

Structure and Properties of Organic Molecules

Reading: Wade chapter 2, sections 2-1- 2-7

Study Problems: 2-25, 2-27, 2-28, 2-30, 2-31, 2-33, 2-34

Key Concepts and Skills:

- Draw the structure of a single, double, and triple bond
- Predict the hybridization and geometry of the atoms in a molecule.
- Draw a three-dimensional representation of a given molecule.

Lecture Topics:

I. Combination of atomic orbitals

Atomic orbitals (s,p) can combine to form more complex wave functions. The number of new orbitals generated equals the number of orbitals started with.

1. When orbitals on different atoms interact, they produce an equivalent number of bonding and antibonding **molecular orbitals**.
2. When orbitals on the same atom interact, they give **hybrid atomic orbitals** that define the geometry of the bonds.

a. Formation of Molecular Orbitals

Sigma Bonding

- In the H₂ molecule, 1s orbitals on H can overlap constructively (in-phase) to produce a bonding molecular orbital known as a σ orbital where there is an increase in electron density in the bonding region between the nuclei.
- The 1s orbitals on H can also overlap destructively (out-of-phase) to produce an antibonding MO known as a σ^* orbital in which there is a node (region of zero electron density) between the nuclei.
- The sigma bonding molecular orbital is lower in energy than either of the isolated hydrogen 1s orbitals, and the σ^* antibonding orbital is higher in energy than either of the isolated hydrogen 1s orbitals. Both electrons in H₂ are thus located in the bonding σ orbital.
- All single bonds in organic compounds are σ bonds, in which most of the electron density in the bond is between the two nuclei on the internuclear axis. Sigma bonds are **cylindrically symmetrical**.
- Sigma bonding for p orbitals follows the same pattern: constructive overlap of two p_x orbitals along the x axis leads to a lower energy σ -bonding MO, and destructive overlap leads to a higher energy σ^* antibonding molecular orbital
- Constructive and destructive overlap of s and p orbitals similarly leads to σ -bonding and σ^* antibonding molecular orbitals.

Pi-Bonding

- π -bonding results from the overlap of p orbitals oriented perpendicular to the internuclear axis (side-ways overlap)
- Constructive and destructive overlap of the p-orbitals leads respectively to lower energy π -molecular orbitals and higher energy π^* -molecular orbitals

- The bonding π molecular orbitals have electron density in plane above and below the internuclear axis; the antibonding π^* molecular orbitals have a nodal plane between the nuclei.
- An example of π -bonding occurs in the molecule ethylene. Double bonds consist of one sigma bond and one π -bond.

b. Hybrid atomic orbitals

• Hybrid atomic orbitals arise from the mixing of orbitals on the same atom. VSEPR theory provides a rationale for the bonding geometries found in organic molecules: The bonding and lone pairs about a central atom will have the largest possible separation.

For 4 pairs of electrons: 109.5° bond angles

For 3 pairs of electrons: 120° bond angles

For 2 pairs of electrons: 180° bond angle

• The hybrid atomic orbitals resulting from combination of s and p orbitals allows the electrons in the hybrid orbitals (and molecular orbitals formed therefrom) a more wide separation in space.

• Combining an s and a p orbital leads to two sp hybrid orbitals pointing in opposite directions, allowing a bond angle of 180° . An example is BeH_2 , which contains 2 Be-H sigma bonds (both formed from overlap of Be sp-H 1s), is a linear molecule. There are two remaining unhybridized and empty p orbitals on Be orthogonal to each other.

• sp^2 hybrid orbitals are formed from the combination of one s and two p orbitals, and the three resulting hybrid orbitals are oriented 120° away each other in space. (trigonal geometry). Note that the atom contains one unhybridized p orbital oriented perpendicular to the trigonal plane containing the sp^2 hybrid orbitals

• An example is BH_3 , containing three B-H bonds (each formed from overlap of B sp^2 -H 1s), which displays trigonal geometry and all atoms are in plane, bond angles 120° .

• Combining one s and three p orbitals results in the formation of four equivalent-in-energy sp^3 orbitals oriented toward the corners of a tetrahedron around the central atom, with an angle of 109.5° between the sp^3 hybrid orbitals.

• Most organic molecules contain carbon atoms with four elements bonded to them, and thus each such carbon displays tetrahedral geometry: example: CH_4 , CCl_4 , etc.

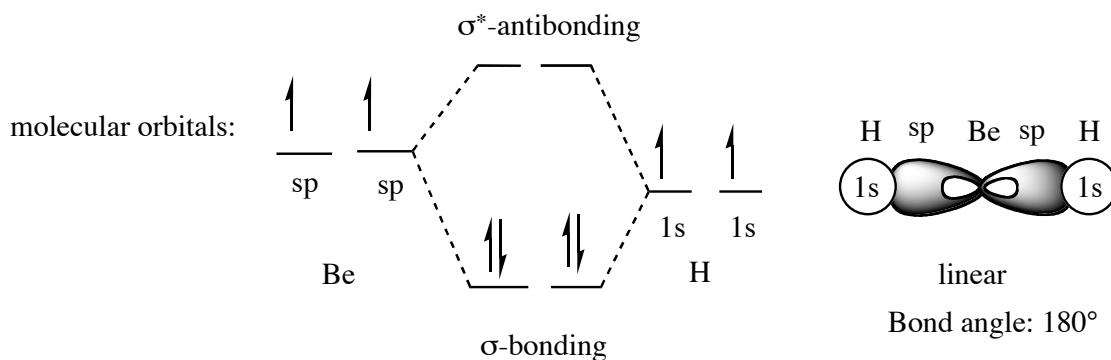
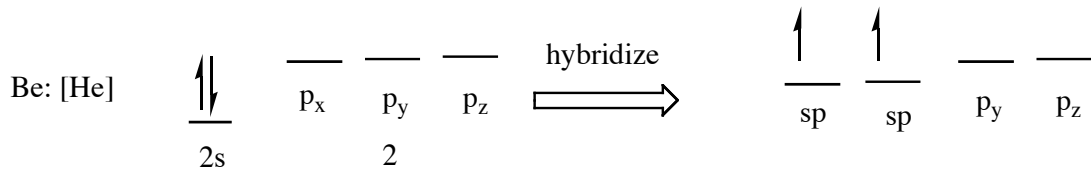
Hybridization Rules:

1. Both sigma bonding electrons and lone pairs occupy hybrid orbitals. The number of hybrid orbitals on an atom is computed from the total number of sigma bonds and lone pairs on the atom (Note: for doubly and triply bonded atoms, only the first bond of the multiple bond is a sigma bond, all others are pi-bonds formed from side-to side overlap of p-orbitals)
2. Use hybridization and geometry that give the widest possible separation of the calculated # of bonds and lone pairs

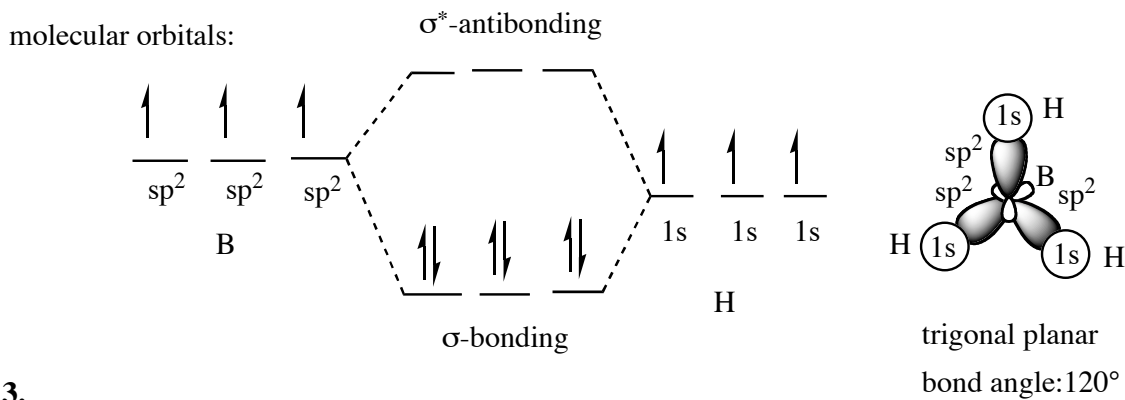
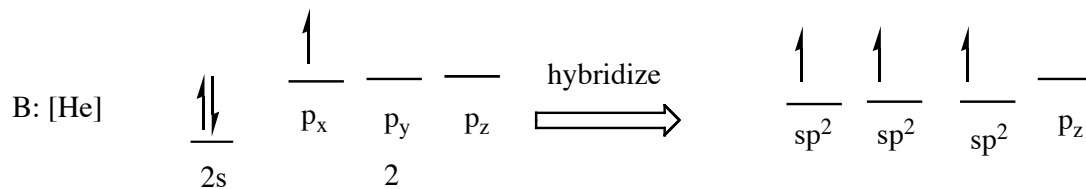
Hybrid orbitals	Hybridization	Geometry	Bond Angles
2	sp	linear	180°
3	sp^2	trigonal	120°
4	sp^3	tetrahedral	109.5°

3. The number of hybrid orbitals = the number of atomic orbitals combined
4. Lone pairs take up more space around an atom and thus compress the bond angles: examples : NH_3 (bond angle 107°), H_2O (bond angle 104°)

sp hybrid orbitals: BeH_2

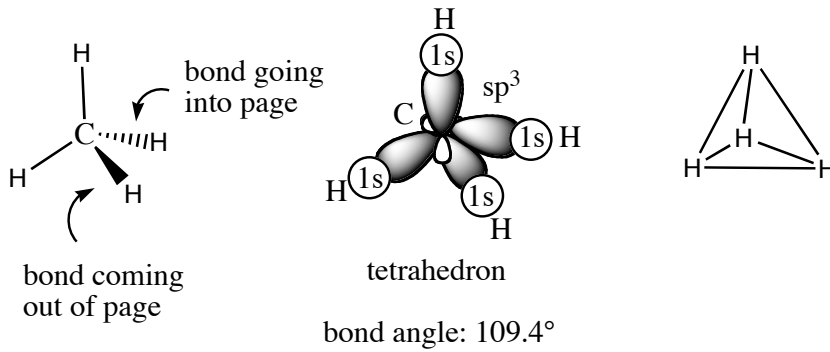
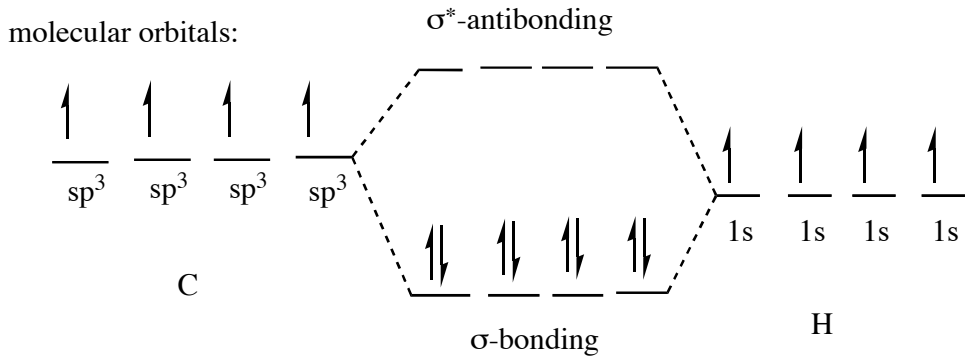
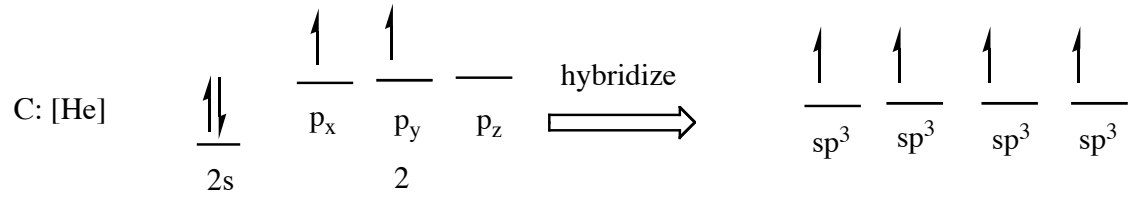


sp² hybrid orbitals: BH_3

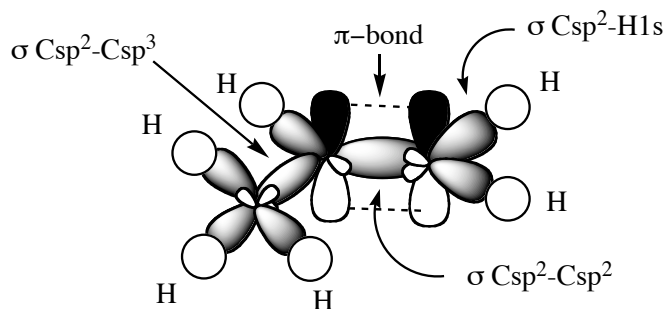
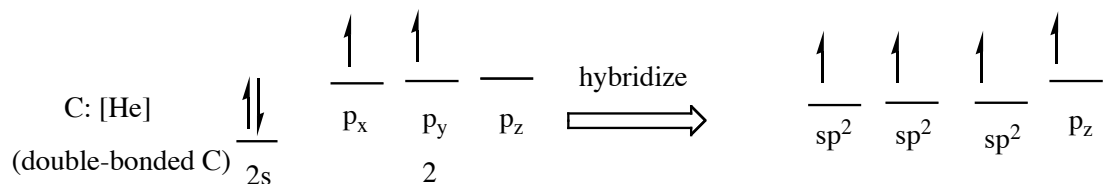


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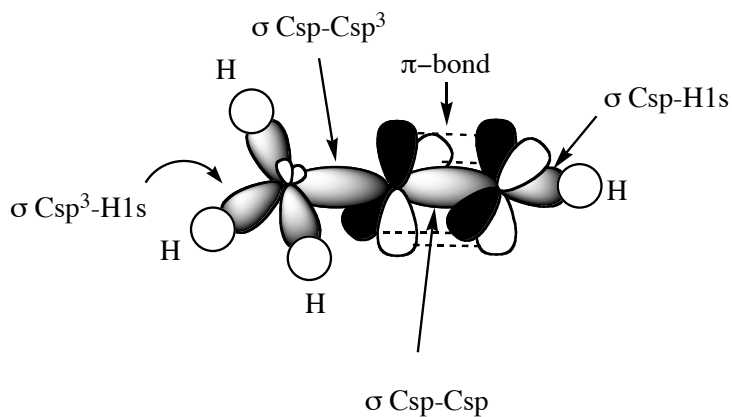
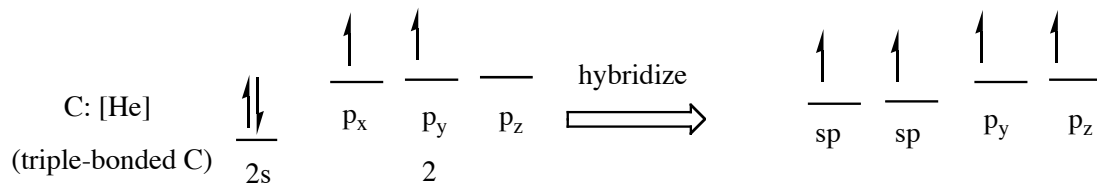
sp³ hybrid orbitals: CH₄



Double bonds: alkenes $\text{CH}_3\text{CH}=\text{CH}_2$



Triple bonds: alkynes CH_3CCH



Bond Rotation

Because of the cylindrically symmetric nature of sigma bonds, rotation about sigma bonds is possible. **Conformations** are structures differing only in rotation about a single bond.

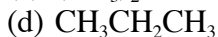
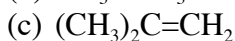
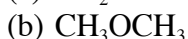
In contrast, double bonds are rigid, and no rotation about a double bond is normally observed. To twist a double bond requires a large input of energy to break a pi bond (twisting the p-orbitals on each atom perpendicular to each other prevents the side-to-side overlap required for pi-bond formation). Because of this high energy barrier to rotation about double bonds, it is easy to isolate cis/trans isomers of compounds containing C=C double bonds.

Additional Problems for practice:

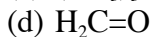
1. Use the VSEPR rules to determine the shape of each of the following molecules:



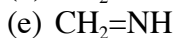
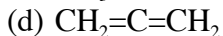
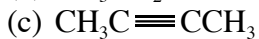
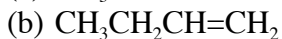
2. Indicate the kind of hybridization you might expect for each carbon atom in these molecules:



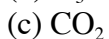
3. What shape would you expect these species to have?



4. Draw the structure of the following molecules, indicating the types of bonds involved and the hybrid orbitals on each atom:



5. Draw an orbital diagram for the following species, showing the hybrid orbitals that combine to form bonds. Indicate the geometry of each:



6. In which of the following molecules do you expect to observe cis/trans isomerism? Draw Lewis structures for the different possibilities.

