

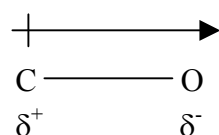
2. BONDING: How atoms are stuck together.

2.1. Covalent vs. Ionic Bonds

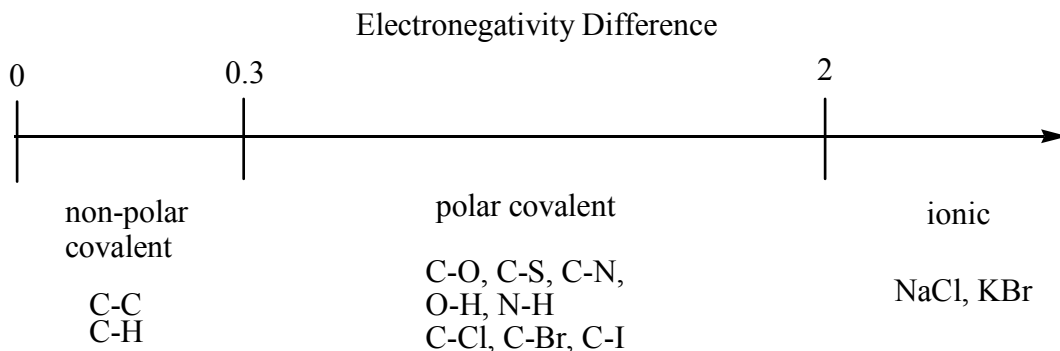
Now, you should already know the difference between these. If not, review your general chemistry. Again, for emphasis, a difference in electronegativity greater than 2 (on the Pauli Scale) between two elements is usually indicative of ionic bonding. Ionic bonds are formed between species that are easily ionizable such as alkali metals and halogens (NaCl), i.e., a metal and a non-metal. A difference of less than 2 between two elements is usually indicative of covalent bonding. Covalent bonds are formed by the sharing of an electron pair...typically between two non-metals (C-O, C-C, C-N, C-H...etc)...between atoms which don't easily gain or lose electrons.

And recall that bonding between atoms is not bimodal in distribution (i.e., *either* ionic *or* covalent). Bonding actually spans a continuum of ionic and covalent character.

And again, recall that despite the "sharing" of electrons between two different atoms (like C and O), there will be a tendency for the electrons to spend most of their time around the more electronegative atom. This gives the covalent bond a polarity that is expressed as δ^+ and δ^- ("partial positive" and "partial negative")...also seen as funny arrows...



Now, this bond is not ionic just because it has small charges associated with it...It is what we call a *polar covalent bond*. When the difference in electronegativity between two atoms is small (say less than about 0.5), like in a C-H bond, then the bond is said to be a *non-polar covalent bond*, with no discernable polarity. However, when the difference in electronegativity is greater than about 0.5, then the bond is polar-covalent...like C-O, C-S, C-Cl, C-Br, C-I.

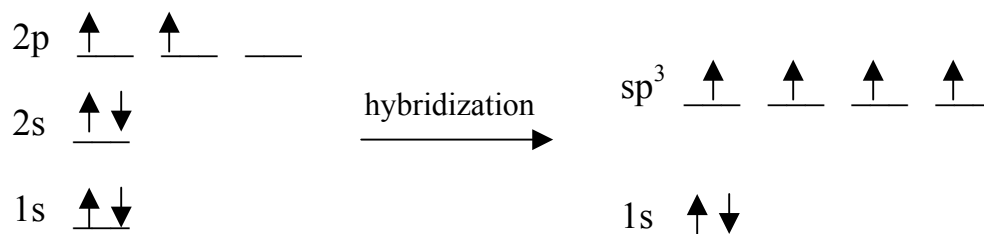


The resulting dipole moment of a molecule is the sum of all polarities in a molecule that results in partial positive and negative ends....symmetrical molecules tend to not have dipole moments (eg, CH₄) while asymmetrical molecules have dipole moments (CH₃Cl). This concept has a direct impact on many properties of organic compounds like solubility, boiling point, vapor pressure. Again, the best example is solubility. Polar compounds will dissolve in polar solvents, while non-polar compounds prefer to dissolve in non-polar solvents. Easily summed up in the saying "like dissolves like".

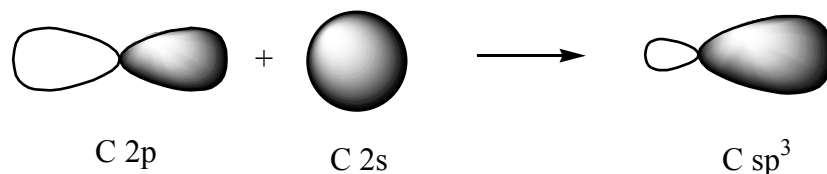
2.2. Hybridization

In organic chemistry, we will deal almost exclusively with covalent bonding involving carbon. So, how does bonding in organic compounds work? One word: Hybridization.

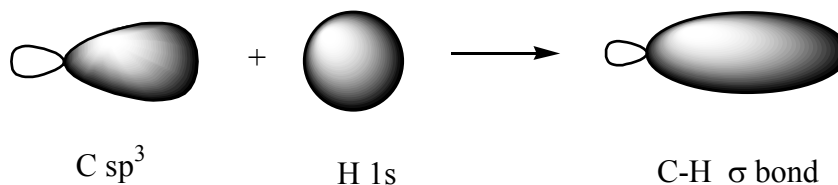
Consider your average carbon atom, complete with 6 electrons. From GenChem, what do the electrons look like in their orbitals? They look like this...



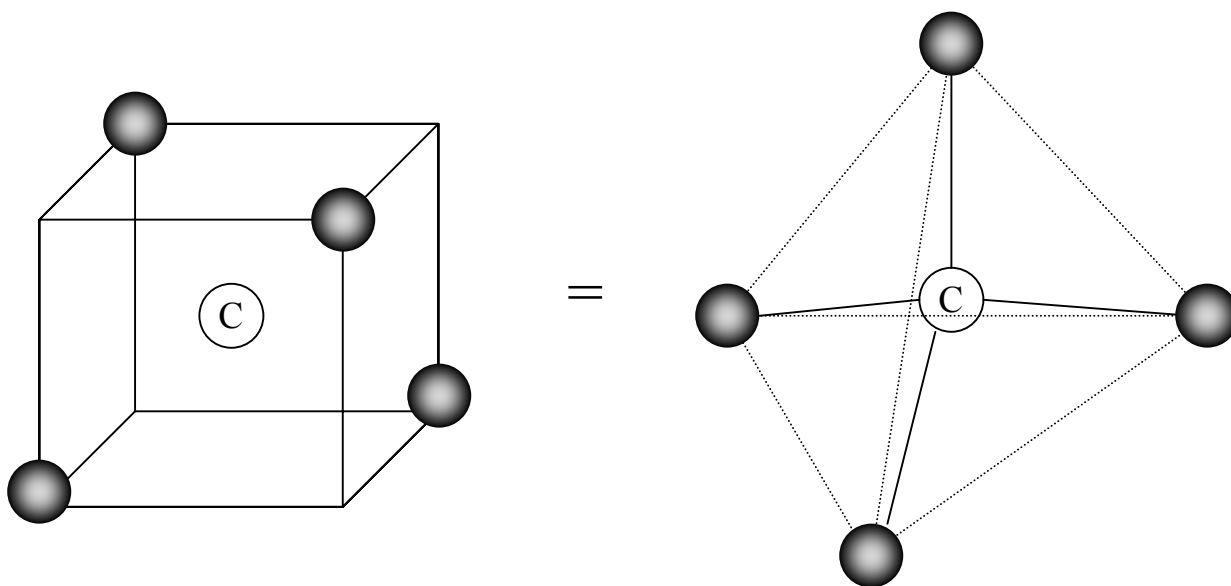
Carbon is 4 electrons away from filling its 2p orbital and satisfying the octet rule. So, in its quest to look like a noble gas, it combines electrons from the 2s and 2p orbitals, it HYBRIDIZES. The 2s orbital combines with the 3 2p orbitals to give 4 sp^3 hybrid orbitals. There are now 4 sp^3 hybrids that are readily available for bonding.



So, let's bond C with something... how about hydrogen to make methane (CH_4). Consider the two bonding pictures of methane. First the Valence Bond picture...

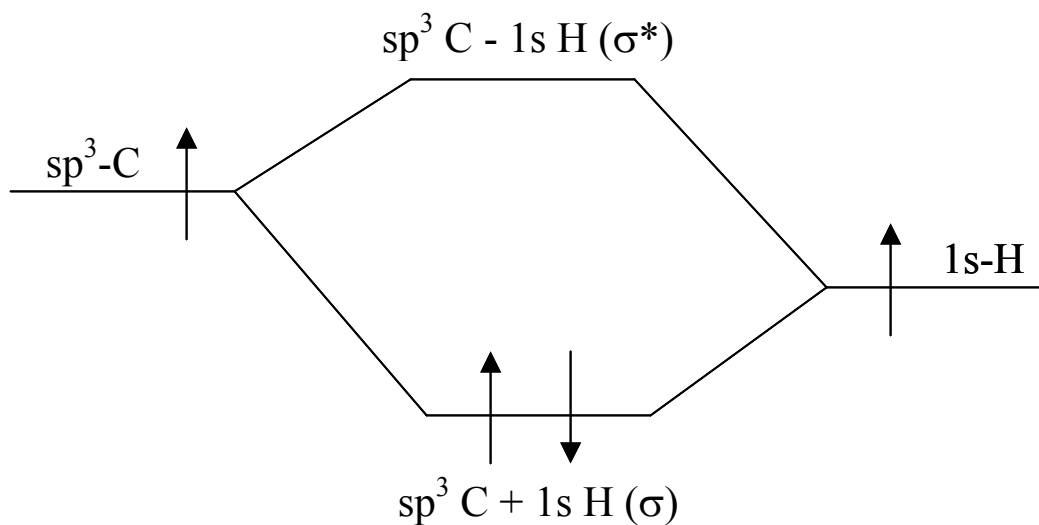


This picture may be crude, but it is instructional. The sp^3 orbital overlaps (adds) with the 1s orbital of the hydrogen to give the C-H covalent (sigma) bond (shown sharing the electron pair). In methane there are 4 such interactions. These interactions and the resulting bound hydrogens want to be as far away from each other as possible. The geometry is therefore tetrahedral (4 farthest corners on a cube)... If we put C in the center of a cube, the H's will be at the 4 farthest points of equal distance, and therefore the molecule takes the shape of a tetrahedron (a 4-sided equilateral pyramid).

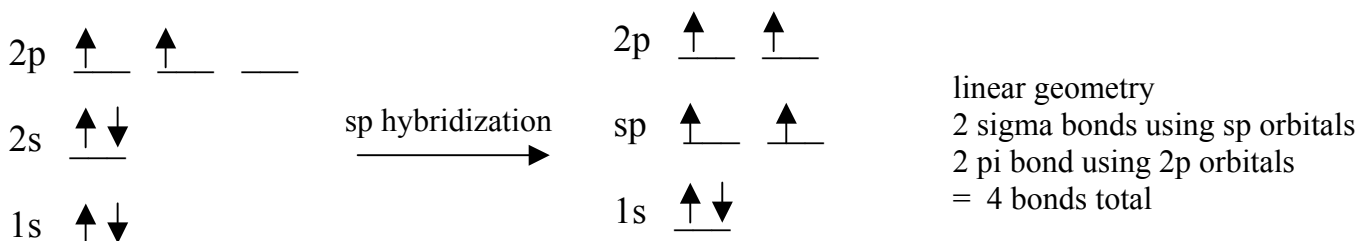
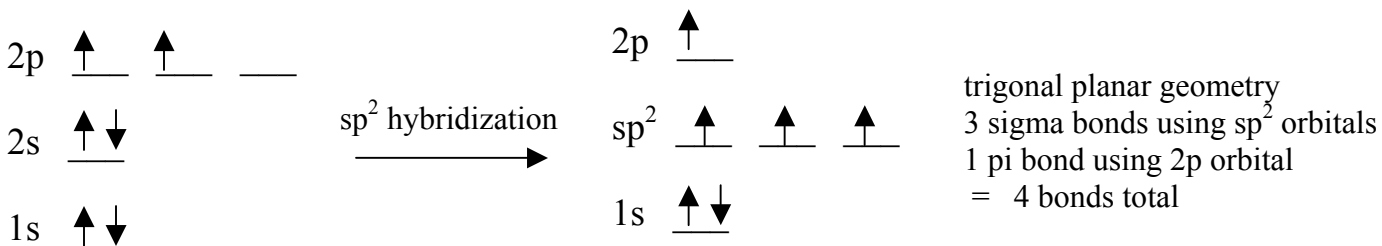


You must get used to visualizing this tetrahedral geometry. Your sanity and your grade will depend on it.

Molecular Orbital Picture. In the MO picture, only the mathematical details change...the two atomic orbitals (sp^3 from the C and $1s$ from the H) can either add and make a bonding orbital (σ) or can subtract and give an antibonding molecular orbital (σ^*). However many atomic orbitals get combined, that is how many molecular orbitals you create. Ugh. More info on this as specific examples warrant.



Now looking back at the valence electron picture on page 10, there are other possibilities for hybridization... $2s + 2 2p$'s and $2s + 1 2p$...the pictures look like this...



A summary of bonding characteristics for the different 3 possible hybridizations schemes are shown below.

s	p	% s	% p	sp^x	bond angle	geometry	examples
1	1	50	50	sp^1	180	linear	BeH_2 , C_2H_2
1	2	33	66	sp^2	120	trigonal	BF_3 , BH_3
1	3	25	75	sp^3	109.5	tetrahedral	CH_4

bond type	C-C length Å	C-C strength kJ/mol	C-H length Å	C-H strength kJ/mol
$sp-sp$	1.20	835		
sp^2-sp^2	1.33	611		
sp^3-sp^3	1.54	376		
$sp-s$			1.06	552
sp^2-s			1.076	444
sp^3-s			1.10	420

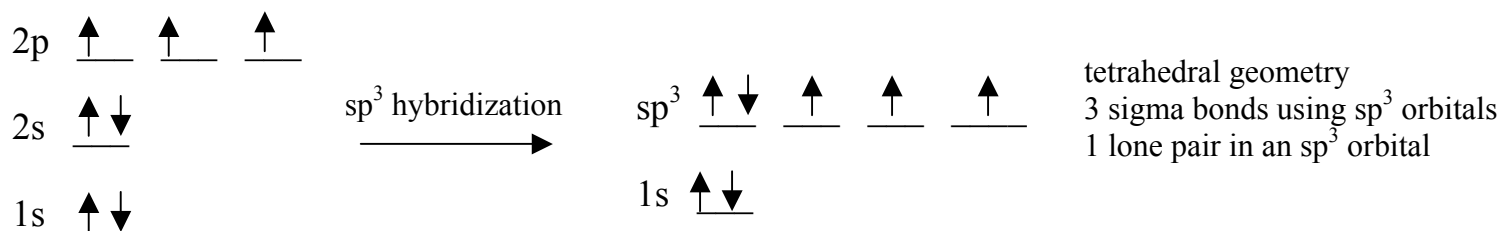
General trends...more "s" character gives shorter, stronger bonds.

Hybridization solves three basic problems...

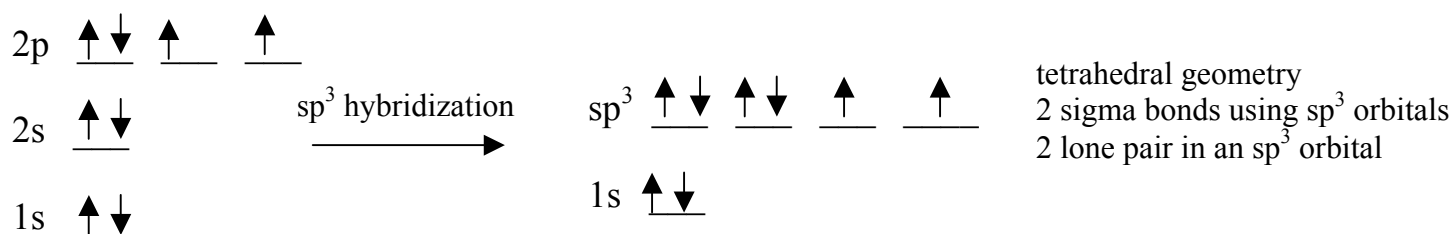
- 1) Proximity...everything (atoms and electrons) in a molecule wants to be as far away from everything else as possible.
- 2) All electrons are in bonding orbitals so the molecule can be held together.
- 3) Nature hates wasted space. Hybrid orbitals create maximum space for electrons to reside.

Hybridization of N and O...

Though we won't discuss it much, or its implications, you should be aware that other atoms central to organic chemistry (N and O) also hybridize for exactly the same reasons as carbon. For example, consider nitrogen. Why does nitrogen typically have three bonds and one lone pair arranged in a tetrahedral if it has three lone electrons occupying p_x , p_y and p_z orbitals?



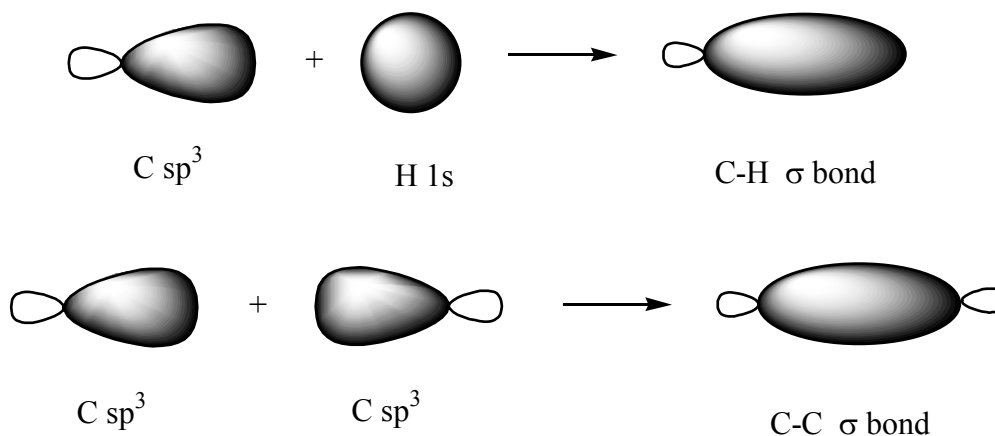
And for oxygen...



2.3. Sigma (σ) vs. Pi (π) Bonds

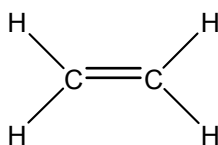
Again, you should remember this from GenChem, but we will refresh because this distinction is vital to your understanding organic chemistry.

On the second page of this section (pg. 11)... Those are sigma bonds. Sigma bonds (denoted by the Greek letter σ), are the result of direct overlap of atomic orbitals. The normal, average, boring sp^3 - sp^3 C-C bond in ethane is a perfect example. In fact, all the C-H bonds are also perfect examples...



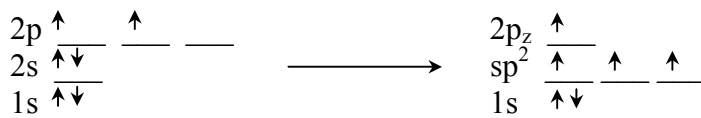
Sigma bonds are usually quite strong. They will bend, but they are hard to break. And, they have one more unique feature that we will exploit later...free rotation.

Pi bonds (denoted by the Greek letter π) result from the indirect, lateral interaction of p orbitals. Pi bonding usually show up in double and triple bond systems. The prototypical example is C_2H_4 , ethene.

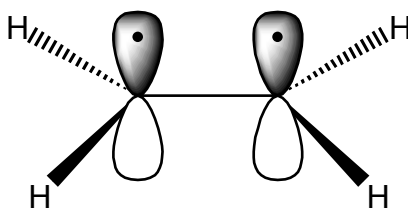


So how does bonding in ethene work?

The requirement: 3 “items” optimally spaced around a carbon instead of 4 comes from sp^2 hybridization...



The result: 3 “items” optimally arranged around a carbon, with 1 electron extra for pi bonding.



C-H bonds are $sp^2 - 1s$
 C-C sigma bond is $sp^2 - sp^2$
 C-C pi bond is $2p_z - 2p_z$

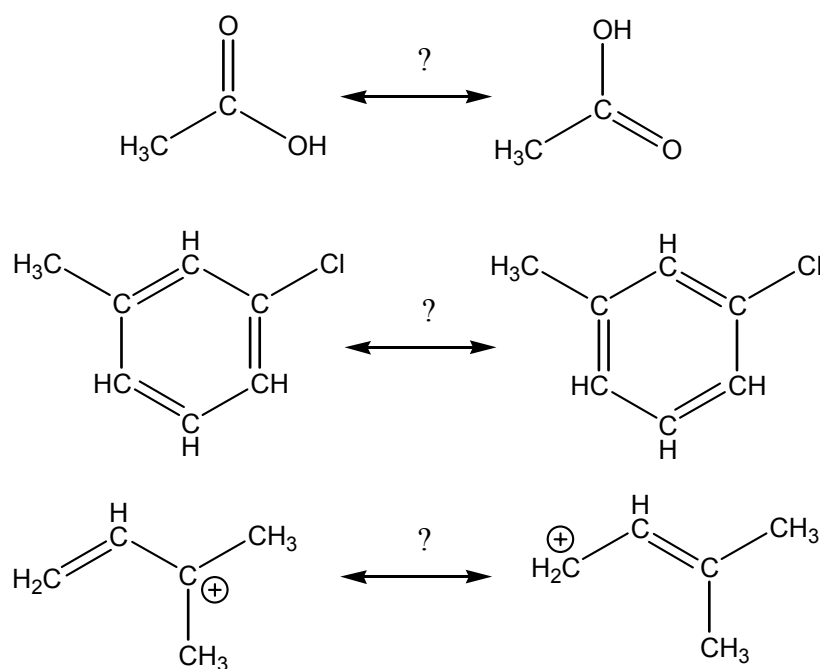
Pi bonds have the unique feature that, when paired with σ bonds, they prevent free rotation about the axis of the bond. More on this and other features of the π bond when we talk about alkenes, alkynes and aromatic compounds.

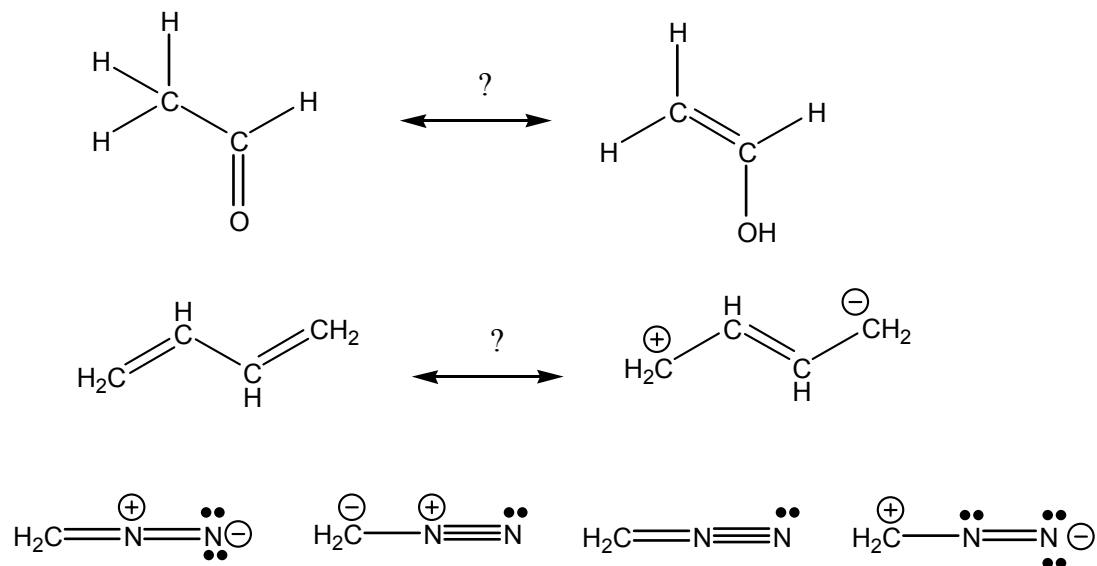
2.4. Resonance

Resonance is a very important concept in organic chemistry and will allow you to assess the relative reactivity of different molecules and specific sites within one molecule. There are 3 basic rules (1,2,3) that guide how we draw resonance structures and 2 basic observations (4,5) that can be made...

- 1) When drawing resonance structures, nuclei of atoms may not be moved, only electrons in conjugated p orbitals.
- 2) Each resonance structure must have the same number of electrons and the same total charge.
- 3) The stability of resonance structures is assessed the same way as the stability of Lewis structures; satisfaction of the octet rule, number and location of formal charges, and the interactions between charges within the structure.
- 4) Resonance stabilization energy increases as the number of important resonance structures increases.
- 5) The actual structure of a molecule most resembles the most stable resonance structure of that molecule.

Examples...





More examples and rules for resonance forms as we come to specific examples or functional groups.