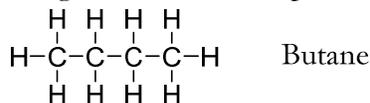# Loudon Ch. 2 Review: Alkanes
Jacquie Richardson, CU Boulder – Last updated 9/2/2020

The simplest organic molecules are hydrocarbons. These contain just carbon and hydrogen. To be most stable, each C wants to have 4 total bonds and each H wants 1 bond. It's possible to link Cs together into long chains. For example, butane has four carbons.


Butane

Hydrocarbons can still have multiple bonds between carbons. This gives us a basis to subdivide them into categories based on what types of bonds they contain: single, double, or triple. Another category is aromatic hydrocarbons, which react very differently and will be covered much later. C=C double bonds aren't considered alkenes if they're part of an aromatic ring.

All single C-C bonds: alkane
At least 1 C-C double bond: alkene } Aliphatic hydrocarbons
At least 1 C-C triple bond: alkyne

Aromatic hydrocarbons: as far as we're concerned for now, anything with a six-membered ring of alternating single and double bonds
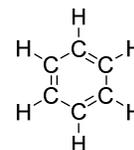
This chapter focuses only on alkanes. If all the carbons in an alkane are in a single, unbranched line, it's a **normal** or **n-alkane**. The names of these are listed below. These names are enough to uniquely identify each compound, but if you want to explicitly show that you're talking about the normal alkane, you can put "n-" at the start of the name. For example, five carbons in a row is pentane, but you can name it as n-pentane if you want to be absolutely clear you're discussing the linear form.

| # of C	Name	Structure
1	Methane	CH_4
2	Ethane	CH_3-CH_3
3	Propane	CH_3-CH_2-CH_3
4	Butane	CH_3-CH_2-CH_2-CH_3
5	Pentane	CH_3-CH_2-CH_2-CH_2-CH_3
6	Hexane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_3
7	Heptane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3
8	Octane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3
9	Nonane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3
10	Decane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3

This is one example of a **homologous series** – each subsequent item in the list has one more –CH_2– unit (also called a methylene group). Usually all members of a homologous series will have physical properties – melting point, boiling point, etc. – that vary in predictable ways.

The more atoms there are in a molecule, the more work it takes to draw out the entire Lewis dot structure. For this reason, there are several different valid ways to draw the same compound, each one progressively more compact. We'll use butane as an example.

- Molecular formula: C_4H_{10} for butane. This one is not actually a unique identifier, since for an alkane with 4 or more carbons, there can be multiple structures possible with the same formula. An example is shown below.
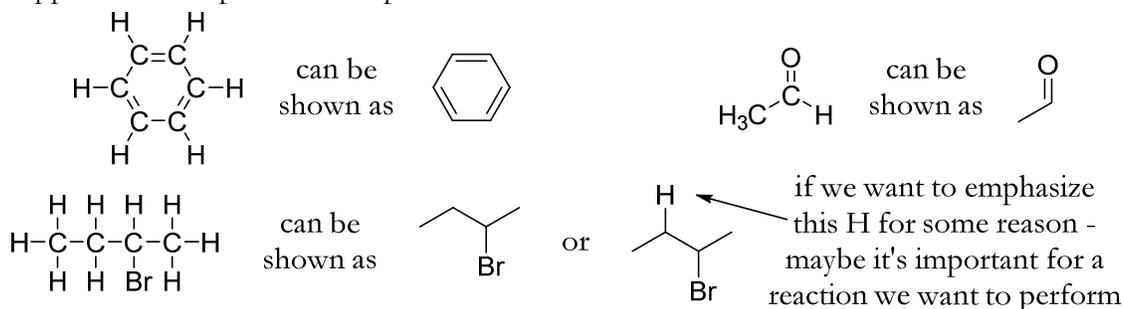
Butane, C_4H_{10}

Isobutane, C_4H_{10}
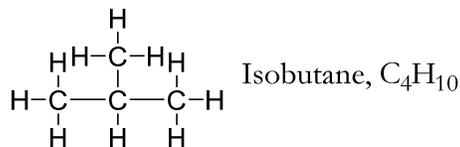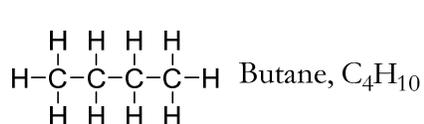
These are called **structural isomers**. The more carbons there are in a molecule, the more structural isomers are possible.

- Structural formula: This is basically just the Lewis dot structure, with bonds indicated by lines rather than two shared dots (like the two examples shown above). This gives us enough information to tell structural isomers apart.
- Condensed structural formula: $CH_3-CH_2-CH_2-CH_3$ for butane. All H atoms are put either right before or right after the carbon atom to which they're attached.
- Highly condensed structural formula: $CH_3-(CH_2)_2-CH_3$ for butane. Any similar groups like the methylenes in the middle of the chain are grouped together with parentheses.
- Skeletal, line-bond or zigzag formula: for butane. In this system, every bend or end of a line is a carbon, unless explicitly stated otherwise. Hydrogen atoms are assumed to be present in the amount needed to fill octets, unless there's a charge on the atom that implies it does not have a filled octet. All heteroatoms (atoms other than C and H) must be shown explicitly, and any C or H can also be shown explicitly if desired. However, if an atom is shown explicitly, its H atoms must also be shown. Note that we have a choice in how much to show explicitly, depending on what parts of the molecule we're focusing on. In the last example here, the H that's shown happens to be important for a particular reaction.

can be shown as

can be shown as

can be shown as   or   if we want to emphasize this H for some reason - maybe it's important for a reaction we want to perform

Carbon atoms can also be linked into a ring. These are called cycloalkanes (assuming they're all C & H with single bonds only) and are named after the alkane with the same number of carbons, but with a "cyclo" prefix. (These are **not** aromatic rings though.)

Cyclopentane
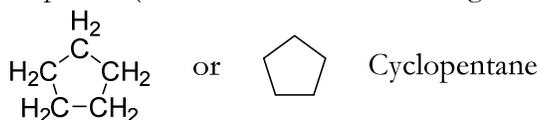
Degrees of Unsaturation
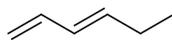
For noncyclic alkanes, the formula is always C_nH_{2n+2}. For example, methane is CH_4, ethane is C_2H_6, and propane is C_3H_8. Each **pair of missing H atoms** from this formula is one **degree of unsaturation**. These can be caused by two things: pi bonds or rings. Remember: in any multiple bond between atoms, the first line of the bond is a sigma bond, and any additional lines are pi bonds.

Loudon Ch. 2 Review: Alkanes
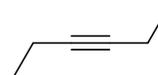**Jacquie Richardson, CU Boulder – Last updated 9/2/2020**
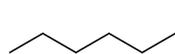
| 0 degrees unsat. C_6H_{14}	2 pi bonds 2 degrees unsat. C_6H_{10}	1 pi bond + 1 ring 2 degrees unsat. C_6H_{10}	2 pi bonds 2 degrees unsat. C_6H_{10}

Functional Groups

These are small groups of atoms that react in a particular characteristic way, usually with no regard for what the rest of the molecule looks like. For example, all alcohols have an –OH group. The rest of the molecule is sometimes just abbreviated as R.
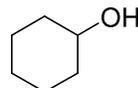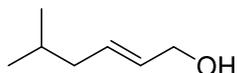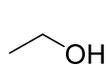
R−OH   Alcohols

Aromatic rings are a subcategory of R. These are called **aryl groups**, or Ar for short. These are often based on benzene, a six-membered ring of alternating single and double bonds. Aromatic double bonds can also be drawn as a circle, for reasons we'll cover later.
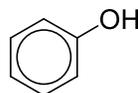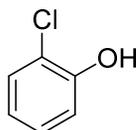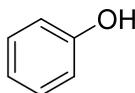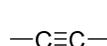
these are all ArOH
(or more generally, ROH)

These are the main functional groups you will need to recognize, although we'll cover others.
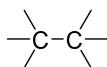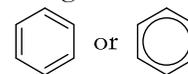
Alkanes (anything with only single bonds between carbons)

Alkenes (anything with double bonds between carbons, except aromatics)

Alkynes (anything with triple bonds between carbons)

Aromatics (for now, six-membered ring of alternating single & double bonds)

—C— (O) Carbonyl - this is a subpart of many FGs, including:	R−C-OH (O) Carboxylic acids	R−C-Cl (O) Acid chlorides	R−C-O-C-R (O)(O) Acid anhydrides	R−NH₂ 1° amines H R−N−R 2° amines
	R−C-OR (O) Esters	R−C-NR₂ (O) Amides	R−C-R (O) Ketones	R−C-H (O) Aldehydes R−OH Alcohols R−O−R Ethers R−X Alkyl halides (X=halogen)

Substitution Patterns

Carbon atoms can be described based on how many bonds they have to other carbon atoms. One bond is primary (1°), two bonds is secondary (2°), three bonds is tertiary (3°), and four bonds is quaternary (4°). In many reactions, these four types of carbon will all react slightly differently.
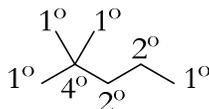
H atoms can also use these descriptors. Because they can each only make one bond, they just get the same descriptor as the carbon atom they're attached to. So the carbon atoms marked 2° in the example above would also have H atoms that are described as 2°.

3

Loudon Ch. 2 Review: Alkanes
**Jacquie Richardson, CU Boulder – Last updated 9/2/2020**

Nomenclature

This is the topic of how to name things – specifically, alkanes in this chapter. We've covered some names of normal alkanes above, but we need to also name branched alkanes. Although there are a lot of old, non-systematic names in use, it's better to use the names that follow rules defined under the **IUPAC system**. (Loudon goes through these steps in a different order but it works out the same as these steps.)

1. **Determine the longest/principal/parent chain.** This gets the same name as the n-alkane of the same length. This is the one with the most carbon atoms, shown in bold here. They won't necessarily be all in a horizontal line. In this example, the longest chain is 6 carbons atoms so it's named as hexane.

$$H_3C-CH_2-CH_2-CH-CH_3$$
$$\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad\quad CH_2-CH_3$$
   or
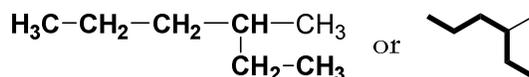
   If multiple paths along the molecule have the same largest number of carbon atoms, choose the one with more branch groups attached to it. For this molecule below, there are two choices, but the one on the right is better because it has two branch groups connected to it.
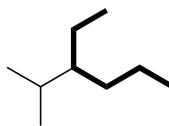
   6 Cs, 1 branch
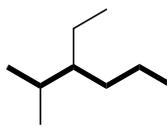
   6 Cs, 2 branches
   Better choice

2. **Name each group coming off the parent chain.** Each branch is named after the n-alkane with the same number of carbon atoms, but you drop "ane" from the name and add "yl". For example, a one-carbon branch group is a methyl group. There are some other groups that are not named after n-alkanes that you should be able to name; these are shown below. Note that "iso" groups (isopropyl, isobutyl, etc.) have a methyl branching off the second-to-last carbon. Also note that the *sec*-butyl group and the *tert*-butyl group have a secondary or a tertiary carbon, respectively, attached to the parent chain. It's also possible to have cyclic groups, like cyclohexyl. During the next couple of steps, you will need to alphabetize all the groups on your molecule. Include unhyphenated prefixes (iso, neo, and cyclo) for alphabetization, but exclude hyphenated prefixes (*sec-* and *tert-*). So *tert*-butyl would be sorted under "B", but isobutyl would be sorted under "I". These letters are underlined below.
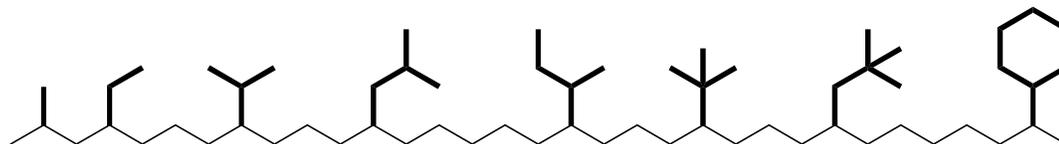
   <u>m</u>ethyl   <u>e</u>thyl   <u>i</u>sopropyl   <u>i</u>sobutyl   *sec*-<u>b</u>utyl   *tert*-<u>b</u>utyl   <u>n</u>eopentyl   <u>c</u>yclohexyl

   Most small alkyl groups have short abbreviations that show up frequently. For example, most organic chemists would write ethanol, CH_3CH_2OH, as EtOH. *tert*-Butyl iodide, or $(CH_3)_3CI$, could also be written as tBuI.

Methyl	**Me**	Propyl	**Pr or nPr**	Isopropyl	**iPr**	*sec*-Butyl	**sBu**	Neopentyl	**Np**
Ethyl	**Et**	Butyl	**Bu or nBu**	Isobutyl	**iBu**	*tert*-Butyl	**tBu**	Cyclohexyl	**Cy**

   One set of substituents that isn't covered in Loudon yet but might show up in Sapling: halogens. These drop "ine" and add "o" when they become a substituent, but other than that they're treated the same as any alkyl substituent.

F   Cl   Br   I

fluoro   bromo
    chloro   iodo
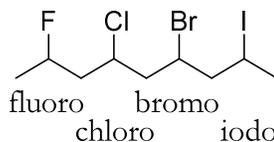
3. **Number the carbons of the parent chain.** Start at the end closest to a branch point.

Branch on 4th C:
Worse choice

Branch on 2nd C:
Better choice

If the parent has multiple substituents and this didn't resolve how to number the parent chain – in other words, if both ends started equally close to a branch point – then compare locations of each branch group and choose the one with the smallest number at the first point of difference.

Branch at 3, 3, 5 - Better choice

First difference - 3 vs. 5

Branch at 3, 5, 5 - worse choice
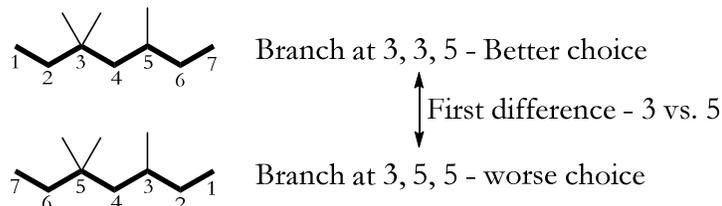
If this still didn't resolve how to number the parent chain – in other words, if there is no point of difference – start numbering closer to the group that is cited first alphabetically.

Methyl at 3, ethyl at 5
Worse choice

Methyl at 5, ethyl at 3
Better choice

4. **Name the compound as "location #"-"substituent""parent".** In general, everything is separated with hyphens, except the last substituent and the parent – these are put together with no space or hyphen. So here "methyl" and "pentane" run together.

2-methylpentane
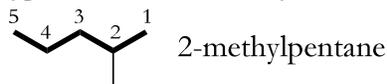
If the parent has multiple copies of identical substituents (e.g. two methyl groups), they get grouped together with a counting prefix like di, tri, tetra, penta, etc. However, each still gets its own location number.

2,2-dimethylbutane

2,3-dimethylbutane
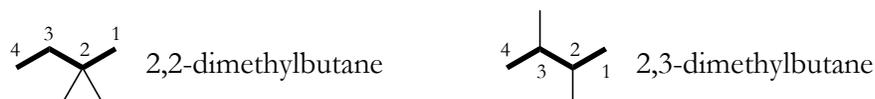
If the parent has multiple different types of substituents, cite groups in alphabetical order, regardless of where they appear on the chain. Remember not to include hyphenated prefixes! Also don't include counting prefixes like di, tri, tetra, penta, etc. So here, dimethyl goes under m, not d.

3-ethyl-5,5-dimethyloctane
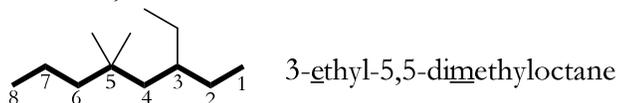
5. **Sometimes the parent is a ring, instead of a chain.** These follow roughly the same rules as for naming branched alkanes, except numbering can hypothetically start with any carbon on the ring. As before, though, you want to choose a point to start numbering that minimizes the location of the first substituent, or if that doesn't resolve it, then the

numbering the minimizes the location at the first point of difference. Also, if there's only one substituent, it's automatically attached to carbon 1 so drop the location prefix.

1,3-dimethylcyclobutane   methylcyclobutane
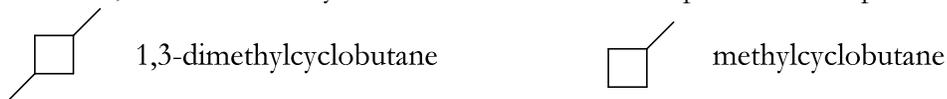
If a ring has fewer carbons than the chain it's attached to, then the chain becomes the parent instead, and the ring is named as a substituent. Don't drop the location prefix in this case, since the ring could attach to one of several points along the chain and we need to specify which.

1-cyclobutylhexane,
**not** hexylcyclobutane
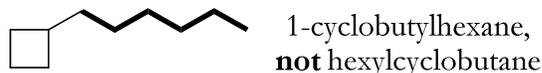
Note that as soon as a carbon is included in part of a ring, it can never be counted as part of a chain. The four ring carbons above do not count toward the length of the parent chain, even though that would make the chain longer.

6. **In some cases, we will see substituents-of-substituents, or complex substituents.** (This is not covered in Loudon). A few of these have their own names covered above, like isopropyl, *tert*-butyl, etc., but not all of them. So you can use those, or use these more generalizable rules instead. To name these groups, find the longest chain within the substituent. Number this chain, starting with the carbon that attaches to the parent. Any groups attached to this are numbered and listed as before, but with a set of parentheses thrown around the entire thing. This group is then alphabetized by the first letter within the parentheses, *even if that letter is part of a counting prefix*. This gives us some alternate naming options for branched groups like *tert*-butyl, but either option is acceptable so long as you pick one consistently. In some cases, choosing one option over another will reorder the groups.

<u>e</u>thyl   (1-<u>m</u>ethylethyl)

(1,1-<u>d</u>imethylethyl)
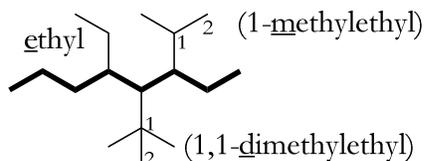
Conformations of Alkanes

The conformation of a molecule is how the molecule arranges itself in space. This can be extremely important in some cases – for example, it dictates how a protein molecule folds up, which can change how it behaves chemically. Since bond length and bond angles are pretty much predetermined, we only have one type of variable to adjust: dihedral angles (a.k.a. torsion angles). As it turns out, some dihedral angles are better than others. We can start looking at simple molecules and use this to make predictions for more complex ones. The simplest alkane where dihedral angles are possible is ethane. We will look at changing the dihedral angle by rotating around the C-C bond.
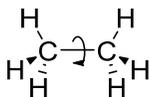
Using this system, we only have three ways to show the direction an H is pointing – either in-plane (regular bond), coming out of the plane (bold bond) or behind the plane (dashed bond). This is not enough detail to see the spatial relationships between Hs as the dihedral
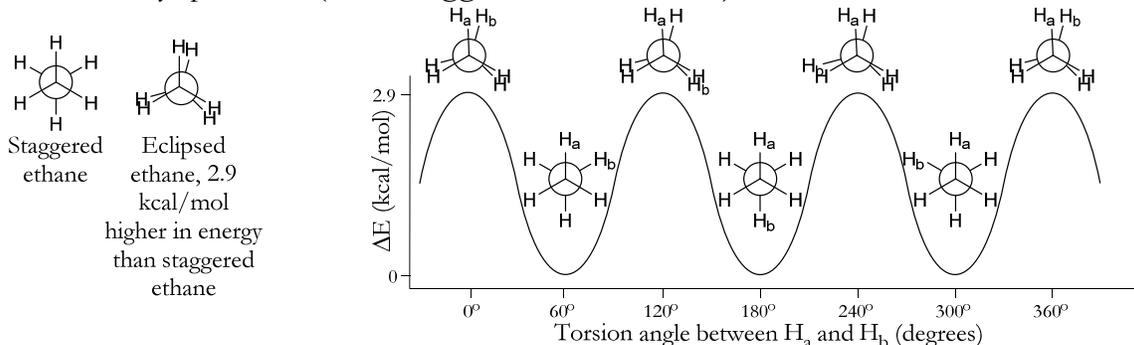
angle changes, so we need a more precise way to show them. We can use a **Newman projection** if we follow these steps:

1. Choose a bond to sight along (for ethane, there's only one choice: the C-C bond).
2. Draw the front atom of this bond (the atom closer to you) as a dot, and the back atom as a circle.
3. Fill in the groups attached to each atom. If the groups are right on top of each other, you can space them out just a little to show them clearly, even though it's implied that the front groups are right in front of the back groups in this case.


converts to

You can define the dihedral angle, θ (theta), as the angle between any two groups. In this case we can pick any H on the front C and any H on the back C to define our dihedral. We'll label these as H_a and H_b. Hold one carbon still (in the example below, this is the front C) and rotate the other carbon in 60-degree increments (in the example below, the back C is rotating clockwise). We can measure the energy experimentally as the back C rotates, and graph it as shown below. As it turns out, the conformations where a front H is covering up a back H (called **eclipsing** conformations) are 2.9 kcal/mol higher in energy than when the Hs are evenly spread out (called **staggered** conformations).

Staggered ethane

Eclipsed ethane, 2.9 kcal/mol higher in energy than staggered ethane

ΔE (kcal/mol)

Torsion angle between H_a and H_b (degrees)

This energy difference is caused by **torsional strain** – the repulsion between electrons in the C-H bonds to the front and back carbons. Even though they're not overlapping in space, they still have a slight preference for being more spaced out from each other. This is not a strong preference though – this barrier is so small compared to the amount of energy available at room temperature that ethane can pass through its eclipsed form about 10^{11} times per second.

As a second example, we will look at the energy diagram for the dihedral angles of butane. In this case we have multiple C-C bonds we could sight along, but we will choose to sight along the middle bond of the molecule (referred to as the C2-C3 bond).


converts to
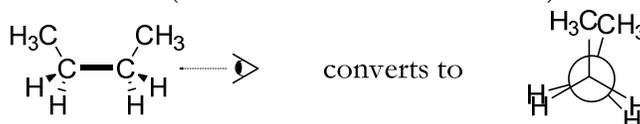
We're going to define our dihedral angle as the angle between the two methyl (CH_3) groups. Again, we can generate a Newman diagram for dihedral angles in increments of 60 degrees, and graph what the values are measured to be. Several things are different compared to ethane. For one thing, there are two different types of eclipsing conformations: one where the two methyl groups are eclipsing each other (costing 5.3 kcal/mol) and one where they're

not (costing 3.6 kcal/mol). There are also two types of staggered interactions: one where the two methyl groups are 60° apart from each other (costing 0.9 kcal/mol) and one where they're 180° apart from each other (costing 0 kcal/mol). The conformation where the two methyl groups are 180° apart is called **anti**. The one where they're 60° apart from each other is called **gauche**, from the French word describing to pass nearby something.
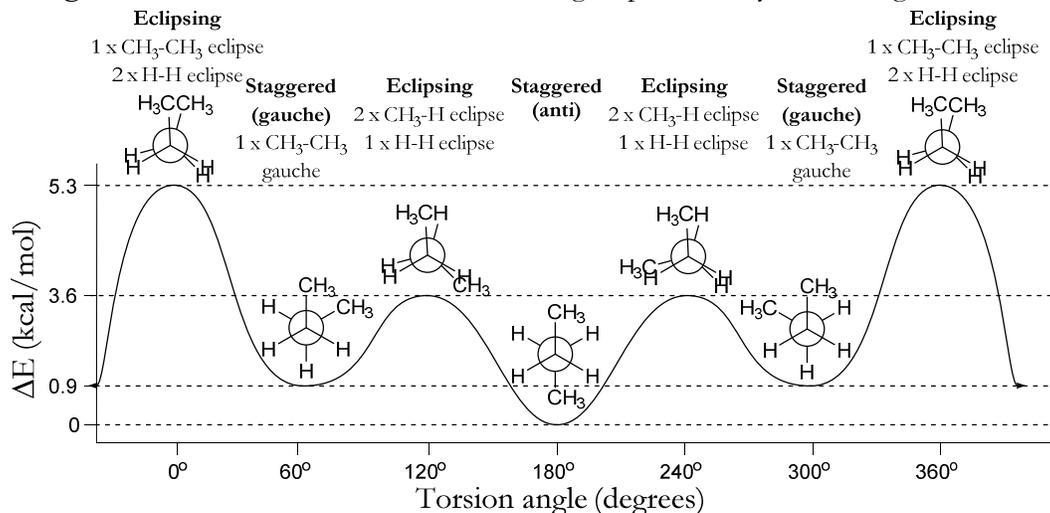

The energy cost of the gauche form is similar to the energy cost of eclipsed ethane: repulsion between electrons. However, something even more severe is happening in the CH_3-CH_3 eclipsed form of butane: not only are the methyl groups feeling electron repulsion, but they are impinging on each other's atomic radii by trying to physically cram into the same area of space. The repulsion they feel from this is called **van der Waals repulsion**, or **steric hindrance**. This is something that is quite important in predicting whether certain reactions will be able to happen or not; if the sterics are too crowded, the molecules cannot bring their reactive atoms together closely enough to react.

From the two graphs above, we can figure out the energy cost of each type of interaction. There is no energy cost for any type of gauche interaction involving H as a group – it's just too small to be affected by other groups gauche to it.

Interaction	Cost	Math
H-H eclipse	~1 kcal/mol	(3 kcal/mol)/3 - from ethane
CH_3-H eclipse	1.3 kcal/mol	(3.6-1) kcal/mol/2 - from butane
CH_3-CH_3 eclipse	3.3 kcal/mol	(5.3-2) kcal/mol - from butane
CH_3-CH_3 gauche	0.9 kcal/mol	0.9 kcal/mol - from butane

We can use this to estimate the energy of different conformations for unknown molecules. These predictions are not always exact but they're close enough to get an idea.
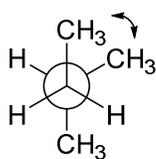
1 gauche interaction, so total cost should be 0.9 kcal/mol.
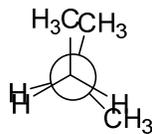
1 CH_3-CH_3 eclipse, 1 CH_3-H eclipse, 1 H-H eclipse, so total cost should be 1+1.3+3.3 = 5.6 kcal/mol.

Loudon Ch. 2 Review: Alkanes
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Physical Properties
These include things like melting point, boiling point, density, and solubility. **Boiling point** (BP) is the point where the vapor pressure of a compound equals the atmospheric pressure (usually set as 1 atm). For n-alkanes, this is a smooth plot.
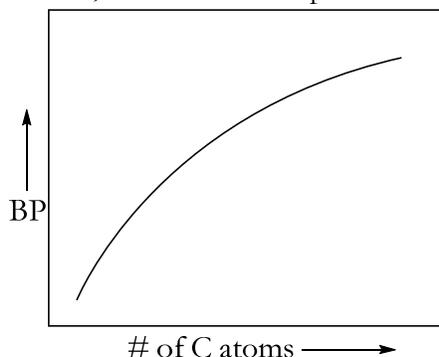
BP measures the **intermolecular forces** (how strongly molecules stick together) in the liquid state. The weakest but most universal intermolecular force is **dispersion** (a.k.a. van der Waals) forces. These are caused by attraction between temporary dipoles, caused by the electron cloud around a molecule "sloshing" back and forth briefly. Other molecules feel these dipoles and make corresponding induced dipoles, which pull the molecules together slightly. The more surface area a molecule has, the stronger this effect is. Having more carbons increases dispersion forces, but branching lowers them because the molecule is rounder and less splayed-out.

Neopentane	n-Pentane
More branching	Less branching
Less surface area	More surface area
BP = 9.4 °C	BP = 36.1 °C
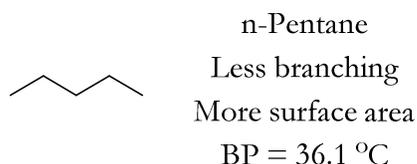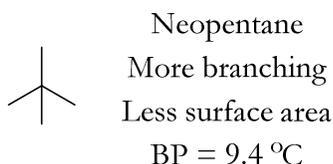
There are other, stronger intermolecular forces, but we'll cover these later.

Melting point (MP) is more dependent on intermolecular forces in the solid state. Higher MP means there are stronger intermolecular forces holding the molecules together into a crystal. Unlike BP, this does not increase linearly but has more of a sawtooth pattern. This is because it is alternating back and forth between two smooth curves – one for even numbers of carbon atoms, and one for odd.
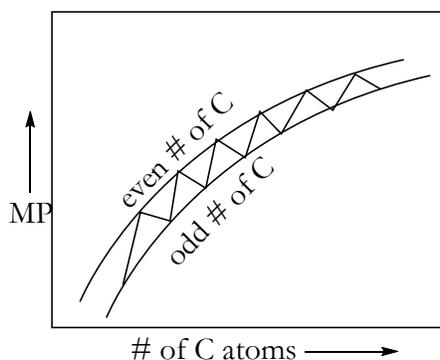
This is because even-numbered molecules form crystals more easily than odd, because they can pack together more efficiently. This has to do with molecular symmetry. For branched molecules, branching usually lowers the MP because it disrupts packing.