

2.2: Background

Organic molecules are often represented using Lewis structures or the line bond formalism. In both molecular representations, a single line between atoms represents a single bond sharing a pair of electrons. Similarly, a double or triple bond, sharing 2 or 3 pairs of electrons, are represented by 2 or 3 lines between atoms respectively. Representing atomic bonding in this manner, however, doesn't always provide an accurate picture of electronic structure. Specifically, some molecular species have electron pairs that are spread over a larger area than just one bond in a concept known as delocalization. For example, the allyl anion, shown in Figure 1, has one carbon-carbon single bond and one carbon-carbon double bond. The actual structure of this allyl anion has two carbon-carbon bonds with a bond order of about 1.5.

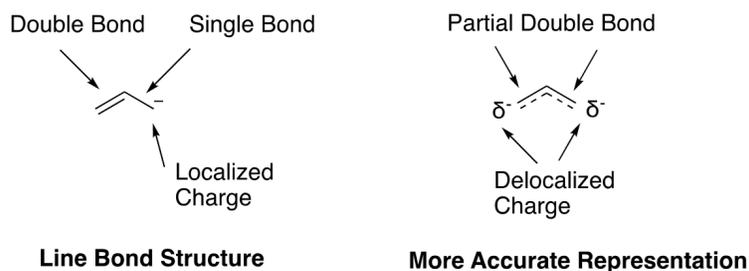


Figure 1. A comparison between the line bond structure and actual structure of the allyl anion.

Rather than throwing the proverbial baby out with the bathwater, chemists decided to adapt the method of drawing molecules using line bond structures to better represent the electronic geometry of species with delocalized electrons. In this method, multiple line bond drawings, known as resonance structures, represent different aspects of a molecule's electronic structure. An observer is then expected to mentally merge the resonance structures together to get a more realistic picture of the molecule. More often, chemists will average the resonance structures to produce a realistic picture known as a resonance hybrid. As shown in Figure 2, two resonance structures of the allyl anion are averaged to make a more accurate resonance hybrid.

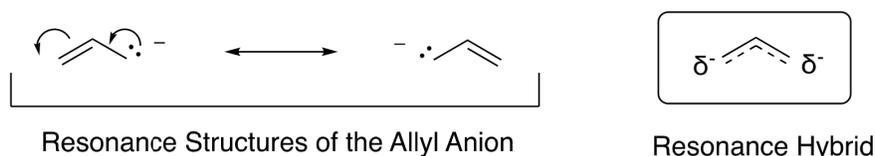


Figure 2. (Left) Two resonance structures of the allyl anion with their interconverting curved arrow shown. (Right) The resonance hybrid produced by the averaging of the two resonance structures.

In lecture, you will have learned how chemists create resonance structures of molecules using a series of curved arrows to push electrons from one part of the molecule to another. In the computational exercise that follows, you will examine resonance by optimizing the geometry of N, N-dimethylacetamide, whose structure is shown in Figure 3.

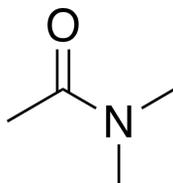


Figure 3. Line bond structure of N, N-dimethylacetamide.

In a previous exercise, we have done basic geometry optimization within Avogadro. This exercise utilizes a more powerful set of techniques based on Density Functional Theory (DFT). On a basic level, DFT assumes that the electrons reside in predefined regions of space around each atom, with a mathematical function describing how likely it is to find each electron in at a given location (its density functional). Starting from a predetermined set of these functions (called a basis set), our software ORCA will try to "wiggle" each atom, looking to see if by moving the atoms it can relax the molecule to a lower energy than its starting position. By successively moving atoms and recalculating the electron energies from the density functionals, ORCA is able to more accurately find the structure of a molecule than Avogadro. This accuracy comes at a price however, as the calculations involved in density functional theory are quantum mechanical and take much more computing power than Avogadro's optimization.

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