the boat form. The half chair has still more *eclipsing* interactions and it is thus higher in energy. The twist-boat form is hard to visualize; it is more stable than both the boat and the half-chair but less stable than the chair form. (see visualization center!)



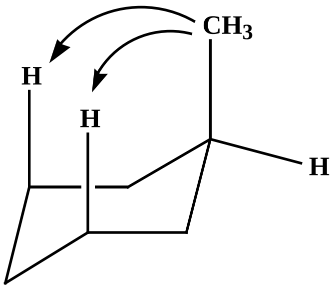
Axial and Equatorial Positions in the Chair Form

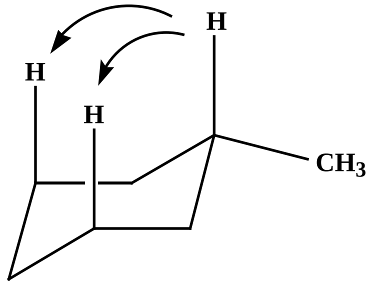
There are two distinctly different kinds of positions for the Hs in the most stable form of cyclohexane. These sets of substituents are the **axial** and the **equatorial** substituents (shown as E and A).



Energetically Non-Equivalent in Substituted Systems

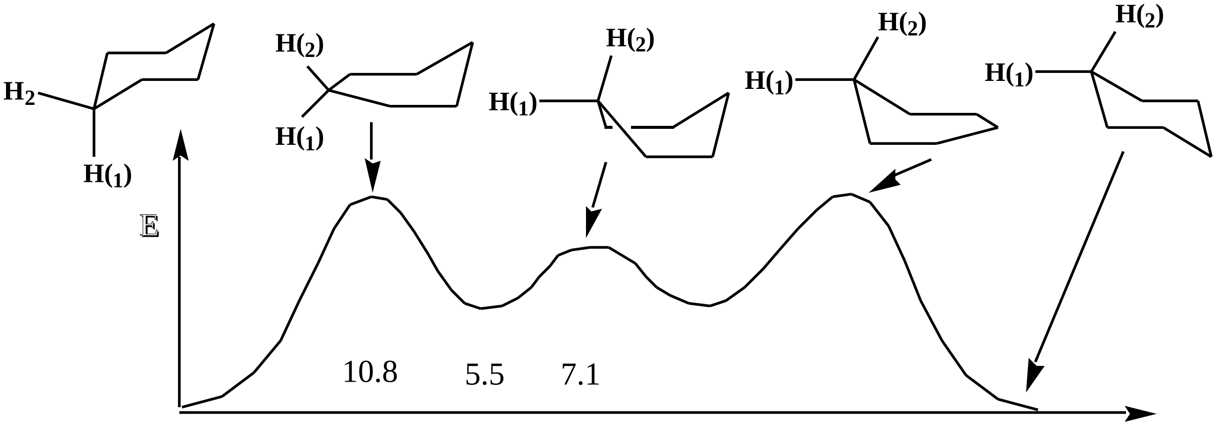
Suppose we have a methyl substituent connected to the ring. Would it be axial or equatorial? It would prefer the equatorial position because the **1,3 repulsive interactions** are minimized. The interconversion between axial and equatorial substituents can happen easily (*vide infra*) and the substituent will thus always be in the preferred position.





Equilibration between Axial & Equatorial Positions

Let’s suppose we have one H in an axial position. Can the structure be interconverted into one that has this H in an equatorial position? Well, yes. These are the conformational changes necessary to do this: *Chair* --> *half chair* --> *twist boat* --> *boat* --> *second twist boat* --> *second half chair* --> *second chair*. The energy required for these interconversions are shown in the energy profile.



The highest activation barrier is 10.8 kcal/mol. So, this type of interconversion can happen at room temperature. For the cyclohexane itself, this interconversion has little consequences, but for substituted derivatives there are important differences.

Relative Stability and Axial/Equatorial Isomer Ratio

Whenever several isomers are capable of fast isomerization, one needs to be concerned about the ratio of these isomers. This ratio depends on two factors, namely, (a) the temperature and (b) the energy difference between the isomers. The equation for the equilibration constant K is K = exp(-ΔE/RT). Inspection of the data shows that rather small energy changes can affect very significant changes in the isomer ratio.

ΔE kcal/mol	More stable isomer	Less stable isomer
0	50	50
0.651	75	25
1.302	90	10
1.744	95	5
2.722	99	1
4.092	99.9 quant.	0.1

Group Size and 1,3 Strain

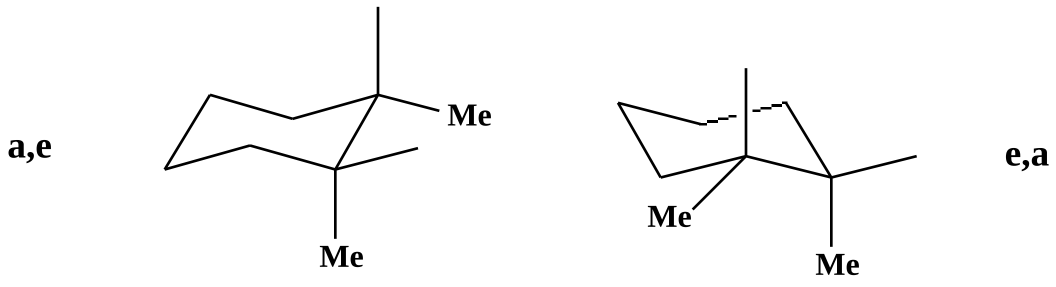
Depends on the size of the group just as one might expect. The Y-H interactions in kcal/mol are:

F	0.12	Me	0.9	Ph	1.5
Cl	0.25	Et	0.95	COOH	0.7
Br	0.25	*iso*-Pr	1.1	CN	0.1
OH	0.5	*tert*-Bu	2.7		

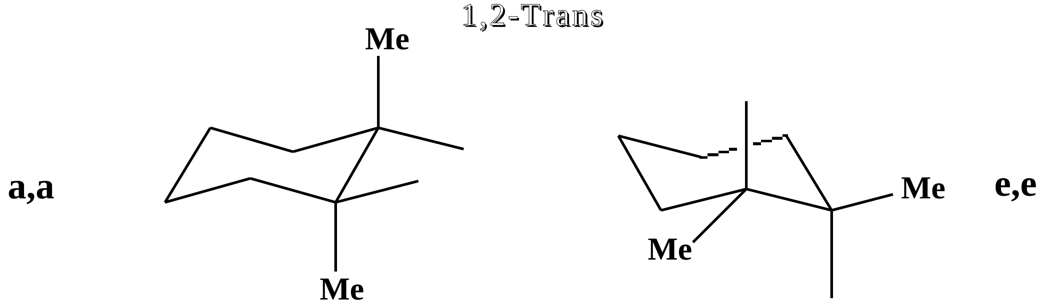
Disubstituted Cyclohexanes

There are several possibilities for isomerism. Let’s first look at the geometrical isomers and begin with the 1,2-disubstituted cyclohexanes. The two substituents can either be *cis* or *trans.*

1,2 Cis



1,2-Trans



The 1,2 *cis* always has one substituent in the axial and one substituent in the equatorial position; they are always on the same side. These two conformations have the same energy.

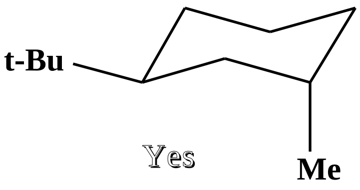
The 1,2 *trans* can be either a,a or e,e. These energies are not the same! The e,e is preferred. Steric repulsion argument.

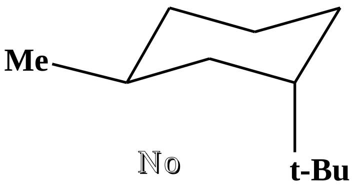
In general, 1,n-disubstituted isomers are *cis* (*trans*) if the substituents are on the same (on opposite) side(s). What does change is the position:

1,2 *cis* is a,e or e,a (same energy)
1,3 *cis* is a,a or e,e (e,e preferred)
1,4 *cis* is a,e or e,a (same energy)

And *vice versa* for the *trans.* Exercise with many examples!

Different substituents cause the a,e and the e,a structures to have different energies. In these cases the larger substituent will be in the equatorial position.
Example:





The actual preference energies can be calculated, to a very good approximation, by addition of the pairwise 1,3-interactions.

Hydrocarbon Properties

Nonpolar molecules, no polar bonds.
Intramolecular bonding strong! C-C and C-H bonds are hard to break. Not very many reactions.
Intermolecular bonding weak! Only London dispersion forces and they are weak. Does not form solutions with polar materials (**hydrophobic**), but does form solutions with other oils and fats (**lipophilic**). The lipohilicity of alkanes is the topic of the News Item to Chapter 3.

Melting and Boiling Points

At room temperature, the alkanes methane - pentane are **gases**. Hexane is the first **liquid** alkane (bp 36˚C) at RT. In Arizona during the summer, hexane would boil. Even heptane (bp 69˚C) would come close to boiling on many days in Death Valley. Hence, gasoline contains mostly octanes and heavier compounds — for very practical reasons as you can see.
At room temperature, the first alkane that could **solidify** is $C_{17}H_{36}$ (mp 23˚C). Yet, it might form an oil.

Branched alkanes melt and boil lower than straight chain alkanes. London dispersion depends on contact surface.

Melting points for even numbered alkanes are a bit higher than for the odd numbered alkanes. The former pack better in the solid. No big deal.

Hydrocarbon Resources and Uses

Boiling Range	Carbons	Name	Use
< 30	1-4	natural gas	🏠 heating
30-180	4-9	gasoline	🚦 cars
180-230	8-12	kerosene	✈ planes
200-320	10-18	diesel oil	🏢🏠🏠🏢🏠 🚦
305-405	18-25	heavy gas oil	🏢🏠🏢🏠🏠🏠🏢🏠

Crude Oils (Petroleum). Created from prehistoric plant biomass (fossil fuel), contains about 500 HCs and many other elements such as nitrogen and sulfur. Distillation aka. refining separates the fractions which are used as shown above.

Cracking. Modern society needs more of the low-C fuels than high-C fuels. The process of breaking down long alkanes into smaller ones is called “**cracking**”. This can be done **catalytically** (metals on silicon) or **with steam**. The alkanes also isomerize in the process (branched octane is a better gas than n octane). Cracking in the absence of hydrogen gas gives smaller alkanes and short alkenes (ethene, propene, butenes, pentenes). (The News Item to Chapter 7: Alkenes will deal with cracking!) Cracking the the presence of hydrogen — **Hydrocracking** — gives smaller alkanes and short alkanes (ethane, propane, butane, pentenes).

Reforming. Arocess that increases the amount of aromatic hydrocarbons (they prevent knocking in cars).

Natural Gas. 70% methane, 10% ethane, 15% propane and 5% other (water, other HCs, other gases).

Gas Additives. Octane numbers. 100 is *iso*-octane (2,2,4-trimethylpentane). 0 is *n*-heptane. Tetraethyllead (helps ignition). 1,2-dichloroethane (cleans up the Pb). Aromatic hydrocarbons. (No lead, more aromatic HCs, Catch22?). Alcohols (promotes more complete burn, higher efficiency, cleaner combustion).

Coal. Destructive distillation gives coal gas (methane and H_2), coal gas (liquids) and coke. Coal gasification and liquification: C and water --> CO and H_2 (“synthesis gas”) Synthesis gas is hydrogenated with Ni (Lurgi) to make methane or with Fe to give alkanes Fischer-Tropsch).

Chemical Properties of Alkanes

Alkanes also are called **paraffines** (latin for too little affinity). They are not very reactive at all. There are two very important reaction of alkanes. First there is the **halogenation**. This reaction provides the alkanes with a functional group and allows us to do further modifications to them. Halogenation of alkanes is thus very important! Then there is **combustion**; the reaction of alkanes with oxygen.

Halogenation

We discuss this reaction in great detail in the next chapter. For now let's just look at it briefly. Halogen molecules, such as Cl_2 and Br_2, react with alkanes under the influence of light to produce a halogenated alkane and HX. UV-Light cleaves the X-X bond and the X radicals do the reaction with the alkane. (This is the problem with chlorinated hydrocarbons in the environment: Eventually they release Cl_2 which is reactive because the sun light makes Cl radicals from it.)

<u>Example:</u> $CH_2 + Cl_2$ ---> CH_3Cl and HCl

Combustion

Reaction with O_2 to form CO_2 and water. If there is not enough oxygen present, then CO (carbonmonoxide) and C (soot) are produced.

Propane + 5.0 O_2 ---> 3 CO_2 + 4 water
Propane + 3.5 O_2 ---> 3 CO and 4 water
Propane + 2.0 O_2 ---> 3 C and 4 water

Environmental impact: CO_2 causes the greenhouse effect. CO is toxic (exhaust). C comes in great variety of forms which are not exactly good for us either. So, we are well advised to keep combustion processes to a minimum. Carbondioxide might well be regarded as the **Molecule of the 20th Century**! No other molecule was produced by mankind in such quantity. And, very likely, carbondioxide will turn out to be the molecule wit the largest effect on mankind.

Heats of Combustion

The energy released by the combustion of one mole of a hydrocarbon. It's about 210 kcal/mol for methane and 157 kcal/mol more for each CH_2 group in the homologues series.

Alternatives to Fossil Fuel Combustion

This topic also is addressed in the News Item to the present Chapter 3.

The three main energy sources are **biomass** (fossil fuels, renewable bio resources), **nuclear fuel** (fission reactions of heavy nuclei), **energy harvesting** (geothermal, sun light, wind power).

Nuclear power and energy harvesting can be used to create electricity and the electricity can be used to produce hydrogen has a s a fuel.

Overall, we have thus access to these **fuels**: Fossil fuel, renewable biomass fuels such as methanol and ethanol, hydrogen gas fuel. Now, what shall we do with them? Just burn them? That used to be the only answer. But now there is **combustion-free oxidation** (Ballard Power Systems).