



Survey of Organic Chemistry and Biochemistry
Handout 1.3
Alkanes Part 2
Properties and Reactions of Alkanes
Cycloalkanes

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Since the bonds in alkanes consist of only nonpolar carbon-carbon bonds (C—C) and carbon-hydrogen bonds (C—H), weak London dispersion forces are the intermolecular forces that hold them together.

London dispersion forces are temporary attractive forces formed as a result of the constant motion of the electrons within molecules. When the electron distribution is averaged over time, their distribution is symmetrical. However, at any instant one end of the molecule may have more electrons than the other which gives the molecule temporary polarity.

As the size of straight-chain alkanes increases, their melting and boiling points increase.

Gases at room temperature and pressure:

methane, ethane, propane, butane

Liquids at room temperature:

Alkanes with 5-15 carbon atoms (pentane, hexane, heptane, octane, etc.)

Low-melting, waxy solids:

Alkanes with 16 or more carbon atoms

A Summary of the Properties of Alkanes

1. Alkanes are nontoxic, colorless, tasteless, and have no odor or a mild odor.
2. As discussed earlier, alkanes are nonpolar. They are soluble with nonpolar organic solvents and are insoluble in water.
3. Alkanes are less dense than water which results in them floating on the water's surface.

4. We will see in the next section that alkanes are flammable when we examine combustion.

5. Physiological effects: although alkanes are relatively nontoxic, suffocation can result from a lack of oxygen. Vapors of higher alkanes can induce loss of consciousness when breathing in high concentrations. Since alkanes are nonpolar, breathing in the droplets of liquid alkanes can dissolve nonpolar substances in lung tissue resulting in pneumonia-like symptoms.

Reactions of Alkanes

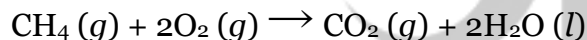
Alkanes have low chemical reactivity and are not reactive to most common laboratory reagents such as acids and bases.

Under certain appropriate conditions, alkanes react with oxygen (combustion) and halogens (halogenation).

Combustion

When an alkane such as methane reacts with oxygen, carbon dioxide and water are formed as products. Heat is also released during combustion.

Complete combustion:



The incomplete combustion of a hydrocarbon results in carbon monoxide and carbon-containing soot as products.

While carbon dioxide (CO₂) is nontoxic and harmless (only posing a problem if there is a high concentration leading to suffocation), carbon monoxide is deadly.

Incomplete combustion:



Inhaling moderate amounts of carbon monoxide in air (even as little as 2% CO in the air) for prolonged periods of time can lead to damage to the respiratory and nervous systems or death. This is because of carbon monoxide's ability to strongly bind to hemoglobin molecules in the blood. As a result, oxygen can't bind to the site where it normally binds to hemoglobin due to the carbon monoxide. Hemoglobin is prevented from carrying oxygen to tissues, and organs such as the brain do not get their supply of oxygen.

Cycloalkanes require an additional C—C bond with a loss of two hydrogen atoms as a result.

The formula for cycloalkanes is C_nH_{2n} .

When drawing cycloalkanes, polygons are used to represent them. The following are a few examples, but the list goes on beyond cyclooctane.

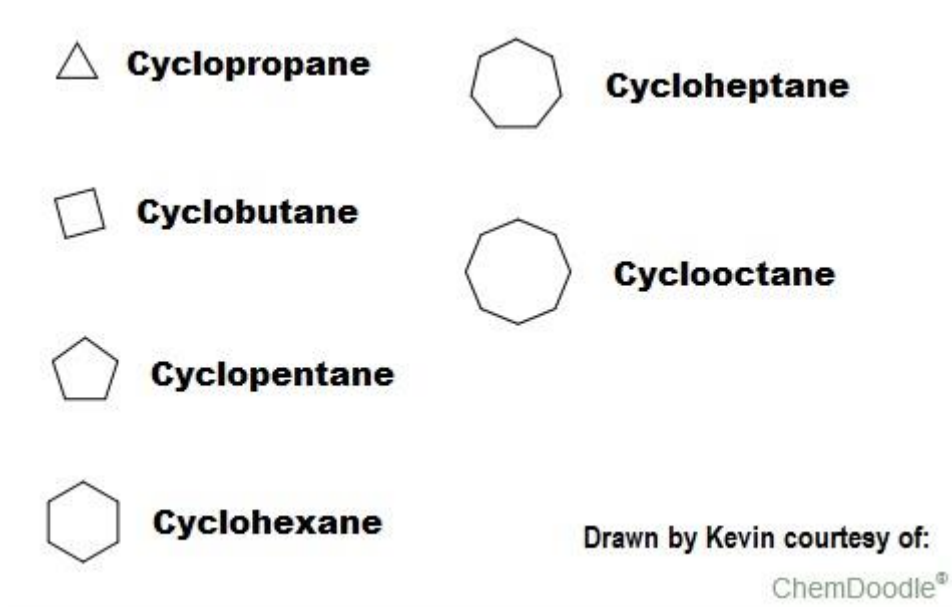


Figure 1.3a Cycloalkanes

Review of Line Structures

So far we would write out the structures of the alkanes (e.g. condensed structures). When we look at Figure 1.3a above, we do not explicitly see the carbon and hydrogen atoms written out.

Line structures are another shorthand where the carbon is understood from the intersections and then mentally adding the appropriate number of hydrogens.

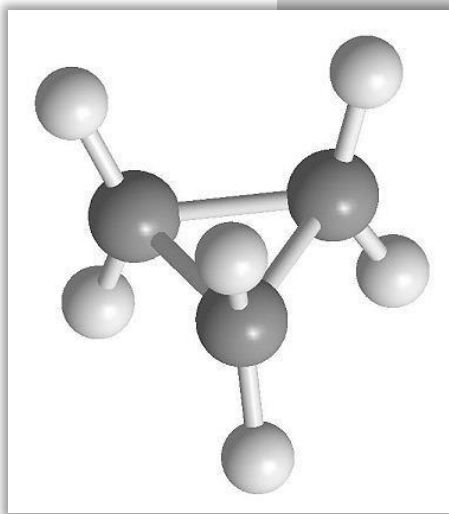
Let's look at cyclopropane above. When we take one of the intersections, we understand that there is a carbon in each intersection. Since carbon is tetravalent (always forms four bonds), we mentally note that the carbon is already attached to the two other carbons so there are two hydrogen atoms bonded to each carbon. When we use the formula above, it verifies this case. Cyclopropane's formula is C_3H_6 .

This is very helpful and efficient because once we get to biochemistry and examine larger organic molecules, it will be time consuming, confusing, and difficult to document each carbon and hydrogen.

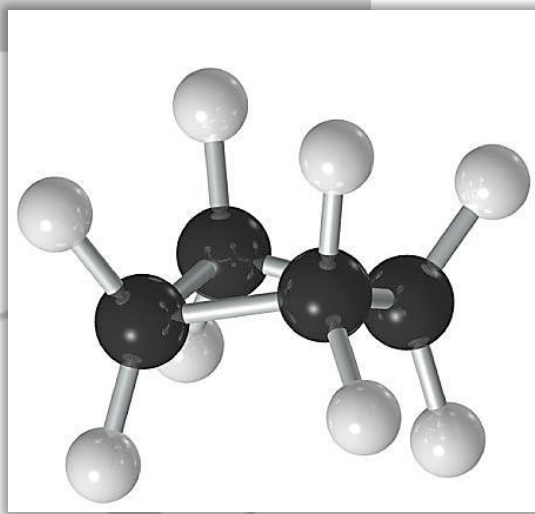
Properties of Cycloalkanes

Cyclic and acyclic alkanes share similar properties. The simpler cycloalkanes such as cyclopropane and cyclobutane are gases while larger cycloalkanes are liquids and solids.

We learned in the previous handout that the carbon atoms in alkanes have a tetrahedral structure. The bonds are identical and the bond angles are near 109.5° . The values are compressed when the rings are flattened for cyclopropane and cyclobutane. The C—C—C bond angle for cyclopropane is 60° and for cyclobutane it is 90° which are compressed from the normal 109.5° tetrahedral value. This results in cyclopropane and cyclobutane being less stable and more reactive than the other cycloalkanes.



Cyclopropane



Cyclobutane

When we look at cyclopentane and above, the bond angles are closer to the ideal tetrahedral value and are more stable.

The properties we had discussed regarding alkanes are also similar to cycloalkanes such as being nonpolar, flammable, and insoluble in water. However, since cycloalkanes have cyclical structures, they have less flexibility and more rigidity than the acyclic (straight-chain) alkanes.

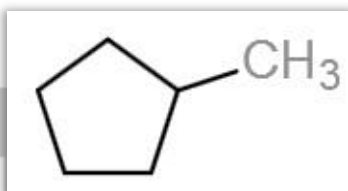
Naming Cycloalkanes

In Figure 1.3a above we named a few cycloalkanes from the simplest cyclopropane with 3 carbons to more complex ones such as cyclooctane.

In the previous handout, we examined in detail how to name straight-chain alkanes. The rules are similar (such as alphabetical priority when naming) with only a few additional steps to keep in mind.

1. Compounds are named as alkyl-substituted cycloalkanes.

This means that the substituents are written before the cycloalkane.



This would be ✓ **methylcyclopentane**, not ✗ cyclomethylpentane.

The cycloalkane name is used as the parent. In Figure 1.3a, we saw a short list of common cycloalkanes. In our current example, cyclopentane is the parent.

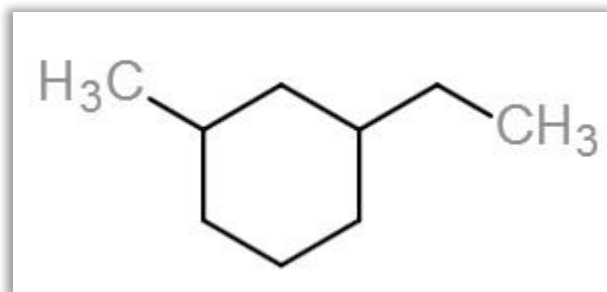
When there is only one substituent (like in our example above), you don't have to specify the number (i.e. 1-methylcyclopentane) since the positions are all the same. If you attach the methyl group to any of the other positions in cyclopentane, you will still end up with methylcyclopentane.

When there are additional substituents attached to the parent compound, then assigning numbers will be necessary.

2. Identify the substituents and assign them a number.

Similar to straight-chain alkanes, the substituents are named based on **alphabetical priority** (e.g. 1-ethyl-4-isopropyl- or 1-isopropyl-2-methyl-). The number 1 is assigned based on alphabetical priority. In our example from the previous sentence, the ethyl group gets assigned the 1 in the first part and the isopropyl group is assigned the 1 in the latter.

From there, move around the ring to give the next substituent the lowest possible number. Let's look at an example.



1-ethyl-3-methylcyclohexane

When we apply the rules, we get:

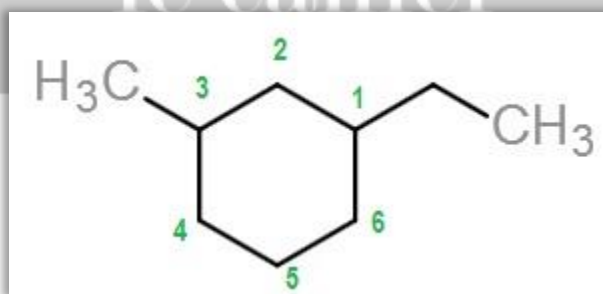


Figure 1.3b
1-ethyl-3-methylcyclohexane

This is the correct way to name cycloalkanes. ✓

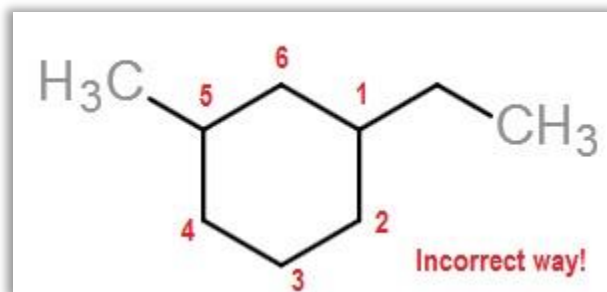
Let's look at it step by step:

1. Identify the parent compound. We note that it is cyclohexane since there are six carbons.

2. Identify the substituents attached to the parent compound. We note that there is an ethyl group and a methyl group attached to the cyclohexane.

3. Assign the priority number (1) to the substituent based on alphabetical priority. We identified the ethyl and methyl groups attached to the cyclohexane. Since "e" comes before "m" in the alphabet, ethyl is assigned the number 1.

4. Move around the ring to give the next substituent the lowest number. In Figure 1.3b, we move to the left (counterclockwise) because it gives methyl the number **3**.

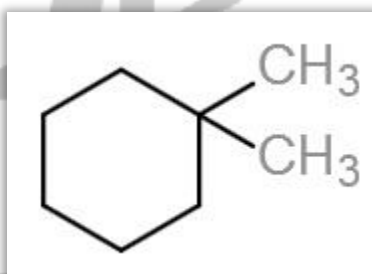


Please be careful not to do this! ✘

If you count to the right and go clockwise, the methyl group will be assigned “5” which is **not** the lowest possible number. This is incorrect and will give 1-ethyl-5-methylcyclohexane ✘.

Also keep in mind the alphabetical priority. Another mistake can be 1-methyl-3-ethylcyclohexane ✘ (mistaking alphabetical priority) or the completely incorrect 1-methyl-5-ethylcyclohexane ✘ (mistaking both alphabetical priority and numbering).

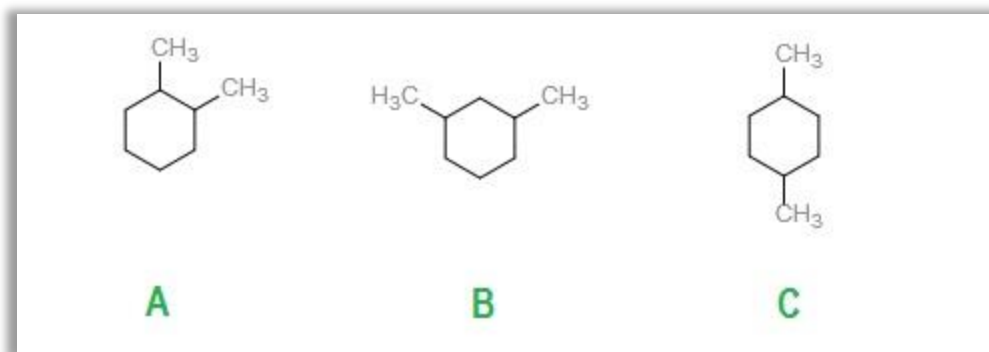
Similar to the open-chain alkanes, if there are similar substituents attached to the parent compound, you use similar prefixes (di-, tri-, etc.).



1,1-dimethylcyclohexane

We discussed earlier that we don't have to add a 1 if there is only one substituent attached to the parent compound. However, we have two substituents in the above example. We can't just say “Dimethylcyclohexane” since we wouldn't know where the location of the second substituent is.

The possibilities can be “1,1-,” “1,2-,” “1,3-,” or “1,4-,” dimethylcyclohexane. This is why it is necessary to note the proper position of each substituent.

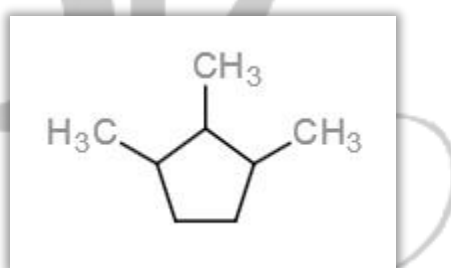


A: 1,2-dimethylcyclohexane

B: 1,3-dimethylcyclohexane

C: 1,4-dimethylcyclohexane

Here is another example with three substituents:



1,2,3-trimethylcyclopentane

This concludes the general overview of alkanes. In the next handout we will start examining alkenes, alkynes, and aromatic hydrocarbons (arenes). Many of the rules that we learned in these first three handouts are important as we progress. You will see that the rules will continue expanding from the foundational rules from the introduction to orgo and alkane handouts.

Next time, we will examine topics such as cis-trans isomerism and organic reactions (addition, elimination, substitution, and rearrangement).