

Bonding and Molecular Structure - PART 2 - Valence Bond Theory and Hybridization

1. Understand and be able to describe the Valence Bond Theory description of covalent bond formation.
2. Understand and be able to describe what is meant by orbital hybridization and hybrid orbitals. Be able to identify the hybridization of an atom in a molecule or polyatomic ion and the orbitals used to form hybrid orbitals.
3. Understand and be able to draw orbital diagrams for atoms before and after hybridization.
4. Understand and be able to describe the difference between sigma (σ) and pi (π) bonds and how they are formed.
5. Understand and be able to describe why pi bonding leads to cis-trans isomerism.

Valence Bond Theory - Description

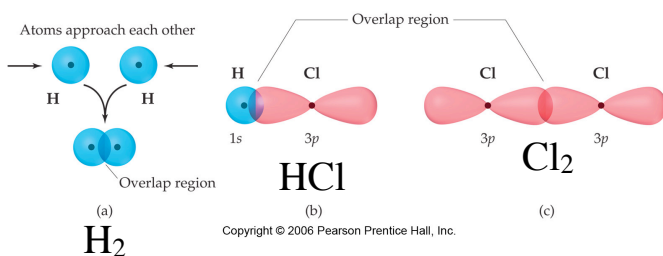
When a covalent bond is formed, there is shared electron density between the nuclei of the bonded atoms.

The simultaneous attraction of the shared electron density for both nuclei holds the atoms together, forming a covalent bond.

In valence bond theory, the shared electron density is described as occurring when a valence orbital from one atom overlaps with a valence orbital from another atom.

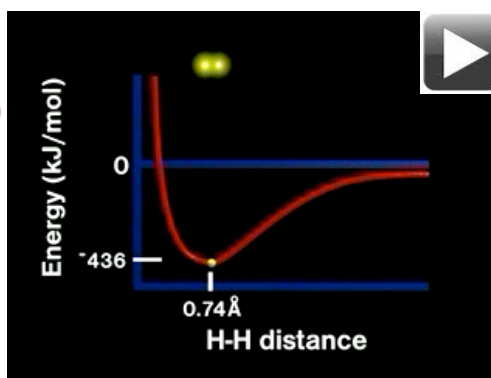
Two electrons with opposite spin are shared in the overlap region, forming a covalent bond.

The greater the extent of orbital overlap, the stronger the bond.



Formation of sigma (σ) bonds in H_2 , HCl and Cl_2 .

A σ bond is formed when the electron density is located along the inter-nuclear axis. Single bonds are always σ bonds.



Valence Bond Theory Description of Bond Formation in H₂

- The electron configuration of hydrogen is 1s¹. Each hydrogen atom has an unpaired electron in its valence 1s orbital.
- As the two hydrogen atoms approach each other, their 1s orbitals begin to merge (overlap). Electron density builds up in this overlap region where two valence electrons with opposite spin are shared, forming a sigma bond.
- As the two H atoms come closer and closer together, the overlap between the 1s orbitals increases and the potential energy of the system decreases to a minimum and then starts to increase as the electrostatic repulsion between the two nuclei starts to become significant at short internuclear distances.
- The internuclear distance at the minimum potential energy corresponds to the observed bond length.
- The energy released (exothermic process) as the bond is formed corresponds to the bond energy (or bond enthalpy). An input of this amount of energy is required to break the bond (endothermic process) that has formed.

Question: The formation of other simple diatomic molecules with single bonds, such as HF and Br₂ can be described in a similar way as the formation of H₂.

In the case of HF, which atomic orbitals are used to form the bond?

In the case of Br₂, which atomic orbitals are used to form the bond?

How do we Explain the Bonding in Covalent Molecules To Give the Correct Shapes Predicted by VSEPR Theory?

How can we use valence bond theory to adequately describe the bonding for polyatomic molecules or ions having electron-domain geometries such as linear, trigonal planar, tetrahedral, trigonal bipyramid or octahedral? Overlap of atomic s, p and d orbitals will not yield structures with these geometries (except linear)! To explain bonding for these geometries, valence bond theory uses the concept of **orbital hybridization**.

Orbital Hybridization (proposed by Linus Pauling): To understand this concept, we need to remember that the atomic s, p, d and f orbitals are described by mathematical functions. These functions are actually probability distributions, giving the probability of finding an electron with a specific energy in an atom.

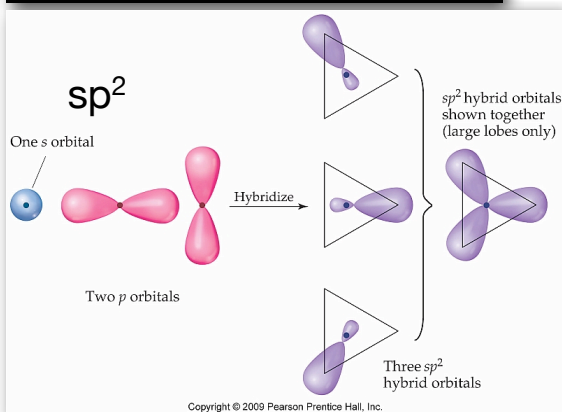
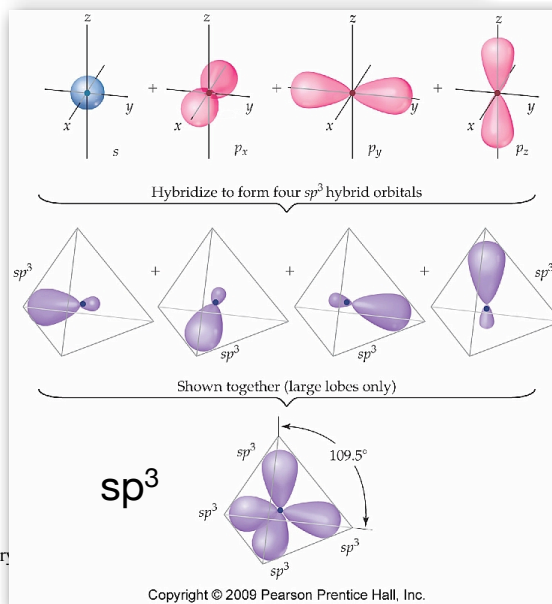
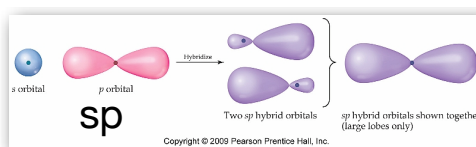
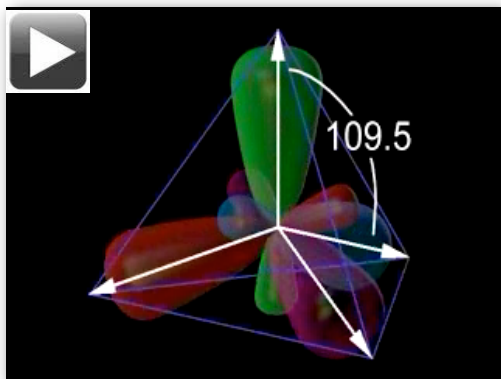
Orbital hybridization is simply the mathematical combination of two or more atomic orbitals (s, p, or d) to form new hybrid orbitals that are used for bonding.

Valence Bond Theory (Hybridization)

Central atoms **do not use** atomic (s, p, d, f) orbitals to form **sigma bonds**.

Central atoms mix **or hybridize** their **valence atomic orbitals** to form new bonding orbitals called hybrid orbitals.

Hybridization - sp, and sp² and sp³ OVERVIEW



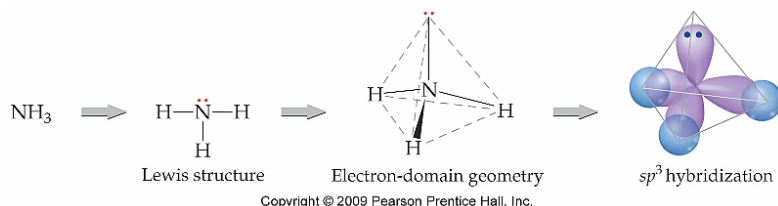
Hybrid Orbital Formation: Orbital Hybridization Basics

1. When forming hybrid orbitals, ***the number of hybrid orbitals formed equals the number of orbitals mathematically combined or "mixed"***. For example, if an s orbital is combined with a p orbital the result is two "sp" hybrid orbitals.
2. Hybrid orbitals have ***orientations around the central atom that correspond to the electron-domain geometry predicted by the VSEPR Theory***.
3. The hybrid orbitals have ***shapes that maximize orbital overlap*** with another atoms orbitals. This increases bond strength.
4. ***Hybrid orbital overlap*** between atoms ***creates SIGMA bonds***.

Correlation Between VSEPR Theory and Hybridization

The logical sequence to determine hybridization is:

Formula → Lewis Structure → VSEPR Electron Domain Geometry → Hybridization



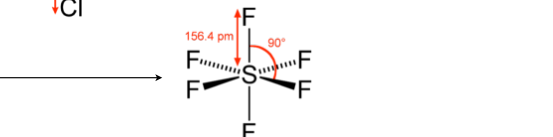
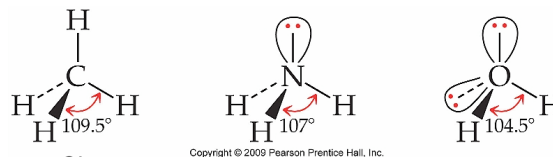
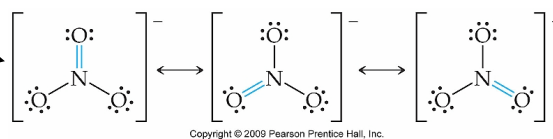
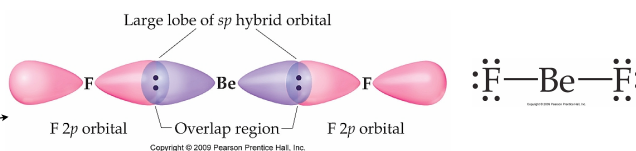
There is a direct correlation between VSEPR electron domain geometry and the hybridization of the central atom.

VSEPR Electron Domain Geometry	Hybridization	Example
Linear	sp	BeF_2
Trigonal Planer	sp^2	NO_3^-
Tetrahedral	sp^3	CH_4
Trigonal Bipyramidal	sp^3d	PCl_5
Octahedral	sp^3d^2	SF_6

Correlation Between VSEPR Theory and Hybridization

TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s, p	Two sp	Linear 180°	$\text{BeF}_2, \text{HgCl}_2$
s, p, p	Three sp^2	Trigonal planar 120°	BF_3, SO_3
s, p, p, p	Four sp^3	Tetrahedral 109.5°	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$
s, p, p, p, d	Five sp^3d	Trigonal bipyramidal $120^\circ, 90^\circ$	$\text{PF}_5, \text{SF}_6, \text{BrF}_5$
s, p, p, p, d, d	Six sp^3d^2	Octahedral 90°	$\text{SF}_6, \text{ClF}_3, \text{XeF}_4, \text{PF}_6^-$

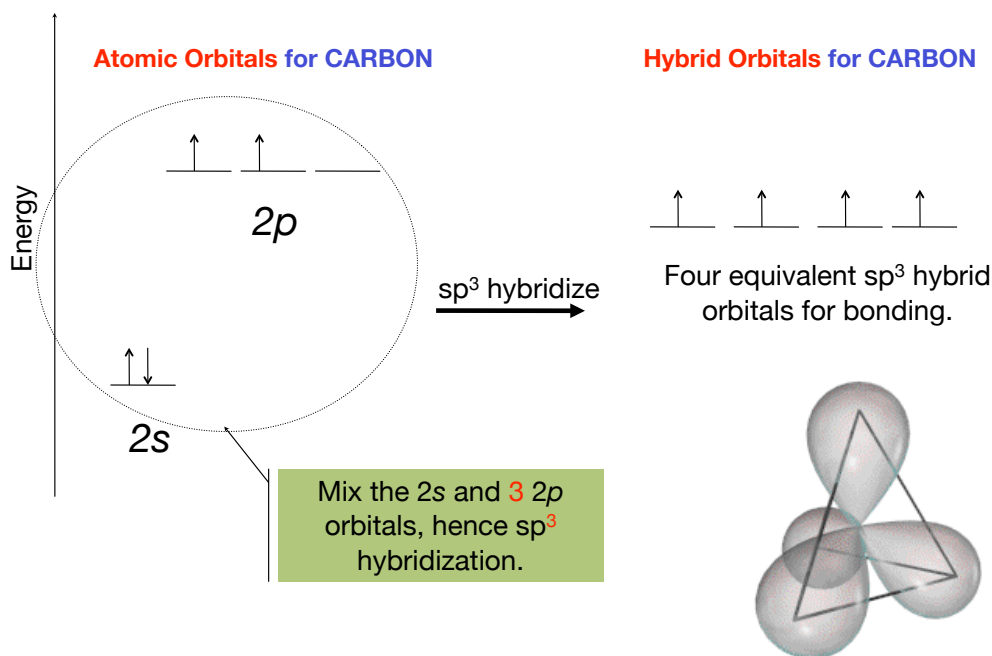


Valence Bond Theory & Hybridization

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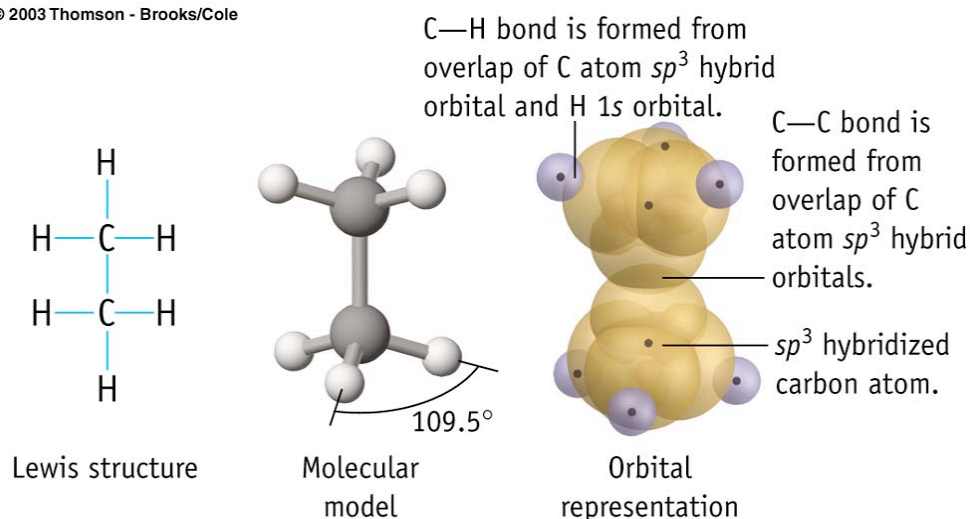
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Energies of Hybridization - sp^3 Hybridization for Carbon (Tetrahedral Electron Domain Geometry)



Carbon Hybridization in Ethane - sp^3

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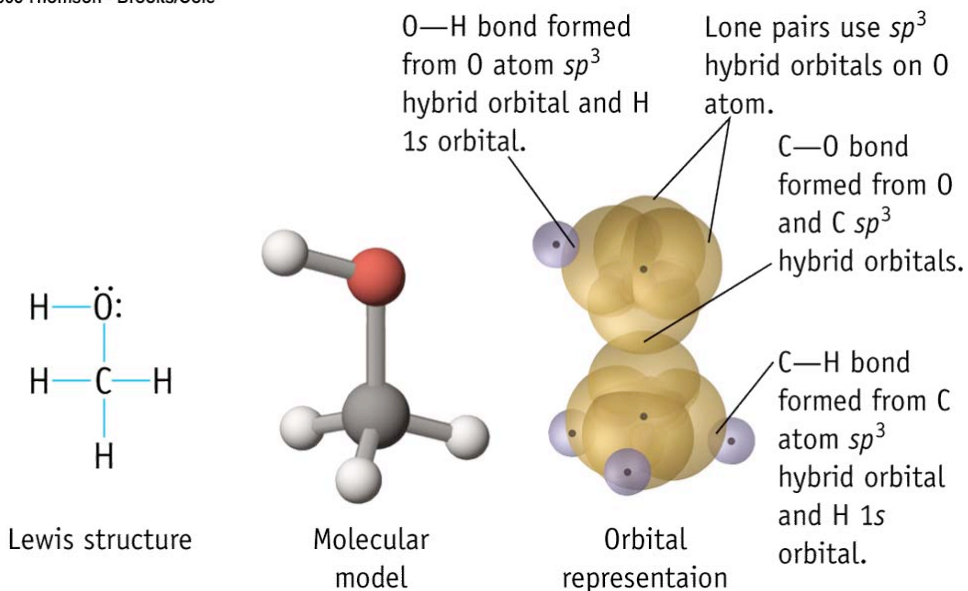
Sigma bond (σ): the first bond formed between two atoms.
All single bonds are **sigma** bonds.

Valence Bond Theory Description of Bonding in H_2O

1. What is the hybridization of the oxygen atom in water?
2. Draw the orbital energy diagram for the valence shell of the oxygen atom before and after hybridization. Show the electrons before and after hybridization. For the hybridized orbitals, indicate below each orbital whether the orbital holds a lone pair or is used to form a sigma bond.
3. Make a sketch of orbitals showing the valence bond theory description of the bonding in H_2O . Label on the sketch the orbitals used by each atom to form each bond.

Hybridization in Methanol - O sp^3 and C sp^3

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Valence Bond Theory & Hybridization

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Expanded Octets: Bonding in SF_4

1. What is the hybridization of the sulfur atom in SF_4 ?
2. Draw the orbital energy diagram for the valence shell of the sulfur atom before and after hybridization. Show the electrons before and after hybridization. For the hybridized orbitals, indicate below each orbital whether the orbital holds a lone pair or is used to form a sigma bond.

Valence Bond Theory & Hybridization

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What about MULTIPLE BONDS?

Valence Bond Theory description of Multiple Bond Formation.

1. Multiple covalent bonds (double and triple) form when more than one orbital from each atom overlap.
2. This additional overlap occurs using **UNHYBRIDIZED atomic orbitals**, not hybrid orbitals. This overlap is called a pi (π) bond formation.

Sigma bond (σ): the first bond formed between two atoms.

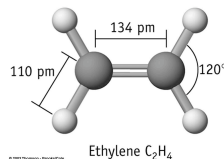
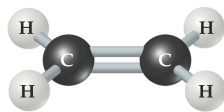
All single bonds are **sigma** bonds.

Pi (π) bond: the second or third bond formed between two atoms.

Single bond = sigma bond (σ)

Double bond = sigma + pi ($\sigma + \pi$)

Triple bond = sigma + pi + pi ($\sigma + \pi + \pi$)



A Double Bond - sp^2 Hybridization of Carbon (Trigonal Planar Electron Domain Geometry, $H_2C=CH_2$)

Energy

One p orbital is not mixed on each carbon.

Three equivalent sp^2 hybrid orbitals.

The three sp^2 hybrid orbitals form sigma bonds with H or the other carbon.

Two lobes of one π bond

The **unhybridized p orbital** from each carbon overlap to form the pi bond.

Complete Bonding Description in H₂CO

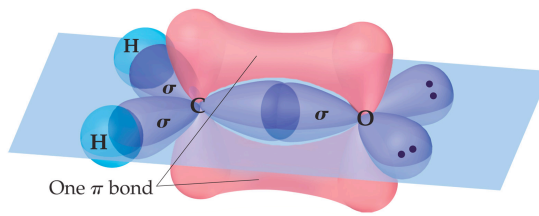
The bonding in formaldehyde can be explained by sp^2 hybridization.

The H-C sigma bonds come from overlap of the $1s$ orbital of H with a sp^2 hybrid orbital on carbon.

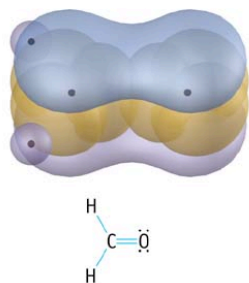
The C-O sigma bond comes from overlap of a sp^2 hybrid orbital on C with another sp^2 hybrid orbital on oxygen.

(O is sp^2 hybridized as well)

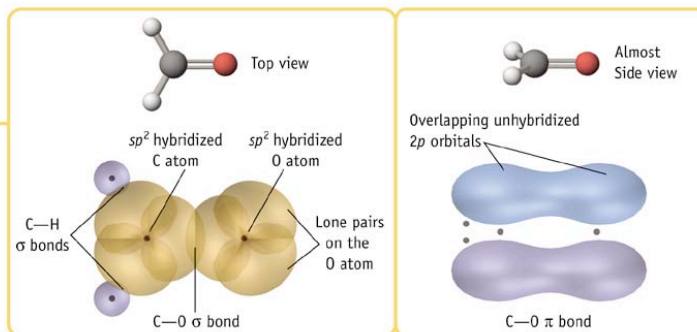
The C-O pi bond comes from overlap of a $2p$ atomic orbital on C with another $2p$ atomic orbital on oxygen.



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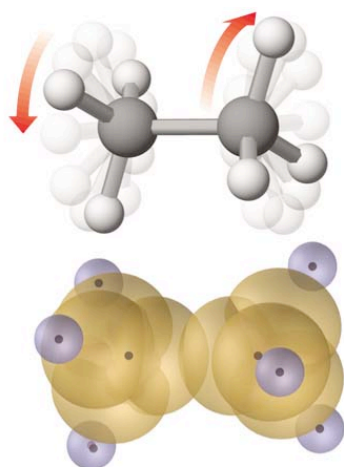
(a) Lewis structure and bonding of formaldehyde, CH₂O.



(b) The C—H σ bonds are formed by overlap of C atom sp^2 hybrid orbitals with H atom $1s$ orbitals. The σ bond between C and O atoms arises from overlap of sp^2 orbitals.

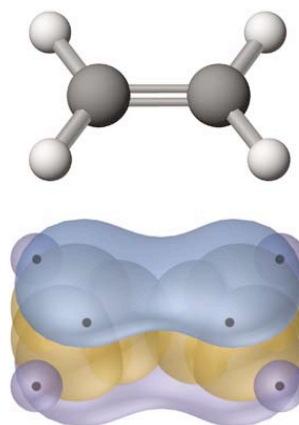
(c) The C—O π bond comes from the side-by-side overlap of p orbitals on the two atoms.

Details: Pi Bonding Restricts Rotation Around the Inter-nuclear Axis at Room Temperature

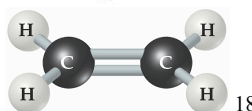


(a) Free rotation can occur around the axis of a single (σ) bond.

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(b) In contrast, rotation is severely restricted around double bonds because doing so would break the π bond, a process generally requiring a great deal of energy.

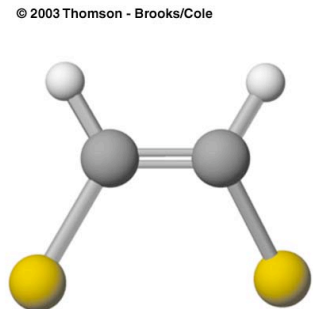


Restricted Rotation Give cis- and trans- Isomers

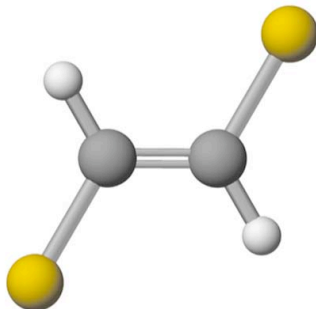
Geometric Isomers: Geometric isomers are compounds that have the same molecular formula and order of attachment of the atoms, but different special arrangement of the atoms relative to each other. Restricted rotation around a pi bond results in a type of geometric isomerism known as cis-trans isomerism.

These are two DIFFERENT MOLECULES that do not interconvert. They exist separately and have different physical properties.

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cis-1,2-dichloroethylene



trans-1,2-dichloroethylene

cis isomer: like atoms are located *on the same side* of the double bond.

Density: 1.28 g/mL Melting pt. -80.5 °C

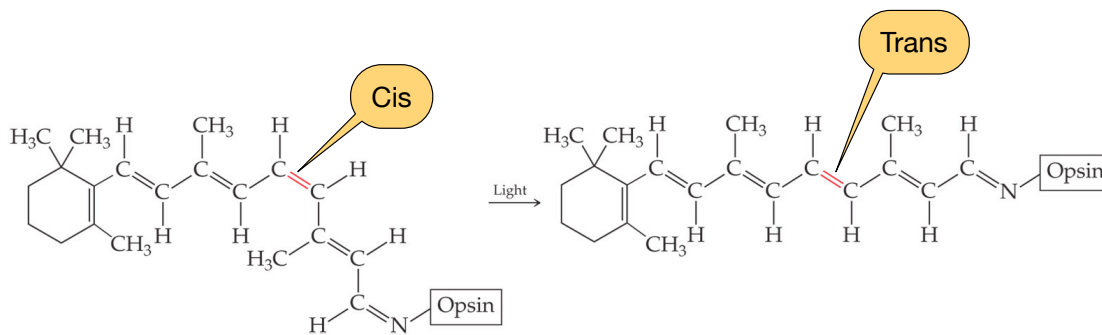
Boiling pt: 60.3 °C Dipole: 1.9 D

trans isomer: like atoms are located *on opposite sides* of the double bond.

Density: 1.26 g/mL Melting pt: -49.5 °C

Boiling pt: 47.5 °C Dipole: 0 D

cis- and trans- Isomers: Vision



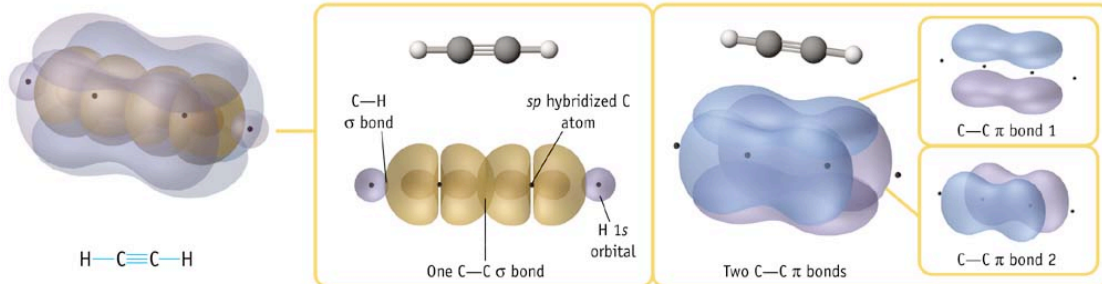
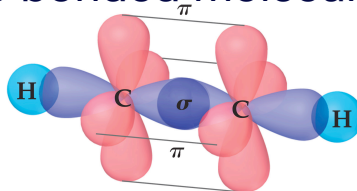
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cis isomer:
rhodopsin in the normal or "relaxed" state.

trans isomer:
rhodopsin after light absorption. Molecular geometry is changed to trans-form. This stimulates our nervous system to "see" the light.

Acetylene, HCCH, a triple bonded molecule

Acetylene has two pi bonds. They are formed from atomic p orbitals on each carbon.



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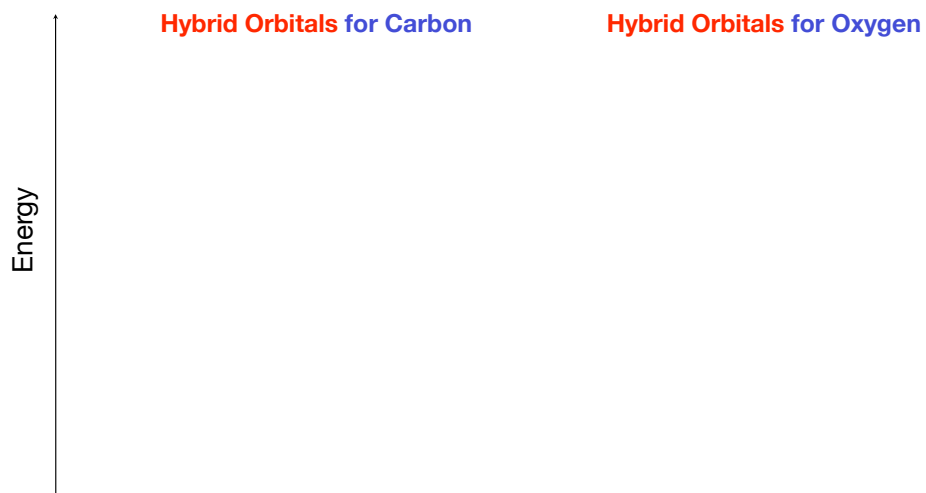
$\uparrow\uparrow$ Two unhybridized p orbitals. Used for π bonding in C_2H_2 .

$\uparrow\uparrow$ Two sp hybrid orbitals. Used for C—H and C—C σ bonding in C_2H_2 .

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Hybridization schemes - sp hybridization of carbon monoxide, CO

Here we need to consider formal charge on each atom!

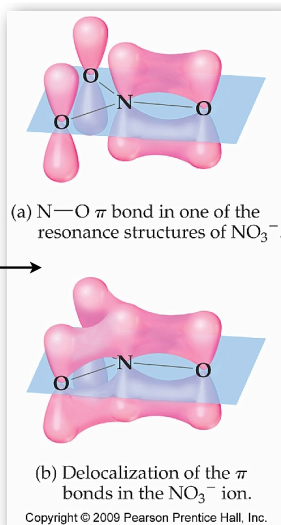
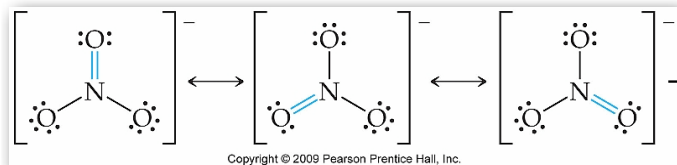
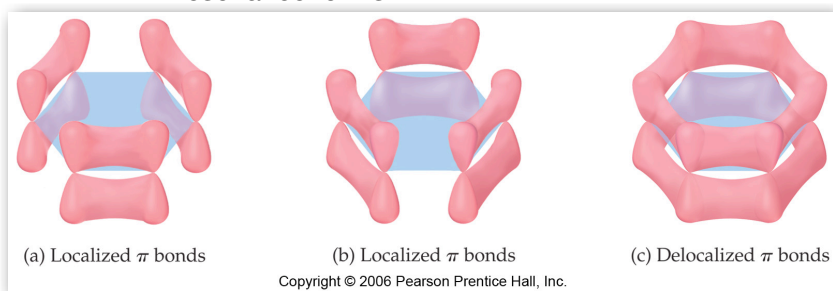


Details: Delocalized pi Bonds - Resonance!

Often when we have resonance the position of the pi bonds are not fixed but delocalized through the resonance structures. A classic example is benzene, C_6H_6 .

Resonance forms

Resonance hybrid



Which of the following molecules or ions can exhibit delocalized bonding:
 SO_3^{2-} , H_2CO , O_3 , NH_4^+ ?

Valence Bond Theory & Hybridization

Details: Pi Bonding with d Orbitals

1. What is the hybridization of sulfur in SO_4^{2-} ?
(Draw an expanded octet to minimize formal charges.)
2. Draw the orbital ENERGY diagram of the sulfur atom after hybridization. Show the arrangement of valence electrons for sulfur after hybridization. For the orbitals, indicate below each orbital whether the orbital holds a lone pair or is used to form a sigma or pi bond with oxygen.

Summary of what you should be able to do:

1. Draw a correct Lewis Structure

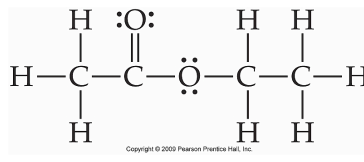
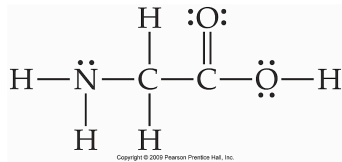
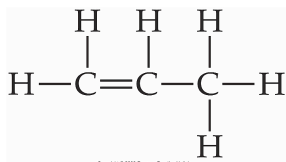
- Expand Octets when necessary to reduce formal charges.
- Predict if there will be resonance:
 - Draw all resonance forms.
 - Use formal charges to predict the stability of any resonance form.
 - Combine resonance forms into a resonance hybrid.
 - Estimate the bond orders in the resonance hybrid.
 - Predict relative bond lengths and bond strengths in the hybrid.
- For any Central Atom:
 - Predict Electron Geometry - Name.
 - Predict Molecular Geometry - Name.
 - Predict any changes to ideal bond angles.
- Identify any polar bonds. Predict their direction and relative magnitude.
- Determine if the molecule as a whole will have a permanent dipole moment.
- Predict Orbital Hybridization of each Central Atom or Multiply Bonded Atom.
 - Match the hybridization and bonding to the LEWIS STRUCTURE!
 - Determine what orbitals overlap to form each sigma (σ) bond.
 - Determine what orbitals overlap to form each pi (π) bond.
 - Draw an energy level diagram for the hybrid orbitals.

2. Draw the molecule in 3D.

Problems

1. For each Lewis Structure

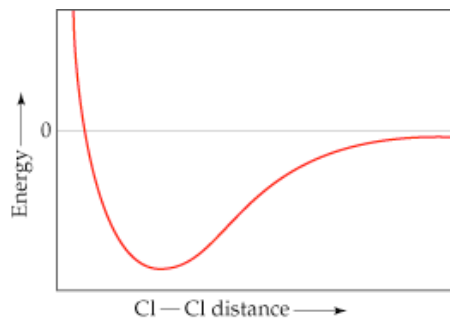
- Give the electron domain geometry and the molecular geometry of each central atom.
- Predict the ideal bond angles and if there are any deviations.
- Identify each bond as polar or nonpolar.
- Determine if the molecule has a permanent dipole moment.
- Give the hybridization of each central atom and each atom with multiple bonds.
- Describe the bonding as sigma and/or pi.
- Describe what orbitals are used to make each sigma and/or pi bond.
- In what orbitals are any lone pairs located?



Problems

Text Problem 9.5: The plot below shows the potential energy of two Cl atoms as a function of the distance between them.

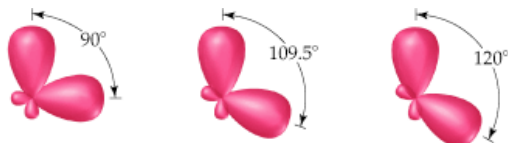
1. To what does an energy of zero correspond in this diagram?
2. According to the valence-bond model, why does the energy decrease as the Cl atoms move from a large separation to a smaller one?
3. What is the significance of the Cl-Cl distance at the minimum point in the plot?
4. Why does the energy rise at Cl-Cl distances less than that at the minimum point in the plot?
5. Label the part of the plot that corresponds to the bond energy of Cl_2 .



Problems from Textbook

Text Problem 9.6:

Shown below are three pairs of hybrid orbitals, with each set at a characteristic angle. For each pair, determine the type or types of hybridization that could lead to hybrid orbitals at the specified angle.



Problems from Textbook

Text Problem 9.49:

(a) Draw a picture showing how two p orbitals can be combined to make a sigma bond.

(b) Sketch a π bond that is constructed from p orbitals.

(c) Which is generally the stronger, a σ bond or a π bond? Explain.

(d) Can two s orbitals make a π bond. Explain.