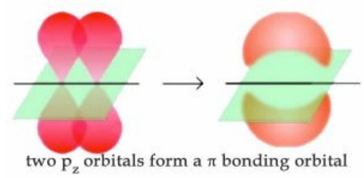
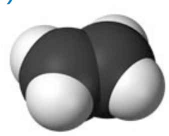
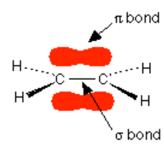
4.3: Double and Triple Bonds



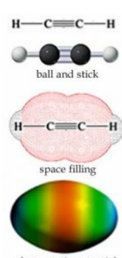
So far, we have considered what are known as single bonds; that is, all the $C-C$ and $C-H$ bonds in alkanes, and all the bonds in diamond. Each single bond involves two (and only two) electrons that are described by a bonding molecular orbital. In such a bonding orbital, most of the electron density is located between the two bonded atoms in a linear sigma (σ) bond. We have, however, already discussed albeit briefly bonds that involve more than one pair of electrons, namely those found in graphite. Recall that for graphite and graphene the bonds between carbon atoms in the sheet plane involve hybridized orbitals that are mixtures of the $2s^2$ and $2p_x$ and $2p_y$ (that is sp^2 hybrid orbitals) leaving an unhybridized $2p_z$ orbital. On bonding, these unhybridized $2p_z$ orbitals reorganize to form what is known as a pi (π) bonding orbital. In π orbitals, the electron density lies above and below the axis connecting the bonded atoms. The combination of \simga and π bonding orbitals produces a double bond. Double bonds are indicated by two lines, for example as in $CH_2{=}CH_2$ (ethene).

Shapes of Molecules with Double (and Triple) Bonds





We can apply the same thinking about the arrangement of bonds around the carbon atoms in $CH_2{=}CH_2$ in much the same manner as we did for CH_3-CH_3. In ethene each carbon atom is surrounded by three centers of electron density, two Hs and one C. Note that the double bond counts as a single center of electron density ($\rightarrow$). There are a number of important points to keep in mind when considering the effects of double bonds on a molecule and its properties. First, a $C=C$ double bond is typically less stable (that is more reactive) than two separate single bonds. When we come to thinking about reactions we will find that replacing a double bond by two single bonds typically produces a more stable system. Second, although there is more or less free rotation around the axis of a single bond at room temperature, rotation is blocked by the presence of a double bond. For a rotation to occur, the π bond (in which there is electron density above and below the axis between the two carbon atoms) must be broken and then reformed. The presence of a double bond has distinct effects on molecular shape. The minimum energy arrangement for three centers is a two-dimensional arrangement in which the groups are oriented at about 120° to one another; an arrangement known as trigonal planar geometry.



There is one more common type of bond that carbon can form, which is a triple bond. For example each carbon in C_2H_2 (ethyne) is surrounded by only two centers of electron density: a single sp hybrid orbital bonds between a carbon atom and a hydrogen atom and a triple bond, which can be thought of as a σ bond and two π bonds between the carbons, shown in the figure ($\rightarrow$). The lowest energy arrangement around each carbon is a line in which the angle between the bonds is 180°. As before, a triple bond is less stable than three single bonds, and reactions can be expected!

We see that under most conditions, a carbon atom can participate in a maximum of four bonds; either four single bonds, two single bonds and a double bond, or one single bond and a triple bond.

? Questions

Questions to Answer

- Given a particular hydrocarbon, what factors would influence your prediction of its melting and boiling points? Can you generate some tentative rules?
- How does the presence of a double bond influence the structure of a hydrocarbon?
- How is the presence a triple bond different from that of a double bond?
- Why do you think there is no tetrabonded from of carbon (that is C four bonds C).

Questions to Ponder

- What limits the size and shape of a hydrocarbon?