

Chapter 10: Bonding & Molecular Structure - Hybridization & Molecular Orbitals

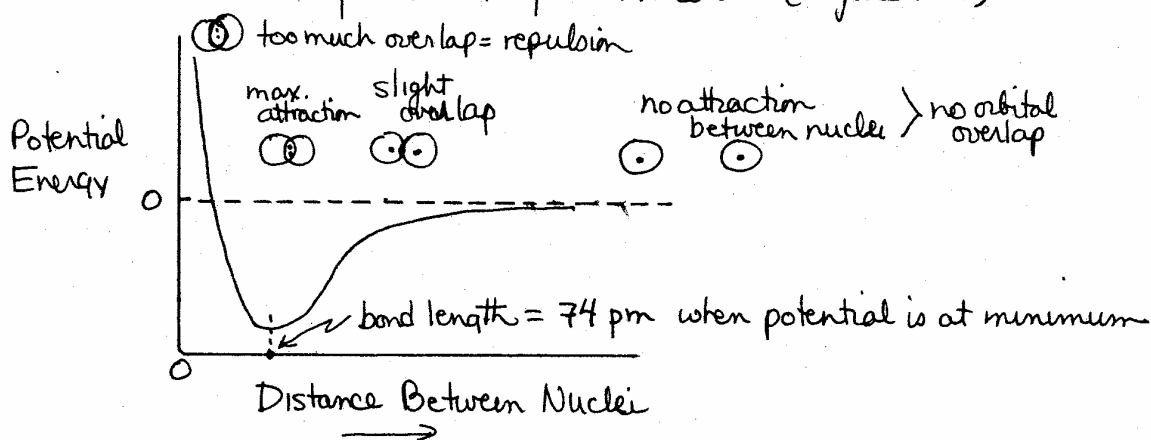
Chemical bonding in covalent compounds can be explained by

- (VB) (1) Valence Bond Theory - bonding results from overlap of atomic orbitals
 (MO) (2) Molecular Orbital Theory - a model of bonding in which pure atomic orbitals combine to produce molecular orbitals that are delocalized over 2 or more atoms.

VB Theory gives a good visual picture of molecular structure

MO Theory gives a quantitative picture of bonding. It is more complex and is only theory that explains why O_2 is paramagnetic.

How does orbital overlap work to form bonds? (Figure 10-1)



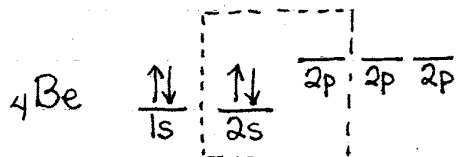
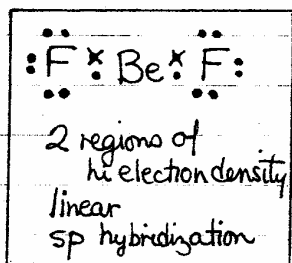
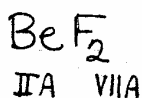
But - how can we have orbital overlap with our familiar s, p and d orbitals to get the shapes we know occur with VSEPR theory? Geometries like trigonal planar? Tetrahedral? etc.

Linus Pauling proposed the theory of orbital hybridization. A new set of orbitals called hybrid orbitals can be created by mixing s, p + d orbitals to get new orbitals.

Let's look at the kind of hybridization that can occur:

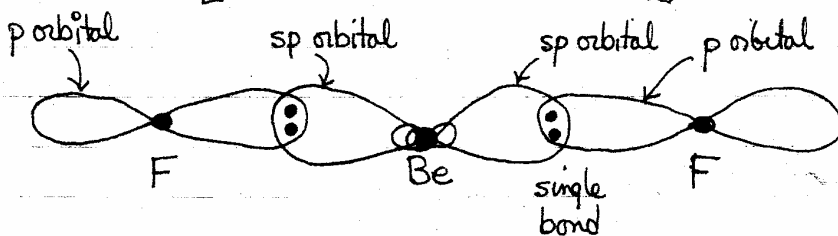
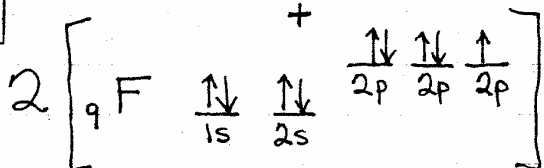
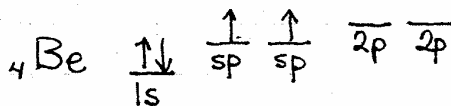
Hybridization	Regions of high electron density around central atom	Electronic Geometry	
sp	2	linear	$s + p$ orbitals $\xrightarrow[\text{(mixing)}]{\text{hybridization}}$ 2 sp hybrid orbitals
sp^2	3	trigonal planar	$s + p + p$ orbitals $\xrightarrow{\text{hyb.}}$ 3 sp^2 hybrid orbitals
sp^3	4	tetrahedral	$s + p + p + p$ orbitals $\xrightarrow{\text{hyb.}}$ 4 sp^3 hybrid orbitals
sp^3d	5	trigonal bipyramidal	$s + p + p + p + d$ orbitals $\xrightarrow{\text{hyb.}}$ 5 sp^3d hybrid orbitals
sp^3d^2	6	octahedral	$s + p + p + p + d + d$ orbitals $\xrightarrow{\text{hyb.}}$ 6 sp^3d^2 hybrid orbitals

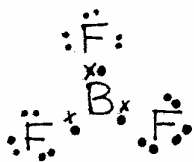
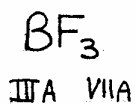
Examples:



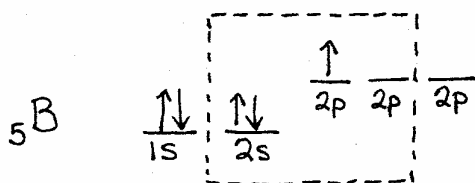
p sublevel has higher energy than s sublevel

\Downarrow hybridization

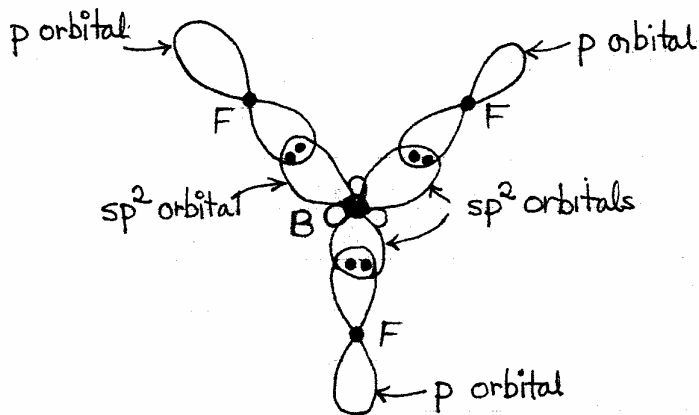
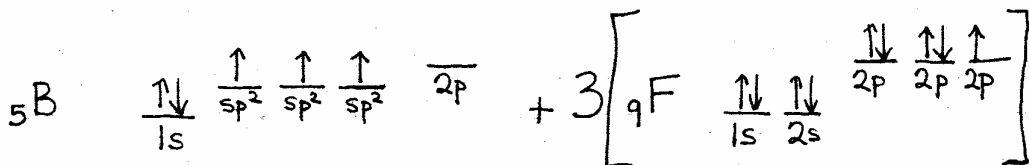




3 regions of high electron density
 Electronic geometry is trigonal planar
 sp^2 hybridization



↓ hybridization



Up to now we have been concerned with ELECTRONIC geometry - referring to the arrangement of the valence shell electrons around the central atom.
 The MOLECULAR geometry refers to the arrangement of atoms around the central atom - ie what the the molecule or ion really looks like.

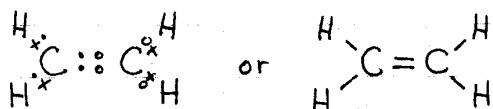
At the same time, we'll talk about the polarity of the molecule or ions whether the species is POLAR or NONPOLAR. A species can contain polar bonds but be nonpolar, when the pulling on the electrons balances out. See Ch. 9.

Compounds Containing Double Bonds

Consider ethylene (ethene) C_2H_4

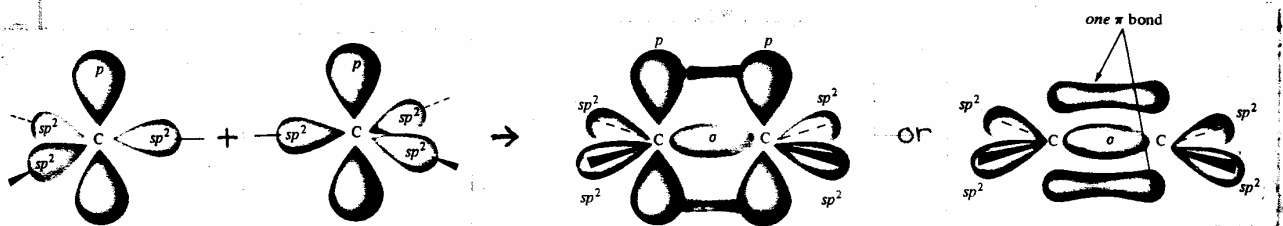
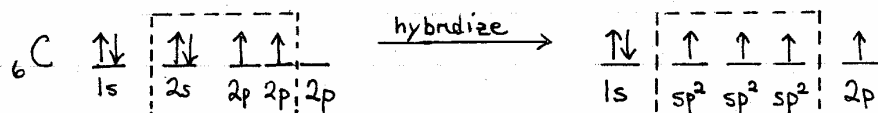
$$S = N - A$$

$$= [4 \times 2 (\text{for H}) + 2 \times 8 (\text{for C})] \\ - (4 \times 1 (\text{for H}) + 2 \times 4 (\text{for C})) \\ = 24 - 12 = 12 \text{ shared electrons}$$

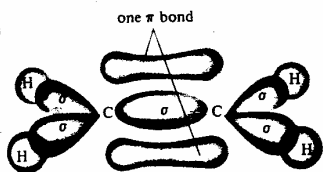


both carbon atoms are sp^2 hybridized (have 3 regions of high electron density)
each carbon is at the center of a trigonal plane
the carbons are connected by a double bond

But what exactly is a double bond?



Therefore, for ethene:



- ∴ double bond is result of 1 σ bond and 1 π bond
- ∴ ethene has a total of 5 σ bonds and 1 π bond

sigma (σ) bond: result of head-on (end-to-end) overlap
there is free rotation around σ bond

pi (π) bond: result of side-on overlap of p orbitals
there is NO free rotation around a π bond — the side-on overlap of p orbitals locks the molecule into place at that point

Compounds Containing Triple Bonds

Consider acetylene (ethyne) C_2H_2



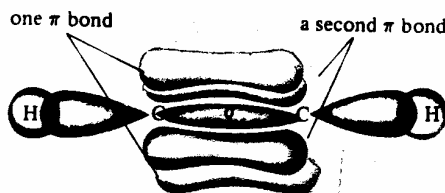
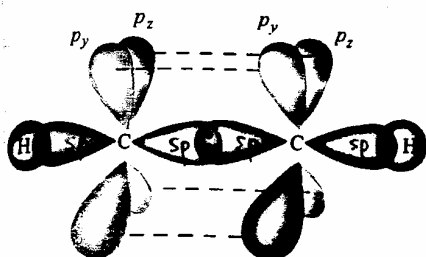
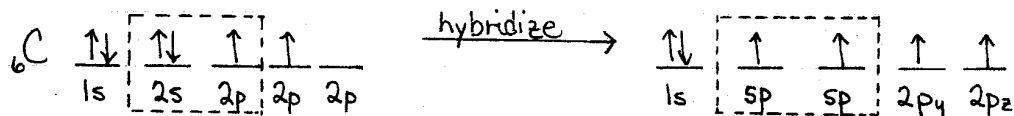
$$\begin{aligned} S &= N - A \\ &= [2 \times 2(\text{for H}) + 2 \times 8(\text{for C})] \\ &\quad - (2 \times 1(\text{for H}) + 2 \times 4(\text{for C})) \\ &= 20 - 10 = 10 \end{aligned}$$

both C atoms are sp hybridized

the molecule is linear

the carbon atoms are connected by a triple bond.

But what is a triple bond?



∴ a triple bond is the result of 1 σ bond and 2 π bonds

∴ ethyne $H-C \equiv C-H$ contains 3 σ bonds and 2 π bonds.

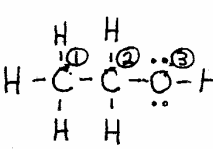
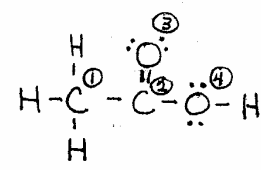
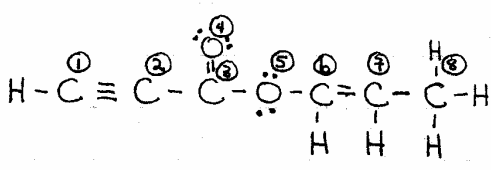
Summary:

- (1) all single bonds are sigma (σ) bonds formed by the normal, head-on overlap of orbitals.
- (2) double bond : 1 σ bond, 1 π bond
- (3) triple bond : 1 σ bond, 2 π bonds

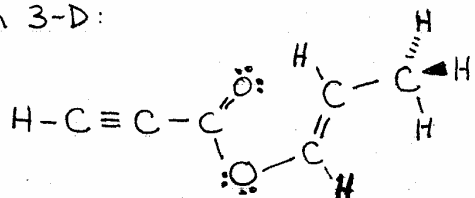
Review of hybridization using organic compounds:

(1) Know organic names & structures on sheet.

(2) Recall that all organic compounds (C-containing compounds) obey the octet rule. Each carbon has 4 bonds around it since there are never any lone pairs of electrons on C.

Examples	Atom	Hybridization	Bond Angle (ideal)
1. C_2H_5OH (ethanol) <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px 0;"> $S = N - A$ $= 36 - 20$ $= 16$ </div>  <p>lone pairs - 2 σ bonds - 8 π bonds - 0</p>	$C^{(1)}$ $C^{(2)}$ $O^{(3)}$	sp^3 sp^3 sp^3	$109^\circ 28'$ $109^\circ 28'$ $109^\circ 28'$
2. CH_3COOH (acetic acid) <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px 0;"> $S = N - A$ $= 40 - 24$ $= 16$ </div>  <p>lone pairs - 4 σ bonds - 7 π bonds - 1</p>	$C^{(1)}$ $C^{(2)}$ $O^{(3)}$ $O^{(4)}$	sp^3 sp^2 sp^2 sp^3	$109^\circ 28'$ 120° 120° $109^\circ 28'$
3.  <p>lone pairs - 4 σ bonds - 13 π bonds - 4</p>	$C^{(1)}$ $C^{(2)}$ $C^{(3)}$ $O^{(4)}$ $O^{(5)}$ $C^{(6)}$ $C^{(7)}$ $C^{(8)}$	sp sp sp^2 sp^2 sp^3 sp^2 sp^2 sp^3	180° 180° 120° 120° $109^\circ 28'$ 120° 120° $109^\circ 28'$

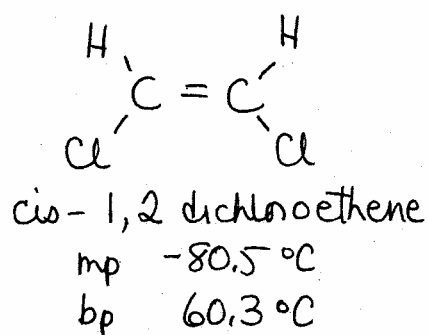
In 3-D:



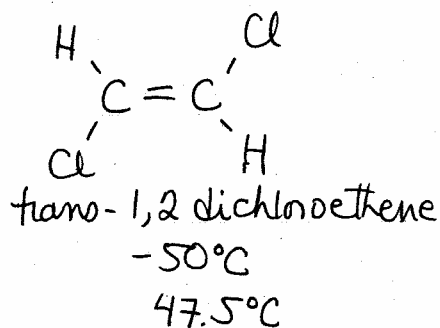
Cis-Trans Isomerism - a consequence of π bonding in double bonds

In a double bond, the π bond "locks" the molecule into place.
(There is free rotation around single bonds - sigma bonds)

Look at



vs



These compounds are isomers because they have same chemical formula
 $\text{C}_2\text{H}_2\text{Cl}_2$
but are different compounds, with different boiling + melting points.