

Alkanes: Nomenclature of Alkanes and Cycloalkanes

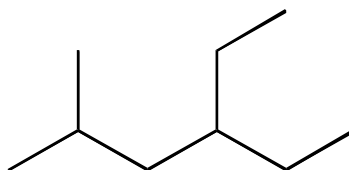
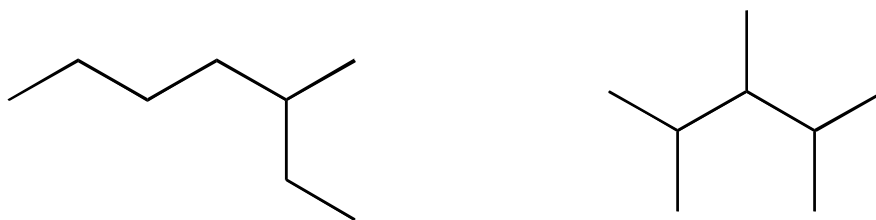
We've already seen how the alkanes are named according to the number of carbon atoms; 1 carbon is methane, 2 carbons is ethane etc. We've also seen how the suffixes change from -ane to -ene and -yne for alkenes and alkynes respectively.

The names of the alkanes from 1 to 100 carbons are given in Table 4.4. We won't see many molecules above C₈ (octyl) in this course.

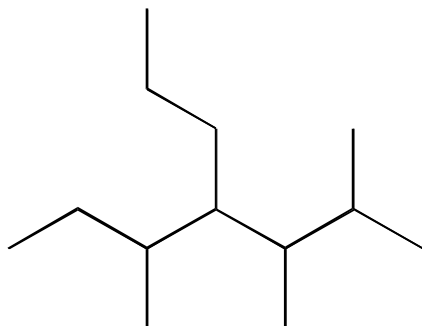
We've also talked about how to name branched alkanes using the **systematic IUPAC** rules:

1. find the longest continuous chain to get the name of the parent alkane
2. number the branches using the lowest possible number(s).

Here are some examples – name them according to IUPAC nomenclature.



There are a couple of rules we haven't seen yet. How do we name this molecule?



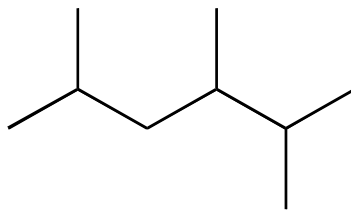
rule: choose the chain with most substituents

One of the heptane chains has two methyls and an isobutyl = three substituents

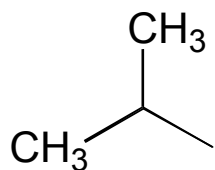
One of the heptane chains has one methyl and an isopentyl = two substituents

One of the heptane chains has three methyls and a propyl = four substituents

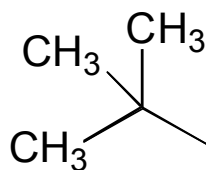
And this one?



A couple of trivial names that get a lot of use



Isopropyl
(1-methylethyl-)



tert-butyl
(1,1-dimethylethyl-)

How the names break down – IUPAC substitutive nomenclature

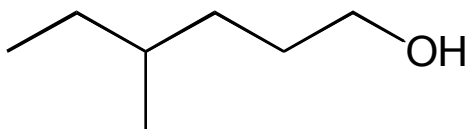
The longest alkane chain gives the **parent** name

The functional group gives the **suffix**. Note that halides don't count as functional groups for naming purposes. Alcohols (-ol), amines (-amine), ketones (-one), aldehydes (-al), multiple bonds (-ene, -yne), acids and esters all count.

Numbering of the chain usually starts at the carbon bearing the functional group

Branches are called **prefixes** – they're listed alphabetically

The number of the prefix is called a **locant**



4-methyl-1-hexanol

Cycloalkanes

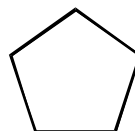
Cycloalkanes are easy to name – the prefix cyclo- then the number of carbons in the ring



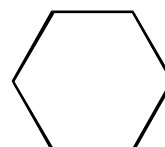
cyclopropane



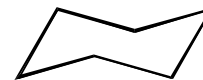
cyclobutane



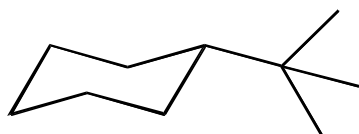
cyclopentane



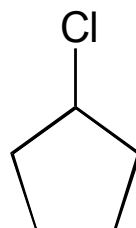
or



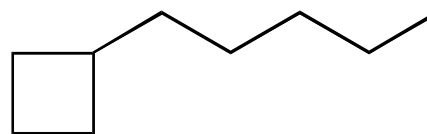
cyclohexane



tert-butylcyclohexane

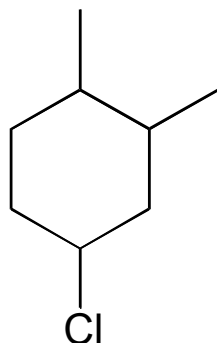


chlorocyclopentane

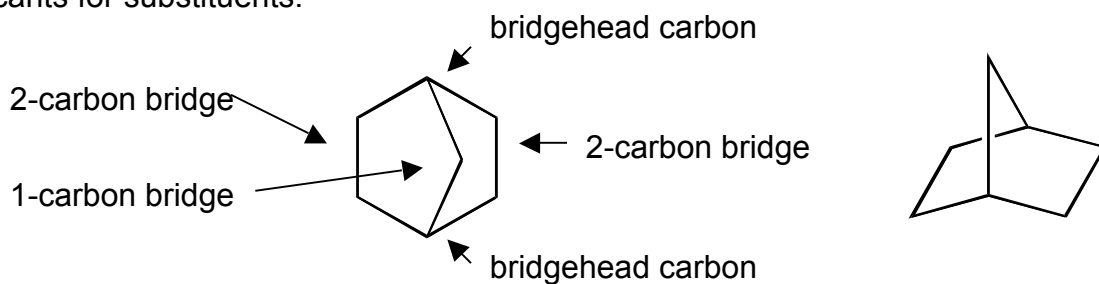


1-cyclobutylpentane

Substituted cycloalkanes are named and numbered like substituted **acyclic** alkanes. Begin numbering at the substituent that leads to the lowest set of locants



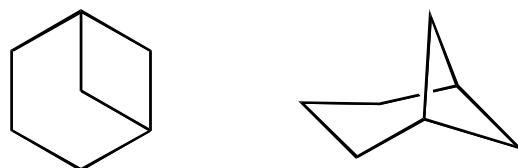
Things get interesting when rings are fused together. Count the number of **bridging** carbons to figure out the numbers that go in the square brackets. Numbering starts at the most substituted **bridgehead**, goes around the largest ring to the next bridgehead, then the next largest ring etc. Bridge sizes are separated by periods. The ring numbers give the locants for substituents.



7 carbons, bicyclic system: bicycloheptane
Then count the bridging carbons: 2, 2, and 1

bicyclo[2.2.1]heptane

And this isomer:



Nomenclature of Alkenes and Alkynes: Alkenes

The alkene is numbered according to the lowest possible sp^2 carbon *unless* the parent is an alcohol, in which case the OH has the lowest locant

Alkenes can have *cis* and *trans* isomers

Alkenes dictate the numbering of rings – the alkene is at position 1. Unless the molecule is an alcohol.

Nomenclature of Alkenes and Alkynes: Alkynes

Same rules as alkenes – the first sp carbon gets the lowest locant, except for alcohols. If there is also an alkene, it takes precedence over the alkyne.

Because of the 180° bond angle, alkynes don't often show up in rings. For a notable exception, check out the structure of calicheamicin on p448. Calicheamicin has 2 alkynes and an alkene in a 10-membered ring!

Alkanes and Cycloalkanes – Physical Properties

Boiling points: alkanes have the lowest boiling points of all the functional groups.

Generally, the more carbons, the higher the bp.

Cyclo C_n have higher bp than linear C_n .

For alkanes with the same C_n , the more branching the lower the boiling point.

This can be argued on the basis of accessible surface area. The more branches, the closer to a sphere (minimum sa/volume ratio). Van der Waals forces are proportional to the surface area available to make contact with other molecules.

Melting points depend on packing in the solid state. Even numbered C pack better and have higher mp.

Conformations of Alkanes: sp^3 σ -bonds

sp^3 hybridized C atoms want to be tetrahedral. Bond angle = 109.5° . We can draw ethane to try to indicate this using wedges and dashes. This is an **eclipsed** conformation.

Two other ways to illustrate the stereochemistry are the **sawhorse** and the **Newman projection**.

Dihedral Angles

Dihedral Angles and Potential Energy

For ethane, the energy difference between the **eclipsed** and **staggered** conformations is 12 kJ/mol. At 300K, RT gives us available thermal energy of 2.5 kJ/mol. At any given moment, most ethane molecules will have a staggered conformation at room temperature.

$$\text{rate} = A \exp(E_a/RT)$$

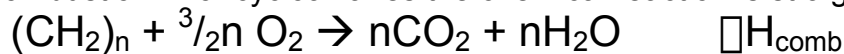
For rotation about the ethane C-C bond, $E_a = 12 \text{ kJ/mol}$, and A is $\sim 10^{13} \text{ s}^{-1}$. At 300K, $k \sim 8 \times 10^9 \text{ s}^{-1}$. So even though the staggered conformation is strongly favored, the C-C bond is in rapid rotation.

Conformational Stereoisomers with Bulky Substituents

If we substitute a methyl group for a hydrogen on each of the C atoms of ethane (to make butane) the conformations no longer repeat every 120° . We now have the familiar eclipsed and staggered conformations, and another conformation where the conformation is staggered, but the bulky groups are not 180° opposed. This is called the **gauche** conformation.

Conformational Energetics of Cycloalkanes

The energy of a molecule can be determined by burning it in oxygen to get the enthalpy of combustion. For cycloalkanes the chemical reaction is straight forward:



	ΔH_{comb} (kJ/mol)	ΔH_{comb} per CH ₂	1g strain per CH ₂
cyclohexane	3952	658.7	0
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cyclopentane	3320	664.0	5.3
cyclobutane	2744	686.0	27.3
cyclopropane	2091	697.0	38.3
cycloheptane	4637	662.4	3.7
cyclooctane	5310	663.8	5.1
clodecane	6636	663.6	4.9

Cyclopropane and Cyclobutane

Part of the reason for strain in cyclopropane and cyclobutane is that the bond angles want to be 109.5°. In cyclobutane they're constrained to be ~90°, and in cyclopropane they're constrained to be 60°!

In addition, the geometry of cyclopropane and cyclobutane forces all the CH bonds to be eclipsed.

Cyclopentane

Look along the C₁,C₂ bond. The CH bonds are staggered. The envelope conformation allows for staggered CH bonds and internal angles close to 109.5°. The C atom at the envelope “flap” alternates. Cyclopentane changes its conformation rapidly at RT.

Cyclohexane

There are significant barriers to conformational change in cyclohexane. The highest barrier to interconversion is 45.2 kJ/mol. This corresponds to a rate of about $9 \times 10^4 \text{ s}^{-1}$ at RT. This is 100,000 times slower than rotation about the C-C bond in ethane.

Substituted Cyclohexanes: Axial and Equatorial Substituents

Most stable configuration is the chair. It can flip between two chair conformations with an energy barrier of 45.2 kJ/mol. This conformational isomerism means that we have to be able to identify the orientation of the substituents with respect to the plane of the ring.

Bulky groups in axial positions can have a **steric clash** with other axial substituents on the same face of the ring. These are called **1,3-diaxial** interactions.

What is the energy penalty associated with the 1,3-diaxial interaction of the methyl group in methylcyclohexane? We can figure this out from butane.

This is relative to a penalty of zero for the axial methyl conformation.

So at room temperature, methylcyclohexane is 95% in the equatorial conformation.

For larger substituents such as the *tert*-butyl group, the penalty is even more severe. The energy difference between axial and equatorial orientation is 21 kJ/mol. At room temperature the equilibrium mixture contains 99.99% equatorial *tert*-butylcyclohexane.

Disubstituted Cyclohexanes: *cis-trans* Isomerism

If two substituents are on the same face of a ring, they're said to be ***cis*** to each other. If they're on opposite faces, they're ***trans***. For cyclohexanes in the chair conformation the 1,2-*cis* isomers are identical. The 1,2-*trans* isomers are ee (equatorial equatorial) or aa (axial axial). These are not the same. The 1,3-*trans* isomers are identical, the 1,3-*cis* isomers are not. The 1,4 *cis* isomers are identical, the 1,4-*trans* isomers are not.