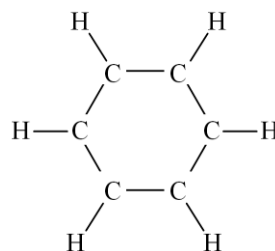
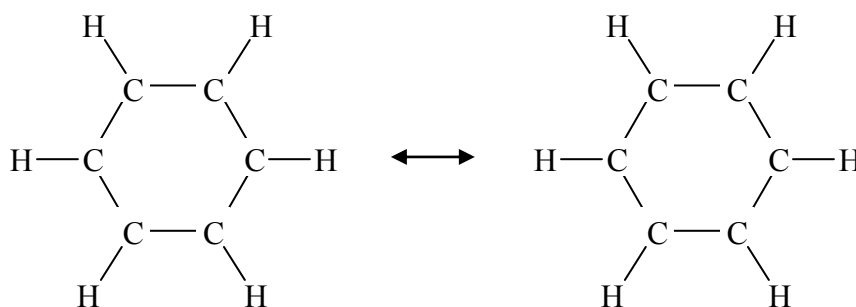


ALE 11. Resonance Structures and Formal Charge(Reference: [Section 10.1 - Silberberg 5th edition](#))**How can a set of Lewis structures be used to represent a compound's structure?****The Model: Resonance Structures**

Benzene, C_6H_6 , is a stable compound with a hexagonal ring of carbon atoms. Each of the 6 carbon atoms is bound to two other carbon atoms and a hydrogen atom, as shown on the right.

**Key Questions**

- 1a. How many electrons must be drawn around a carbon atom in a valid Lewis structure of a stable compound?
 - b. How many electrons are currently represented around each carbon atom in the structure of Benzene in the above Model?
2. The solution to the problem brought up by Questions 1a&b is to recognize that in the Lewis structure of Benzene the carbon atoms are not simply singly bound to each other. Complete the two Lewis structures below DIFFERENTLY so that they are both "valid".

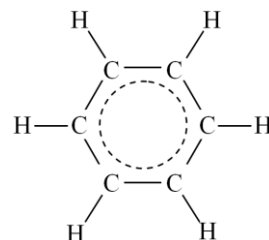


- 3a. Draw Lewis structures for Ethane (CH_3CH_3) and for Ethene (CH_2CH_2).
- b. The **bond length** between the two carbon atoms is 0.154 nm in Ethane and 0.134 nm in ethene ($1 \text{ nm} = 10^{-9} \text{ m}$). We say that a single bond has a **bond order** or 1 and a double bond has a bond order of 2. What is the relationship between bond length and the bond order? As bond order _____, bond length _____.

- 4a. We can use **spectroscopy** to measure the distances between atoms in compounds. When we use spectroscopy to see Benzene, we observe that all six of the C—C bonds are equivalent and have a length of 0.139 nm. Are any of the C—C bonds in Benzene single bonds? Briefly explain your answer.
- b. True or False: It is possible for all six of the C—C bonds in Benzene to be double bonds. Briefly explain your answer.
- c. In the answer to Question 2, the two Lewis structures are separated by a double-headed arrow. The \leftrightarrow symbol is used by chemists to denote two (or more) structures that are in “**resonance**”. Dr. Kenneth Fountain, a physical organic chemist at Truman State University, once told me the following wonderful analogy of the concept of resonance:

“Picture a dragon. Next picture a unicorn. Now picture a rhinoceros. There is no such thing as a dragon or a unicorn, but there is such a thing as a rhinoceros.”

We might say the Lewis structure of Benzene on the left in Question 2 is a “dragon”, and that would make the structure on the right be a “unicorn”. Then we could say that the depiction shown here on the right is the “rhinoceros”.

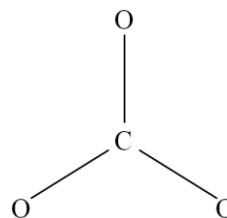


In your own words, explain what resonance is.

- d. As mentioned in the Model, all six of the C—C bonds in Benzene are equivalent to each other since they all have the same bond length. And the two resonance structures you completed in Question 2 are equally valid. So what is the bond order of a C—C bond in Benzene? *Briefly explain.*

The Model: Formal Charges

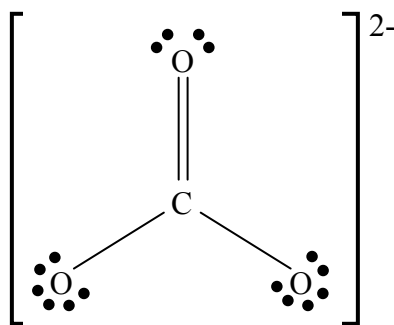
The carbonate ion (CO_3^{2-}) has a central carbon atom bonded to three oxygen atoms. We start out writing the Lewis structure as what is on the right:



Total # of valence e^- :

$$1\text{C} + 3\text{O} + \text{charge} = 1(4) + 3(6) + 2 = \mathbf{24}$$

We can give each of the oxygen atoms an octet of valence electrons by placing three lone pairs of electrons on each of them. That exhausts the 24 valence electrons that were available. But then the Lewis structure would still be invalid because the central carbon atom would not have an octet. So the carbon atom shares another pair of electrons with *one* of the oxygen atoms, resulting in the following valid Lewis structure:



Now the central carbon atom has its preferred number of bonds (which is four). When an atom has its preferred number of bonds, it is sharing as many electrons as it wants to with the atoms it is bound to. Such an atom neither has too much nor too little electron density around it. The atom will, therefore, carry no **formal charge**.

The formal charge of an atom may be calculated by the following equation:

$$\text{Formal charge} = \left(\begin{array}{c} \text{valence } e^- \text{ of} \\ \text{neutral atom} \end{array} \right) - \left(\begin{array}{c} \# \text{ bonds atom has} \\ \text{in Lewis structure} \end{array} \right) - \left(\begin{array}{c} \# \text{ nonbonding } e^- \\ \text{drawn around atom} \end{array} \right)$$

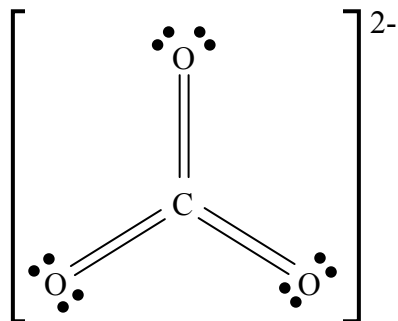
Using this formula, we see that the formal charge of the central carbon atom is $(4 - 4 - 0) = 0$.

Key Questions

- Calculate the formal charge of the oxygen atom that is doubly bound to the carbon atom.
- What is the formal charge of each oxygen atom that is singly bound to the carbon atom?
- How many bonds does an oxygen atom prefer to have? Explain why the sign of the formal charge of the singly-bound oxygen atom makes sense in terms of sharing too little electron density. (What is the charge of an electron?)

6. What is the sum of all of the formal charges of the four atoms in CO_3^{2-} equal to?
- 7a. What are the bond orders for the three C—O bonds in the drawn Lewis structure of the carbonate ion?
- b. Draw the Lewis structures of Methanol (CH_3OH) and Formaldehyde (H_2CO).
- c. What are the bond orders of the C—O bonds in Methanol and Formaldehyde?
- d. When spectroscopy is used to see the carbonate ion, we see that each of the three C—O bonds is 0.129 nm long. The C—O bond lengths in Methanol and Formaldehyde are 0.143 nm and 0.123 nm, respectively. What does this suggest about the bond order for the C—O bonds in the carbonate ion?

8. Can we use the Lewis structure on the right to represent the structure of the carbonate ion? Explain why or why not?



- 9a. Back in the Model, we said that for the carbon atom to be given an octet of valence electrons, *one of the three* oxygen atoms needed to share one of its lone pairs as a bonding pair with the carbon atom. So we drew the Lewis structure with a double bond between the carbon atom and the oxygen atom at the top. Did we have to choose the oxygen at the top to double bond with the carbon? Yes or No

- b. Draw all possible valid resonance structures of the carbonate ion that are different from each other.
- c. If all three of the resonance structures are understood to exist simultaneously, what is the:
- order of each C—O bond? (There is only *one* answer.) _____
 - formal charge on the carbon atom? (There is only *one* answer.) _____
 - formal charge on each oxygen atom? (There is only *one* answer.) _____
 - sum of all of the formal charges for the four atoms? _____

Exercises

10. Assuming that there are no bond orders greater than 2 in the chlorite ion, there are four possible resonance structures to describe the structure of the chlorite ion, ClO_2^- . *Draw all four. Hint:* one resonance of the resonance structure has all single bonds; another has all double bonds, while the other two have one single bond and one double bond.)
11. Assign formal charges to each atom in each of the four resonance structures of ClO_2^- . (Please, write the formal charges next to each atom in each of the four structures above.)
12. When there are multiple resonance structures, they will very often not be “equally valid”. A resonance structure that minimizes formal charges is more reasonable than another that depicts atoms having larger formal charges. Also, if given the choice between two atoms on which a negative charge will be found, it is most likely that the electrons will be found on the more electronegative atom. (An atom’s electronegativity is a measure of how much it “wants or attracts” electrons compared to another atom that it is covalently bonded to. The greater the electronegativity of an atom, the more that atom “wants” electrons. Like electron affinity, electronegativity increases from *left to right across a period* and increases from *the bottom to the top of a group*.)

Decide between the four resonance structures of ClO_2^- that you drew in Exercise #10 which one is the most reasonable representation of the structure of the chlorite ion. Circle that resonance structure. (If more two are equally valid, circle both of them.)