

CHAPTER 1. INTRODUCTION TO ORGANIC CHEMISTRY

(Arthur Cammers, Ashley Jolly Steelman, and Susan Odom, University of Kentucky, 2019)

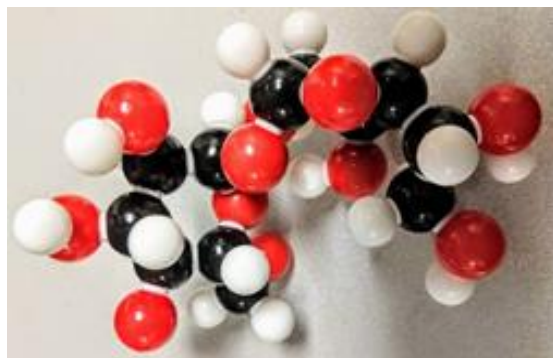
Learning Objectives:

1. Explain chemistry in terms of its small pieces: electrons, protons, nuclei, and photons.
2. Draw Lewis structures and bond-line structures from molecular formulas.
3. Use chemical formulas to calculate degrees of unsaturation in molecular structures.
4. Explain what a resonance structure is, and why they are required.
5. Develop chemical intuition about low-energy and high-energy resonance contributors.
6. Know what the resonance arrow (\longleftrightarrow) indicates, and how it differs from the equilibrium arrow (\rightleftharpoons).
7. Show electronic motion in the conversion of one resonance structure to another using curved arrow formalism.
8. Explain how X-ray crystallography works – including how data is acquired and interpreted – to locate atoms in crystalline molecules.

1.1 WHAT IS ORGANIC CHEMISTRY?

(Arthur Cammers, 2019) (Image: Molecular model of sucrose. Credit: Arthur Cammers, 2019)

← 1.5 nm →



The question about the definition of organic chemistry can go on forever and indeed would change depending on the decade in which you asked the question. Certainly, chemists would have answered the question differently in 1920 than in 2020 – the age of LCDs, polymer processing, industrial catalysis, modern instrumentation, and new drug discovery. We can simplify the question by removing ‘organic’ and ask, “What is chemistry?” I need to give a broad definition that may initially confuse you, and then I will work to clear things up.

Chemistry studies the [emergent](#) properties of the electromagnetic force (EM) at approximately nanometric length scales and below (go to the link: [electromagnetic force](#); look at the table, ‘*The four fundamental interactions of nature*’ and take note of the row entitled, ‘*Bound states formed*.’ You will see ‘*atoms and molecules*’ under the column heading ‘*Electromagnetic*’). Take note of the other universal forces and their bound states. This one row in the table neatly puts chemistry in terms of scale and topic as it compares to other topics in the physical sciences. The length scale of atoms and molecules is about 0.1 to 100 nm. For example, the sucrose molecule, table sugar, is about 1.5 nm from end to end. **Chemistry** also studies emergent properties of the electromagnetic force extrapolated to length scales that correspond to the human experience, extrapolated from the nm-Å scale to the μm-m scale, the scale at which humans usually build. This includes everything from the conductivity of a copper wire to the setting time of epoxy cement.

Now I must apologize! That definition was probably too dense because one must know quite a bit to parse it into anything sensible. Let us talk about some broad examples of the EM force at

atomic length scales. We need to spend some time on this because the definition of chemistry will put us on the same page.

Consider the periodic table and apply the definition of chemistry to it. When we compare the chemical behavior of hydrogen (^1H) to one of its isotopes, deuterium (^2H), they are nearly identical even though the atomic mass is double. Likewise, the chemistries of the other common isotopes in the periodic table are nearly identical, e.g. ^{12}C compared to ^{13}C . Obviously, the force of gravitation and the property of mass do not determine what we call chemistry! Neither does the force that sticks an extra neutron to the nucleus to give us different isotopes determine the chemistry. The forces between charged components (nuclei and electrons) determine the chemistry. This is the electromagnetic force; everything chemistry derives from it.

The periodic table organizes atoms according to their chemistries. This is the reason Li^+ and Na^+ have similar chemistries. One is much heavier than the other is, but the arrangement of the electrons with a single positive charge is similar. Both atomic species are prone to interact with other electrons. Chemistry always focuses on the electromagnetic force and – in particular – the energy of the electrons in the chemical system. Logically, if we add an electron to both we get atomic Li and Na which also have similar chemistries with some clear differences. The chemistries of the atoms in the periodic table determine how they stick to one another to form molecules and determine how molecules interact with each other to determine measurable properties of gases, liquids, and solids. This macroscopic, emergent behavior of *electrons* comprises a large part of what we study in chemistry.

Light as we see it is a small portion of the [■ electromagnetic spectrum](#). The electromagnetic field is a property of space. When the value is zero, space is dark. When the value is non-zero, space gets more interesting because we can see reds to blues with our eyes; we can detect infrared or ultraviolet with instruments; we can detect radio signals; etc., depending on the wavelength of the EM phenomena. EM waves interact strongly with atoms and molecules. We use this interaction to learn about the chemistries of the material we are studying. [■ Spectroscopy](#) is the theory and activity of interpreting the interaction between EM radiation and atoms or molecules. Go back to the link [■ electromagnetic force](#); look at the table, '*The four fundamental interactions of nature*' and take note of the row entitled, '*mediating particles*.' You will see '*photon*' under the column heading '*Electromagnetic*'. For a charged body to repel or attract another charged body they exchange photons. Molecules contain charged components, which exchange photons to stay with the molecule (vs. floating away), so the absorption of another photon changes the nature of the association between electron and molecule (average distance changes, average energy changes, etc.). The photon is the mediating particle of the electromagnetic force, and chemistry relies on EM; thus, molecules interact strongly with light.

Without spectroscopy, we would be blind to most of chemistry; spectroscopy, therefore, is the epistemological aspect of EM that allows us to construct theories about chemistry. To tell someone about chemistry without referencing spectroscopy would be describing what we know without describing how we know it. Throughout these introductory chapters we include important aspects of EM that pertains to the chapter content.

What is Organic Chemistry? Look at the [periodic table](#); find atom number 6; it is the fourth atom in the second row, the carbon atom. The C atom has diverse options to bond with itself and many other atoms. This rich variability to make connections and to react ...or not...makes life possible. That's right, the nature of life is chemical. Concrete aspects of life like bone, blood and muscle are chemical, but even abstract aspects of life like your thoughts and memories are also chemical in nature. Besides life, the chemistry of the carbon atom is central to many other aspects of our daily lives, such as multi-billion-dollar industries of many types. The chemistry of the carbon atom *is* organic chemistry!

6	C
carbon	
12.011	

many other atoms. This rich variability to make connections and to react ...or not...makes life possible. That's right, the nature of life is chemical. Concrete aspects of life like bone, blood and muscle are chemical, but even abstract aspects of life like your thoughts and memories are also chemical in nature. Besides life, the chemistry of the carbon atom is central to many other aspects of our daily lives, such as multi-billion-dollar industries of many types. The chemistry of the carbon atom *is* organic chemistry!

Most of the elements we will encounter in Chapters 1-9 of this book are contained in the portion of the periodic table represented below. Later we will use transition metals (e.g. Os, Cr, Zn, Cu, Ni, Pd, Pt), but for now, let us focus on knowing the position of a subset of elements in the periodic table. Remembering in which Group an element resides will help you more quickly count its valence electrons and predict its reactivity.

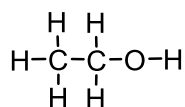
Exercise 1.1.1 In the empty boxes, insert the symbol for each missing element.

	Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	1							2
2	3	4	5	6 C	7	8	9	10
3	11	12	13	14	15	16	17	18
4	19	20	31	32	33	34	35	36
							53	54

1.2 BOND-LINE STRUCTURES: ELECTRONS, BONDS, AND FORMAL CHARGES

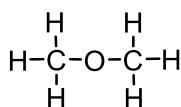
(Arthur Cammers, 2019)

Why are molecular formulas inadequate to define molecules? Let's examine the molecular formula C_2H_6O . Ethanol and dimethyl ether bear very different chemical properties despite having the same molecular formula. Molecules that have the same molecular formula but differ in atomic connectivity, are termed **constitutional isomers**. The way that atoms are arranged play a major role in how they react in solution with other molecules. Therefore, discussing electronic properties of molecules is the first thing we need to accomplish.



ethanol

boiling point: 78.5 °C at 1 atm



dimethyl ether

boiling point: -25 °C at 1 atm

Much of what follows will be review for you because the prerequisite of Organic Chemistry is General Chemistry, which always introduces ■ [Lewis](#) dot structures. Lewis structures represent molecules by demonstrating their atom connectivity allowing us to communicate symbolically. There are a few concepts that you need to bear in mind to apply Lewis Structures effectively in organic chemistry:

1. Electrons connect nuclei by virtue of their attraction to two or more nuclei.
 - a. Yes, one-electron can bond two nuclei, but two electrons bond them much better.
 - b. When only two electrons bond two nuclei we call this a σ bond (pronounced “sigma” like the corresponding Greek letter).
 - c. Only two electrons ‘fit’ in a bond, but double and triple bonds can form between nuclei. In the following chapters we will unpack this concept further.
 - d. When more than two electrons bind to two nuclei, these extra electrons must occupy π bonds (pronounced “pi” like the corresponding Greek letter).
2. ■ [Valence bond theory](#) states that only valence electrons make bonds.
 - a. There are other electrons, often referred to as core electrons or inner shell electrons, that we can think of as very low-energy lone pairs that do not participate in chemical change.
3. Better Lewis structures have 8 electrons around any second-row elements (Li to Ne) and 2 electrons around the first-row elements (H and He) whenever possible. Remember your many discussions of the ■ [octet rule](#) when you studied General Chemistry.

Tackling a few example problems is the best approach from here to review the construction of Lewis structures. In these examples while you are reading try to remember your General Chemistry and do the problem first before you look at the stepwise solution to the problem.

Example 1.2.1 Draw a bond-line structure of ammonia, NH_3 .

Solution: First, we will count electrons. Then we will find a reasonable way to connect the atoms and place remaining electrons in our structure without violating any rules.

Step 1. Count the valence electrons.

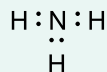
When we consult the ■ periodic table, we note that nitrogen is element number 7 and it is the fifth element in the second row. To balance the charge of the 7 protons in the N atom we need 7 electrons, but 2 of those are first row electrons. The five electrons in the second row concern us the most as these are the valence electrons – the electrons that reside in the outermost shell surrounding the atomic nucleus. The number of valence electrons for each neutral atom is equal to the atom’s main group number found in the periodic table. These electrons determine the chemistry of the atom. The hydrogen atoms have one valence electron each and there are three of them. Counting the valence electrons in NH_3 gives us:

$$\text{N: } 1 \text{ atom} \times 5 \text{ e}^- = 5 \text{ e}^-$$

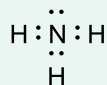
$$\text{H: } 3 \text{ atoms} \times 1 \text{ e}^- = 3 \text{ e}^-$$

$$\text{Total} = 8 \text{ valence electrons}$$

Step 2. Place the atoms together so they share pairs of electrons to make complete octets.

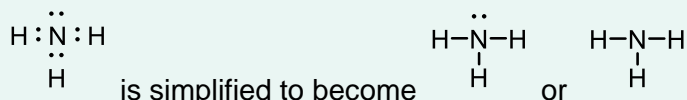


After we use 6 electrons to share between N and the three H atoms, we are left with two electrons ($8 - 6 = 2$) which can sit on the N atom.



Now counting all the electrons, we see that we have used 8 valence electrons in the structure.

Step 3. In organic chemistry we will show the bonded electrons as lines and use dots for the non-bonded electrons.



It is okay to draw either structure when referring to ammonia. In the case on the right, the lone pairs are understood to be there.

Sometimes people draw structures with implicit lone pairs; in other words, sometimes people do not draw them on the structure. The rule of thumb is that lone pairs do not have to be drawn on bond-line structures, but ***formal charges should always be shown***. Charges always are explicit; if the electrons were really missing, we would have to indicate the molecule has +2 formal charge (we will discuss how to calculate formal charge in Section 1.2.1); thus, the lone pair is implied on the last structure above.

Instead of Lewis structures, we call these **bond-line structures**. Bond-line structures, which are also called **line structures** and **skeletal structures**, are quicker to draw, but we *always* understand them as Lewis structures, meaning we know that each single bond is made of two electrons.

1.2.1 Formal Charge

The formal charge (+ or -) is a number that we ascribe to *atoms* in line structures. **Formal charge** is simply the number of protons in the nucleus minus the number of electrons around the nucleus. It is a way of keeping track of electrons and doesn't necessarily represent the location of charge in a molecule, but nonetheless, it is necessary to know how to assign formal charges to become proficient in organic chemistry.

The calculation of formal charge is below:

$$\text{FC} = \text{valence charge} - (\text{non-bonded valence electrons}) - \frac{1}{2} (\text{bonded valence electrons})$$

The valence charge is a positive number: It is simply the charge of the nucleus without the valence electrons. To determine this number, start with the left side of the [periodic table](#) and count from left to right until you get to the atom of interest. For example, the B atom has 3 valence electrons, C has 4 valence electrons, etc.

Example 1.2.2 Draw the Lewis structure of the cation $^+\text{NH}_3$, which could also be written as NH_3^+ or $[\text{NH}_3]^+$. Put formal charges on the appropriate atoms.

Note: There is one fewer electron than there are protons in the molecule.

Solution: When determining the Lewis structure for an ion, we must adjust the number of electrons to account for the net electric charge of the ion. A negative charge on an ion represents an excess of electrons; however, a positive charge on an ion represents a loss of electrons.

Step 1. Count the valence electrons:

N: 1 atoms x 5 e⁻ = 5 e⁻

H: 3 atoms x 1 e⁻ = 3 e⁻

- 1 for the positive charge

Total = 7 valence electrons

Step 2. Put the molecule together as indicated by the formula.

Using the logic above, we now have this $\text{H}:\overset{\oplus}{\underset{\cdot\cdot}{\text{N}}}\text{:H}$, which should be written as $\text{H}-\overset{\oplus}{\underset{\text{H}}{\text{N}}}-\text{H}$.

Step 3. Check your formal charge assignments before concluding work on a problem.

For the H atoms, FC = 1 - 0 - ½ (2) = 0

For the N atom, FC = 5 - 1 - ½ (6) = +1

Note: In all structures, the sum of the formal charges must equal the molecular charge.

Note: When including a formal charge, you should circle it. This will help make sure that your positive charge is not mistaken for a plus sign and that your negative charge is not mistaken as a stray pencil mark.

Note: When including +1 or -1 formal charge, do not write the number 1. Only the + or - symbol surrounded by a circle is needed: \oplus or \ominus .

Exercise 1.2.1 How did we know to draw the molecule with a positive formal charge on N (left) rather than a half charge each on N and one of the H atoms (right)?



Example 1.2.3 Draw the Lewis structure of (CH₃)₂CNH₂⁺.

Note: In this case, the way we should connect the atoms is indicated by the formula. This is not always the case. The formula could have been presented as C₃H₈N⁺, and in that case we would have more liberty in how we could correctly connect the atoms with electrons.

Solution:

Step 1. Count the valence electrons: C = 4, H = 1, N = 5, -1 for the positive charge.

C: 3 x 4 = 12

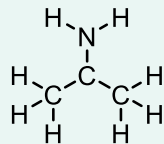
H: 8 x 1 = 8

$$\text{N: } 1 \times 5 = 5$$

- 1 for the positive charge

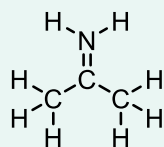
Total = 24 valence electrons

Step 2. Put the molecule together as indicated by the formula.



Step 3. Count the electrons used so far and compare that to the number available: There are 11 bonded pairs of electrons = 22 electrons. There are 24 electrons that we must use (they must go somewhere).

Step 4. Notice in the structure above C and N do not have 8 electrons. They both have 6 electrons around them. We can fix this by connecting C and N with the remaining two electrons.



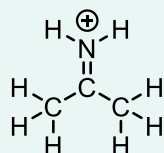
Still something is missing. Even our new method to abbreviate Lewis structures never omits formal charges. When we calculate the formal charges for the C atoms, we get zeros because the valence of C = 4 and there are 8 bonded electrons to the C atoms in every case:

$$\text{FC} = 4 - \frac{1}{2} (8) = 0$$

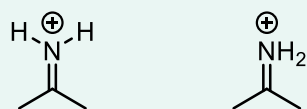
When we calculate the formal charge for the N atom:

$$\text{FC} = 5 - \frac{1}{2} (8) = +1$$

We finish the structure by adding the FC to the N atom.



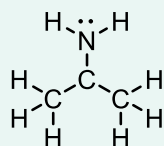
Since organic structures have so many C atoms with H atoms connected, we further abbreviate these atoms in bond-line structures implicitly. In the structure above, we drew it with C and H explicit. The same molecule with C and H atoms implicit is shown below. It is okay to draw the N-H bonds or represent the group as "NH₂".



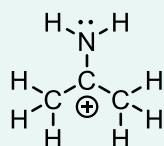
Note: All heteroatoms (anything besides C and H) and any hydrogen that is attached to a heteroatom must always be shown when drawing bond-line structures.

Alternate Solution for Example 1.2.3

Step 2. Put the molecule together as indicated by the formula and put the electrons on the most **electronegative** atoms.



Step 3. Calculate the formal charges.



Example 1.2.4 Draw the Lewis structure of the methoxide anion, CH_3O^- .

Solution:

Step 1. Count the valence electrons for 1 C atom, 3 H atoms, 1 O atom, and add an electron to account for the negative charge.

$$\text{C: } 1 \times 4 = 4$$

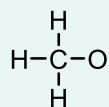
$$\text{H: } 3 \times 1 = 3$$

$$\text{O: } 1 \times 6 = 6$$

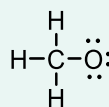
+ 1 for the negative charge

Total = 14 valence electrons

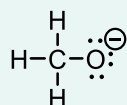
Step 2. Put the molecule together as indicated by the formula. Since we know that carbon generally forms 4 bonds, we can assume all 4 additional atoms will bond to carbon.



Step 3. Count the electrons used so far and compare that to the number available: There are 4 bonded pairs of electrons = 8 electrons. If we satisfy the octet rule for oxygen, then we will need to add three lone pairs of electrons to the O. This makes 14 valence electrons, which equals the amount calculated.



Step 4. We know from the formula that the molecule has an overall negative formal charge. Upon calculating formal charge, we find that it belongs on O.



Note: In the examples above, when formal charges were included, the charge was either +1 or -1. While ions can have net charges of +2 and -2 and greater, you will never see a formal charge on an atom other than 0, +1, or -1 in a reasonable representation of an organic molecule or ion.

Example 1.2.5 Draw a bond-line structure for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2$.

Solution:

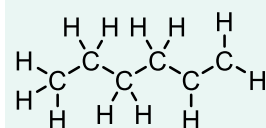
Step 1. Count the valence electrons for 6 C atoms and 12 H atoms

$$\text{C: } 6 \times 4 = 24$$

$$\text{H: } 12 \times 1 = 12$$

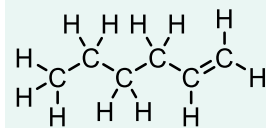
Total = 36 valence electrons

Step 2. Put the molecule together as indicated by the formula.

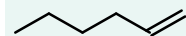


Notice that all the C atoms are connected to C or H by 4 bonds except the two C atoms on the right side.

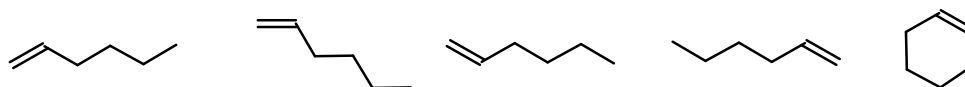
Step 3. The two C atoms on the right side do not have a full octet of electrons. They each have 6 total valence electrons. If we examine the total number of valence electrons in our molecule from Step 2 you will recognize that we have utilized 34 valence electrons and still have 2 additional valence electrons to add. We should use this pair of electrons to make another bond between the two C atoms filling each of the C atom's valence shell with 8 electrons.



Step 4. Draw the structure again, removing implicit C and H atoms, using bond-line structure.



Note: We don't care how the structure is oriented. All these structures indicate the same molecule.



Exercise 1.2.2 Draw a bond-line structure for $\text{CH}_3\text{CHCHCH}_2\text{CHCH}_2$.

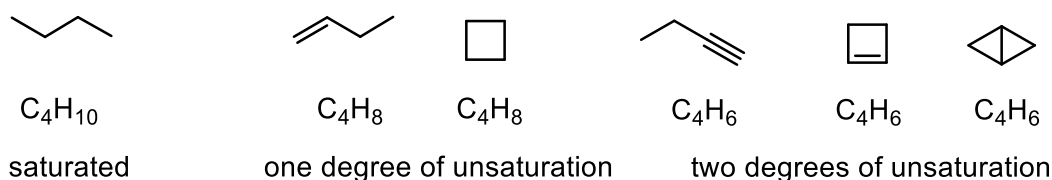
Exercise 1.2.3 Draw a bond-line structure for $(\text{CH}_3)_2\text{CHCO}_2\text{H}$.

1.3 DEGREES OF UNSATURATION (DU)

(Arthur Cammers, 2019)

A molecule is termed **saturated** when it possesses its maximum number of hydrogen atoms. A compound with fewer than its maximum number of H atoms is termed **unsaturated**. Decreasing the number of hydrogen atoms by two adds a **degree of unsaturation (DU)**. In some textbooks, you may see this term called the **hydrogen deficiency index**.

Each DU indicates a ring or a π bond. For a saturated compound, in which there are no degrees of unsaturation, there will be no rings and no π bond. Compounds with one DU have either one π bond or one ring. A compound with 2 DUs will have two π bonds, one π bond and one ring, or two rings. In the examples below in which all compounds have four carbon atoms, the molecular formula is the same when the number of degrees of unsaturation is the same.



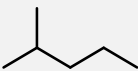
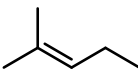
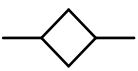
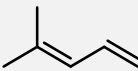

Calculating the degrees of unsaturation is a very useful shortcut that chemists use when the task involves going from formula to structure.


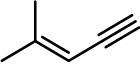





For any neutral molecule,

$$\text{DU} = 1 + \#E4 - \frac{1}{2} \#E1 + \frac{1}{2} \#E3$$

where #E4 = number of elements that bond 4 times, and #E3 = number of elements that bond 3 times, and #E1 = number of elements that bond one time with neutral formal charge.

Upon calculating the DU for a molecular formula, we can determine several structural features of the molecule. The chart depicts possible combinations of structural features depending on what DU you calculate. If a DU of zero is obtained this means the molecule must be fully saturated and therefore have no rings, double or triple bonds.

DU	Structural Components		Examples Containing 6 Carbon Atoms
	π bonds	rings	
0	0	0	
1	1	0	
	0	1	
2	2	0	
	0	2	

	1	1	
3	3	0	
	0	3	
	2	1	
	1	2	
4	4	0	
	0	4	N/A for C ₆ H ₆
	3	1	
	etc., as long as the sum of π bonds + rings = 4		

Note: The molecule cannot possess a charge and must have an even number of electrons to simply apply DU to the molecular formula to unveil possible structural features!

Example 1.3.1 Draw a bond-line structure for the formula C₆H₁₀.

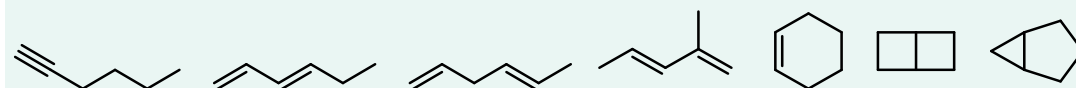
Solution:

Step 1. Determine the degrees of unsaturation based on the molecular formula.

$$\text{DU} = 1 + 6 - \frac{1}{2}(10) = 2$$

Two degrees of unsaturation means that there is some combination of two bonds in excess of a single bond between any two atoms or a ring. In other words, structures matching this formula will have two π bonds, two rings, or a π bond and a ring.

Step 2. Draw structures with the correct number of C atoms and the correct DU features. You don't have to count electrons, or hydrogen atoms. Molecular formulas do not indicate how the atoms are connected. If you need to draw a structure for C₆H₁₀ you are free to present any structure of the family of molecules with this molecular formula. Some examples are shown below.



Twins or triplets are people with the same parents, likewise we call these molecules isomers because they were built with the same number and kinds of atoms. We are going to revisit the concept of isomers in much greater detail soon.

Exercise 1.3.1. Can you think of a few more isomers with molecular formula C_6H_{10} ? Keep the definition of DU in mind when answering this question.

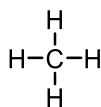
1.3.1 Using DU for Molecules with Other Atoms

We have more to discuss about using DU to go from molecular formulas to molecular structures. *How do you know which elements are E4 or E1 and so on?* Let us reflect on our General Chemistry background while we look at the [periodic table](#). Remember that simple application of DU to the molecular formula is only feasible if the molecule is neutral and has an even number of electrons.

#E4 Elements: Due to the manner electrons occupy space around elements, the C atom tends to bond 4 times. It has a valence of 4 and atomically the chemistry of the carbon atom is thought of as



which can combine with elements that bond once like $H\cdot$ to make methane, CH_4 .

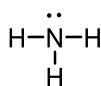


This structure obeys the octet rule with 8 electrons around the C atom. The elements below the second row in the periodic table have similar chemistry, so Si is also a #E4 element.

#E3 Elements: To the right of C we find N which has 5 valence electrons. In its obedience of the octet rule, the chemistry of the nitrogen atom is thought of as having one lone pair, making three electrons available to form bonds.

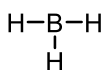


Nitrogen combine with elements that bond once like $H\cdot$ to make ammonium, NH_3 .



Thus, N is an E3 element in the DU formula for neutral molecules.

B in neutral structures, like BH_3 , also bonds 3 times. In these structures, the B atom violates the octet rule, which is fine for neutral structures that include boron.



We will see in our studies that the octet rule still operates with molecules that include B because boron atoms tend to bond with electrons to make charged structures, but remember when this happens, these structures are beyond the scope of DU because they are charged. The elements below the second row in the periodic table have similar chemistry, so P is also a #E3 element.

#E2 Elements: Beryllium (Be) and oxygen (O) are E2 elements in neutral molecules; they bond 2x. Oxygen has 6 valence electrons, in obedience to the octet rule the chemistry of oxygen.



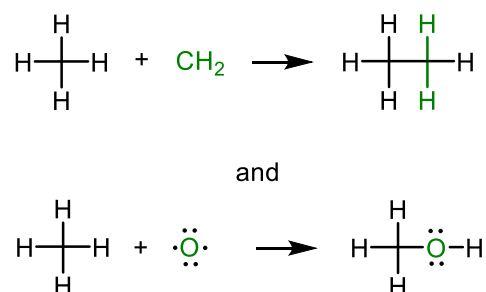
Oxygen tends to bond 2x and obey the octet rule by also having two lone pairs.

In neutral structures the chemistry of Be is mandated by its two valence electrons, so it is a #E2 element. It violates the octet rule (see example BeCl_2). However, similar to boron, in molecules the Be atom tends to want to fill its octet by bonding with electrons in other atoms.



Think about why #E2 does not appear in the DU formula. Think about why we count half the H atoms and all the C atoms in the formula. Let us start with molecular hydrogen, H_2 , which must be $\text{DU} = 0$ because logically it can have no rings or double bonds without violating the bonding rules for the H atom, and $\text{DU} = 1 - \frac{1}{2}(2) = 0$. The atoms in H_2 are the reason we have the 1 in the formula.

Between the two H atoms we can put CH_2 to get CH_4 and the structure still has $\text{DU} = 0$. This is why we add one DU unit for every C atom and subtract half a DU unit for each H atom in the DU formula. This is also why we can ignore the elements that bond 2x because we can use the O atom and other atoms that bond 2x in the same manner that we used CH_2 without changing DU. For example:



Both the ethane and methanol molecules have no degrees of unsaturation. Therefore, atoms or structural fragments that bond 2x must contribute zero to the DU of the formula. In the case of CH_2 , we add 1 and subtract $\frac{1}{2}(2)$ to get zero; in the case of the O atom, we ignore it.

#E1 Elements: Of course, the H atom is an E1 element and so is the F atom because octet occupation leads us to chemistry wherein only one bond can form.



Single vs. Double vs. Triple Bonds: For now we are using multiple bonds simply to satisfy the octet rule, but you may already know that there is a difference between multiple lines we draw between atoms in molecular structures when there is more than one bond between two atoms, i.e. when we introduce unsaturation in the structure. In the case where there are two bonds between two atoms, one of these is a single bond, a sigma (σ) bond and the other is a pi (π) bond. In the case where there are three bonds between two atoms one of these is a σ bond and the other two are π bonds. We will soon have to discuss the intrinsic differences in structure and reactivity of these two bonds in detail, but we will need more theory to do so.

Summary: We know from our general chemistry background that the elements in the columns of the periodic table have similar chemistries. Thus H, Li, F, Cl, Br are all #E1 elements in the DU formula. Likewise, O, S, and Be are #E2 elements, and B, Al, N, P, and As are #E3 elements. Finally, C, Si, and Pb are #E4 elements.

Example 1.3.2 Draw a bond-line structure for the formula $\text{C}_{20}\text{H}_{35}\text{NOSi}_2\text{BrCl}$.

Solution: The scale of this problem is big, but with the background above, scale becomes more trivial. This ridiculously large scale of atomic content and possible structural features for this example was chosen to show that scale becomes manageable with good formulism.

Step 1. Find out something about the structure by calculating $DU = 1 + 22 - \frac{1}{2}(37) + \frac{1}{2} = 5$;
 22 because there are 20 C and 2 Si atoms; C and Si form 4 bonds in neutral molecules
 37 because there are 35 H atoms and 2 halogen atoms; these bond once
 + $\frac{1}{2}$ is for the N atom

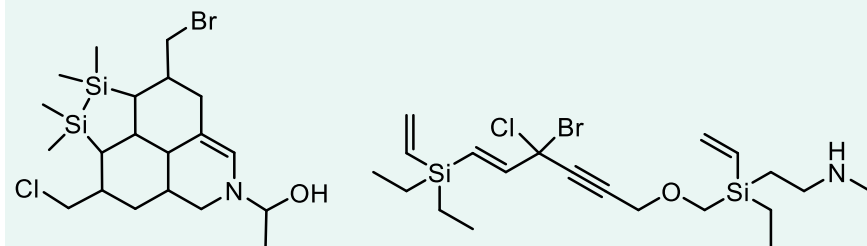
DU = 5 means that there are 5 bonds in excess of a single bond between any atom or some combination of rings and multiple bonds to equal DU = 5.

Step 2. We can just draw neutral bond-line structures (Lewis structures) that answer the formula without thinking about counting electrons or H atoms.

While drawing, make sure there is one Cl, one Br, two Si, one O and one N atom in the molecule. Make the Si and C atoms bond 4x and the O atom bond 2x and the N atom bond 3x. We make sure that there is enough unsaturation to equal DU = 5 by including structural features like double bonds, triple bonds, and /or rings.

In the first structure below there are 4 rings and a double bond which gives DU = 5. In the next structure there is a triple bond and 3 double bonds which also sum to DU = 5.

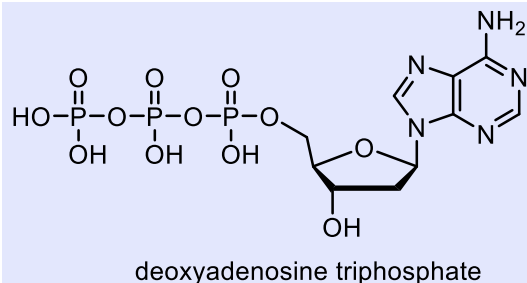
Two Solutions (there are many, many more):



When you look at the structures remember that the H atoms on the C atoms are implied. The C atoms are also implied when the lines change direction or terminate; at the end of every single 'line' there are 3 H atoms on a C atom unless it bears a formal charge. At each vertex there are two H atoms if there are only single bonds at the C atom and there is one H atom if there is a double bond at the C atom, and so on.

Note: These structures may seem random ... these structures are random. There are zillions of isomers for this formula. Organic Chemistry is amazing! Due to the diversity in bonding and atomic content, a chemist with a little training can make the world's supply of something in a few days in the lab!

Exercise 1.3.2 dATP is an important molecule in the synthesis of DNA and energy production. Add the missing lone pairs to dATP.



Exercise 1.3.3 Consider possibilities for the bond-line structure for the diol propylene glycol, $C_3H_8O_2$. This is a common ingredient in [antifreeze](#); you can click the link and check the line structure. Did you happen to guess right? Did you draw an isomer?

Note: Even looking up encyclopedic information on antifreeze contains a bond-line structure for a common ingredient; this fact should pique your curiosity about the importance of and the broad information in organic chemical bond-line structures. After you take this course, you will look for these structures and tap your chemical education to learn more about the substances that you research!

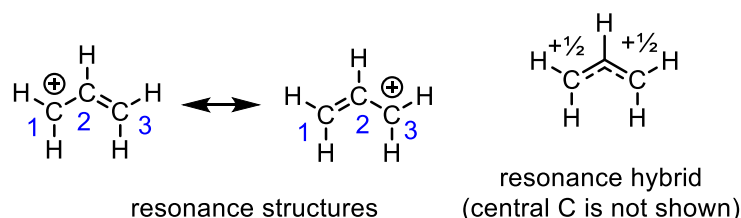
1.4 RESONANCE AND ELECTRON PUSHING

(Ashley Jolly Steelman and Susan Odom, 2019)

As chemists started to develop a deeper understanding of the bonding in molecules, it was found that there are inadequacies in numerous bond-line structures. In order to resolve these inaccuracies, chemists draw resonance structures. A **resonance structure** is drawn when one bond-line or Lewis structure cannot fully describe the bonding that takes place between neighboring atoms. Examine the two structures of the allyl cation. The positive formal charge is **delocalized** onto C_1 and C_3 , meaning the charge is spread over two locations. The formal charge cannot be isolated at the two different locations, because in the real structure electrons move freely. Experiments have shown that the structures below must represent the same molecule. Shown below are the two resonance structures of the allyl cation, $[CH_2CHCH_2]^+$. Both resonance structures, which are shown to either side of the double headed **resonance arrow** (\longleftrightarrow), contribute equally to the electronic structure of the allyl cation.

It is important that you know that resonance structures depict the location of electron density within one molecule. The actual structure of the allyl cation is a combination of all resonance structures melded together. This is represented by a **resonance hybrid** – a combination of each individual resonance structure.

Note: The double headed resonance arrow is not the same as an equilibrium arrow. Resonance structures are not in equilibrium with each other.



Note: any time that two resonance structures are mirror images of each other, they will contribute equally to a species' electronic structure.

Two structures are **resonance structures** if they only differ in the placement of π bonds and electron lone pairs; the position of σ bonds do not change. In the next few sections, we will learn more about resonance structures, including converting between multiple structures as well as determining what structures are reasonable and are the most important contributors.

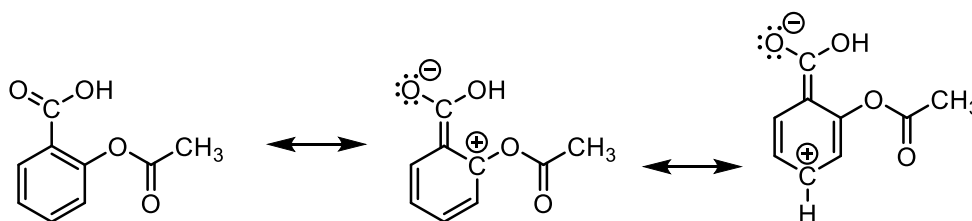
You might wonder why it is important to consider multiple representations of the same molecule or ion when each valid resonance structure is a Lewis structure that represents the species of interest. The structures are only different because we rearranged bonds and charges. The reason we need to consider resonance structures is that considering the position of charges and electrons will allow us to begin analyzing the reactivity of a molecule specifically looking at where a molecule's electron density is located. In order to draw and recognize resonance structures of a given species, we need to talk about a couple rules:

1) We tend to move electrons located in π bonds or in electron lone pairs because disrupting σ bonds drastically increases the energy. These electrons must be isolated in a p orbital, which we will talk about in a deeper sense later. However, recall from general chemistry what single, double, and triple bonds consist of:

- single bond: one σ bond
- double bond: one σ bond and one π bond
- triple bond: one σ bond and two π bonds

This means that we will avoid breaking a single bond in a resonance structure. We will avoid breaking a π bond without having the structure recover electron occupation at an electronegative atom. We should focus on moving electrons in double bonds, triple bonds, or electron lone pairs.

2) The overall charge of a system must remain the same. Examine the three resonance structures of Aspirin and note that the net charge is the same in each structure. The first structure is neutral and therefore, we will see that the second and third structure carries a positive and a negative formal charge, which cancel one another out so that the structure remains overall neutral.



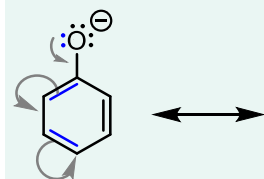
3) The bonding framework must remain intact. We will use curved arrows to depict the movement of electrons throughout this entire course. A common mistake of beginning organic chemists is to use curved arrows to indicate the movement of atoms or positive charges but this will NEVER occur. A curved arrow is only used to depict the movement of valence electrons in resonance structures or reaction mechanisms. Every curved arrow has a tail and a head. Each arrow indicates where a pair of electrons originates (tail of the arrow) and where they are moving to (head of the arrow).



tail - where electrons originate **head** - electrons' destination

Let us tackle the following example to demonstrate how curved arrows are used to push valence electrons.

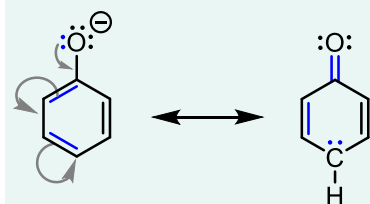
Example 1.4.1 Draw the resonance structure that is indicated by the curved arrows shown. Be sure to include formal charges.



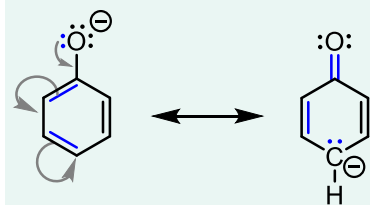
Solution: First, we will draw what did not change from our original structure, then – for the electrons that moved (highlighted here in blue) – we will determine their location in the second resonance structure, then assign formal charges.

Step 1. The tail of each arrow depicts where each set of electrons is moving. The lone pair of electrons on oxygen will move to form a double bond between oxygen and carbon. The double bond at the top left of the ring is being moved to a carbon-carbon double bond to the left of the ring. The double bond at the bottom left of the ring is being moved to a lone pair of electrons on the bottom carbon of the ring.

Note: The tail and head of each arrow needs to be placed in very precise locations. Specifically, if you are moving a pair of electrons to form a double bond then you need to place the head of your arrow in the middle of the bond. However, if you are moving a pair of electrons to a lone pair on a specific atom then the head of the arrow needs to be drawn directly to the atom.

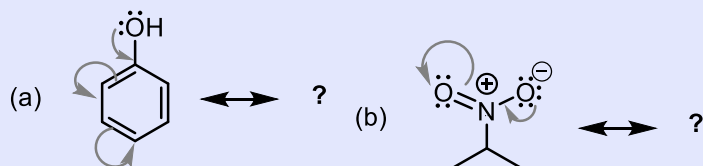


Step 2. We now must assign formal charges. Recall that the overall charge of the molecule must remain the same. Our structure started with an overall negative formal charge and we will find that the newly drawn resonance structure will also have an overall negative formal charge that has been moved to carbon.



Give the exercise below a try. Make sure you can do this problem correctly before proceeding!

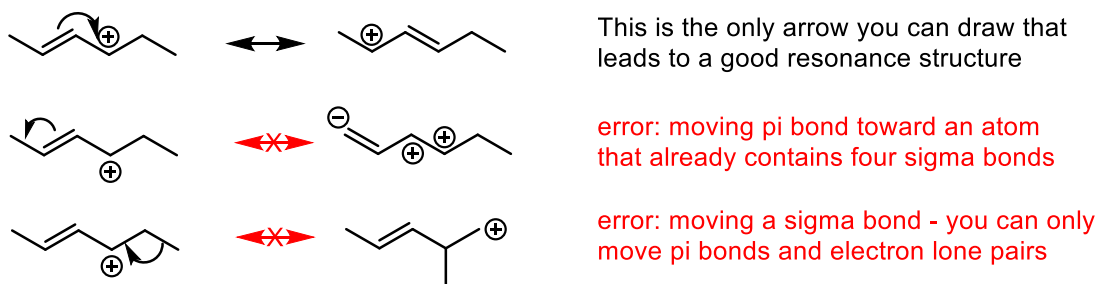
Exercise 1.4.1 For each of the structures below, draw the resonance structure that is indicated by the curved arrows shown, showing all electron lone pairs. Be sure to include formal charges.



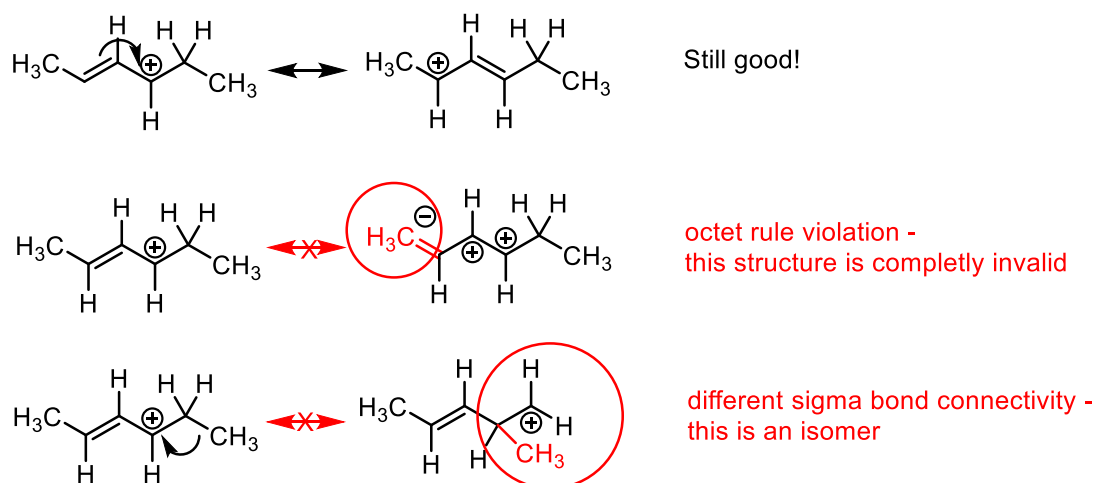
1.4.1 Moving Electrons without Violating Rules

When you first start drawing resonance structures, it is easy to get confused about which way to move π bonds and electron lone pairs. Especially when you're working with bond-line structures in which H atoms are implied, you can move bonds and violate the octet rule without realizing it. Therefore, it is a really good idea to add implicit H atoms and implicit electron lone pairs to your drawings until you are sure that you're comfortable drawing resonance structures without making errors.

Let us look at an example of a right and wrong way to move electrons to create a second resonance structures from the same starting point. In this conjugated system, we can only use three of the carbon atoms to house delocalized electrons.

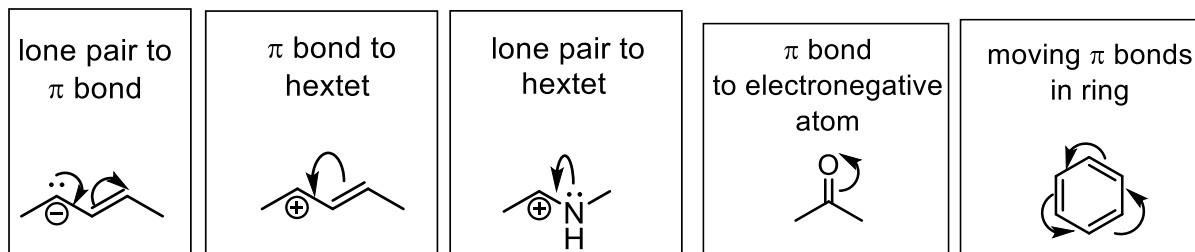


With the implicit H atoms incorporated into the structure, we can be more specific about why the second and third options are incorrect.



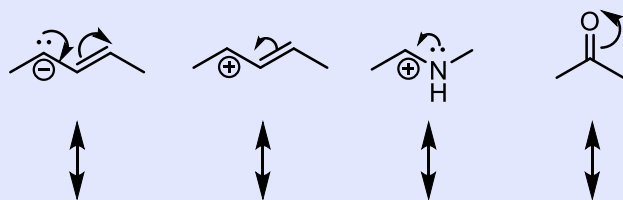
This brings us to recognizing some common patterns in moving delocalized electrons to draw resonance structures. A summary of common arrow pushing patterns in drawing resonance structures is shown below. If you follow these patterns, your resultant structure should be reasonable and without octet violations. If ever in doubt, though, add implicit H atoms to your structures, which will make it easier for you to catch errors.

Acceptable Curved Arrow Use to Yield Reasonable Resonance Structures



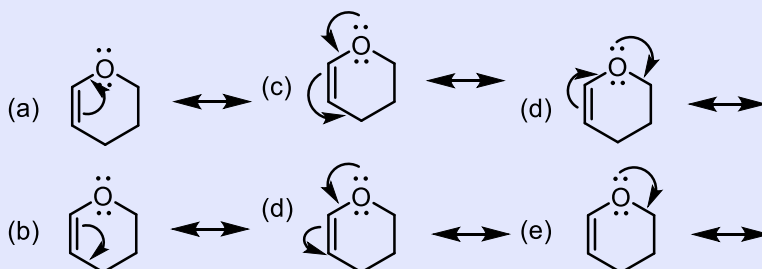
Let us practice some arrow pushing by drawing the resonance structures and resonance hybrids that represent each pair of resonance structures.

Exercise 1.4.2 (a) Redraw the following bond-line structures to show all implicit H atoms and implicit electron lone pairs; retain the curved arrows. (b) Then draw the resonance structures that result from the curved arrows, again showing implicit H atoms and implicit electron lone pairs. (c) For each example, draw a resonance hybrid that represents a combination of each of your pairs of resonance structures.



Note: Always check to make sure your charges are balanced (same net charge in each resonance structure) and that you have not violated the octet rule for second row atoms.

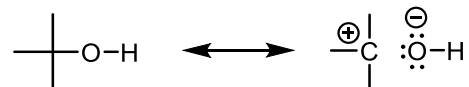
Exercise 1.4.3 For dihydropyran, shown below, examine the curved arrows showing movement of an electron lone pair and/or the π bond. Only one example, a-e, shows the arrow(s) that would lead to a valid resonance structure. Without adding implicit H atoms, can you tell which one choice leads to a resonance structure?



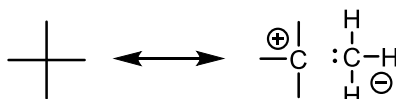
Now, draw the structures again and include the implicit H atoms. Is it easier to see how all but one set of arrows violates the octet rule?

1.4.2 Estimating the Importance of Resonance Structures

Not all resonance structures contribute equally to the overall resonance hybrid. This is the reason we avoid showing resonance structures that involve the movement of electrons in σ bonds without some energetic recovery from putting electrons on electronegative atoms.



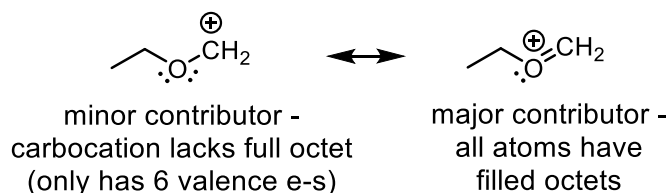
NOT A GOOD RESONANCE STRUCTURE! (Left structure) major contributor - all atoms have filled octets and σ bonds are intact. (Right structure) a minor contributor to the real structure that shows the polarity of the C–O bond. The C atom lacks an octet; it only has six valence electrons.



A WORSE RESONANCE STRUCTURE THAN THE ONE ABOVE! (Left structure) major contributor - all atoms have filled octets and σ bonds are intact. (Right structure) a RIDICULOUSLY minor contributor to the real structure. Unlike the molecule with the O atom, the hydrocarbon resonance structure (above lower right) recovers nothing from putting the extra electrons on a relatively electronegative atom.

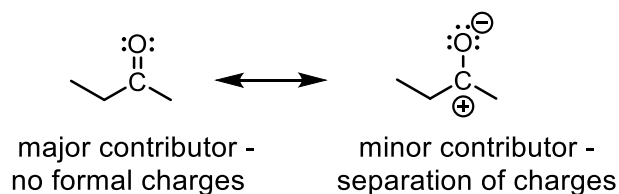
We need to be able to recognize the quality of each resonance structure. The resonance with a better (lower energy) Lewis structure will be a more significant contributor to the overall structure of the molecule. The following rules will help you to evaluate which resonance structures are major vs. minor contributors.

1) Look for the resonance structure where every atom has filled valence shells (completed octets). Examine the structures below.



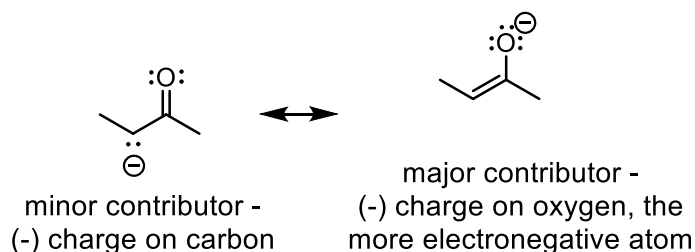
A GOOD RESONANCE STRUCTURE! Because the difference in energy is not so big. The π bond is weaker than the σ bond, but the π bond is better than no bond.

2) The structure with fewer formal charges. The separation of charge costs energy. This is [Coulomb's Law](#) which states that the potential energy increases as a function of the square of the distance between two charged bodies.

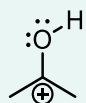


3) If a resonance structure bears a negative formal charge, the structure that places the negative charge on the most [electronegative](#) atom will be more significant (lower in energy). Do you remember that term from General Chemistry? If not refresh your concept by clicking the link. It is

the rough measure of atoms to attract electrons. The lower the energy of the electrons around an atom the more electronegative the atom is.

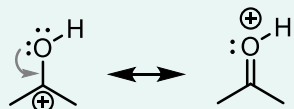


Example 1.4.2 Draw all significant resonance structures for the molecule below and determine which structure would be considered the most significant.

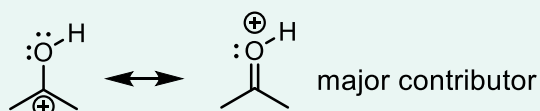


Solution:

Step 1. Locate the π electrons that can move in resonance. A positive formal charge represents an atom that has lost electron density and means that, in most cases, that atom can accept electron density. A pattern that you will notice is that π electrons can be moved towards carbocations because they can accept electron density. You might also notice that oxygen has two lone pairs of electrons. One of these lone pairs can be moved towards the positive charge.

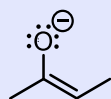


Step 2. In this example, one resonance structure is more significant than the other. The structure on the left exhibits a carbon atom that lacks a full octet (six total valence electrons). The structure on the right exhibits atoms that all have filled octets and a π bond. Therefore, the resonance structure on the right is the major contributor.

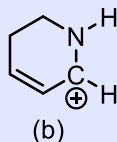
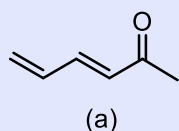


Now, use what you just learned in the example to try your hand at the following exercise involving drawing and comparing resonance structures.

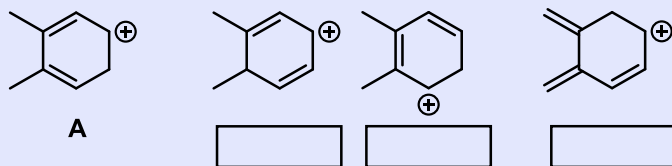
Exercise 1.4.4 (a) Draw a second resonance structure for this anion, showing all electron lone pairs. (b) Determine which structure contributes more to the resonance hybrid.



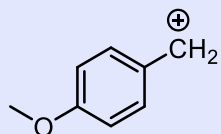
Exercise 1.4.5 (a) Draw the remaining resonance structures for each species below. (b) In each case, determine which of the resonance structures (of the originally provided structure and the answers you provided) would be the most significant contributor to the ground state electronic structure of each species.



Exercise 1.4.6 How are the following structures related to cation A? Your choices are resonance structures, isomers, and neither.



Exercise 1.4.7 (a) Draw all good resonance structures for the benzyl cation. (b) Does the methoxy group (OMe) help to stabilize the cation compared to having an H atom in its place? Explain your answer.



1.5 X-RAY CRYSTALLOGRAPHY FINDING POSITIONS OF ATOMS

(Arthur Cammers, 2019)

Now we come full circle. Due to the strong interaction of light with charged particles and with systems composed of such particles (molecules), we can use electromagnetic radiation at X-ray wavelengths to look for atoms in molecules. This phenomenon has a strong relationship to the discussion in the [first section](#) about the electromagnetic force and its pertinence to chemistry.

■ [X-ray crystallography](#) is utilized to find the relative positions of atoms in molecules. The term indicates that the method involves visualizing some hidden aspect of crystals with X-rays.

1.5.1 Why X-Rays?

One must use wavelengths at about atomic sizes for this to work, typically $\sim 0.1 \text{ \AA}$ range. Confirm this size range by looking at the [periodic table](#). Click on the carbon atom and look for the parameter: 'covalent radius'. This is the typical size of the atom in a bond. This wavelength of X-ray has energy just below the energy required to make ions out of neutral molecules (■ [electromagnetic spectrum](#) just at the upper end of soft X-rays see the table in the link). Light at this wavelength bounces off **electron clouds** around atoms in molecules in crystals. Remember from your General Chemistry course that the electron cloud determines atomic and molecular

dimensions. If the X-ray wavelength is longer, the reflections lack the resolution to 'see' the atoms. If the wavelength is any shorter, molecules decompose.

1.5.2 The Spatially Periodic Crystalline State

For the technique to work, we also need crystals which have repeat patterns of atoms or molecules in 3D. Many substances crystallize and we have everyday experience of this phenomenon in the kitchen with sugar and salt. ■ [NaCl](#) forms a simple cubic lattice (click the link; have a look at the perfectly periodic placement of Na and Cl in the solid), but crystalline sucrose is more interesting. In the crystal, sucrose molecules align in three dimensions due to attractive and repulsive interactions when the **electrons** around the nuclei pack together.

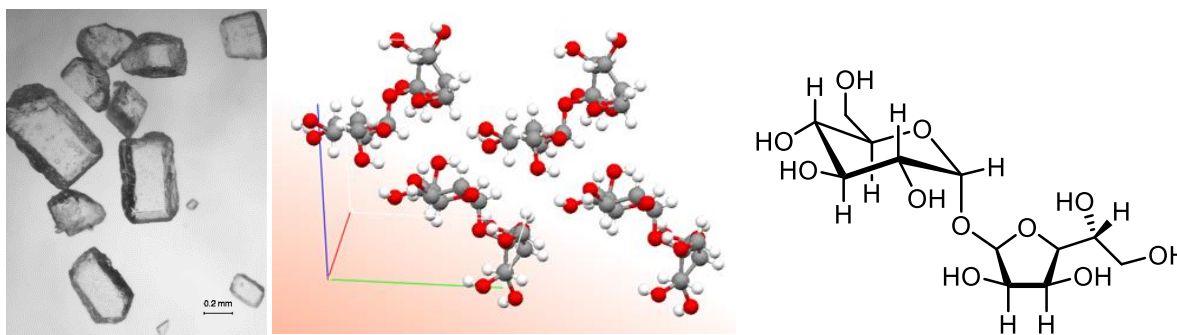


Figure A. Left: Sucrose crystals under a light microscope. Middle: Four molecules arranged by Mother Nature in sucrose crystals. White = H, Grey = C, Red = O atoms. Right: The bond-line structure of sucrose. The experiment finds the C atoms; however, placement of the H atoms on the molecule in this crystal structure are not experimental. The positions of H atoms are more difficult to determine.

1.5.3 How It's Done

The crystallographer mounts a small (~0.2 mm) crystal on a glass fiber, nylon loop, or similar non-crystalline material and puts it in an X-ray beam. Decreasing the temperature (for example to -40 °C) decreases thermal motion in the crystal which affords better atomic resolution. The instrument systematically rotates the crystalline sample in 3D while imaging the diffraction pattern produced by the reflected X-rays. A computer algorithm back-calculates from the positions of the spots in the data to determine the relative positions of blobs of electron density, i.e. 'atoms' in the crystal.

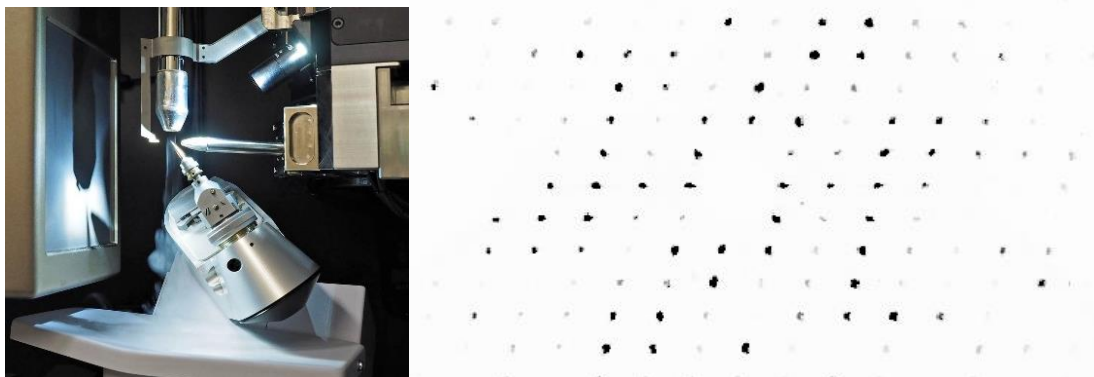


Figure B. Left: goniometer on which a crystal is mounted in preparation for data collection. Right: A 2D diffraction pattern obtained for a crystal of sucrose at $-183\text{ }^{\circ}\text{C}$. Turning and tilting the crystal reveals different 2D parts of the 3D diffraction pattern. The diffractometer digitizes thousands of these images as a function of the tilt angle to the X-ray beam, and enough data piles up to calculate relative positions of the C and O atoms in the molecule. Data Credit: Sean Parkin, U. of Kentucky, ■ [UK X-Ray Crystallography Facility](#).

In this way, we unveil relative positions of atoms in molecules. When we draw a double bond for example, we expect that the two atoms connected by the double bond should be closer (atoms are held together more tightly) than the average value we would get from a single bond between the same two atoms. X-ray structures also show us the geometry of atoms—whether the bonding pattern is planar (2D) or whether the atom in question has bonded atoms in a 3D atom array.

Exercise 1.5.1 Test your understanding. (a) Why are the H atoms more difficult to determine with X-ray in crystallography? (b) What might you do to make them more apparent? Does this pose further problems?

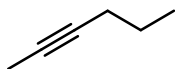
KEY TO CHAPTER 1 EXERCISES

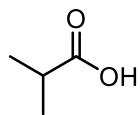
(Susan Odom, 2019)

Exercise 1.1.1 Answer: See the ■ [Periodic Table](#).

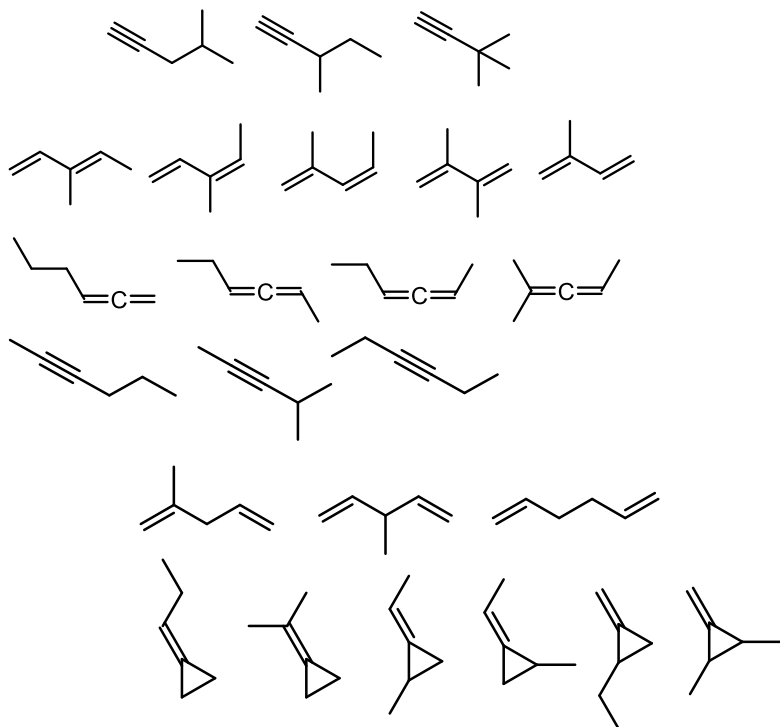
Exercise 1.2.1 Answer: We always want to show general structures as lowest-energy structures. When we worry about chemical potential energy, we are referring to the energy of electrons. The electrons participating in bonding are low in energy so the missing electron will be ‘missing from the non-bonding (lone) pair of electrons instead one of the bonded pair of electrons. You are going to have to make decisions like this in the future when you draw organic chemical structures.

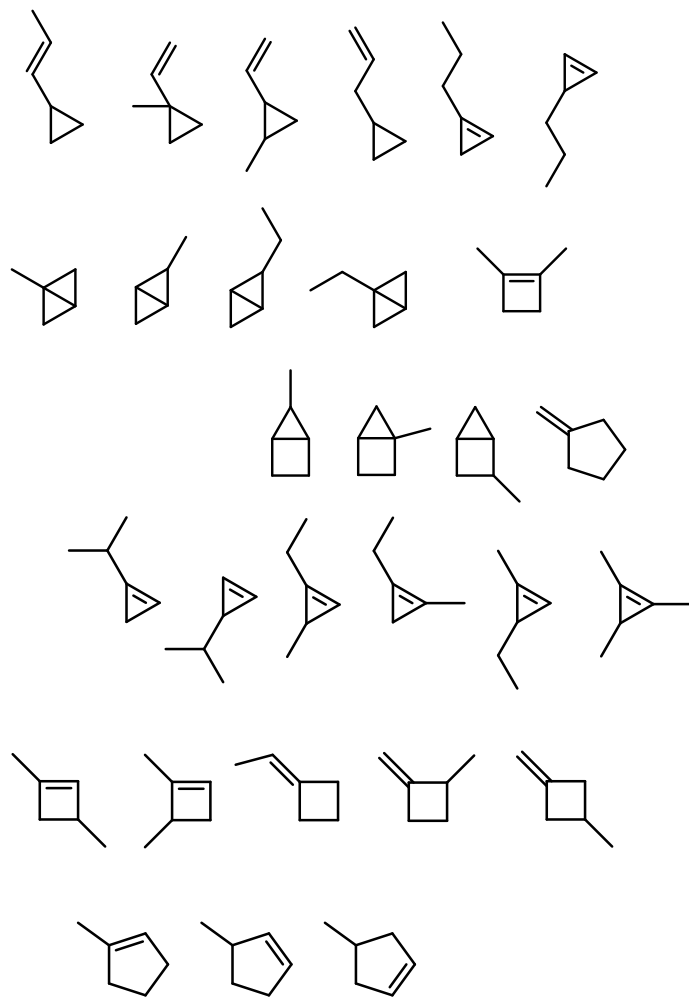
Exercise 1.2.2 Answer:



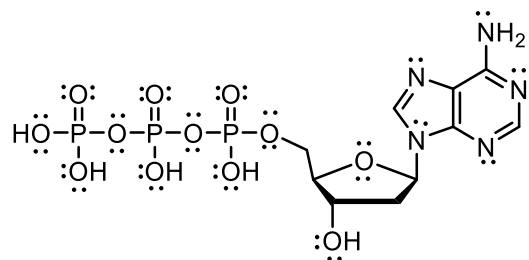
Exercise 1.2.3 Answer:

Exercise 1.3.1 Answer: There are many correct answers to this problem. See if yours match any of these.

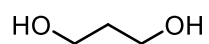




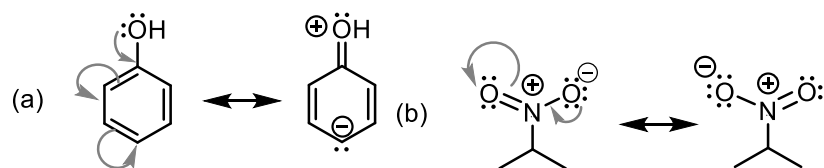
Exercise 1.3.2 Answer:



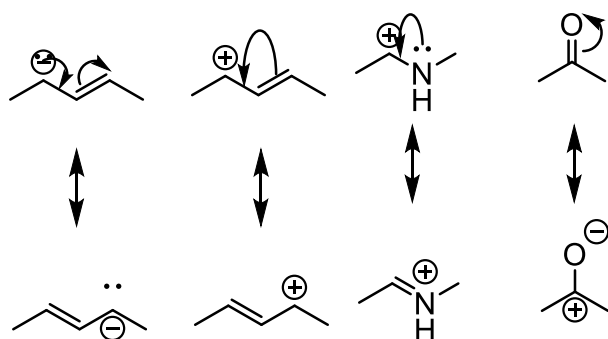
Exercise 1.3.3 Answer:



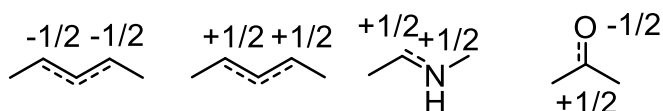
Exercise 1.4.1 Answer:



Exercise 1.4.2 Answer:

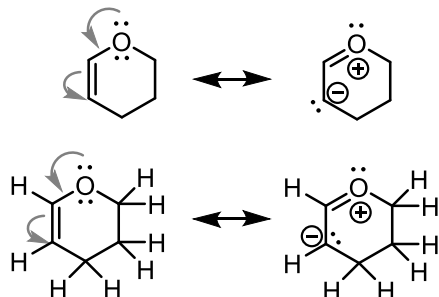


resonance structures that result from curved arrows

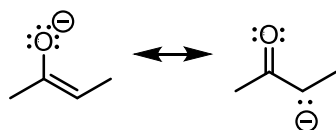


resonance hybrids based on the two resonance structures drawn above weighted equally. There is no reason that they should be weighted equally, in general.

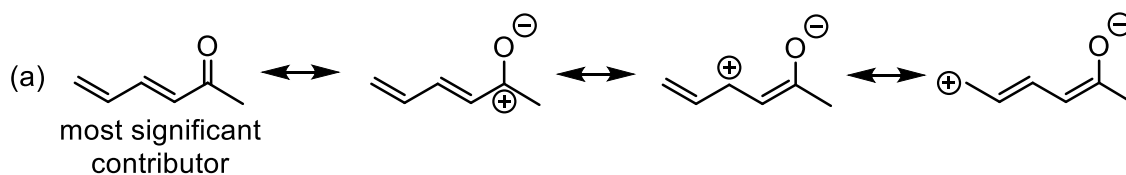
Exercise 1.4.3 Answer: Only the curved arrows in example D does not result in structure that contains an octet rule violation. See the answer with and without implicit H atoms.

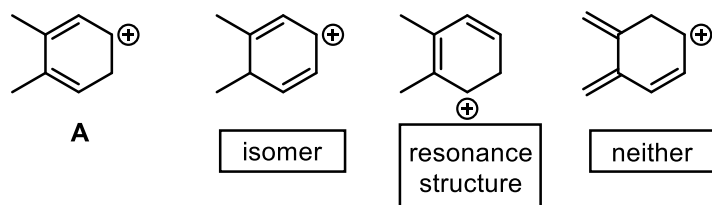


Exercise 1.4.4 Answer:

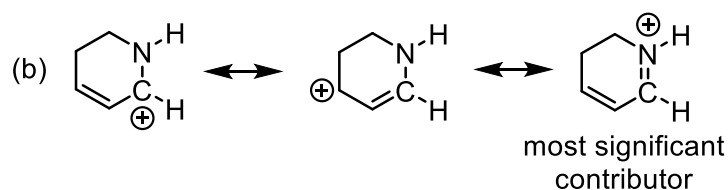
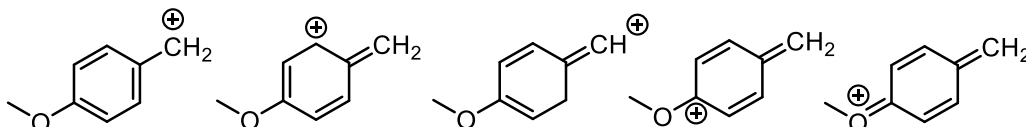


Exercise 1.4.5 Answer:



Exercise 1.4.6 Answer:**Exercise 1.4.7 Answer:**

(a)



(b) Yes, because the electron lone pair is part of the π system and can share the positive charge, this leads to greater stabilization than if an atom without a lone pair were connected to the ring.

Exercise 1.5.1 Answer: (a) H atoms are more difficult to determine than other atoms because they only have one electron. (b) Work with shorter wavelength X-rays. A problem is increasing the risk of materials decomposition.

CHAPTER 1 PRACTICE PROBLEMS

(Ashley Jolly Steelman and Susan Odom, 2019)

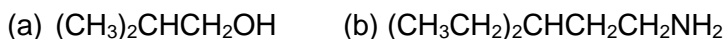
PP 1-1 Draw a bond-line structure that has two rings for $C_{10}H_{18}$.

PP 1-2 Draw a bond-line structure that has one ring for $C_{10}H_{18}$.

PP 1-3 Draw a bond-line structure that has one ring for $C_9H_8O_4$.

PP 1-4 The bond-line structure for $C_9H_8O_4$ matches that of aspirin (acetylsalicylic acid). Look at the structure of [aspirin](#). How many CC double bonds are there? How many CO double bonds are there?

PP 1-5 Draw the bond-line structure for each of the following compounds.



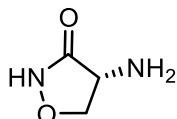
PP 1-6 Draw 4 constitutional isomers with the molecular formula $C_5H_{10}O$ using bond-line structures. Assume all non-hydrogen atoms have an octet of electrons and no formal charge.

PP 1-7 A compound with molecular formula $C_5H_{11}N$ has no π bonds. Determine a potential structure of the compound.

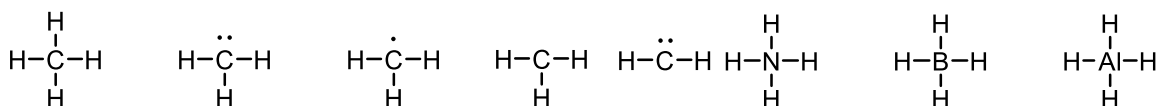
PP 1-8 The bond-line structure for ■ cocaine has 8 degrees of unsaturation. (a) Confirm this with the formula: $C_{17}H_{21}NO_4$; show the math. (b) Look at the structure in the link. In which structural features of the molecule do we find the degrees of unsaturation?

Note: Any common molecular substance that we look up in Wikipedia or elsewhere usually includes a bond-line structure. The structures we are leaning about here are common information for any chemist to gain insight about a substance, examples: (1) ■ capsaicin, (2) ■ GABA, (3) ■ RNA, (4) ■ DDT, (5) ■ oxycodone, etc. This list is functionally infinite because it grows annually.

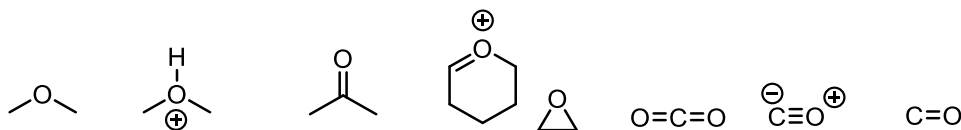
PP 1-9 Determine the molecular formula for the molecule cycloserine, an antibiotic used to treat tuberculosis.



PP 1-10 Add formal charges to the following molecules or ions where necessary.

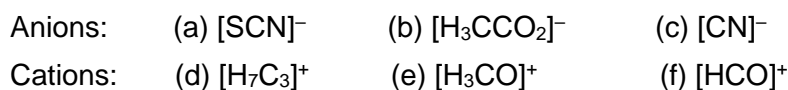


PP 1-11 To each molecule or ion below, add any implied electron lone pairs. Then add formal charge where necessary to complete each structure.

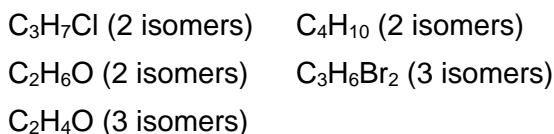


PP 1-12 The bicarbonate anion, HOCO_2^- , has two equally good resonance structures. Draw them and the resonance hybrid that results when taking them into account.

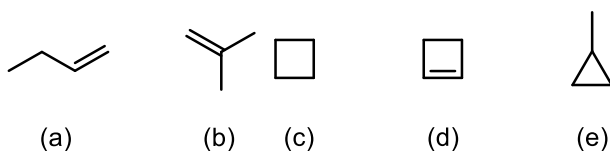
PP 1-13 For each of the anions and cations, draw the best resonance structure – the best being defined as the one that contains the most bonds and fewest formal charges. In some cases, there are two acceptable answers.



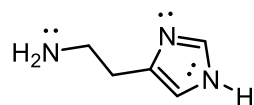
PP 1-14 For each chemical formula, draw all possible constitutional isomers. The number of possible isomers is indicated after each chemical formula.



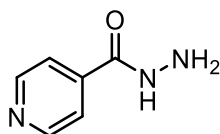
PP 1-15 Which compound is *not* a constitutional isomer of 2-butene, $\text{CH}_3\text{CH}=\text{CHCH}_3$?



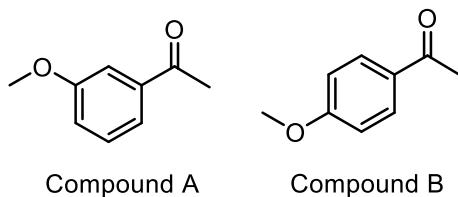
PP 1-16 For the following compound, determine whether each electron lone pair localized or delocalized.



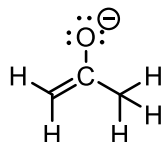
PP 1-17 Isoniazid is a drug used in the treatment of tuberculosis and multiple sclerosis. Add all implicit electron lone pairs to the drawing of the compound isoniazid – a drug used in the treatment of tuberculosis. Then identify each lone pair as either localized or delocalized.



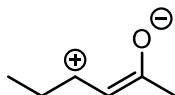
PP 1-18 Consider the following two compounds and identify which has greater resonance stabilization. Provide a brief explanation of your choice.



PP 1-19 Draw another resonance contributor to the anion below in which all atoms have an octet. Show all electron lone pairs.

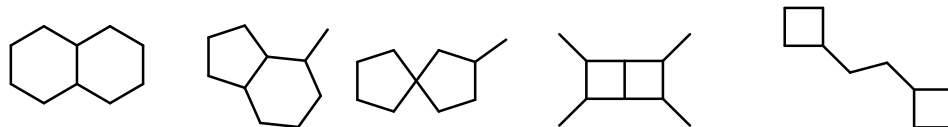
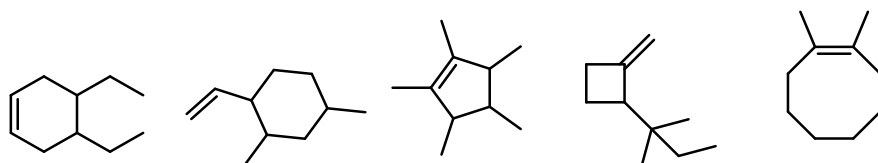
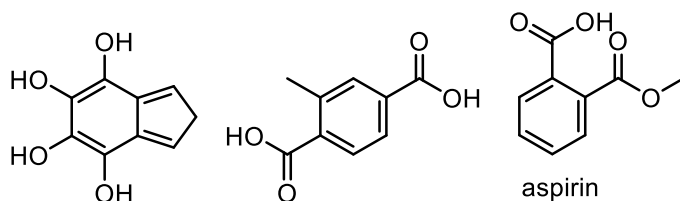
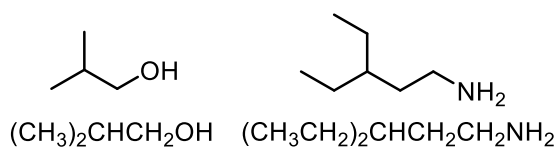
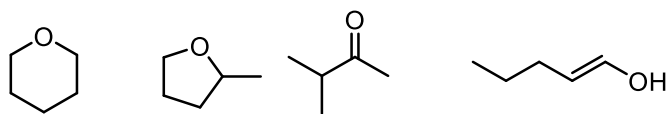
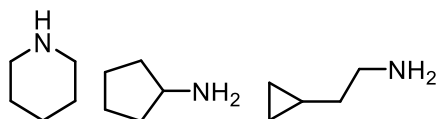


PP 1-20 Draw another resonance contributor of the molecule below in which all atoms have an octet. Do not show implied electron lone pairs and implied C and H atoms.

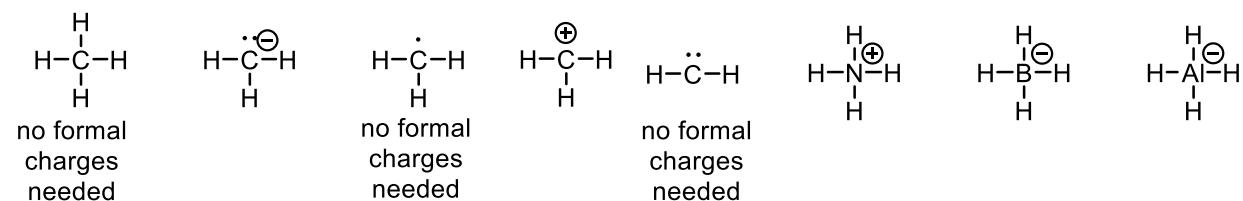


KEY TO CHAPTER 1 PRACTICE PROBLEMS

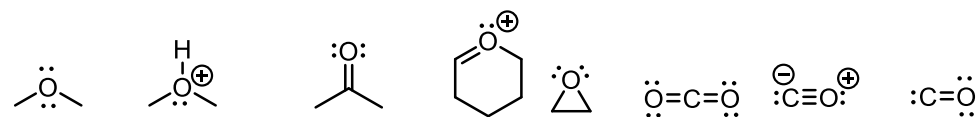
(Susan Odom, 2019)

PP 1-1 Answer: Here are a few examples of many correct possibilities.**PP 1-2 Answer:** Here are a few examples of many correct possibilities.**PP 1-3 Answer:** Here are a few examples of many correct possibilities.**PP 1-4 Answer:** Aspirin has 3 C=C bonds and two C=O bonds.**PP 1-5 Answer:****PP 1-6 Answer:** Here are a few examples of many correct possibilities.**PP 1-7 Answer:** Here are a few examples of many correct possibilities.**PP 1-8 Answer:** (a) DU = 8. (b) Degree of unsaturation include 3 for rings, 3 C=C bonds, and 2 C=O bonds.**PP 1-9 Answer:** $\text{C}_3\text{H}_6\text{N}_2\text{O}_2$

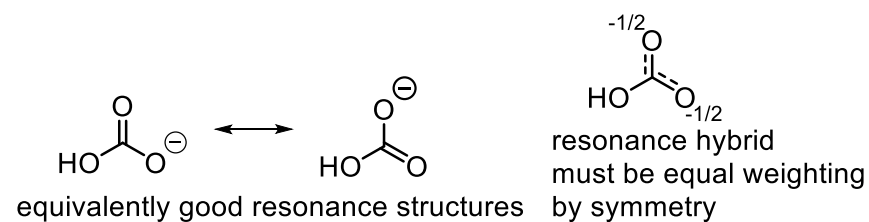
PP 1-10 Answer:



PP 1-11 Answer:

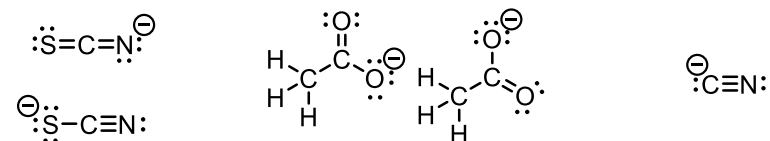


PP 1-12 Answer:

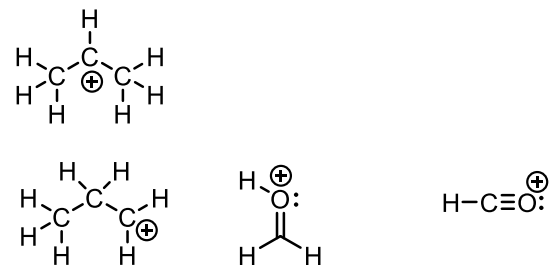


PP 1-13 Answer:

Anions: (a) [SCN]⁻ (b) [H₃CCO₂]⁻ (c) [CN]⁻



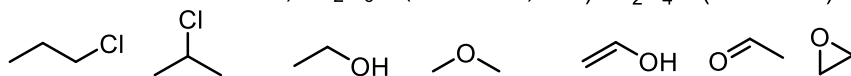
Cations: (d) [H₇C₃]⁺ (e) [H₃CO]⁺ (f) [HCO]⁺

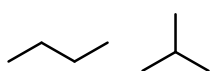
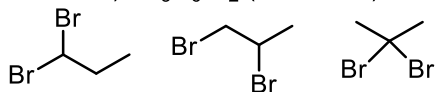


While this structure does not violate the rules, we will later see that a hexet at a carbon atom with only one alkyl group - a primary carbon - is very unstable. This molecule spontaneously rearranges.

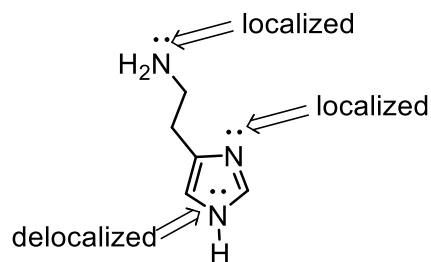
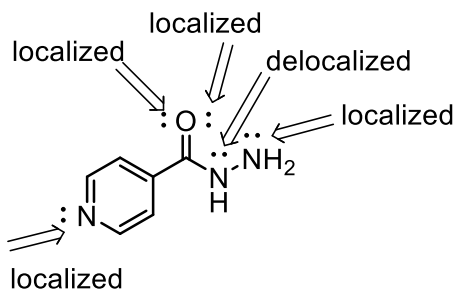
PP 1-15 Answer:

a) C₃H₇Cl (2 isomers) b) C₂H₆O (2 isomers) c) C₂H₄O (3 isomers)

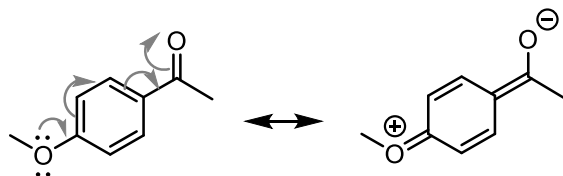


d) C_4H_{10} (2 isomers)e) $C_3H_6Br_2$ (3 isomers)

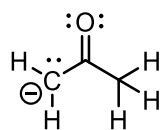
PP 1-15 Answer: D is the only one with a different chemical formula. Without counting H atoms, by acknowledging that it has 2 degrees of unsaturation, you know it has 2 fewer H atoms than 2-butene and structures A, B, C, and E – all of which have 1 D.U. and the formula C_4H_8 .

PP 1-16 Answer:**PP 1-17 Answer:**

PP 1-18 Answer: Compound B has greater resonance stabilization because one of the electron lone pairs in the methoxy (CH_3O) group is part of the π system. See the resonance arrows and resultant second-best resonance structure below. If you try to use the same set of arrows pushing for compound A – pushing the methoxy group's lone pair toward the carbonyl – you'll end up violating the octet rule.



If you haven't tried doing the same with compound A, try it! It's worth seeing why it won't work!

PP 1-19 Answer:**PP 1-20 Answer:**