2.1: Structures of Alkanes

2.1.1 Structures and Different Structure Formulas

Alkane is the simplest hydrocarbon with only C-C single bonds. The chain alkane fits the general formula of $\mathbf{C_nH_{2n+2}}$ (**n**: positive integer), and the number of H atoms reaches the maximum level in chain alkanes. The names and structures of straight-chain alkanes up to ten carbons are listed in the table below.

Number of Carbons	Name	Formula (C_nH_{2n+2})	Condensed Structure
1	methane	CH_4	CH_4
2	ethane	C_2H_6	CH_3CH_3
3	propane	C_3H_8	$CH_3CH_2CH_3$
4	butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Table 2.1 Names and Structures of Straight-Chain Alkanes

The primary sources of alkanes are natural gas and petroleum. Natural gas contains mainly methane (70 –90%) and some ethane. Petroleum refining separates crude oil into different fractions and each fraction consists of alkanes of similar number of carbons. Propane and butane are common fuels in propane gas burners and cigarette lighters. Alkanes with 5 to 8 carbons are the major components of gasoline, while diesel contains alkanes ranging from 9 to 16 carbons. As the number of carbons increase, the boiling point and viscosity of alkanes increase.

There are a variety of formats to show the structural formulas of organic compounds, it is important to be able to recognize different formula drawings, and use them correctly to represent the structures.

Kekul **é Structure**

We have had some discussions on Kekulé structures in **section 1.2.4**. They are similar to Lewis structures with all the bonding electrons shown in short lines and all the atoms included as element symbols. However, *the lone-pair electrons are left out* in Kekulé structures, which is the major difference between Kekulé structures of organic compound and Lewis structures.

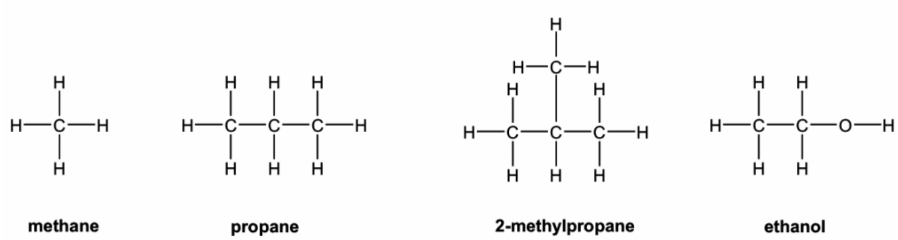


Figure 2.1a Examples of Kekulé Structures

Condensed **Structure Formula**

In **condensed structure formulas**, the C-H bonds are omitted and all the H atoms attached to a certain carbon (or other atoms) are usually shown as a group like CH_3, CH_2, NH_2, OH. The structures in **Table 2.1** are shown as condensed structures. The C-C bond sometimes can be omitted as well (as for 2-methylpropane and 2-hexanol in the examples below). Usually, if the structure has a branch, the bonding between the parent structure to the branch needs to be shown with a short line. It is faster to draw a structure with condensed structure formula, and the structure does not look as bulky as Kekulé structures.

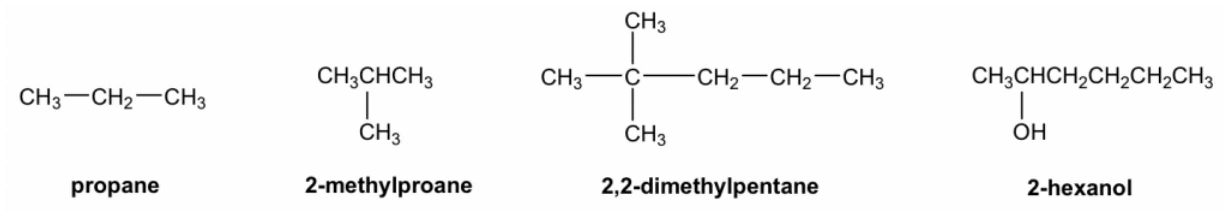
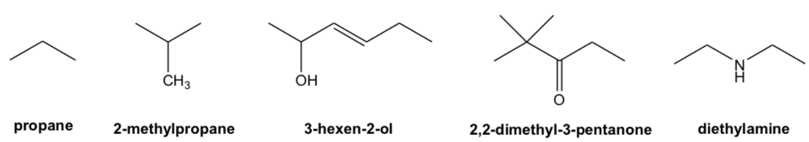


Figure 2.1b Examples of Condensed Structures

Short-Line Structure Formula

The structure drawing can be further simplified by short-line structure (or “bond-line structure”, “skeletal formula” in other books) with most atoms omitted, it is also the very common type of structure formula used in Organic Chemistry because of its simplicity. To apply and interpret the short-line structures correctly, it is very important to understand the conventions of this type of drawing clearly.

- Each short line represents a bond.
- The carbon chains are shown in a zig-zag way.
- No carbon atoms are shown (as an exception, it is optional to show the CH_3 group at the end of the chain, or as a branch); each **bend** in a line or **terminus** of a line represents a **carbon** atom, unless another atom is shown explicitly.
- Hydrogen atoms bonded to carbons are **not** shown; hydrogen atoms bonded to other atoms are shown explicitly.
- Atoms other than C and H, for example N, O, Cl, need to be shown explicitly.



Examples of Short-line Structures

Figure 2.1c Examples of Short-line structures

In short-line structures, the number of hydrogen atoms attached to each carbon can be *calculated* by applying the octet rule and checking formal charges involved.

Perspective Formula **of 3D Structure**

When it is necessary to highlight the spatial arrangement of groups around a tetrahedral sp^3 carbon for conformation (Chapter 4) or stereochemistry (Chapter 5) purposes, the **perspective formula** with solid and dashed wedges are used. Out of the four bonds on a tetrahedral carbon, two bonds lie within the paper plane and are shown as ordinary lines, the solid wedge represents a bond that points out of the paper plane, and the dashed wedge represents a bond that points behind the paper plane.

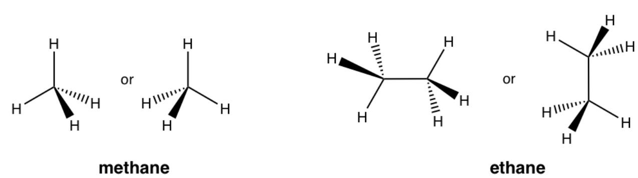
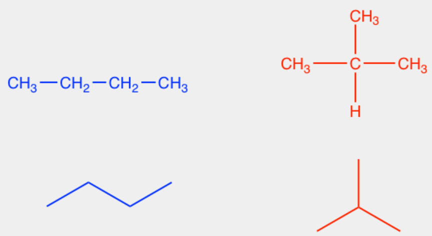


Figure 1.2d Examples of Perspective Formula

2.1.2 Constitutional Isomers

For methane, ethane and propane, there is only one way of carbon arrangement. As the number of carbon increases to 4 carbons, there are **two** ways for the carbon atoms to be connected, one as a straight-chain (blue structure below), and the other one as a branch on the chain (red structure below).

Two Constitutional Isomers with Formula C_4H_{10}	
	
Butane	Isobutane (i-butane) “iso” means “isomeric”
b.p. = 0 °C	b.p. = -12 °C
density: 0.622 g/mL	density: 0.604 g/mL

As we can see, these two different structures represent two different compounds, with different names and different physical properties; however, they both have the same formula of C_4H_{10}, and they are called Constitutional (Structural) isomers. **Constitutional (Structural) isomers** are different compounds with the same molecular formula, but their atoms arranged in a different order. (i.e. the atoms are bonded in different ways.)

Let’s see more examples of constitutional isomers.

For alkanes with 5 carbons, there are a total of three constitutional isomers. Check the notes besides for the strategy to build constitutional isomers.

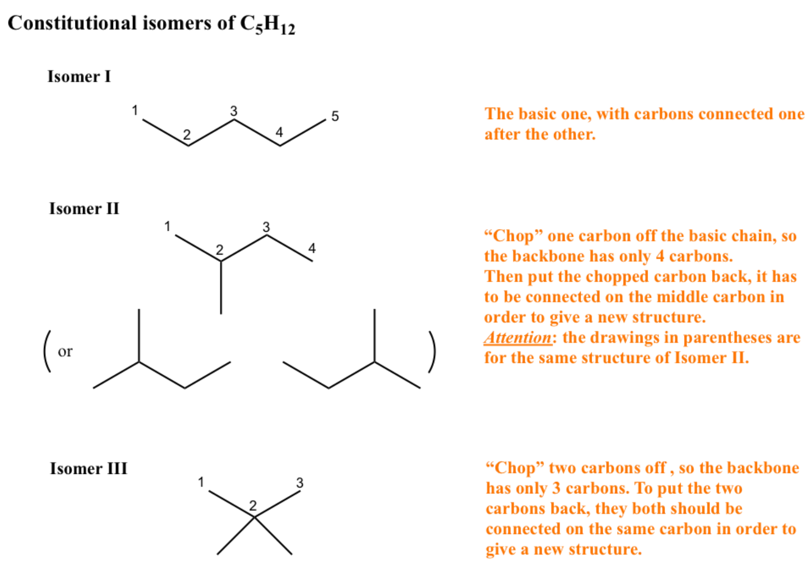
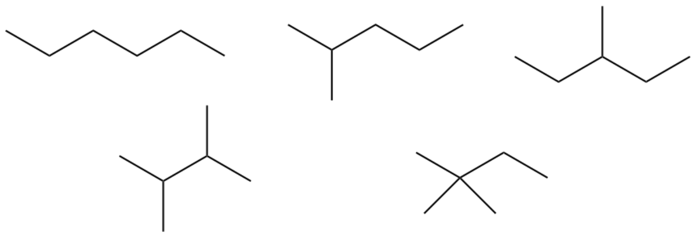


Figure 2.1e Constitutional isomers of C5H12

For alkanes with 6 carbons, there are a total of five constitutional isomers.

Constitutional isomers of C_6H_{14}



Exercises 2.1

Draw all the constitutional isomers with a formula of C_7H_{16}.

Answers to Practice Questions Chapter 2

The constitutional isomers we have so far have different lengths of carbon "backbones", and are also called **skeletal constitutional isomers**. The other possible situations include **positional** and **functional constitutional isomers** that we will encounter later.

As the number of carbons increase, the number of constitutional isomers increases dramatically. For the example of alkanes with 20 carbons, that is $C_{20}H_{42}$, there are 366,319 constitutional isomers. While there is no simple formula allowing us to predict the total number of isomers for a certain amount of carbons, the phenomena of constitutional isomers partially explains the high diversity of organic structures.

2.1.3 Recognition of 1 ° , 2 ° , 3 ° , 4 ° carbons

The carbon atoms in organic structure can be categorized as primary (1°), secondary (2°), tertiary (3°) and quaternary (4°), depending on how many other carbons it connects with. Specifically:

- Primary (1°) carbon: attached directly to only one other C atom;
- Secondary (2°) carbon: attached directly to two other C atoms;
- Tertiary (3°) carbon: attached directly to three other C atoms;
- Quaternary (4°) carbon: attached to four other C atoms.

The hydrogen atoms attached on 1°, 2° and 3° carbon, are labeled as 1°, 2° and 3° hydrogen respectively.

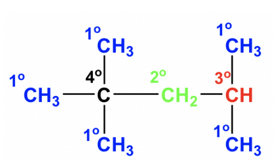


Figure 2.1f Hydrogen atoms attached on 1°, 2° and 3° carbon

In one compound, carbons (or hydrogens) that belong to different category show different structural and reactive properties. This concept has a lot more applications in later sections.