ELECTRONIC EFFECTS IN A COVALENT BOND

Electromeric effect

The term though a bit outdated is important for understanding changes in electronic density in a molecule in the presence for other species. This also involves movement of electrons but in this case due to some external agent. For example if a positive charge like H⁺ is brought near a double bond (say CH₂=CH₂), the double bond which is electron rich (a double bond has pi electrons, remember?), the bond is polarized towards the proton, which can be shown as follows:

![Figure 2. +E effect](image)

This shifting of electrons or polarization of the covalent bond is termed as Electromeric effect. This case is called +E, as the polarization occurs due to the presence of a positive charge. A –E effect can be seen when some negatively charged species like OH⁻ attacks a double bond:

![Figure 3. -E effect](image)

Resonance

Resonance is one of the most fundamental concepts of chemistry with the most applications in organic chemistry. Resonance is a phenomenon where a molecule is represented in more than one form when a single Lewis structure cannot represent all of its properties. An example is CH₃=CH-CH=CH₂, which from the Lewis structure shown consists of two double bonds and a single bond. So C1-C2 and C3-C4 bond lengths should be substantially shorter than that between C2 and C3, but all bonds are found to be of the same length in reality. So the above representation of bonds and electrons is not entirely accurate.

In reality this inadequacy of accurate representation of covalent molecule is inherent in the Lewis model. So we use multiple structures to represent the actual molecule which exists in nature and these structures represent one or more properties of the actual molecule. Philosophically it is like human nature, where we are made p of many different traits, but a person cannot be described by any single one of those traits.
To extend the example above CH=CH-CH=CH₂ can be written as CH₃-CH=CH₂⁻ by moving the electrons in the following manner:

![Figure 4. Resonance structures](image)

These structures are called resonance structures of the main molecule; now we can understand why all the bonds have equal length as structure 2 has a double bond character on C₂-C₃ and 1 and 3 have double bonds on C₁-C₂ and C₃-C₄. So overall all C-C bonds have some double bond character so the actual representation of the molecule found in nature would be something like:

![Figure 5. Resonance hybrid](image)

This structure now would be called a resonance hybrid of all the resonance structures sometimes also referred to as canonical forms. An analogy can be used here.

A foreigner comes to India and sees a rhino for the first time…then when he goes back to his country he tries to describe the animal he saw and he does it by saying the animal was a combination of a unicorn (a fairy-tale horse with one horn above its nose) and a dinosaur. So we can see that these two animals carry distinctive features of the rhino, so the rhino can be considered to be a resonance hybrid of the two. The most important thing here is that neither the unicorn nor the dinosaur exists in real life but the rhino does; resonance structures do not exist but are merely used to describe the actual molecule—the resonance hybrid which exists in nature. So the movement of electrons shown by the arrows to obtain those resonance structures are also superficial and only drawn for easier understanding.

A few points about Resonance hybrids would summarize the concept:

- A resonance hybrid is the actual representation of the molecule.
- It has properties from all the resonance structures.
• It has the least energy of all the resonance structures (that is why it exists in nature) and the structures which have energy close to it contribute the most towards it. This means if X is the hybrid of A, B and C, if C has the lowest energy (or is the most stable) X will look the most like C.

• This extra stabilization of the resonance hybrid is denoted by Resonance energy.

Hyperconjugation

This is very similar to resonance, sometimes referred to a No-bond resonance or Baker-Nathan effect. In case of classical resonance we had seen the involvement of lone pair of electrons and pi bonds (double/triple bonds). In hyperconjugation single bonds are involved in the electron delocalization circuitry. This effect is still not fully understood in detail but would serve the purpose of basic organic chemistry.

The following example would illustrate this effect.

![Figure 6. Formation of a carbocation](http://padakshep.org/otp/subjects/chemistry/organic-chemistry/steric-electronic-effects/)

The cation formed is called a carbocation as we will learn later. This positive charge is stabilized by hyperconjugation as follows:

![Figure 7. Hyperconjugation](http://padakshep.org/otp/subjects/chemistry/organic-chemistry/steric-electronic-effects/)

Notice that the sigma bond is involved in resonance and breaks in order to supply electrons for delocalization.