

1.6: Resonance

Learning Objectives

- Understand the concept of resonance and how it stabilizes molecules.
- Draw resonance contributors and predict equal, major, and minor resonance contributors.
- Predict resonance stabilization and factors that affect it.
- Predict the relative strength of a π -bond based on orientation and sizes of p-orbitals.

Prelude to resonance

C not only makes straight chains and branched chains but makes cyclic chains, as illustrated in Figure 1.6.1. Benzene is a member of a class of hydrocarbons called aromatic hydrocarbons. A set of characteristics of aromatic compounds will be described later. Here only the nature of bonds in benzene is described to introduce the concept of resonance.

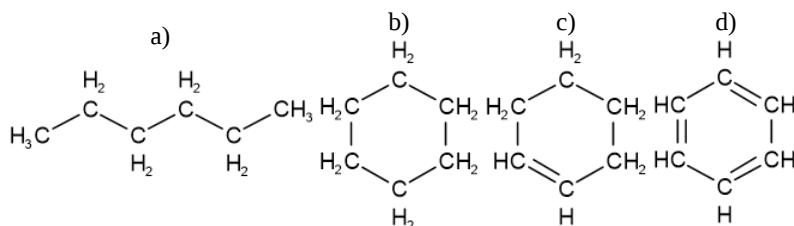


Figure 1.6.1: Semi-condensed formulas of a) a six C straight chain with all single bonds called n-hexane, b) a six C cycle with all single bonds called cyclohexane, c) six C cycle with one double bond called cyclohexene, and d) a six C cycle with all C's sp^2 hybridized called benzene. (Copyright; Public domain)

More than one correct Lewis structure can be drawn for some compounds or polyatomic ions.

If more than one Lewis structure can be drawn for a compound, these are called **contributing structures** or **resonance contributors**.

The contributing structures of a compound are separated from each other by double-headed arrows, as shown in Figure 1.6.2, for the case of benzene molecule and carbonate (CO_3^{2-}) polyatomic anion.

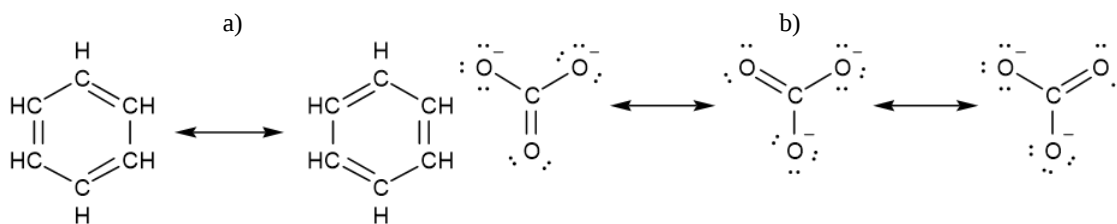


Figure 1.6.2: The resonance contributors of benzene (C_6H_6) and carbonate (CO_3^{2-}) ion. (Copyright; Public domain)

Are the compounds or polyatomic ions with more than one contributing structure a mixture of these structures? The answer is no; none of the contributing structures exist. For example, both the contributing structures of benzene imply that there are three C—C single bonds and three C=C double bonds. Experimental results show that all six C—C bonds in benzene are equal. Similarly, all three contributing structures of CO_3^{2-} imply one double bond and two single bonds. Experimental results show that all three C—O bonds in CO_3^{2-} are equal. The concept of resonance was introduced to deduce the actual structure in the cases of compounds having two or more contributing structures.

What is resonance?

- **Resonance** is a way of describing bonding in molecules and polyatomic ions by a combination of contributing structures into the actual structure.
- The hybrid of the contributing structures -the actual structure, is called a **resonance hybrid**.

Consider the structure of a benzene molecule: every C in benzene is sp^2 hybridized with three σ -bonds in a trigonal planar geometry and a p-orbital perpendicular to the plane, as illustrated in Figure 1.6.3a. All C's and H's are in one plane, and all the p-orbitals are perpendicular to them and parallel to each other. Assuming p-orbitals in benzene simultaneously make a half- π -bond with two adjacent p-orbitals, it can be concluded that all of the C-to-C bonds are equal, i.e., each one is composed of one σ and a half π -bond, as illustrated in Figure 1.6.3b. The same structure is assumed by a fifty%-fifty% hybrid of its two contributing structures. The bonding in the resonance hybrid of benzene agrees with the experimental results, i.e., all six C—C bonds in benzene are equal. Similarly, the resonance hybrid of CO_3^{2-} , arrived at by assuming it is a hybrid of its three equal contributing structures, is illustrated in Figure 1.6.3c. The bonding in the resonance hybrid of CO_3^{2-} agrees with the experimental results, i.e., all three C—O bonds in CO_3^{2-} are equal.

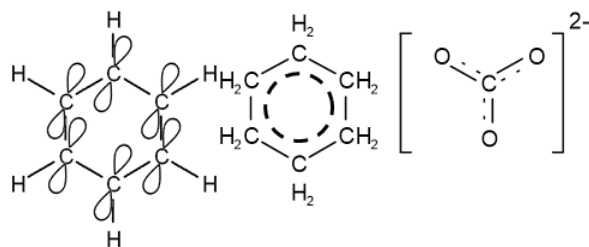


Figure 1.6.3: Illustration of a) sp^2 hybridization of each carbon of a benzene ring, b) a resonance hybrid of benzene, and c) a resonance hybrid of CO_3^{2-} ion. (Copyright; Public domain)

Note that the π bond is not localized between two adjacent atoms in resonance hybrids; it is spread over three or more adjacent atoms.

The π -bond spread over three or more adjacent atoms is called a **delocalized π -bond** and the elections in the delocalied π -bond are called **delocalized electrons**.

For example, the delocalized π -bonds are represented by a dashed-lined circle inside the benzene ring or by dashed lines in the case of CO_3^{2-} resonance hybrids.

How is an sp^3 atom bearing a lone pair involved in resonance?

An sp^3 -hybridized atom with lone pair changes its hybridization from sp^3 to sp^2 and places its lone pair in the p-orbital for resonance to happen when it is adjacent to an sp^2 - or sp -hybridized atom.

Delocalization of π - or nonbonding electrons results in more bonding, i.e., delocalized electrons are spread over more than two nuclei. It results in lowering the potential energy, called resonance stabilization. The resonance hybrid is always more stable than the predicted stability of any of its contributing structures.

Summary of facts about resonance

1. When more than one correct Lewis structure can be drawn for a compound, these are called **resonance contributing structures**.
2. The actual structure of the compound that is deduced by assuming it is a hybrid of the contributing structures is called the **resonance hybrid**.
3. The extra stability of the resonance hybrid due to the resonance is called **resonance stabilization**.
4. The **contributing structures do not exist**; they are just the correct Lewis structures that help deduce the resonance hybrid. Consequently, the double-headed arrow does not show a chemical reaction; it is used only to separate the contributing structures of a compound.

How to draw a resonance contributor?

If one Lewis structure is already drawn, its resonance contributor can be drawn by the following rules, as illustrated with examples:

- Move π -electrons or lone pair only (do not move σ -electrons) to create a new π -bond or lowne pair.

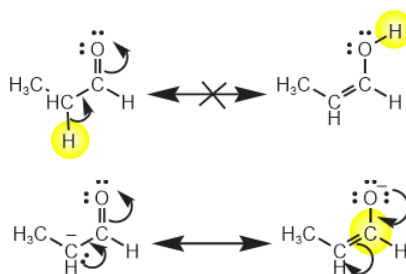
- Curved arrows show the movement of electrons, the arrow starts where the electrons are located, and the arrowhead points where they are going to create a new π bond or a new nonbinding electron (do not make a new σ -bond).
- The electron movement often creates formal charges. Calculate the formal charge and show it if it is not zero. For example, π -electrons are moved to create a new lone pair and formal charges in the following example.



- For resonance to happen, there must be at least two adjacent sp^2 or sp atoms. Resonance can not happen involving sp^3 atom.
 - An exception is an sp^3 atom carrying a lone pair; it changes its hybridization to sp^2 and places its lone pair in the p-orbital for resonance, as shown in the following example.



- Atoms do not move, i.e., a σ -bond is not broken or created during regular resonance. The first example below is not resonance because a $C-H$ σ -bond from a $-CH_2-$ is broken and a $O-H$ σ -bond is formed. It is a chemical reaction, not a resonance. The second example is resonance, as only a lone pair and a π -bond pair are moved.

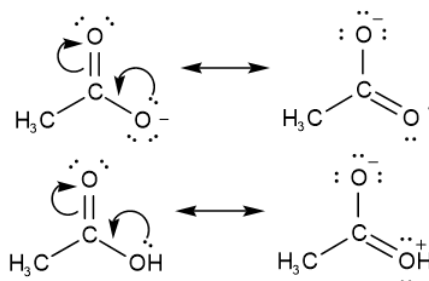


- A H can not have more than two valence electrons (duet rule), and second-row elements, like C, N, O, F, etc. can not have more than eight valence electrons (octet rule) in any of the resonance contributors. (Third-row and higher-row elements are exceptions and may have up to twelve valence electrons in molecules). For example, the movement of a lone pair to create a π -bond in the following example is not allowed as it makes a C with ten valence electrons (five bonds). Simultaneous movement of the $C=O$ π -bond avoids this problem, as in the previous example.

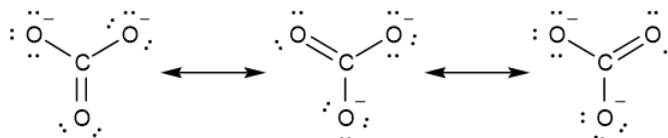


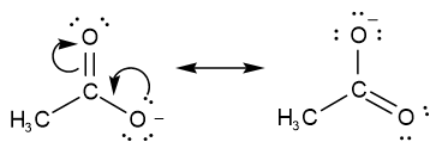
The relative importance of the contributing structures

- There is more resonance stabilization for equal resonance contributors than for unequal resonance contributors. The first example below has more resonance stabilization due to equal contributors than the second one with unequal contributors.



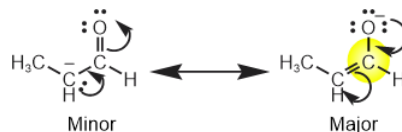
- More the number of equal contributors means more resonance stabilization. For example, resonance stabilization is more for CO_3^{2-} with three equal contributors than for CH_3COO^- with two equal contributors.





In the cases of unequal contributors, the following factors determine the major contributor:

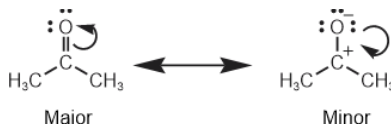
- The negative charge on a more electronegative atom or positive charge on a less electronegative atom is more stable than otherwise. The contributor on the right in the following example with a negative charge on more electronegative O is a major contributor, and the other is minor.



- A contributor with an octet incomplete on an atom is significantly less stable than the contributor with all atoms octet complete.
- A contributor with more bonds is significantly more stable than one with fewer bonds. In the following example, the contributor on the left with octet incomplete on one C and fewer bonds is a negligible contributor relative to the other.



- A contributor with more formal charges is significantly less stable than a contributor without formal charges. The contributor on the left, with two formal charges and fewer bonds, is a negligible contributor compared to the other.



Strength of the π -bond and resonance in relation to size and orientation of the p-orbitals

Both the π -bond and, consequently, the resonance are strong when the two p-orbitals are of the same size and parallel. The strength of the π -bond and the resonances become weaker when

- the two p-orbitals are out of parallel orientation and become zero when the two p-orbitals are perpendicular to each other, and
- when the size of the two p-orbitals differ, the more significant the difference, the weaker the overlap.

These two effects are illustrated in the Figure below.



The two p-orbitals are parallel, resulting in the maximum π -bond strength and the maximum resonance



The two p-orbitals are perpendicular, with no π -bond and no resonance



The two p-orbitals are parallel but of different sizes resulting in a weaker π -bond and weaker resonance.

- In addition to the two effects described above, the third factor is electronegativity, i.e., the less electronegative the atom donating a lone pair of electrons for the resonance, the stronger the resonance.

The following examples support the three effects described above.

The N in pyridine can donate its lone pair of electrons to a proton, i.e., it is a base (pK_b 8.8) because the lone pair is in an sp^2 -orbital which is perpendicular to the other p-orbitals and not occupied in resonance. The N in pyrrole is not able to donate its lone pair of electrons to a proton, i.e., it is a very weak base (pK_b 17.8) because the lone pair is in a p-orbital parallel to other p-orbitals and occupied in resonance and not that much available to protons, as shown in Figure 1.6.4.

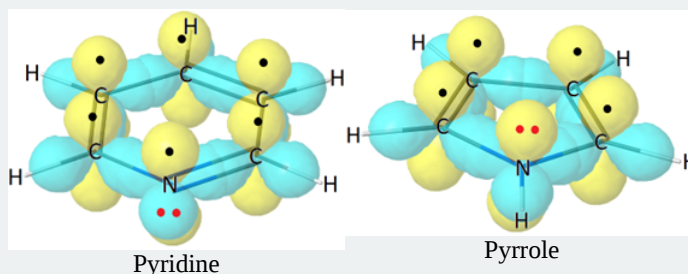


Figure 1.6.4: Illustration of p-orbitals (yellow lobes) and sp^2 -orbitals (blue lobes) in pyridine (C_5H_5N) and pyrrole (C_4H_4NH). Note: the lone pair (red dots) in sp^2 -orbital is perpendicular to the other p-orbitals in pyridine but in a p-orbital parallel to the other p-orbital in pyrrole. (Copyright; Public domain)

Three examples of resonance are shown below, where the second contributor in each case is minor because there is charge separation, and +ve charge is placed on an electronegative atom. However, there are differences in these three cases, i.e., i) the second contributor is minor in the 1st example where 2p-orbital of O is in resonance with 2p-orbital of C which are similar in sizes, but negligible in the second example because 3p-orbital of Cl is in resonance with 2p-orbital of C which are different in sizes, ii) the second contributor is minor in the 1st example but significant in the 3rd example because the p-orbitals are similar in size but N is less electronegative and more willing to donate its lone pair than the O in the 1st example.

