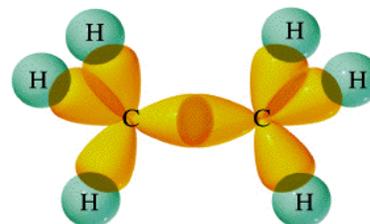# HYBRID TYPES AND MULTIPLE BONDS

We have already seen how sp hybridization in carbon leads to its combining power of four in the methane molecule. Two such tetrahedrally coordinated carbons can link up together to form the molecule **ethane C2H6**.

In this molecule, each carbon is bonded in the same way as the other; each is linked to four other atoms, three hydrogens and one carbon. The ability of carbon-to-carbon linkages to extend themselves indefinitely and through all coordination positions accounts for the millions of organic molecules that are known.

Trigonal hybridization in carbon: the double bond

Carbon and hydrogen can also form a compound **ethylene (ethene)** in which each carbon atom is linked to only three other atoms. Here, we can regard carbon as being trivalent. We can explain this trivalence by supposing that the orbital hybridization in carbon is in this case not sp3, but is sp2 instead; in other words, only two of the three porbitals of carbon mix with the 2s orbital to form hybrids; the remaining p-orbital, which we will call the i orbital, remains unhybridized.

Each carbon is bonded to three other atoms in the same kind of plane trigonal configuration that we saw in the case of boron trifluoride, where the same kind of hybridization occurs. Notice that the bond angles around each carbon are all 120°.

This alternative hybridization scheme explains how carbon can combine with four atoms in some of its compounds and with three other atoms in other compounds. You may be aware of the conventional way of depicting carbon as being tetravalent in all its compounds; it is often stated that carbon always forms four bonds, but that sometimes, as in the case of ethylene, one of these may be a double bond. This concept of the multiple bond preserves the idea of tetravalent carbon while admitting the existence of molecules in which carbon is clearly combined with fewer than four other atoms.
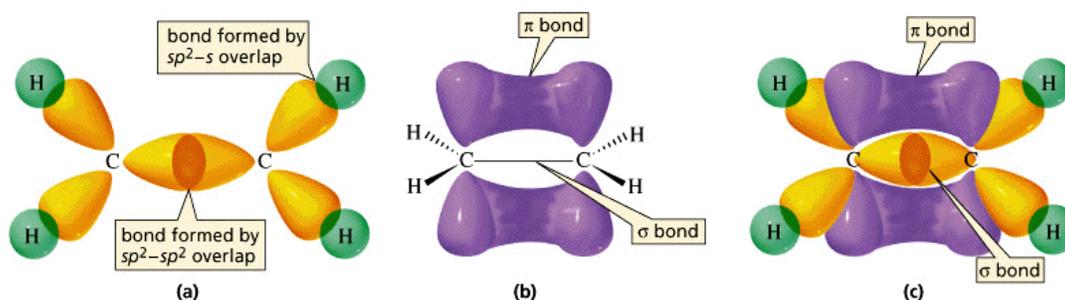
These three views of the ethylene molecule emphasize different aspects of the disposition of shared electron pairs in the various bonding orbitals of ethene (ethylene). **(a)** The "backbone" structure consisting of σ (sigma) bonds formed from the three sp2-hybridized orbitals on each carbon.

(b) The π (pi) bonding system formed by overlap of the unhybridized pz orbital on each carbon. The π orbital has two regions of electron density extending above and below the plane of the molecule. **(c)** A cutaway view of the combined σ and π system.

As shown above, ethylene can be imagined to form when two -CH2 fragments link together through overlap of the half-filled sp2 hybrid orbitals on each. Since sp2 hybrid orbitals are always in the same plane, the entire ethylene molecule is planar. However, there remains on each carbon atom an electron in an unhybridized atomic pz orbital that is perpendicular to the molecular plane. These two parallel pz orbitals will interact with each other; the two orbitals merge, forming a sausage-like charge cloud (the π bond) that extends both above and below the plane of the molecule. It is the pair of electrons that occupy this new extended orbital that constitutes the "fourth" bond to each carbon, and thus the "other half" of the double bond in the molecule.

More about sigma and pi bonds

The σ (*sigma*) bond has its maximum electron density along the line-of-centers joining the two atoms (below left). Viewed end-on, the σ bond is cylindrically symmetrical about the line-of-centers.

It is this symmetry, rather than its parentage, that defines the σ bond, which can be formed from the overlap of two s-orbitals, from two p-orbitals arranged end-to-end, or from an s- and a p-orbital. They can also form when sp hybrid orbitals on two atoms overlap end-to-end.

Pi orbitals, on the other hand, require the presence of two atomic p orbitals on adjacent atoms. Most important, the charge density in the π orbital is concentrated above and below the molecular plane; it is almost zero along the line-of-centers between the two atoms. It is this perpendicular orientation with respect to the molecular plane (and the consequent lack of cylindrical symmetry) that defines the π orbital. The combination of a σ bond and a π bond extending between the same pair of atoms constitutes the double bond in molecules such as ethylene.

Carbon-carbon triple bonds: sp hybridization in acetylene

We have not yet completed our overview of multiple bonding, however. Carbon and hydrogen can form yet another compound, acetylene (ethyne), in which each carbon is connected to only two other atoms: a carbon and a hydrogen. This can be regarded as an example of divalent carbon, but is usually rationalized by writing a triple bond between the two carbon atoms.

We assume here that since two geometrically equivalent bonds are formed by each carbon, this atom must be sp-hybridized in acetylene.

On each carbon, one sp hybrid bonds to a hydrogen and the other bonds to the other carbon atom, forming the σ bond skeleton of the molecule.

In addition to the sp hybrids, each carbon atom has two half-occupied p orbitals oriented at right angles to each other and to the interatomic axis. These two sets of parallel and adjacent p orbitals can thus merge into two sets of π orbitals.

σ bonds

A

Two π bonds

B
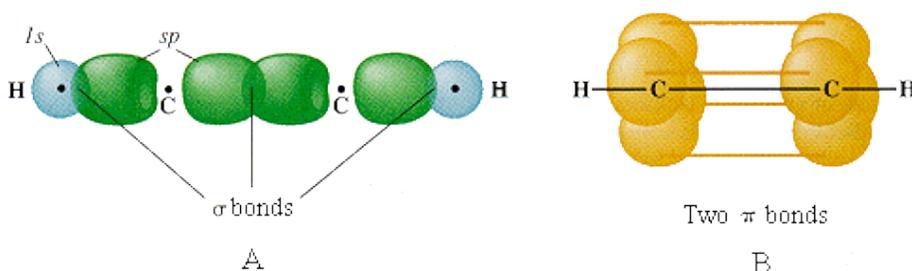
The triple bond in acetylene is seen to consist of one σ bond joining the line-of-centers between the two carbon atoms, and two π bonds whose lobes of electron density are in mutually-perpendicular planes. The acetylene molecule is of course linear, since the angle between the two sp hybrid orbitals that produce the s skeleton of the molecule is 180°.

Multiple bonds between unlike atoms

Multiple bonds can also occur between dissimilar atoms. For example, in **carbon dioxide** each carbon atom has two unhybridized atomic porbitals, and each oxygen atom still has one porbital available.
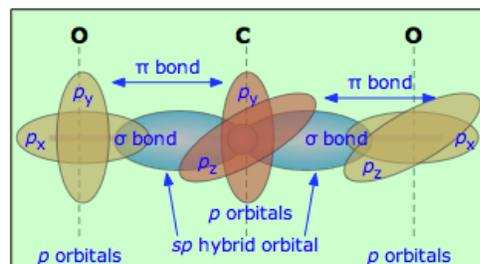
When the two O-atoms are brought up to opposite sides of the carbon atom, one of the p orbitals on each oxygen forms a π bond with one of the carbon p-orbitals. In this case, sp-hybridization is seen to lead to two double bonds. Notice that the two C–O π bonds are mutually perpendicular.

Similarly, in **hydrogen cyanide**, HCN, we assume that the carbon is sp-hybridized, since it is joined to only two other atoms, and is hence in a divalent state. One of
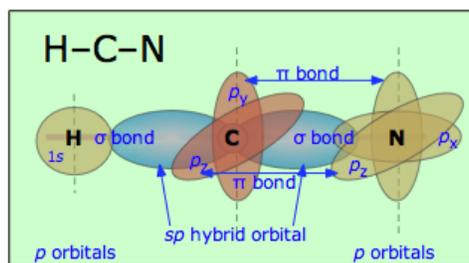
the sp-hybrid orbitals overlaps with the hydrogen 1s orbital, while the other overlaps end-to-end with one of the three unhybridized porbitals of the nitrogen atom. This leaves us with two nitrogen p-orbitals which form two mutually perpendicular π bonds to the two atomic p orbitals on the carbon. Hydrogen cyanide thus contains one single and one triple bond. The latter consists of a σ bond from the overlap of a carbon sp hybrid orbital with a nitrogen p orbital, plus two mutually perpendicular π bonds deriving from parallel atomic p orbitals on the carbon and nitrogen atoms.
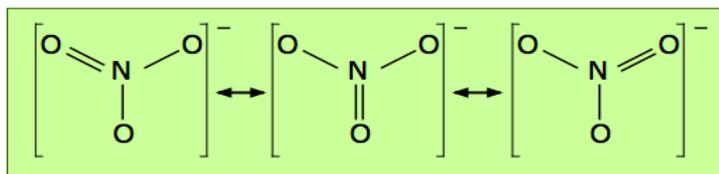
The nitrate ion

Pi bond delocalization furnishes a means of expressing the structures of other molecules that require more than one electron-dot or structural formula for their accurate representation.

A good example is the nitrate ion, which contains 24 electrons:
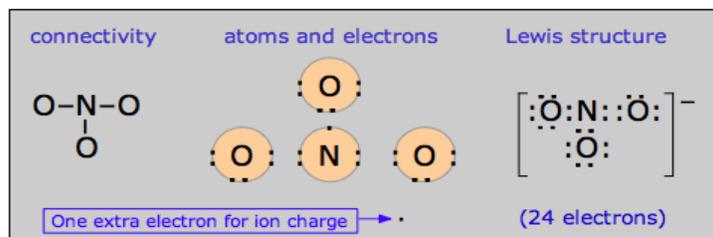
The electron-dot formula shown above is only one of three equivalent resonance structures that are needed to describe trigonal symmetry of this ion.


Nitrogen has three half-occupied p orbitals available for bonding, all perpendicular to one another. Since the nitrate ion is known to be planar, we are forced to assume that the nitrogen outer electrons are sp2-hybridized. The addition of an extra electron fills all three hybrid orbitals completely. Each of these filled sp2 orbitals forms a σ bond by overlap with an empty oxygen 2pz orbital; this, you will recall, is an example of **coordinate covalent bonding**, in which one of the atoms contributes both of the bonding electrons. The empty oxygen 2p orbital is made available when the oxygen electrons themselves become sp hybridized; we get three filled sp hybrid orbitals, and an empty 2p atomic orbital, just as in the case of nitrogen.

The π bonding system arises from the interaction of one of the occupied oxygen sp orbitals with the unoccupied 2px orbital of the nitrogen. Notice that this, again, is a coordinate covalent sharing, except that in this instance it is the oxygen atom that donates both electrons.

Pi bonds can form in this way between the nitrogen atom and any of the three oxygens; there are thus three equivalent π bonds possible, but since nitrogen can only form one complete π bond at a time, the π bonding is divided up three ways, so that each N–O bond has a bond order of 4/3.
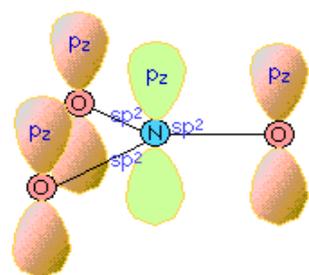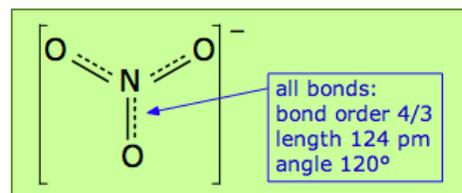
Unhybridized atomic p orbitals and σ-bonding backbone
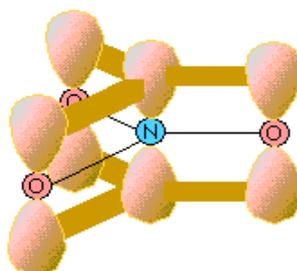
The π bonds are formed by overlap of the pz orbitals
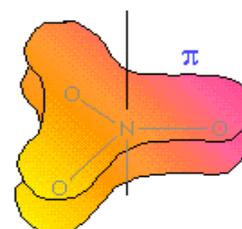
A representation of the entire NO_3^- molecule