
1

COMPOSITION

Carbon forms a vast variety of covalent compounds, many of which occur naturally in biological systems. Besides their importance to plant and animal life, these compounds offer examples of a wide array of structures that challenge chemists to synthesize them. Most carbon compounds are composed of only a small number of elements: carbon, hydrogen, oxygen, nitrogen, and the halogens.

When a chemist prepares or encounters a new substance, the first question that arises is “What elements are present?” After this is determined, the questions become increasingly sophisticated: What is the weight ratio of the elements? How are the atoms of the elements bonded to one another? What is the geometric arrangement of the atoms? For organic compounds, in which the elements are generally attached by covalent bonds to form molecules, the chemist ultimately would like to know the three-dimensional (3D) shape of the molecule. This shape, or structure, can determine how the molecule reacts with various reagents and can also affect physical properties such as boiling point and density. In the following section we progress from the question of the weight ratio of the elements to a series of formulas that reveal different aspects of the structure of molecules. Our goal is to produce a formula that expresses the shape of the entire molecule.

PERCENT COMPOSITION

The simplest way to express the composition of a compound is the mass percentage of its constituent

elements. Let's make sure that you remember how to convert percent composition to the empirical formula.

Q The organic compound benzene contains 92.3% carbon and 7.7% hydrogen. Calculate the empirical formula of benzene.

A Probably the simplest way to proceed is to assume that you have a sample of benzene that weighs 100 g. In 100 g of benzene there are

$$0.923 \times 100 \text{ g} = 92.3 \text{ g of carbon}$$

$$0.077 \times 100 \text{ g} = 7.7 \text{ g of hydrogen}$$

The *empirical formula* presents the simplest whole-number ratio of the number of moles of each element in the compound. The number of moles of each element is easily obtained by dividing by the atomic weight of each element.

$$92.3 \text{ g C} / 12.01 \text{ g/mol} = 7.69 \text{ mol C}$$

$$7.7 \text{ g H} / 1.008 \text{ g/mol} = 7.6 \text{ mol H}$$

These numbers are the same within experimental uncertainty; hence, the ratio of the number of moles of carbon to that of hydrogen is one to one. The formula CH therefore represents the simplest whole-number ratio of the number of moles of carbon to the number of moles of hydrogen. ■

Benzene, like most organic compounds, is a molecular covalent compound.

Q

How would you know that benzene is a covalent compound, rather than an ionic compound?

A

In general, the bonding between two elements becomes more ionic as the difference in electronegativity of the elements increases. In CaCl_2 the difference is so large [$3.0 (\text{Cl}) - 1.0 (\text{Ca}) = 2.0$] that the calcium is present as the +2 cation and chlorine as the -1 anion. For methane, on the other hand, the difference in electronegativity is small [$2.5 (\text{C}) - 2.1 (\text{H}) = 0.4$] and the electrons are shared within a covalent bond. For a compound that contains only carbon and hydrogen, such as benzene, we can reasonably assume that the bonding is covalent. The majority of organic compounds that you will study are *molecular*; that is, the atoms are held together by covalent bonds within a molecule. ■

We now need to determine how many atoms of each element are present in one molecule of benzene. You may be thinking that if CH is the simplest ratio of atoms in the compound, then each molecule should contain one carbon and one hydrogen atom. However, the empirical formula does not tell us how many atoms of each element are present in each molecule. For example, there could be two atoms of carbon and two atoms of hydrogen, or three and three, and so on, in one molecule.

MOLECULAR FORMULA

In order to determine the molecular formula from the empirical formula, we need to know the molecular mass (molecular weight). This value is the mass of one mole of molecules and can be determined experimentally by a number of methods, including mass spectrometry. For benzene the molecular weight is 78 g/mol.

Q

How can you use the molecular weight to convert the empirical formula to the molecular formula?

A

Assume for a minute that CH is the molecular formula; the molecular weight would then be $12.01 + 1.008 = 13.02 \text{ g/mol}$. If we divide the molecular weight of 78 g/mol by the molar mass of the unit CH

$$(7.8 \text{ g/mol}) / (13 \text{ g/mol}) = 6$$

we find that there are six “CH” units in each molecule of benzene. The molecular formula may be written as $(\text{CH})_6$, but it is customary to write it as C_6H_6 . ■

STRUCTURAL FORMULA

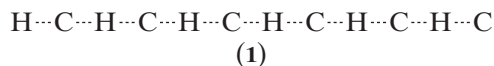
The next step in determining the structure of a compound is to determine how the atoms are arranged or attached to one another. Now that we know that a molecule of benzene has six carbons and six hydrogen atoms, we can speculate about some ways in which these atoms can be arranged.

Q

Can you think of a simple way to arrange six carbons and six hydrogens in a line?

A

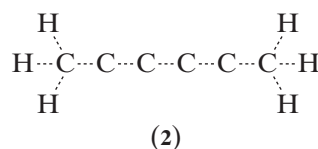
One arrangement of these atoms is as follows:



This sequence of atoms represents the connectivity of atoms; that is, the specific way that atoms are connected to one another.

Statement. The structural formula expresses the connectivity within a molecule.

You should remember that normally hydrogen does not form more than one covalent bond, so arrangement (1) is not very likely. You could imagine groupings of hydrogen atoms around atoms such as



Statement. In both representations above it is important to realize that the dashed lines are used to indicate attachments or connectivities of atoms.

These lines do not indicate electron-sharing bonds. Eventually, however, we will need to determine whether the atoms *could* be attached to one another by covalent bonds and that will require use of the Lewis model.

For organic compounds we use a number of models to explain covalent bonding, one of the most important of which is the Lewis (electron dot) model.

Statement. Good Lewis structures usually involve four bonds at carbon, three to nitrogen, two to oxygen, and one to hydrogen or a halogen.

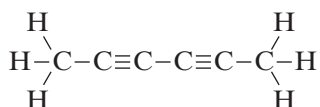
Of course, Lewis structures must contain the appropriate number of electrons and, where possible, must obey the octet rule (for hydrogen, only two electrons). In order to determine whether either structure **1** or **2** *might* be a reasonable structure, we should see if we can write a conventional Lewis structure for each.

Q

Write a Lewis structure for structure **2**.

A

For structure **2**, we could write a perfectly acceptable Lewis structure:



Although a good Lewis structure can be written for structure **2**, this does not mean that structure **2** is the correct structural formula for benzene. In order to determine whether this representation is the structural formula, we must perform either chemical or spectroscopic tests. For example, the Lewis structure for structure **2** contains both carbon–carbon triple bonds and carbon–carbon single bonds. We need a method that can tell us if these two types of bonds are present in benzene. ■

Although chemical methods can be used to determine whether a double or triple bond is present, this determination is more commonly accomplished using spectroscopic methods. These methods, all of which involve irradiating a sample with electromagnetic radiation, include infrared (IR) and ultraviolet–visible (UV–VIS) spectroscopy, as well as nuclear magnetic resonance (NMR) spectroscopy. The colorimeter (e.g., the common Spectronic 20) that you may have used in general chemistry courses employed radiation in the visible region to change the electronic energy levels of the molecule. Infrared spectroscopy, which uses lower frequencies of “light,” changes the energies of the vibrations of different groups of atoms within a molecule. You need not worry at the moment about learning about the various spectroscopic methods, but we use a few such methods below to demonstrate how the structures of molecules are determined.

Q

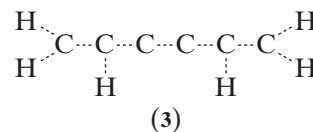
Although we will not discuss infrared spectroscopy in any detail, it is helpful to know that different types of bonds absorb different frequencies of IR light. In general, the stronger the bond, the higher the frequency of the light required to increase the vibrational amplitude of the bond vibration. Look at the carbon–carbon bonds in structure **2** and determine whether the carbon–carbon single or triple bonds will absorb higher frequencies of infrared radiation.

A

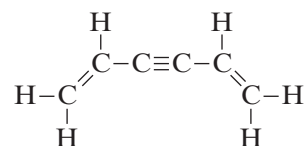
Because the triple bond is stronger than the single bond, the triple bond requires higher frequencies of radiation. Therefore structure **2** would have at least two peaks in the carbon–carbon region of its IR spectrum. However, when the infrared spectrum of benzene is examined, there is no peak due to a triple bond. Consequently, structural formula **2** is not correct for benzene. ■

Q

Write a Lewis structure for the connectivity of atoms portrayed by the following structure:



A



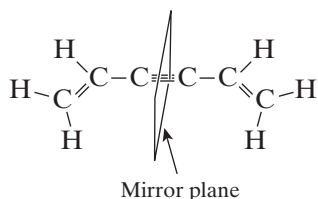
This arrangement contains carbon–carbon single, double, and triple bonds, and at least two different environments for hydrogen atoms. In order to determine whether this is a reasonable structural formula, we will use another spectroscopic technique—nuclear magnetic resonance (NMR) spectroscopy—to determine the number of chemically different carbons in a molecule. When carbons are “chemically different,” they generally have different electron densities around them. The number of chemically different carbon atoms in a molecule can be determined from the symmetry of the molecule. For the structure immediately above, there is a plane of symmetry that divides the molecule in half. The plane (see next structure below) cuts through the triple bond in the center of the molecule. ■

Q

Examine the structure above and determine how many chemically different carbons there are. Remember that there is a plane of symmetry cutting the molecule in two halves. These two halves are mirror images of one another.

A

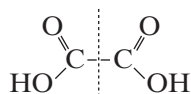
The mirror plane makes the two terminal carbon atoms the same (see the following structure); the two C–H carbons are the same, and the two atoms of the triple bond have the same electronic environment. Thus, there are three chemically different carbon atoms. If we obtain the NMR spectrum of the carbon atoms in this structure, the spectrum would indicate three different carbons.



■

Q

How many different carbons are there in a molecule of oxalic acid as shown below?

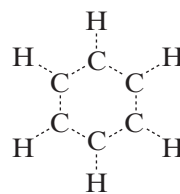


A

The plane of symmetry running through the carbon–carbon bond in the center of the molecule makes the two carbons equivalent. Therefore, this compound has only one type of carbon. ■

The actual NMR spectrum for the carbon atoms of benzene contains evidence for only one type of carbon in benzene, and structure **3** is not the correct structural formula for benzene.

If we continue this process of writing and testing structural formulas long enough, we will eventually arrive at one that satisfies all of the spectroscopic and chemical information. It is the structure shown below, in which the carbon atoms are at the corners of a perfect hexagon with a hydrogen attached to each of the carbons.



It is not obvious from this structural formula that the molecule is planar (i.e., with all atoms lying in one plane), as we will see during our discussion of three-dimensional structural formulas. This structure was first suggested in 1865 by the German chemist Friedrich August Kekule (1829–1896), who claimed that he derived the structure from a dream about a snake biting its own tail.

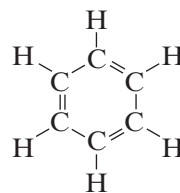
Now that we know how the atoms in benzene are arranged, we will learn how the electrons are arranged by writing the Lewis structure.

Q

Write a Lewis structure for benzene. Notice that the molecule has a total of 30 valence electrons (4 from each carbon and 1 from each hydrogen) that must be arranged to give each atom eight electrons, except hydrogen, which must have two. If you do not remember how to write Lewis structures, rest easy because we will cover this topic in more detail in Chapter 3.

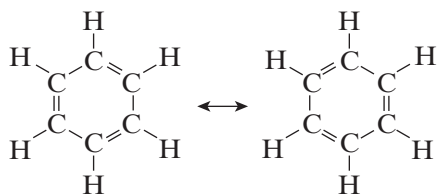
A

The Lewis structure below satisfies the octet rule and has the correct number of electrons.



■

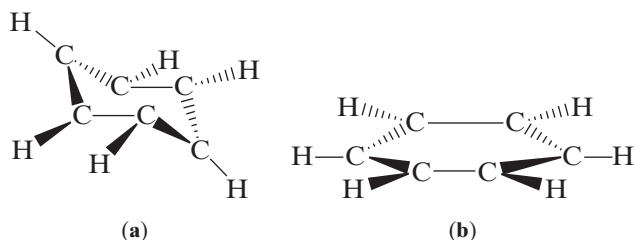
We will find later that this Lewis structure does not do justice to some of the properties of benzene and that it must be modified to make all carbon–carbon linkages the same. (The word *linkage* refers to the connection between two atoms. Normally, the word *bond* is used, but this also connotes a shared pair of electrons.) This modification, known as *resonance hybridization*, is shown below by writing two Lewis structures with a double-headed (double-barbed) arrow between them. The resonance hybrid of the two individual Lewis structures is a better representation of the electronic formula of benzene:



In the resonance hybrid each carbon is identical to the other carbons, and each carbon-carbon bond is the same as the other carbon-carbon bonds. Therefore, this structure is consistent with the carbon NMR spectrum.

3D Structural Formulas

Because much of the behavior of organic compounds depends on their shapes, we need to go one step farther and determine the geometry of the benzene molecule. We could speculate that the hexagonal structure of benzene could have a 3D shape like one of the following:

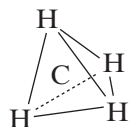


These diagrams are somewhat limited in their ability to portray three-dimensional structure, and we must therefore rely on some conventions to show spatial orientation.

Statement. The solid wedges indicate bonds that come out of the paper toward the reader; the dashed lines or dashed wedges indicate bonds that go behind the paper away from the reader; solid lines are used to represent bonds in the plane of the paper (or parallel to the plane of the paper).

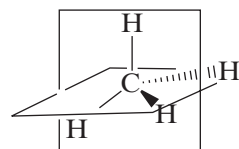
Q

Use the convention given above to draw a 3D structural formula for methane. Remember that methane has a carbon at the center of a tetrahedron with a hydrogen atom at each corner of the tetrahedron.



A

The tetrahedron can be visualized as two perpendicular planes, each containing the carbon and two hydrogen atoms. You will need a model to fully appreciate this geometry. The formula below conveys these two planes quite clearly.



Let's return now to the shape of benzene. The correct shape of benzene is shown by representation **b** above. In this representation all of the carbon atoms and all of the hydrogen atoms are in the same plane. This geometry for benzene is also shown in Figure 1.1 with a ball-and-stick representation, with the atoms in the front drawn larger to give a 3D perspective.

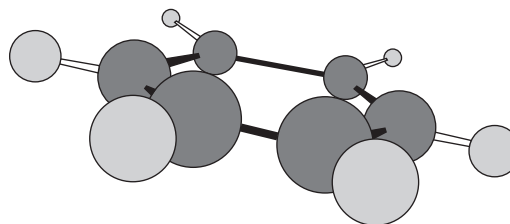


Figure 1.1. A ball-and-stick representation of benzene. The atoms closer to the reader are drawn larger to give a 3D perspective.

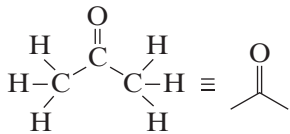
Line Formulas

Representation of organic molecules, many of which are large and complex, is greatly simplified by using line formulas or line structures. A *line structure* for benzene is shown below.



If the line structure is compared to our previous representations, we can see that each intersection of line segments represents a carbon. Because the line structure is a Lewis formula, *each neutral carbon atom must have sufficient hydrogen atoms surrounding it to produce an octet of electrons*. In the line structure of propanone (CH_3COCH_3), shown below, notice that the lines going to the $\text{C}=\text{O}$ group represent methyl (CH_3) groups. In other words, carbons appear at the *intersection* of line

segments and at the *terminus* of a line segment unless another atom appears at those points.

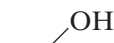


Propanone (also known as *acetone*) is another good compound to commit to memory.

Q

Give the line formula for ethanol. Because ethanol is an important compound, try to remember the formula $\text{CH}_3\text{CH}_2\text{OH}$.

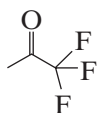
A



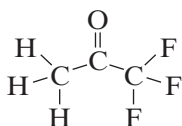
Q

Draw the line formula for 1,1,1-trifluoropropanone. The nomenclature 1,1,1-trifluoro- tells you that there are three fluorines attached to one of the terminal carbons of propanone.

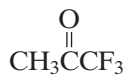
A



Be sure that you can also write formulas with all of the atoms “written out” and as *condensed formulas*. Here are these two types of formulas for 1,1,1-trifluoropropanone:



“Written out” formula



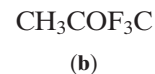
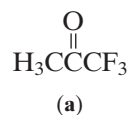
or



Condensed formulas

Q

Condensed formulas can be written in a variety of different ways. Which one of the following formulas is not correct for 1,1,1-trifluoropropanone?

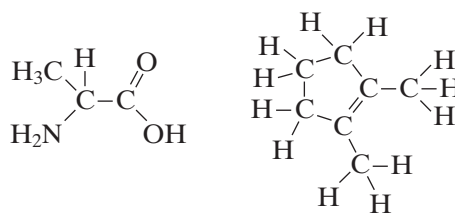


A

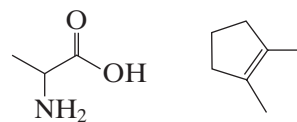
In structure **a** the hydrogens are written before the carbon to indicate that they are attached to the carbon. This is an acceptable formula. In structure **b** the fluorines are written before the terminal carbon, but this formula is unacceptable because of the convention that attached atoms always follow the atom to which they are attached. Exceptions to this rule only occur on the left side of the formula where there can be no confusion about the meaning of either CH_3 or H_3C . ■

Q

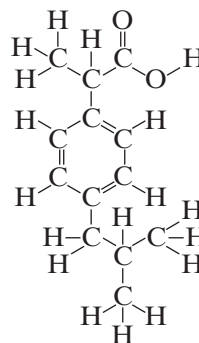
Provide line structures for each of the following:



A

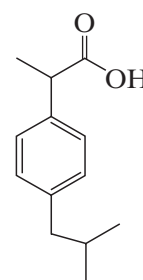


Now, look at structure **a** of the common pain reliever ibuprofen below and compare it to line structure **b**. The line structure **b** should look less cluttered and confusing to you.



(a)

ibuprofen



(b)

