CH-110 Advanced General Chemistry I

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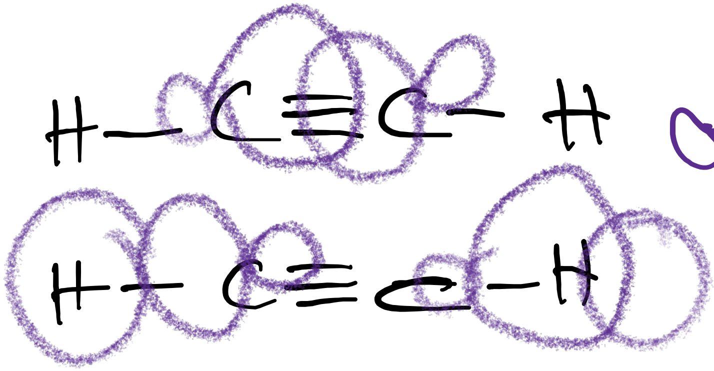
2F.2 Electron promotion and the hybridization of orbitals

Self-test 2F.2B

$H-C\equiv C-H \rightarrow sp$

Suggest a structure in terms of hybrid orbitals for each carbon atom in ethyne, C_2H_2.

$2 \times C2sp, 2p_x, 2p_y$



$\sigma(C2sp, C2sp)$

$\sigma(C2sp, H1s) \times 2$

$H-C\equiv C-H$

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2F.2 Electron promotion and the hybridization of orbitals

Self-test 2F.2B

Suggest a structure in terms of hybrid orbitals for each carbon atom in ethyne, C_2H_2.

2F.2 Electron promotion and the hybridization of orbitals

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2F.2 Electron promotion and the hybridization of orbitals

Summary

The **promotion** of electrons and formation of hybrid orbitals occurs if, overall, it leads to a lowering of energy by permitting the formation of more bonds. A **hybridization** scheme is adopted to match the electron arrangement of the central atom.

Valence-Bond Theory and Hypervalent Compounds

Topic 2F.3

2F.3 Valence-bond theory and hypervalent compounds

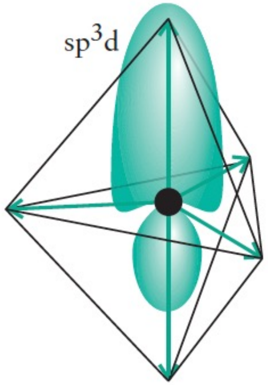
Hypervalency

- Concepts of promotion and hybridization work well to describe the tetravalence of carbon.
- What about hypervalent molecules?
- Two approaches to describe hypervalent compounds with VB theory

2F.3 Valence-bond theory and hypervalent compounds

PCl$_5$ example of hypervalency

Figure 3.17 (old book)



- Consider PCl$_5$:
  - Five Cl atoms attached to central P atom, five equal bonds
  - Five atomic orbitals → five hybrid orbitals
  - 1 s-orbital + 3 p-orbitals. **What is the fifth orbital?**
  - d-orbitals are close in energy: electron can be promoted to a d-orbital
  - Results: **sp^{3}d orbitals** (trigonal bipyramidal)
    - Two axial orbitals (Figure a)
    - Two equatorial orbitals (Figure b)

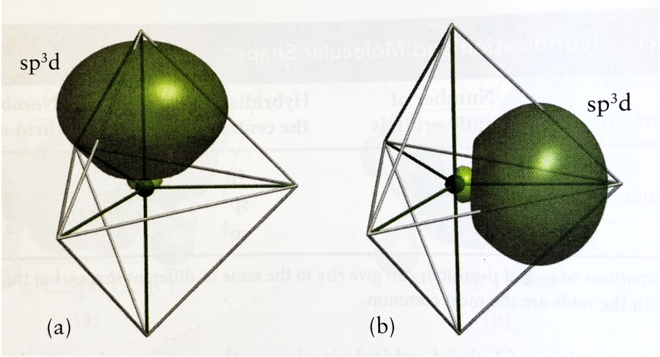


Figure 2F.10 (new book)

2F.3 Valence-bond theory and hypervalent compounds

SF_6 example of hypervalency

- Consider SF_6:
  - Six equivalent S–F bonds, octahedral
  - Six AOs → Six MOs
  - Two sulfur d-orbitals: **sp^3d^2 orbitals**
  - **Six identical orbitals** (no axial and equatorial distinction)

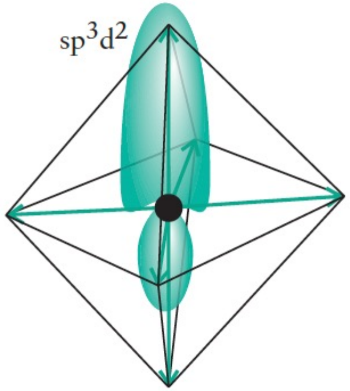


Figure 3.18 (old book)

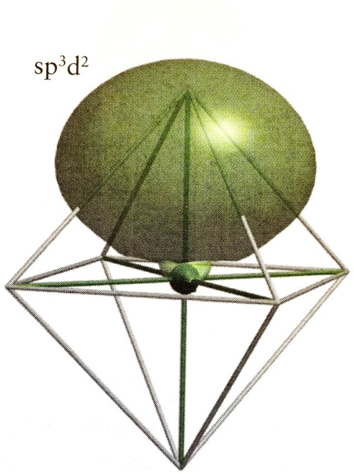


Figure 2F.11 (new book)

2F.3 Valence-bond theory and hypervalent compounds

Table 2F.2

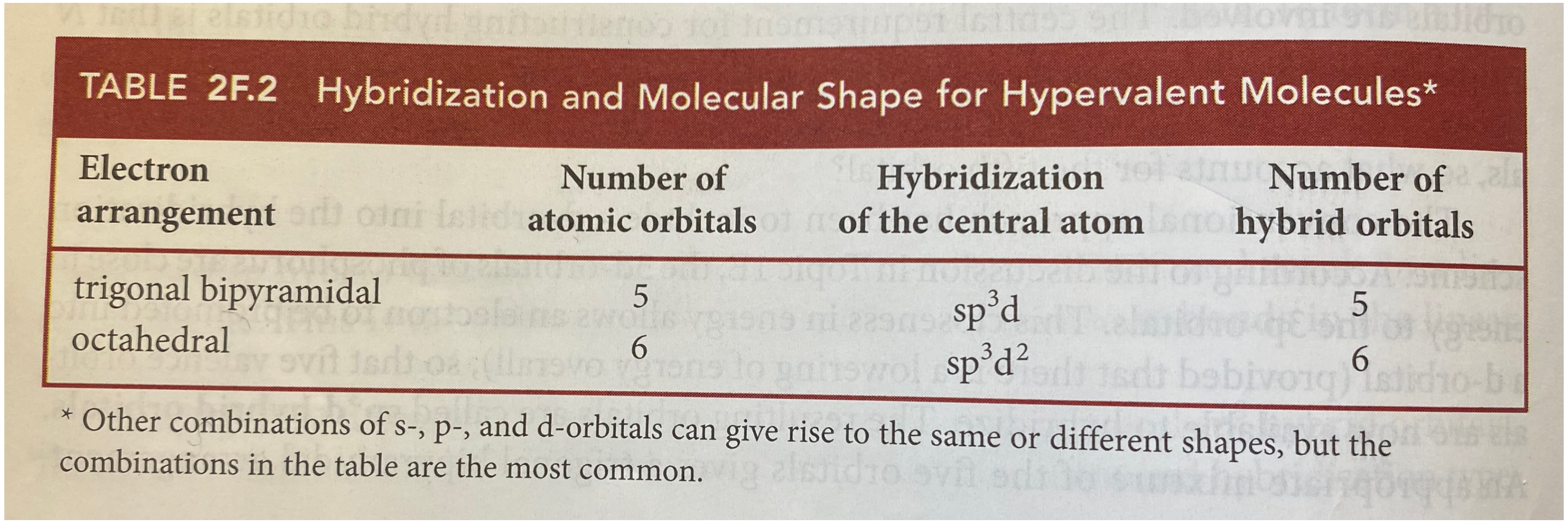


TABLE 2F.2 Hybridization and Molecular Shape for Hypervalent Molecules*

Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

* Other combinations of s-, p-, and d-orbitals can give rise to the same or different shapes, but the combinations in the table are the most common.

- **This type of hybridization only occurs in Period 3 and later**

2F.3 Valence-bond theory and hypervalent compounds

Alternative approach to hypervalency

- Approach 1 includes d-orbitals
- An alternative is to view compounds as extremes of ionic-covalent character (see Topic 2C).

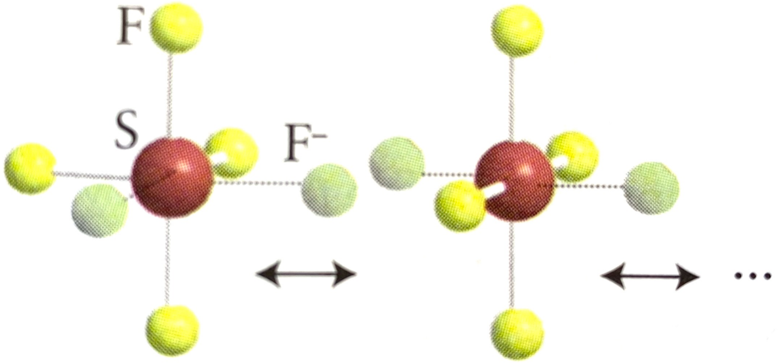


Figure 2F.12 (new book)

The structure of SF_6 can be accounted for by allowing for resonance between 15 structures of the form $(SF_4^{2+})(F^-)_2$, two of which are shown here.

Twelve of these structures have the F^- ions in the *cis* positions; the remaining three have the F^- ions in the *trans* positions.

Which model is more accurate? Would need to run calculations!

2F.3 Valence-bond theory and hypervalent compounds

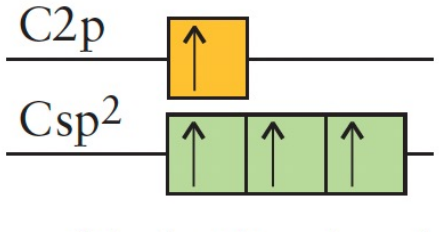
Summary

The bonding in hypervalent compounds can be described in two ways: hybridization schemes that incorporate d-orbitals and the use of ionic-covalent resonance.

Characteristics of Multiple Bonds

Topic 2F.4

2F.4 Characteristics of multiple bonds



Alkenes: Ethene (ethylene)

- Each carbon makes three sp^2 sigma-bonds and one pi-bond.
- 120 ° angles

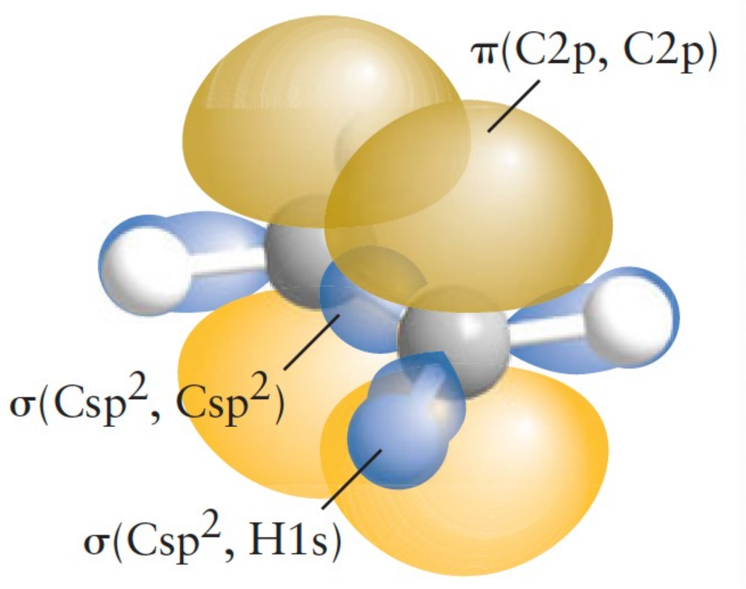


Figure 3.19 (old book)

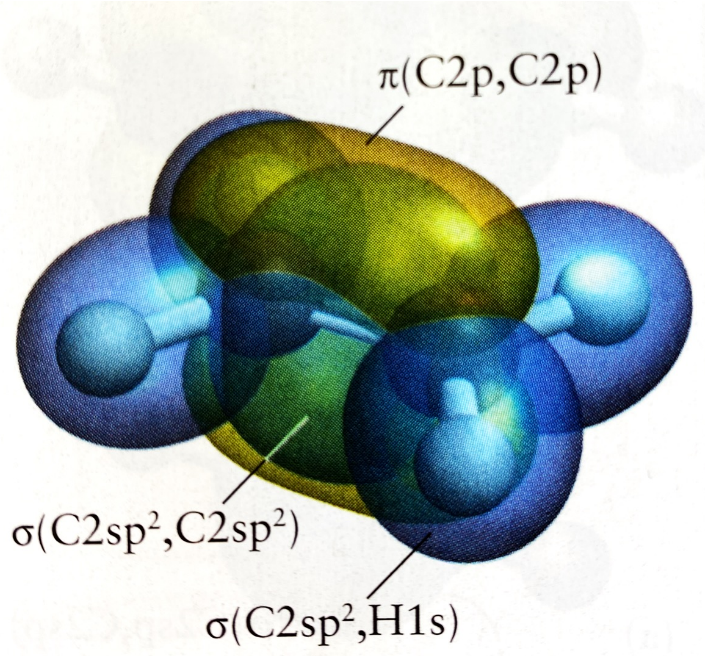


Figure 2F.13 (new book)

2F.4 Characteristics of multiple bonds

Alkenes: Ethene (ethylene)

2F.4 Characteristics of multiple bonds

Alkenes: Ethene (ethylene)

2F.4 Characteristics of multiple bonds

Benzene

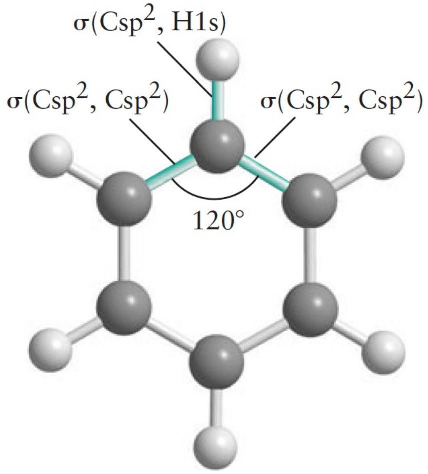


Figure 2F.14 (new book):

The framework of sigma-bonds in benzene.

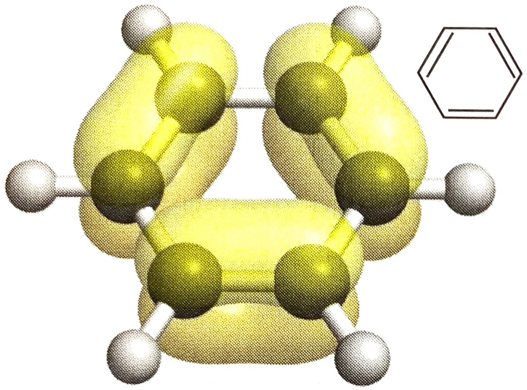


Figure 2F.15 (new book):

Unhybridized 2p-orbitals can form a pi-bond with either of their immediate neighbours. Two arrangements possible, one shown here.

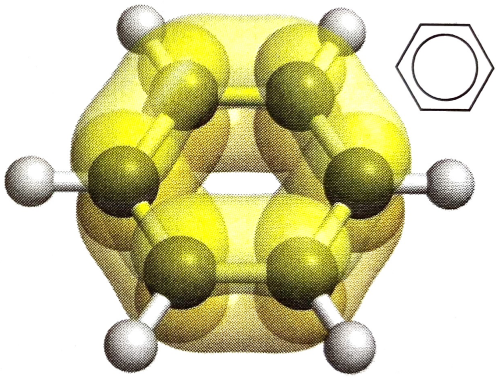


Figure 2F.16 (new book):

Resonance between two structures (one shown in Figure 2F.15) results in double doughnut-shaped cloud above and below the plane of the ring.

2F.4 Characteristics of multiple bonds

Rotation around double bonds

- Double bonds prevent one part of a molecule from rotating relative to another part.
- Double bond hold molecules flat.
- 2p-orbital overlap in ethene is best if all six atoms are in the same plane. In order for the molecule to rotate about the double bond, the π-bond would need to break and re-form.

2F.4 Characteristics of multiple bonds

Alkynes

- Each carbon makes two sp sigma-bonds and two pi-bonds.
- 180 ° angles

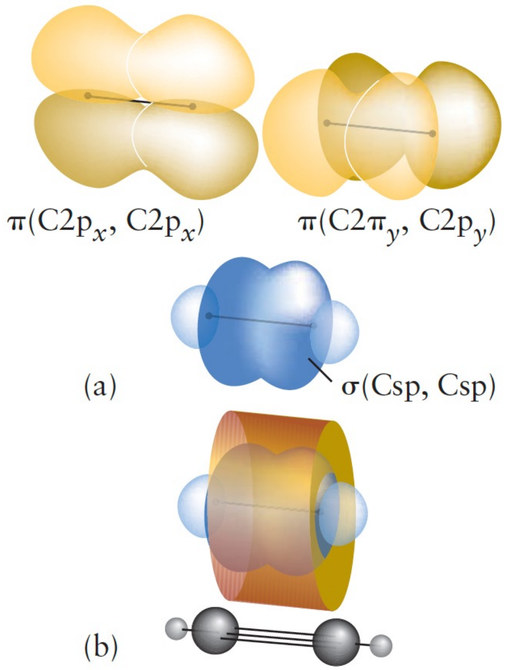


Figure 3.23 (old book)

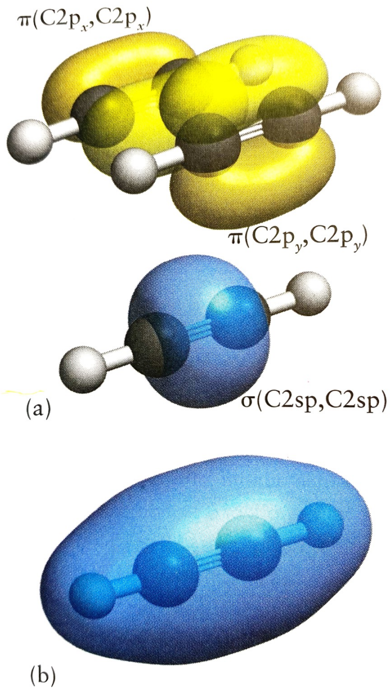


Figure 2F.17 (new book)

2F.4 Characteristics of multiple bonds

Example 2F.1 Accounting for the structure of a molecule with multiple bonds

- Account for the structure of a formic acid molecule (methanoic acid, HCOOH) in terms of hybrid orbitals, bond angles, and σ- and π-bonds. The C atom is attached to an H atom, a terminal O atom, and an –OH group.

2F.4 Characteristics of multiple bonds

Example 2F.1 Accounting for the structure of a molecule with multiple bonds

2F.4 Characteristics of multiple bonds

Summary

Multiple bonds are formed when an atom forms a σ-bond by using an sp or sp^2 hybrid orbital and one or more π-bonds by using unhybridized p-orbitals. The side-by-side overlap that forms a π-bond makes a molecule resistant to twisting, results in bonds that are weaker than σ-bonds, and prevents atoms with large radii from forming multiple bonds.

The skills you have mastered are the ability to

- ☐ Describe the difference between σ- and π-bonds and identify the composition of single, double, and triple bonds.
- ☐ Account for the occurrence and significance of promotion.
- ☐ Describe the formation of hybrid orbitals from the mixing of atomic orbitals.
- ☐ Account for the structure of a molecule in terms of hybrid orbitals and σ- and π-bonds.
- ☐ Account for hypervalent compounds by using the d-orbital hybridization and ionic-covalent resonance models.
- ☐ Explain the torsional rigidity of double bonds between atoms.

Summary: You have learned that according to valence-bond theory, a covalent bond forms when electrons in atomic orbitals pair their spins and the orbitals overlap. You have learned that there are two main types of covalent bonds (σ and π) and that electron promotion occurs if the increased number of bonds that can form repays the energy investment. Finally, You have encountered the concepts of hybridization, which enables the description of bond formation to be matched to the observed molecular shape, and the two alternative approaches to the desription of bonding in hypervalent molecules.