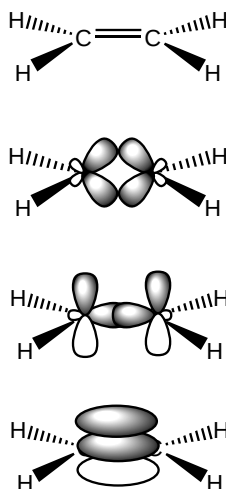


## Multiple Bonds

### Skills to Develop

- Define multiple bonds (name, characteristics)
- Describe and draw resonance structures
- Predict hybridization and numbers of  $\sigma$  and  $\pi$  bonds

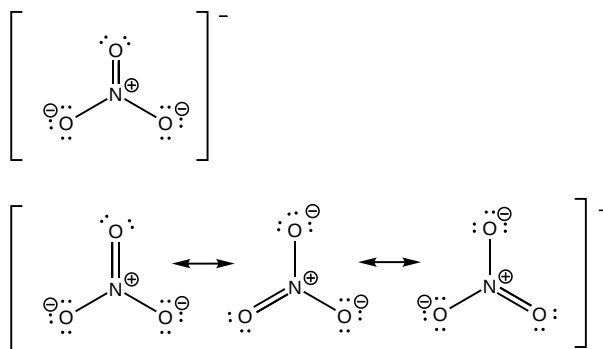
You already know that sometimes we have to use multiple bonds (double or triple bonds) to draw good Lewis structures. Lewis' idea of multiple bonds suggests that they should be shorter than single bonds (because the tetrahedra share an edge or a face, not just a point). This turns out to match the data from crystal structures. In the previous section, we used hybrid orbitals to show how we can make bonds using overlapping orbitals. This actually matches Lewis' image of the tetrahedra pretty well! So we could think about multiple bonds being made with hybrid orbitals just in the way that Lewis pictured, which are now called "bent bonds" because the electron density doesn't seem to be on the line between the nuclei. This isn't a bad way to think for some molecules. However, it becomes very confusing in cases of multiple bond resonance!



Ethylene ( $\text{C}_2\text{H}_4$ ) shown (top to bottom) as a Lewis dot structure, using "bent bonds" and  $\text{sp}^3$  hybridization, and using  $\sigma$  and  $\pi$  bonds with  $\text{sp}^2$  hybridization ( $\sigma$  and  $\pi$  bonding orbitals shown separate, then combined).

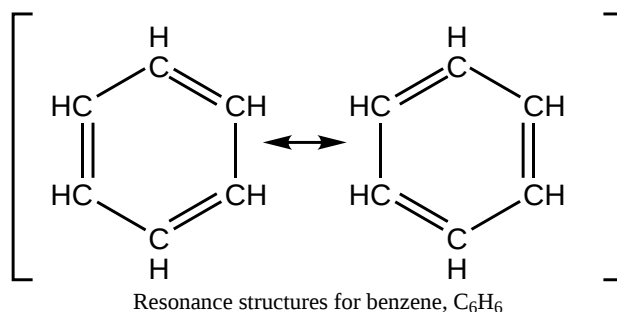
### Multiple Bond Resonance

Let's think about Lewis structures for the nitrate ion,  $\text{NO}_3^-$ . We have to draw 1 double bond and 2 single bonds between N and O to give N exactly 8 electrons. This suggests that there should be 1 short bond and 2 long bonds in nitrate ion. However, there is no difference between the O atoms, so how would we choose which one gets the double bond? We could put it in any position, giving 3 different structures with the same energy. If you remember the idea of resonance energy you might expect that the availability of 3 different structures with the same energy allows resonance between the structures, so that each bond is actually  $4/3$  of a bond, and the molecule is much more stable because of the resonance energy.



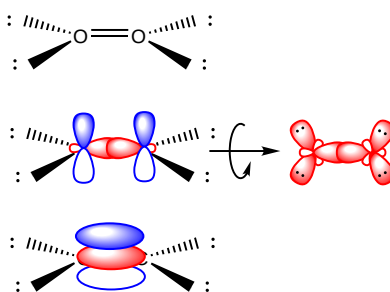
Two Lewis structure descriptions of nitrate ion. Top: nitrate with 1 short double bond and 2 long single bonds. Bottom: nitrate shown using resonance structures, indicating that each bond is equivalent, with the double bond shared over all 3 oxygens.

When we study the structure of nitrate, we can't find any difference between the oxygens. If we do X-ray crystallography on  $\text{CsNO}_3$ , say, we can check what all the bond lengths and bond angles are, and they appear equal. Other methods give the same result. Molecules or ions in which multiple bond resonance is important (just like bonds in which ionic resonance is important) are more stable than we would otherwise predict, and they appear to have "fractional" bonds. Benzene, another important example of resonance, is shown in the figure. Other examples include the sulfate and phosphate ions. Try drawing resonance structures for these ions, using the "resonance arrow"  $\leftrightarrow$ .



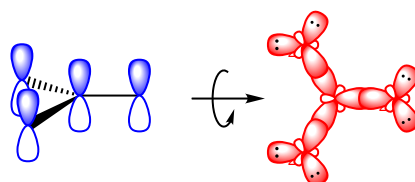
### Orbitals for Multiple Bond Resonance

It's hard to imagine how multiple bond resonance can happen using the "bent bond" idea. However, we can use a different model of multiple bonds that makes it much clearer. Think about a molecule of oxygen. Each atom makes 2 bonds and has 2 lone pairs. We could think about doing this with  $\text{sp}^3$  hybrids, but there's another way as well if we assume that the second bond is different from the first. Imagine using  $\text{sp}^2$  hybrids on each atom. One p orbital is leftover, perpendicular to the 3 hybrids. We make a normal straight bond with one hybrid from each atom, which we will call a  $\sigma$  bond. We put the lone pairs in the other hybrids. The last bond pair goes in a bond made of the leftover p orbitals. This is called a  $\pi$  bond. This is illustrated in the figure.



Formation of  $\sigma$  and  $\pi$  bonds in  $\text{O}_2$ . The  $\sigma$  bond and lone pairs use  $\text{sp}^2$  hybrids, shown in red. The  $\pi$  bond is made of the leftover p orbital, shown in blue.

Now imagine orbitals for nitrate ion. N makes 4 bonds and has no lone pairs. We want to make 3 normal bonds, and one more bond shared over all 3 oxygen atoms. Each oxygen atom has a normal bond to N, and 2 or 3 lone pairs. Let's use  $\text{sp}^2$  hybrids on each atom. N makes 3  $\sigma$  bonds using the  $\text{sp}^2$  hybrids and has 1 p orbital leftover. Each O makes a normal  $\sigma$  bond with one hybrid and puts lone pairs in the other 2. All the hybrid orbitals on each atom are in the same plane, and the leftover p orbitals on each atom are sticking up and down from this plane. The 4 leftover p orbitals hold 3 electron pairs, and all these orbitals can mix together. We can't easily tell from this model which electrons are lone pair electrons and which are bonding electrons, but we can see that the bond is shared equally over all 3 O atoms.



Orbitals in nitrate ion. Left: the  $\pi$  system, using p orbitals, shown in blue. Right: the  $\sigma$  system, including  $\sigma$  bonds and lone pairs, using  $\text{sp}^2$  hybrids, in red.

Ethylene,  $\text{C}_2\text{H}_4$ , is a planar molecule (all atoms are in the same plane). This makes sense using either the bent bond description or the  $\sigma$  and  $\pi$  bond description. In the latter case, if we twist the molecule around the double bond, the p orbitals won't line up with

each other, so the double bond would break. Because double bonds can't rotate easily, the molecule can be different if there are different groups attached to each end of the double bond. These are called **isomers**.

### Predicting Hybridization and Numbers of $\sigma$ and $\pi$ Bonds

Only 1  $\sigma$  bond can be made between 2 atoms. If more bonds or partial bonds are present, they must be  $\pi$  bonds. So it's easy to count the number of  $\sigma$  and  $\pi$  bonds in a Lewis structure. Once you've done that, you can easily find what type of hybrids each atom makes (only for atoms with 8 total electrons; you shouldn't use hybrids for atoms that have more than 8). Each  $\pi$  bond needs a p orbital. The hybridization will be  $sp^x$ , where

$$x = 3 - (\text{number of } \pi \text{ bonds}) \quad (1)$$

For example, an atom that makes 2 double bonds makes 2  $\pi$  bonds, so it will be  $sp$  hybridized, just like an atom that makes 1 triple bond. An atom that makes 1 double bond is  $sp^2$  hybridized.

### Contributors and Attributions

- [Emily V Eames](#) (City College of San Francisco)

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