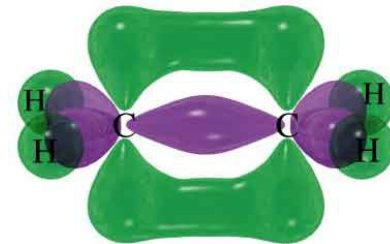


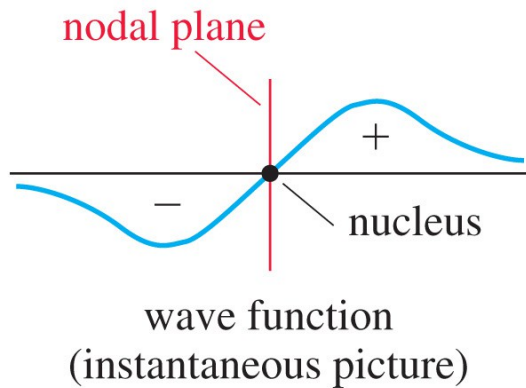
Organic Chemistry, 7th Edition
L. G. Wade, Jr.



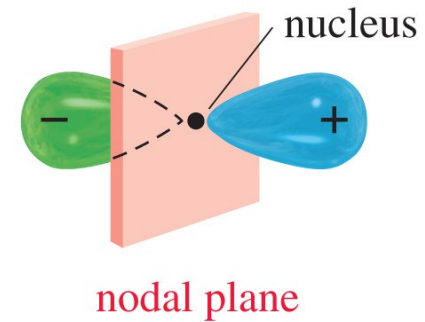
Chapter 2

Structure and Properties of Organic Molecules

Wave Properties of Electrons



represented by



- Standing wave vibrates in fixed location.
- Wave function, ψ , is a mathematical description of size, shape, and orientation.
- Amplitude may be positive or negative.
- **Node**: Amplitude is zero.

Wave Interactions

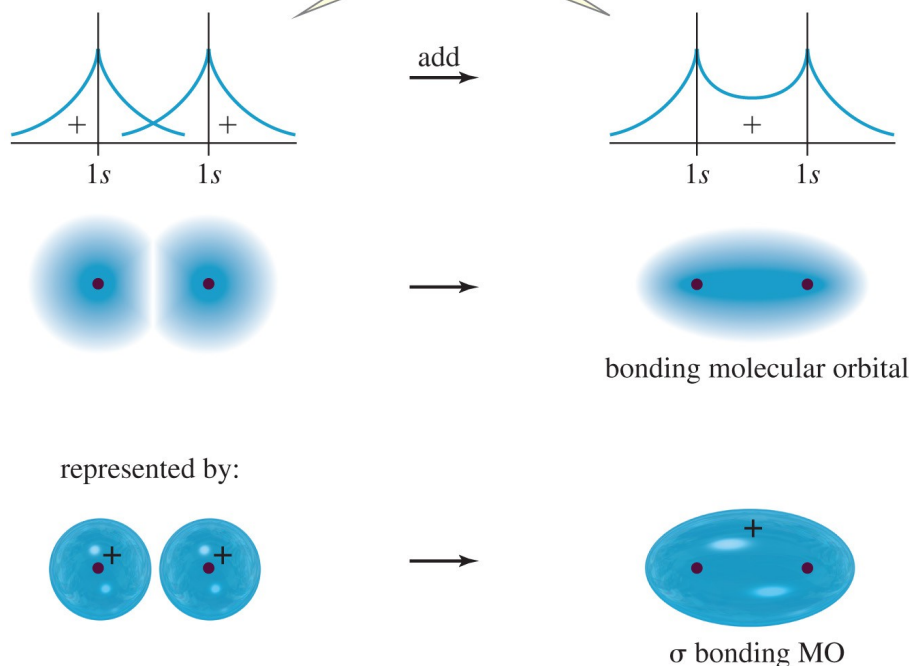
- Linear combination of atomic orbitals:
 - between different atoms is ***bond formation***.
 - on the same atom is ***hybridization***.
- Conservation of orbitals
- Waves that are in phase add together. Amplitude increases.
- Waves that are out of phase cancel out.

Sigma Bonding

- Electron density lies between the nuclei.
- A bond may be formed by $s-s$, $p-p$, $s-p$, or hybridized orbital overlaps.
- The bonding molecular orbital (MO) is lower in energy than the original atomic orbitals.
- The antibonding MO is higher in energy than the atomic orbitals.

Bonding MO

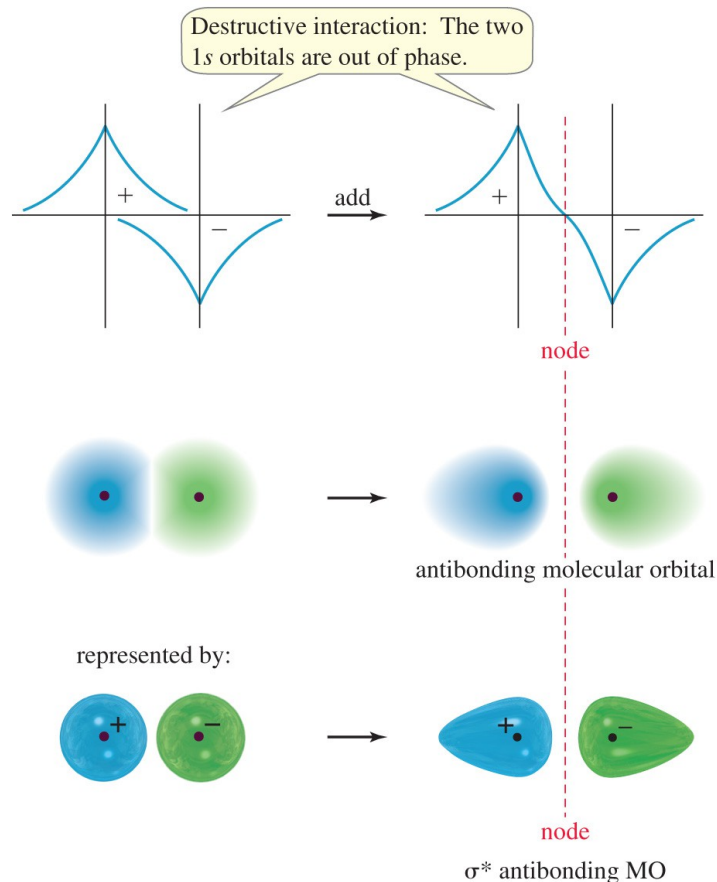
Constructive interaction: The two 1s orbitals are in phase and have the same sign.



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Formation of a σ -bonding MO: When the 1s orbitals of two hydrogen atoms overlap in phase with each other, they interact constructively to form a bonding MO.

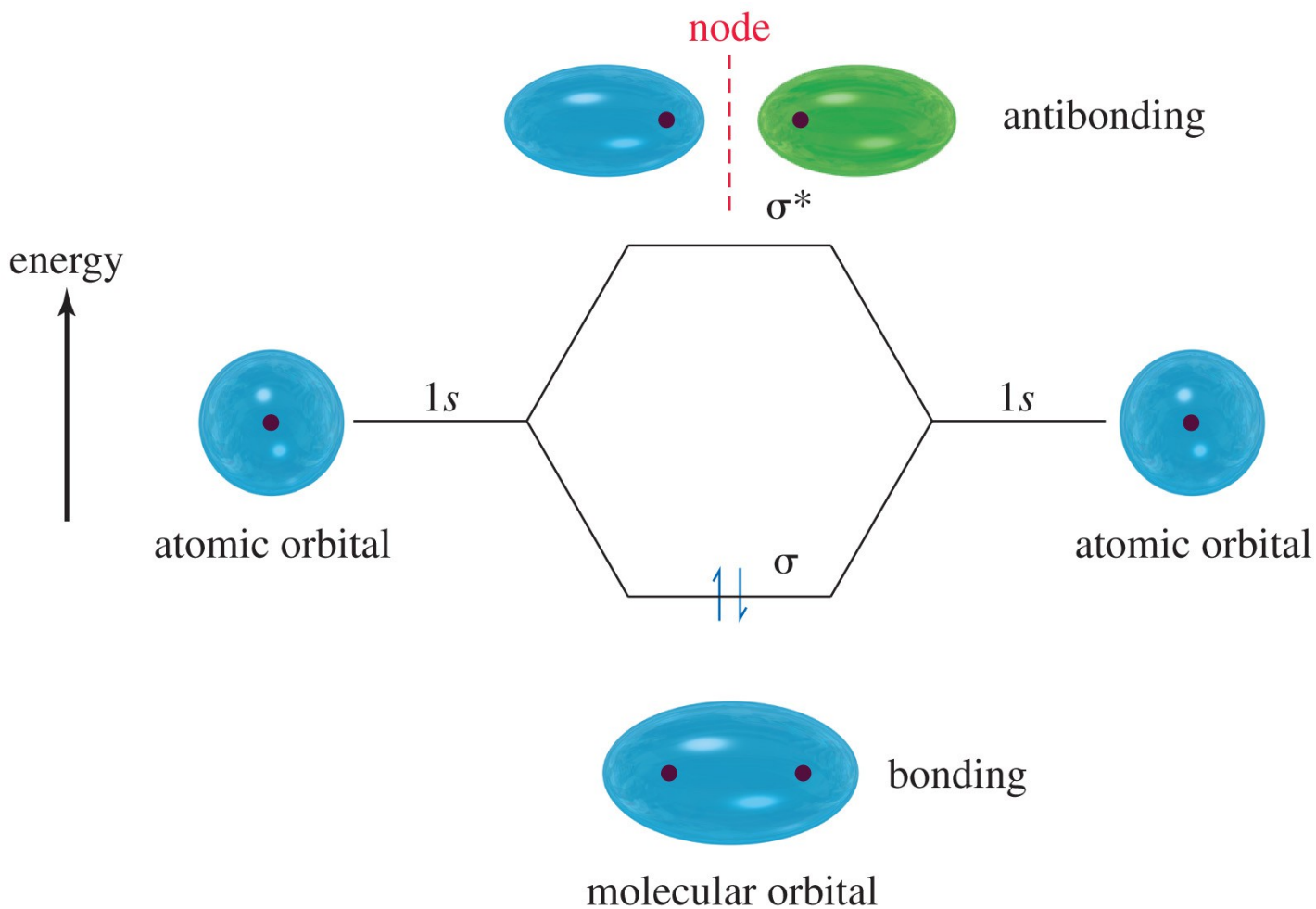
Antibonding MO



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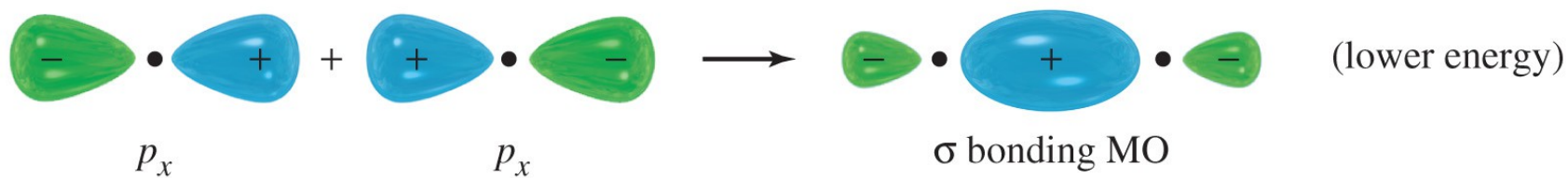
Formation of a σ^* antibonding MO: When two 1s orbitals overlap out of phase, they interact destructively to form an antibonding MO.

H₂: s—s Overlap



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Cl₂: $p-p$ Overlap



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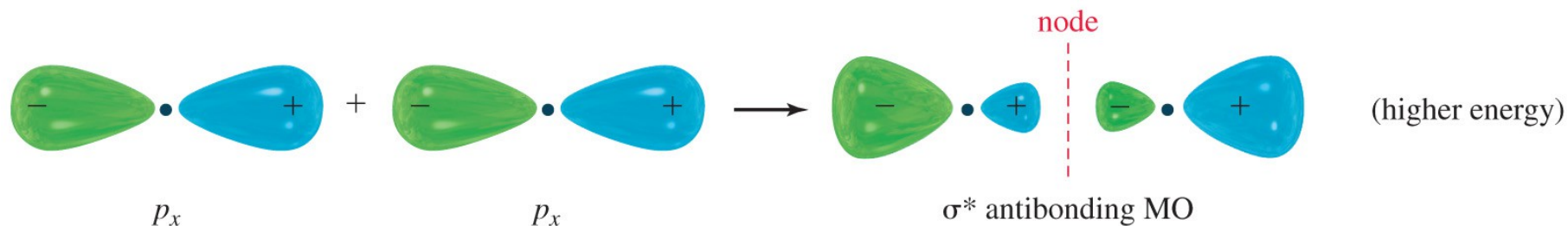
- When two p orbitals overlap along the line between the nuclei, a bonding orbital and an antibonding orbital result.
- Most of the electron density is centered along the line between the nuclei.
- This linear overlap is another type of sigma bonding MO.

Solved Problem 1

Draw the σ^* antibonding orbital that results from the destructive overlap of the two p_x orbitals just shown.

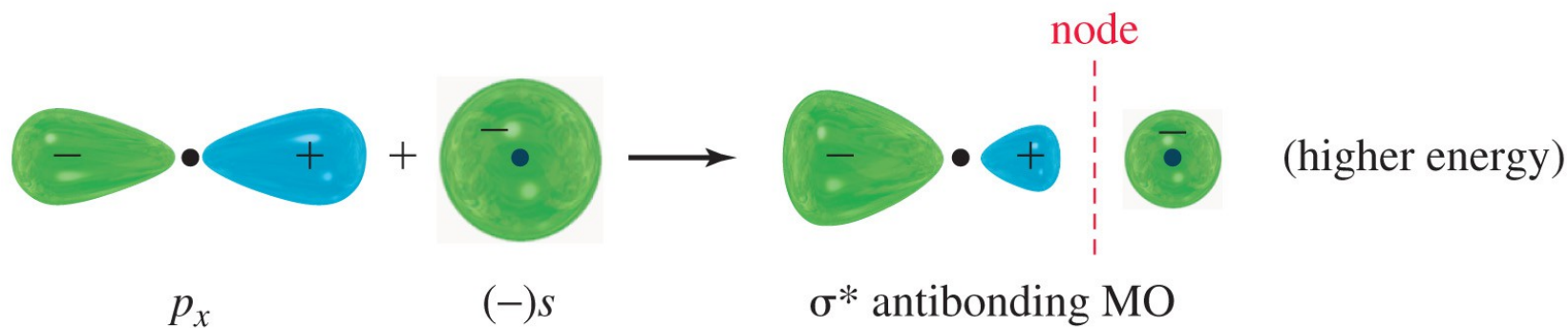
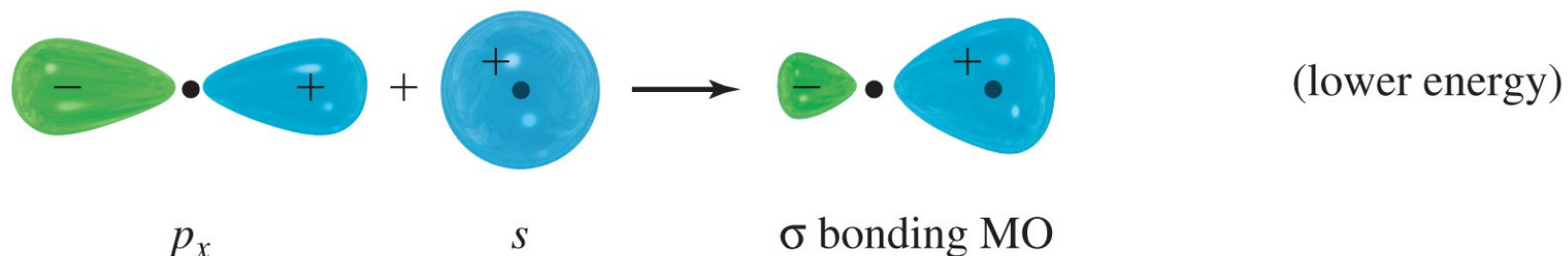
Solution

This orbital results from the destructive overlap of lobes of the two p orbitals with opposite phases. If the signs are reversed on one of the orbitals, adding the two orbitals gives an antibonding orbital with a node separating the two nuclei:



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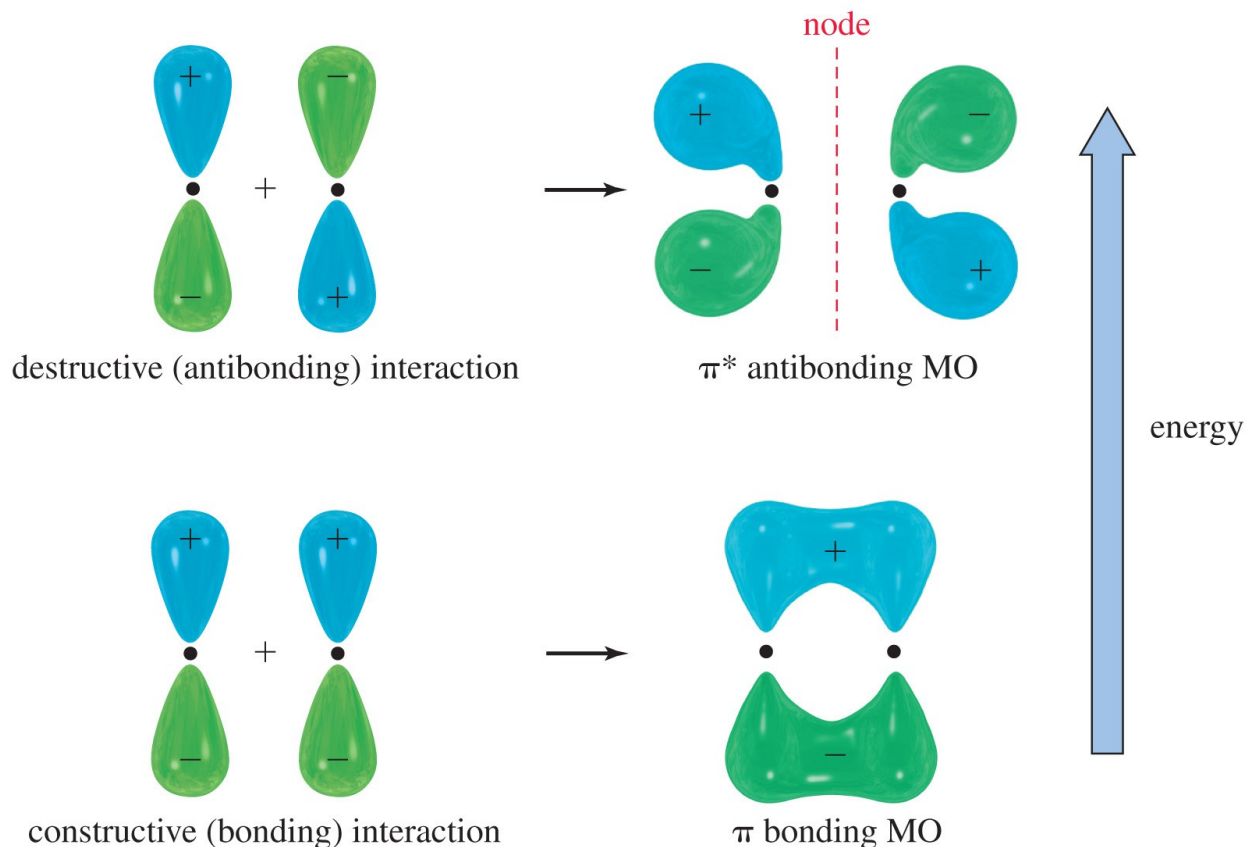
s and p Orbital Overlap



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- Overlap of an s orbital with a p orbital also gives a bonding MO and an antibonding MO.

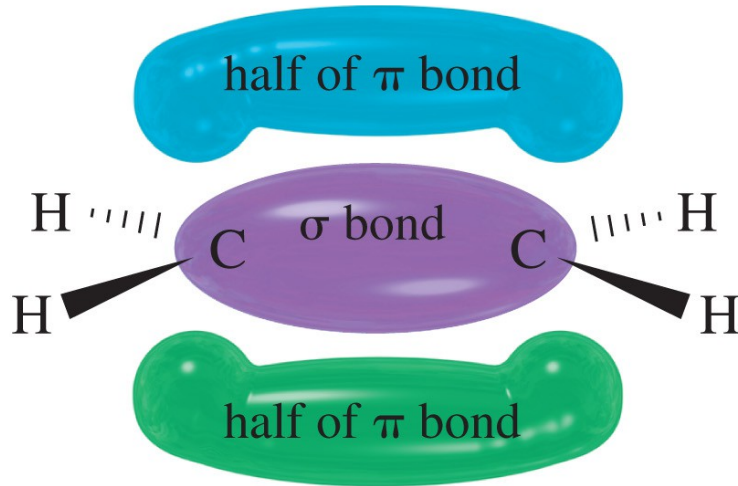
Bonding and Antibonding



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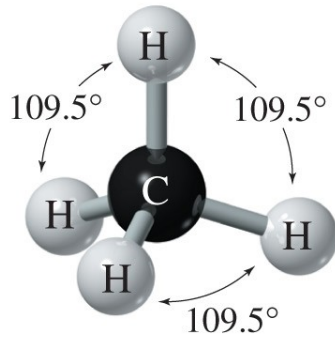
The sideways overlap of two p orbitals leads to a bonding MO and a antibonding MO. A pi bond is not as strong as most sigma bonds.

Multiple Bonds

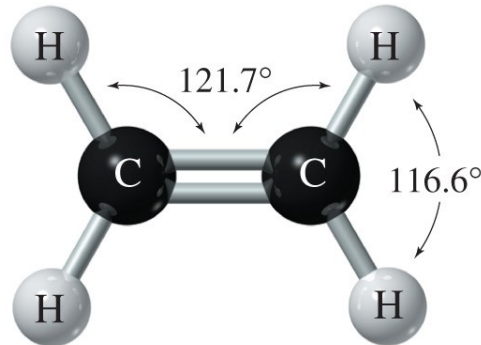


- A double bond (2 pairs of shared electrons) consists of a sigma bond and a pi bond.
- A triple bond (3 pairs of shared electrons) consists of a sigma bond and two pi bonds.

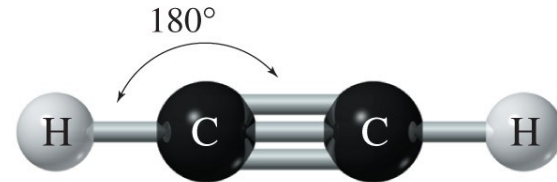
Molecular Shapes



methane, 109.5°



ethylene, close to 120°



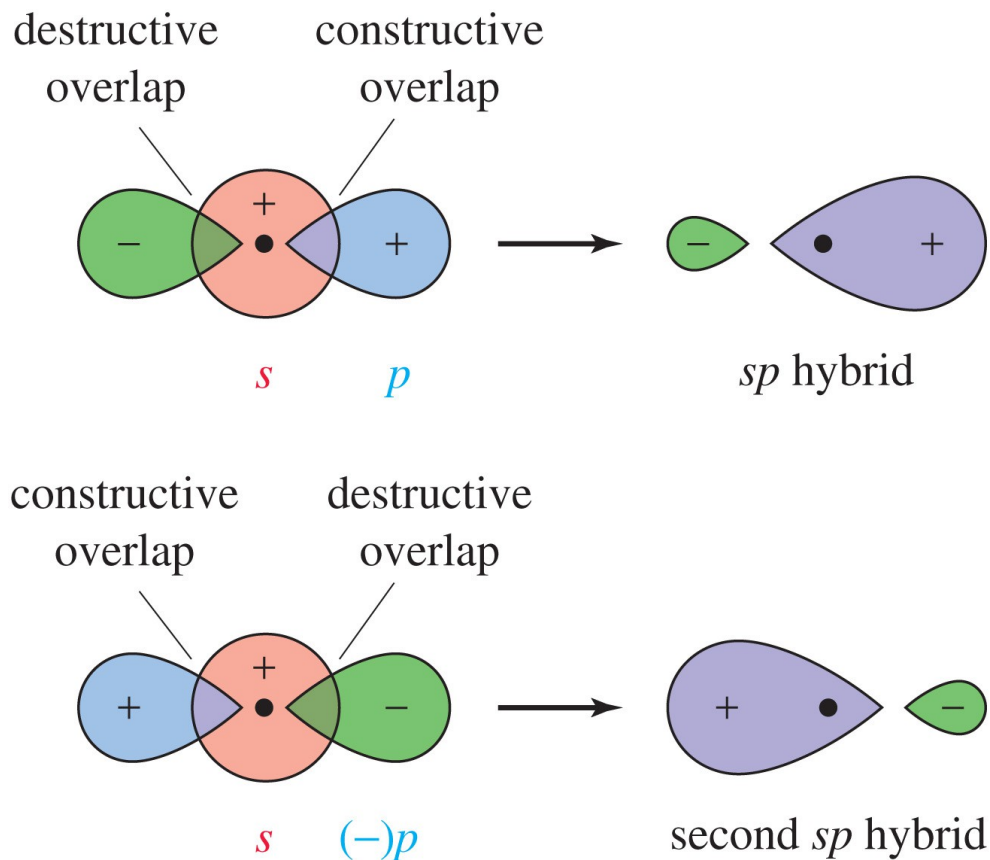
acetylene, 180°

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- Bond angles cannot be explained with simple s and p orbitals.
- Valence-shell electron-pair repulsion theory (VSEPR) is used to explain the molecular shape of molecules.
- Hybridized orbitals are lower in energy because electron pairs are farther apart.

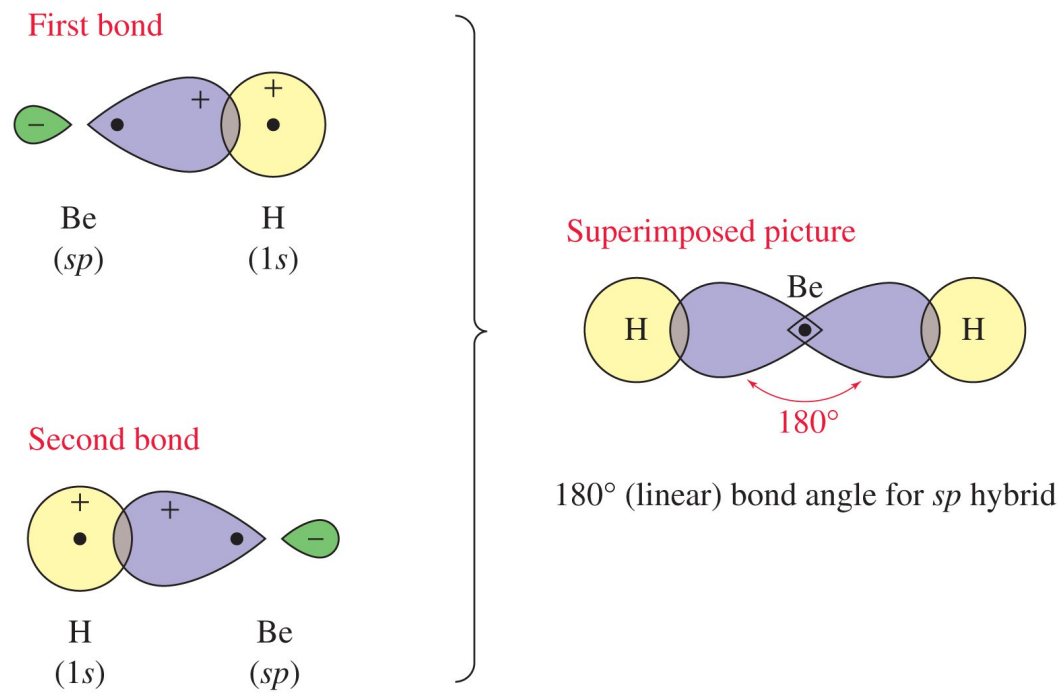
sp Hybrid Orbitals

- Have 2 VSEPR pairs.
- Linear electron pair geometry.
- 180° bond angle.



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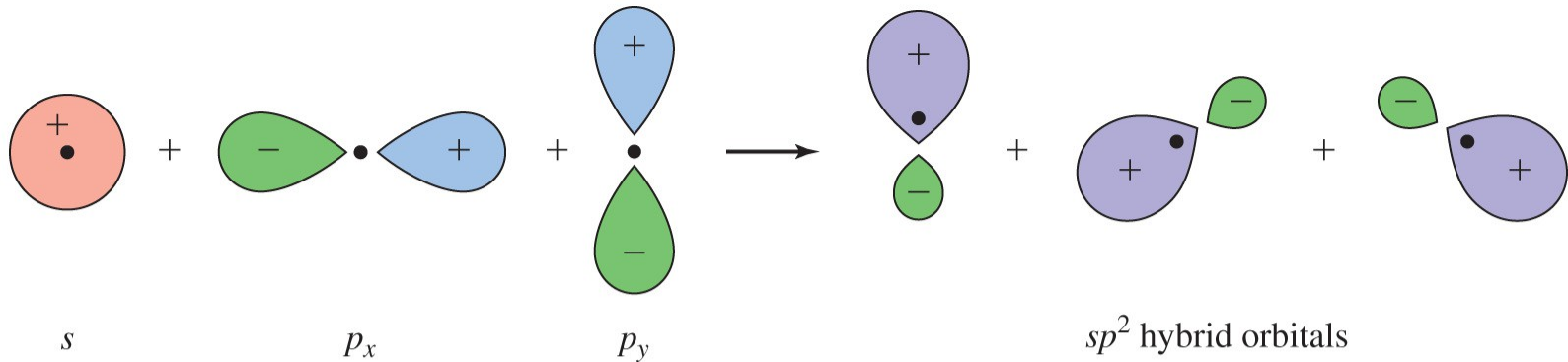
The Bonding of BeH₂



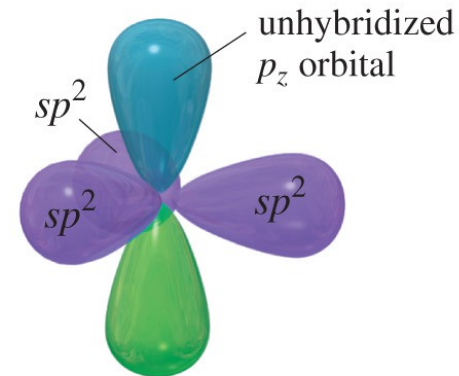
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- The bond angle in BeH₂ is 180° and the geometry is linear.

sp^2 Hybrid Orbitals



- 3 VSEPR pairs
- Trigonal planar geometry
- 120° bond angle



sp^2 hybrid carbon atom
(viewed from the side)

Solved Problem 2

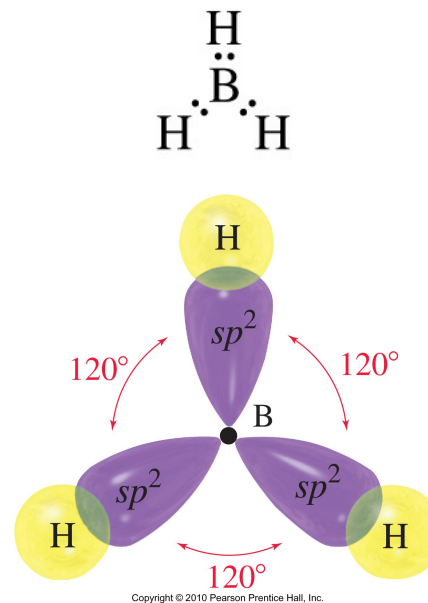
Borane (BH_3) is not stable under normal conditions, but it has been detected at low pressure.

(a) Draw the Lewis structure for borane. (b) Draw a diagram of the bonding in this molecule, and label the hybridization of each orbital. (c) Predict the H–B–H bond angle.

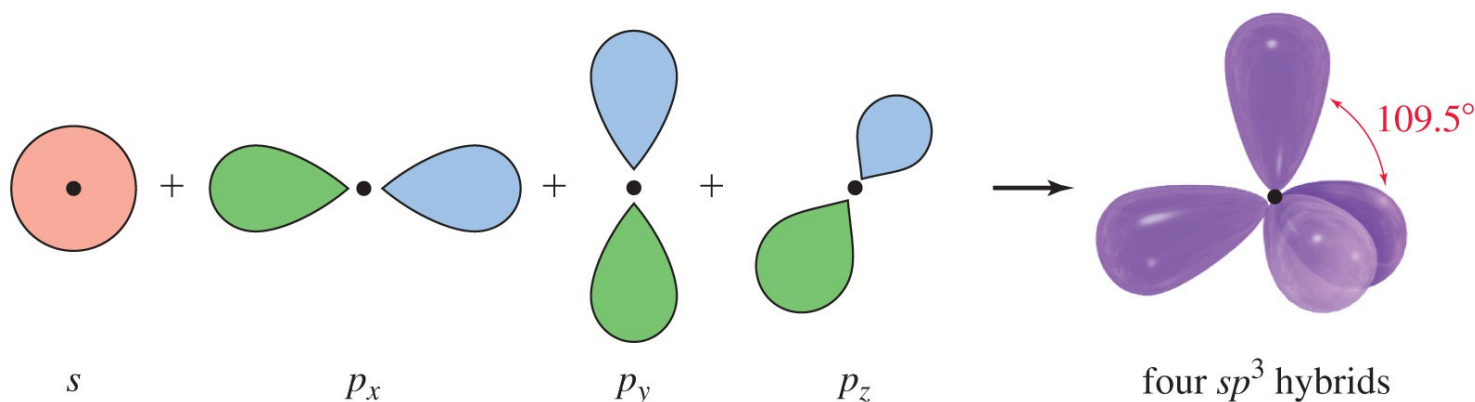
Solution

There are only six valence electrons in borane. Boron has a single bond to each of the three hydrogen atoms.

The best bonding orbitals are those that provide the greatest electron density in the bonding region while keeping the three pairs of bonding electrons as far apart as possible. Hybridization of an s orbital with two p orbitals gives three sp^2 hybrid orbitals directed 120° apart. Overlap of these orbitals with the hydrogen $1s$ orbitals gives a planar, trigonal molecule. (Note that the small back lobes of the hybrid orbitals have been omitted.)



sp^3 Hybrid Orbitals



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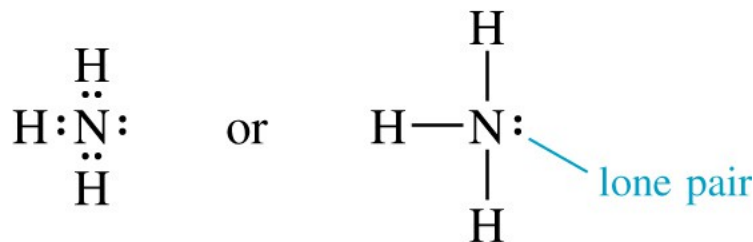
- There are 4 VSEPR pairs.
- The atoms has tetrahedral electron pair geometry.
- 109.5° bond angle

Solved Problem 3

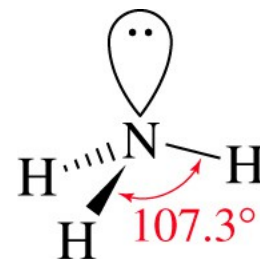
Predict the hybridization of the nitrogen atom in ammonia, NH_3 . Draw a picture of the three-dimensional structure of ammonia, and predict the bond angles.

Solution

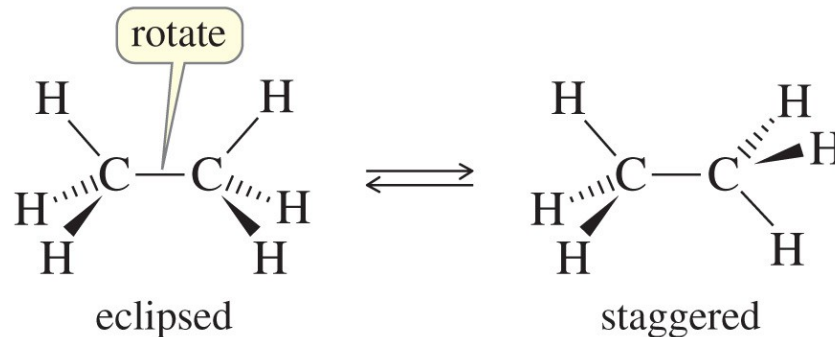
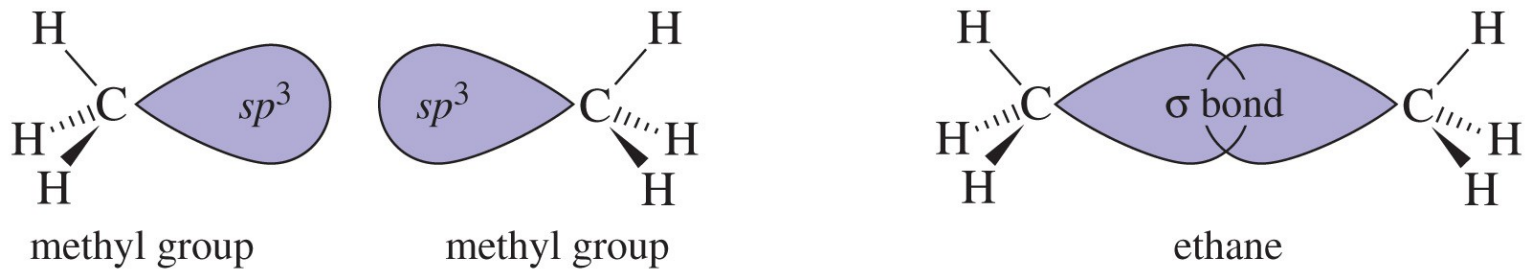
The hybridization depends on the number of sigma bonds plus lone pairs. A Lewis structure provides this information.



In this structure, there are three sigma bonds and one pair of nonbonding electrons. Four hybrid orbitals are required, implying sp^3 hybridization and tetrahedral geometry around the nitrogen atom, with bond angles slightly smaller than 109.5° .



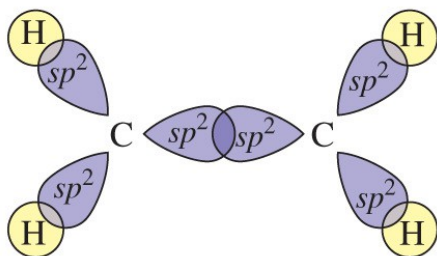
Bonding in Ethane



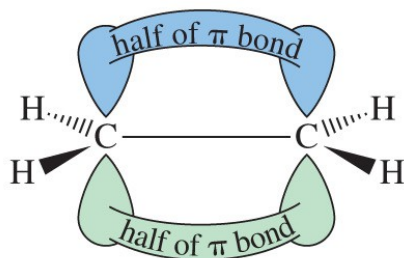
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- Ethane is composed of two methyl groups bonded by the overlap of their sp^3 hybrid orbitals.
- There is free rotation along single bonds.

Bonding in Ethylene



σ bond framework
(viewed from above the plane)



π bond
(viewed from alongside the plane)

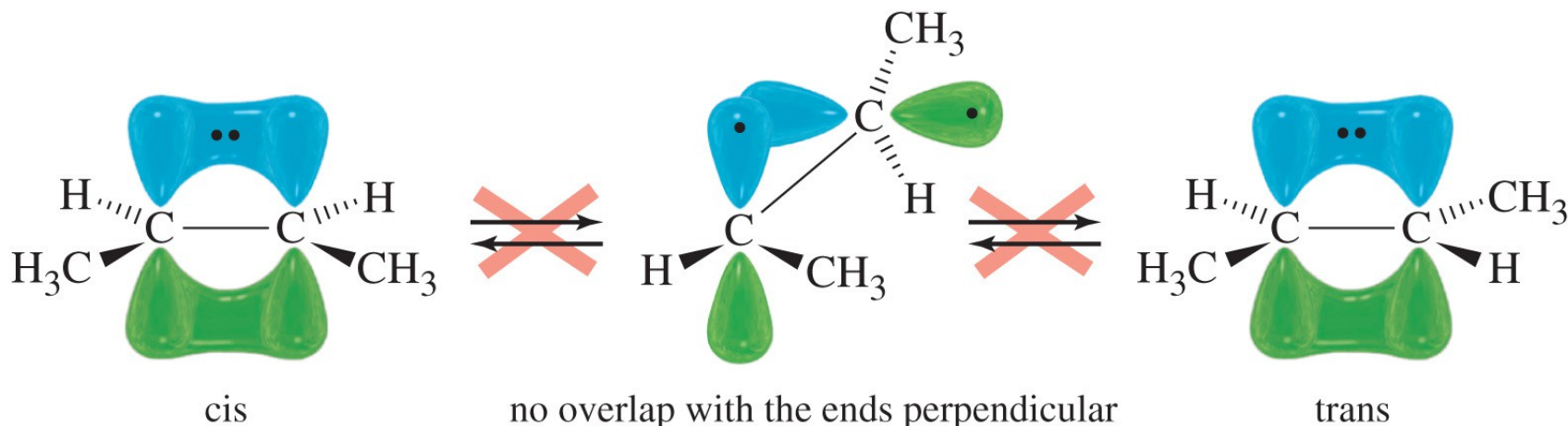


ethylene

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- Ethylene has three (3) sigma bonds formed by its sp^2 hybrid orbitals in a trigonal planar geometry.
- The unhybridized p orbital of one carbon is perpendicular to its sp^2 hybrid orbitals and it is parallel to the unhybridized p orbital of the second carbon.
- Overlap of these two p orbitals will produce a pi bond (double bond) which is located above and below the sigma bond.

Rotation Around Double Bonds



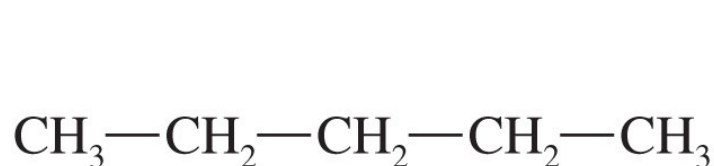
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- Single bonds can rotate freely.
- Double bonds cannot rotate.

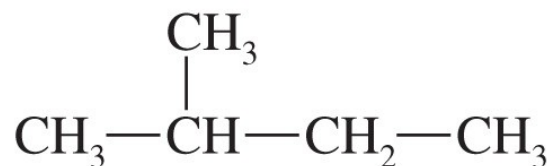
Isomerism

- Molecules that have the same molecular formula, but differ in the arrangement of their atoms, are called ***isomers***.
- Constitutional (or structural) isomers differ in their bonding sequence.
- Stereoisomers differ only in the arrangement of the atoms in space.

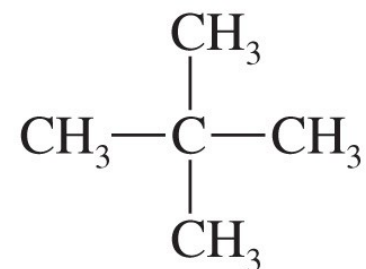
Constitutional Isomers



n-pentane



isopentane

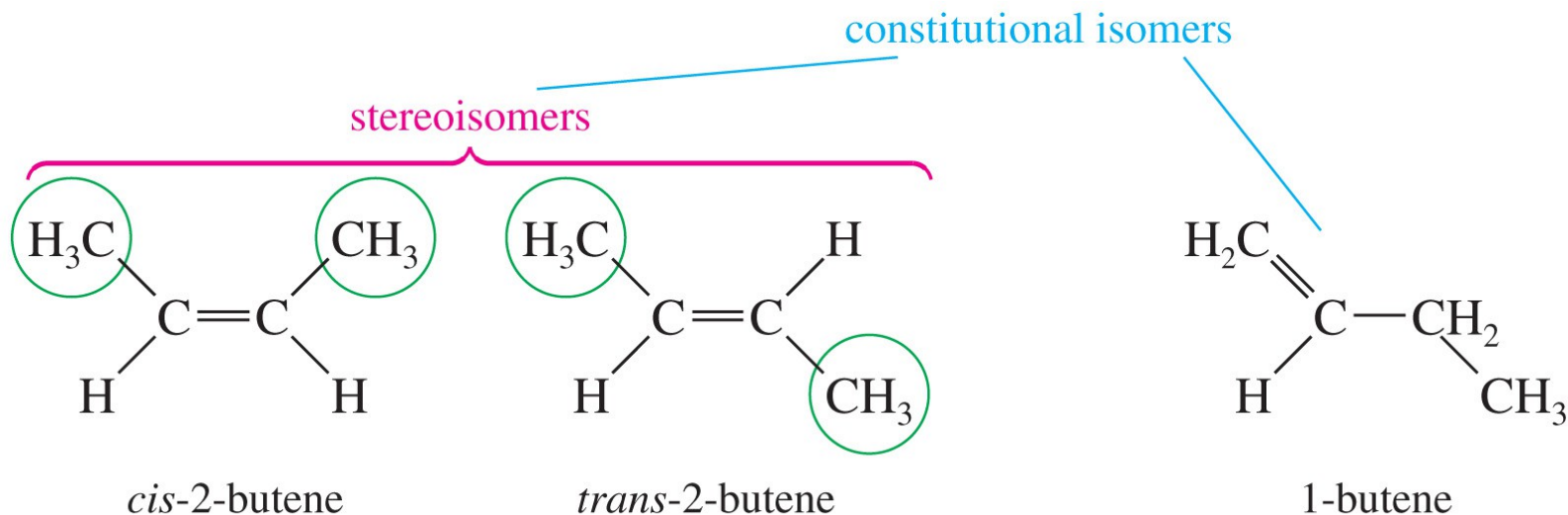


neopentane

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- Constitutional isomers have the same chemical formula, but the atoms are connected in a different order.
- Constitutional isomers have different properties.
- The number of isomers increases rapidly as the number of carbon atoms increases.

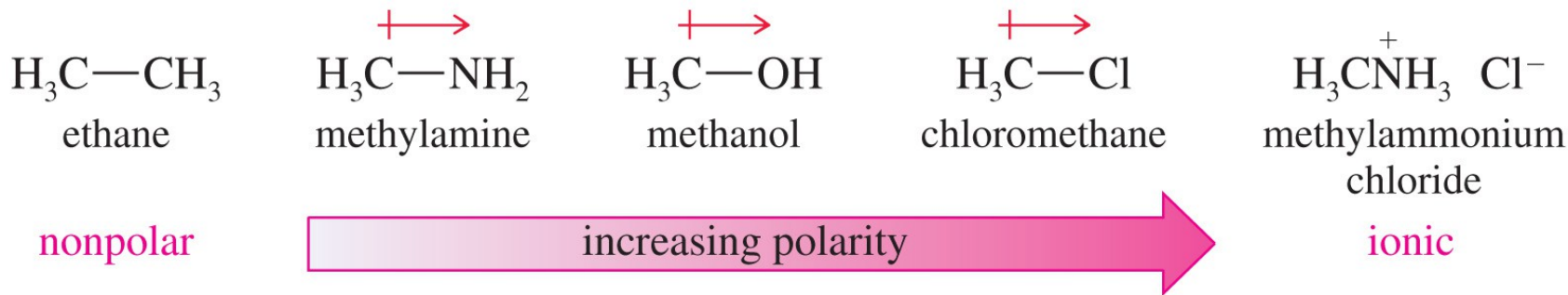
Geometric Isomers: Cis and Trans



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- Stereoisomers are compounds with the atoms bonded in the same order, but their atoms have different orientations in space.
- Cis and trans are examples of geometric stereoisomers and they occur when there is a double bond in the compound.
- Since there is no free rotation along the carbon–carbon double bond, the groups on these carbons can point to different places in space.

Bond Dipole Moments



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- Dipole moments are due to differences in electronegativity.
- They depend on the amount of charge and distance of separation.
- They are measured in debyes (D).

Bond Dipole Moments for Some Common Covalent Bonds

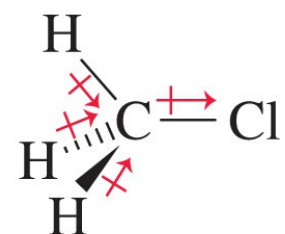
TABLE 2-1

Bond Dipole Moments (Debye) for Some Common Covalent Bonds

Bond	Dipole Moment, μ	Bond	Dipole Moment, μ
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{N}}$	0.22 D	$\overset{+}{\text{H}}-\overset{\rightarrow}{\text{C}}$	0.3 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{O}}$	0.86 D	$\overset{+}{\text{H}}-\overset{\rightarrow}{\text{N}}$	1.31 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{F}}$	1.51 D	$\overset{+}{\text{H}}-\overset{\rightarrow}{\text{O}}$	1.53 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{Cl}}$	1.56 D	$\overset{+}{\text{C}}=\overset{\rightarrow}{\text{O}}$	2.4 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{Br}}$	1.48 D	$\overset{+}{\text{C}}\equiv\overset{\rightarrow}{\text{N}}$	3.6 D
$\overset{+}{\text{C}}-\overset{\rightarrow}{\text{I}}$	1.29 D		

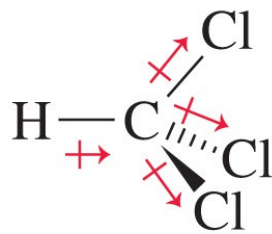
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Molecular Dipole Moments



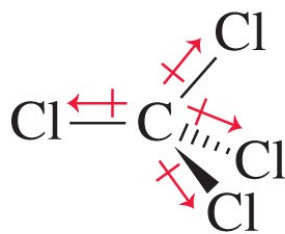
$$\mu = 1.9 \text{ D}$$

chloromethane



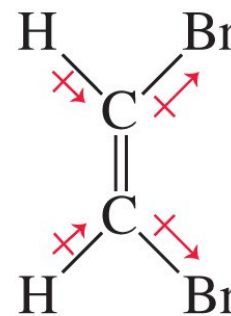
$$\mu = 1.0 \text{ D}$$

chloroform



$$\mu = 0$$

carbon tetrachloride



$$\mu = 1.9 \text{ D}$$

cis-1,2-dibromoethene

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- The molecular dipole moment is the vector sum of the bond dipole moments.
- Depend on bond polarity and bond angles.
- Lone pairs of electrons contribute to the dipole moment.

Intermolecular Forces

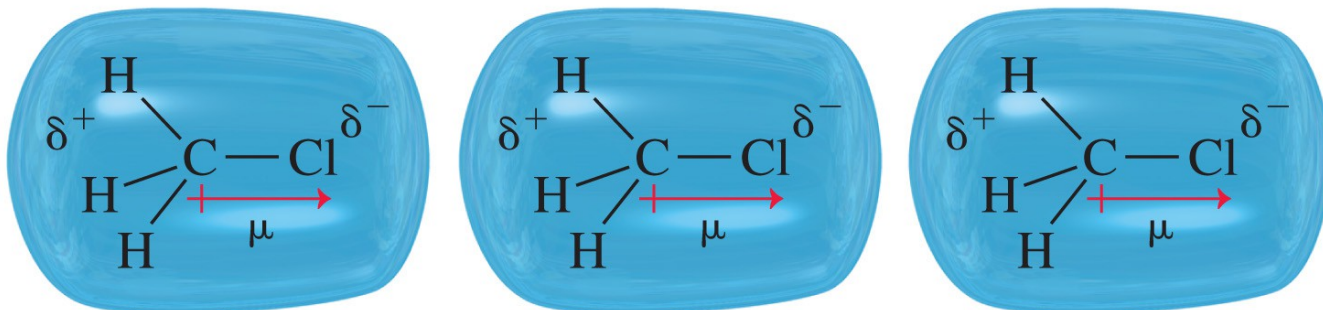
- Strength of attractions between molecules influences the melting point (m. p.), boiling point (b. p.), and solubility of compounds.
- Classification depends on structure:
 - Dipole–dipole interactions
 - London dispersions
 - Hydrogen bonding

Dipole–Dipole Interaction

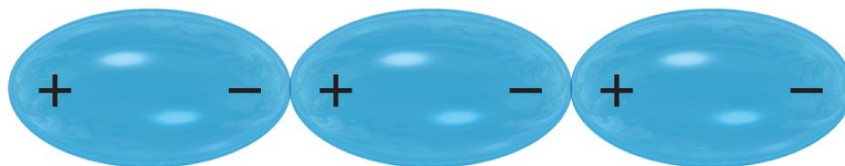
- Dipole–dipole interactions result from the approach of two polar molecules.
- If their positive and negative ends approach, the interaction is an attractive one.
- If two negative ends or two positive ends approach, the interaction is repulsive.
- In a liquid or a solid, the molecules are mostly oriented with the positive and negative ends together, and the net force is attractive.

Dipole–Dipole

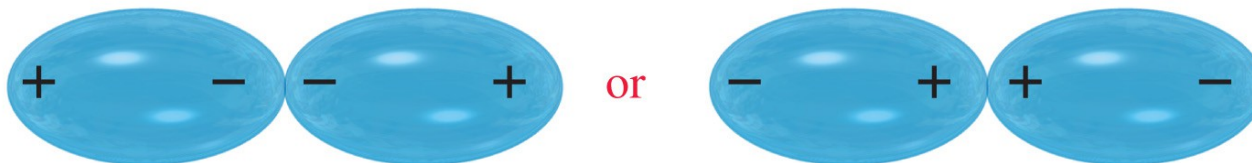
attraction (common)



symbolized by



repulsion (uncommon)

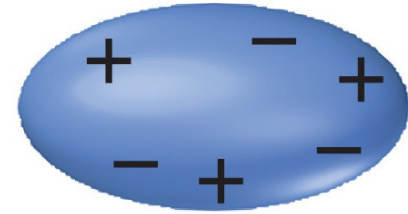
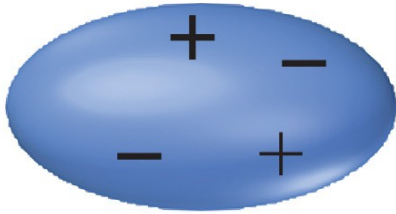


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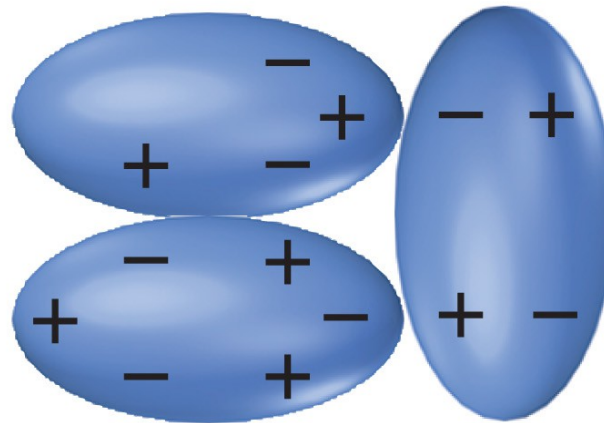
London Dispersions

- One of the Van der Waal forces.
- A temporary dipole moment in a molecule can induce a temporary dipole moment in a nearby molecule.
- An attractive dipole–dipole interaction results for a fraction of a second.
- Main force in nonpolar molecules.
- Larger atoms are more polarizable.
- Branching lowers b. p. because of decreased surface contact between molecules.

Dispersions



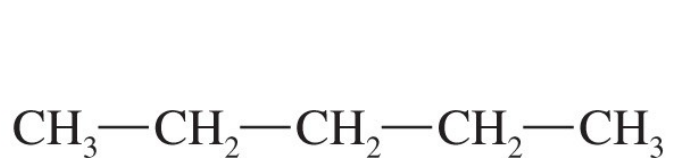
random temporary dipoles when separated



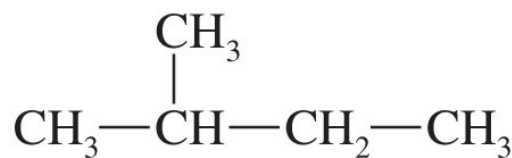
correlated temporary dipoles when in contact

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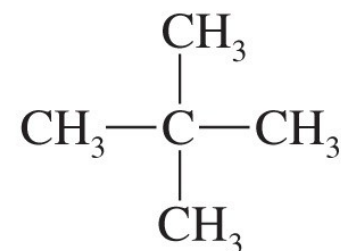
Effect of Branching on Boiling Point



n-pentane, bp = 36 °C



isopentane, bp = 28 °C



neopentane, bp = 10 °C

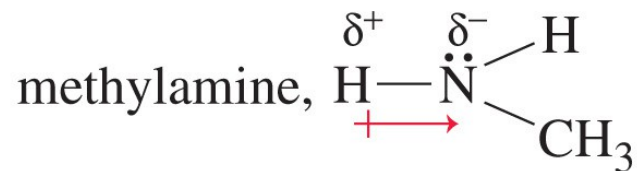
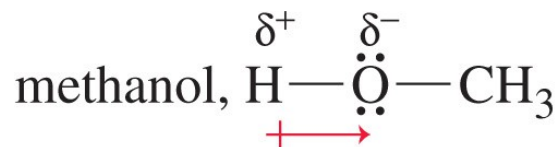
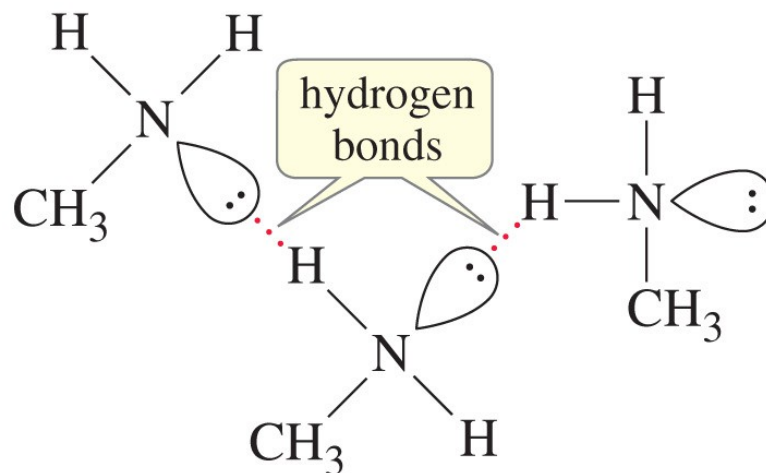
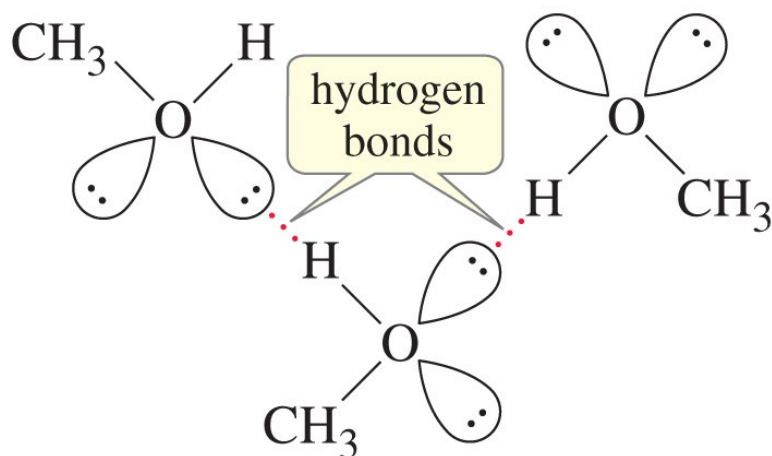
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- The long-chain isomer (*n*-pentane) has the greatest surface area and the highest boiling point.
- As the amount of chain branching increases, the molecule becomes more spherical and its surface area decreases.
- The most highly branched isomer (neopentane) has the smallest surface area and the lowest boiling point.

Hydrogen Bonding

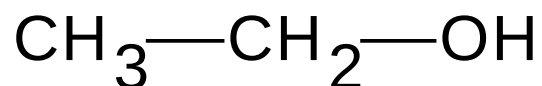
- Strong dipole–dipole attraction.
- Organic molecules must have NH or OH to be able to hydrogen bond.
- The hydrogen from one molecule is strongly attracted to a lone pair of electrons on the oxygen of another molecule.
- O—H more polar than N—H, so alcohols have stronger hydrogen bonding.

H Bonds

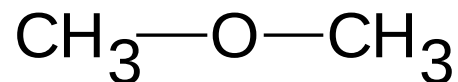


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Boiling Points and Intermolecular Forces

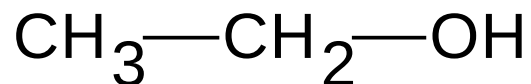


ethanol, b.p. = 78°C



dimethyl ether, b.p. = -25°C

Hydrogen bonding increases the b. p. of the molecule.



ethanol, b.p. = 78°C

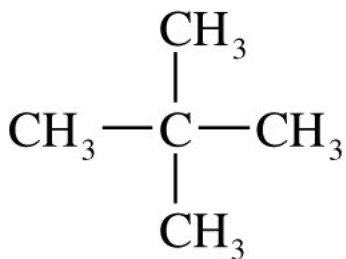


ethyl amine, b.p. 17°C

O—H is more polar than N—H, so alcohols have stronger hydrogen bonding.

Solved Problem 4

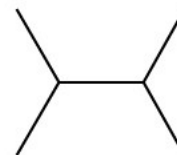
Rank the following compounds in order of increasing boiling points. Explain the reasons for your chosen order.



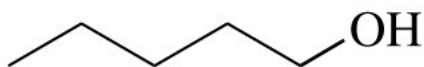
neopentane



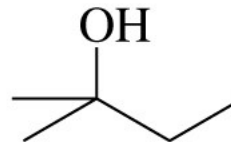
n-hexane



2,3-dimethylbutane



pentan-1-ol



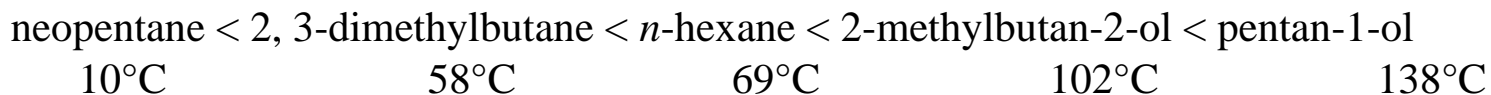
2-methylbutan-2-ol

Solution

To predict relative boiling points, we should look for differences in (1) hydrogen bonding, (2) molecular weight and surface area, and (3) dipole moments. Except for neopentane, these compounds have similar molecular weights. Neopentane is the lightest, and it is a compact spherical structure that minimizes van der Waals attractions. Neopentane is the lowest-boiling compound.

Neither *n*-hexane nor 2,3-dimethylbutane is hydrogen bonded, so they will be next higher in boiling points. Because 2,3-dimethylbutane is more highly branched (and has a smaller surface area) than *n*-hexane, 2,3 dimethylbutane will have a lower boiling point than *n*-hexane.

The two remaining compounds are both hydrogen-bonded, and pentan-1-ol has more area for van der Waals forces. Therefore, pentan-1-ol should be the highest-boiling compound. We predict the following order:

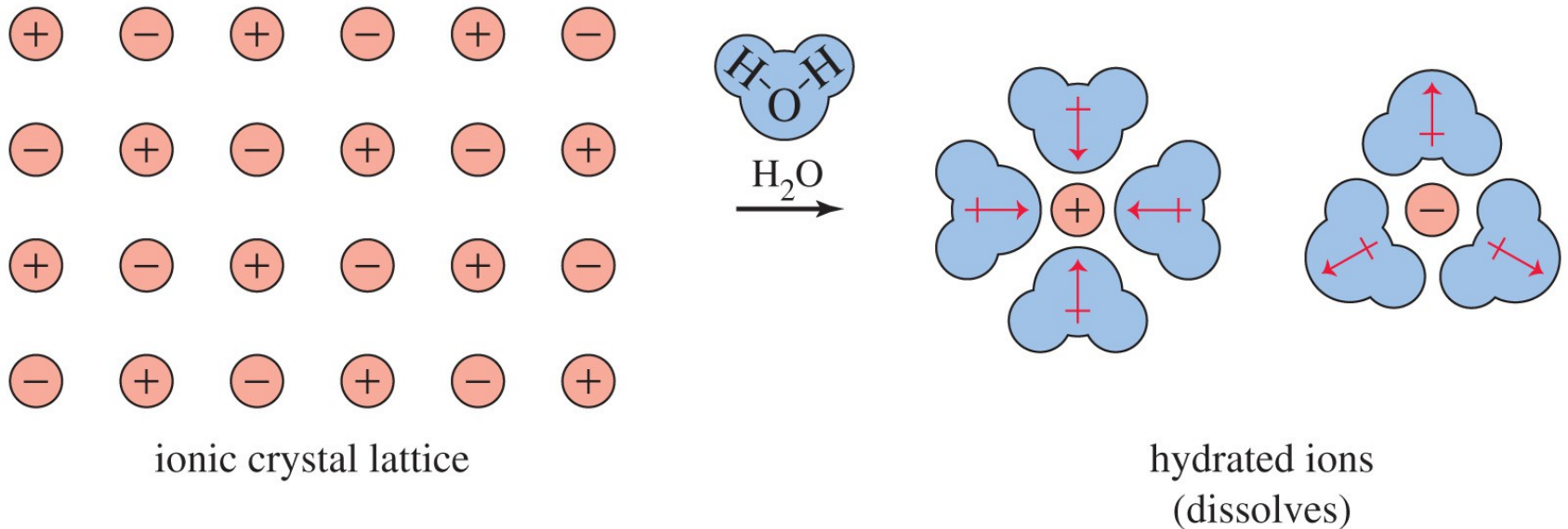


The actual boiling points are given here to show that our prediction is correct.

Solubility

- Like dissolves like.
- Polar solutes dissolve in polar solvents.
- Nonpolar solutes dissolve in nonpolar solvents.
- Molecules with similar intermolecular forces will mix freely.

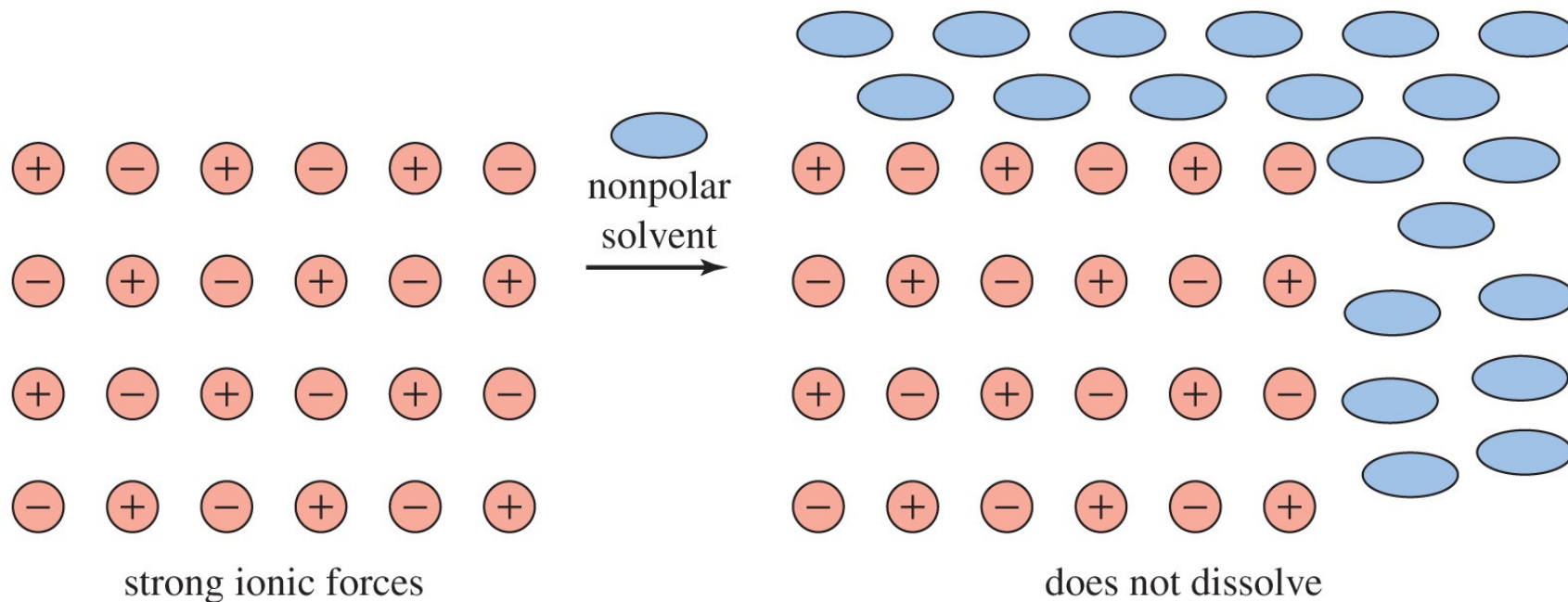
Polar Solute in a Polar Solvent Dissolves



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Hydration releases energy; entropy increases.

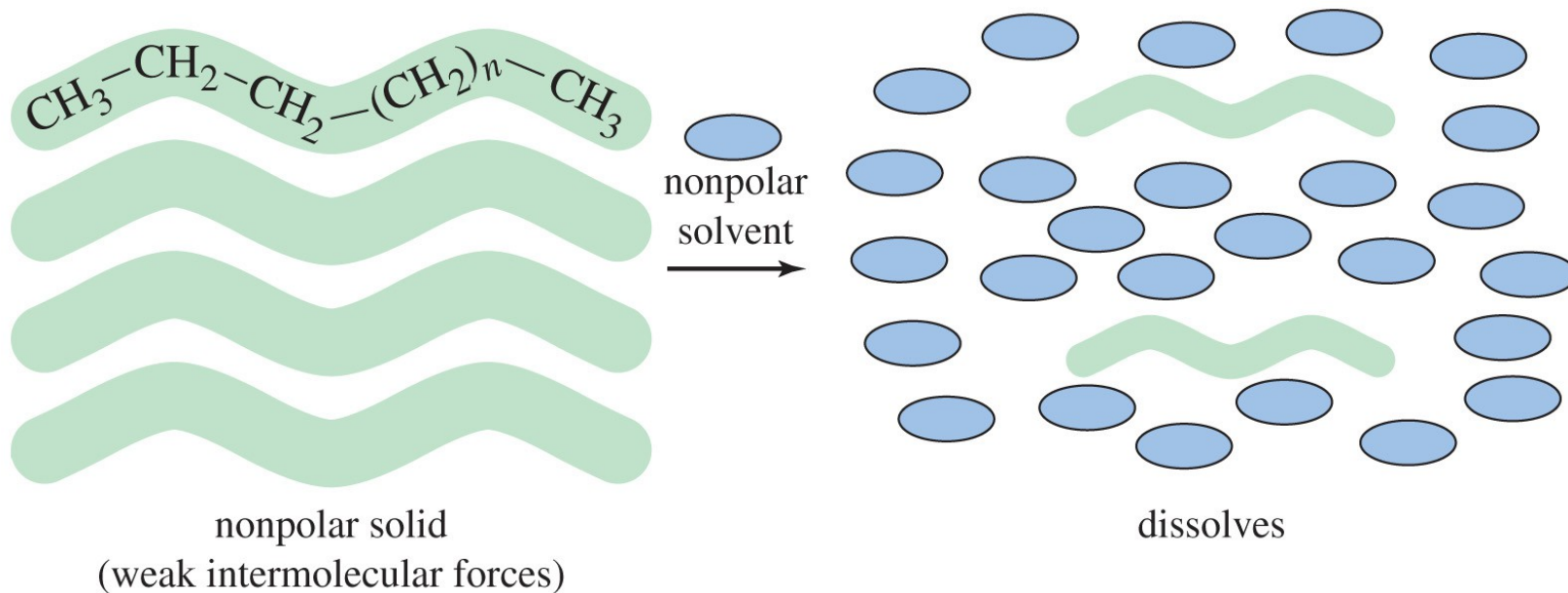
Polar Solute in Nonpolar Solvent



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The solvent cannot break apart the intermolecular interaction of the solute, so the solid will not dissolve in the solvent.

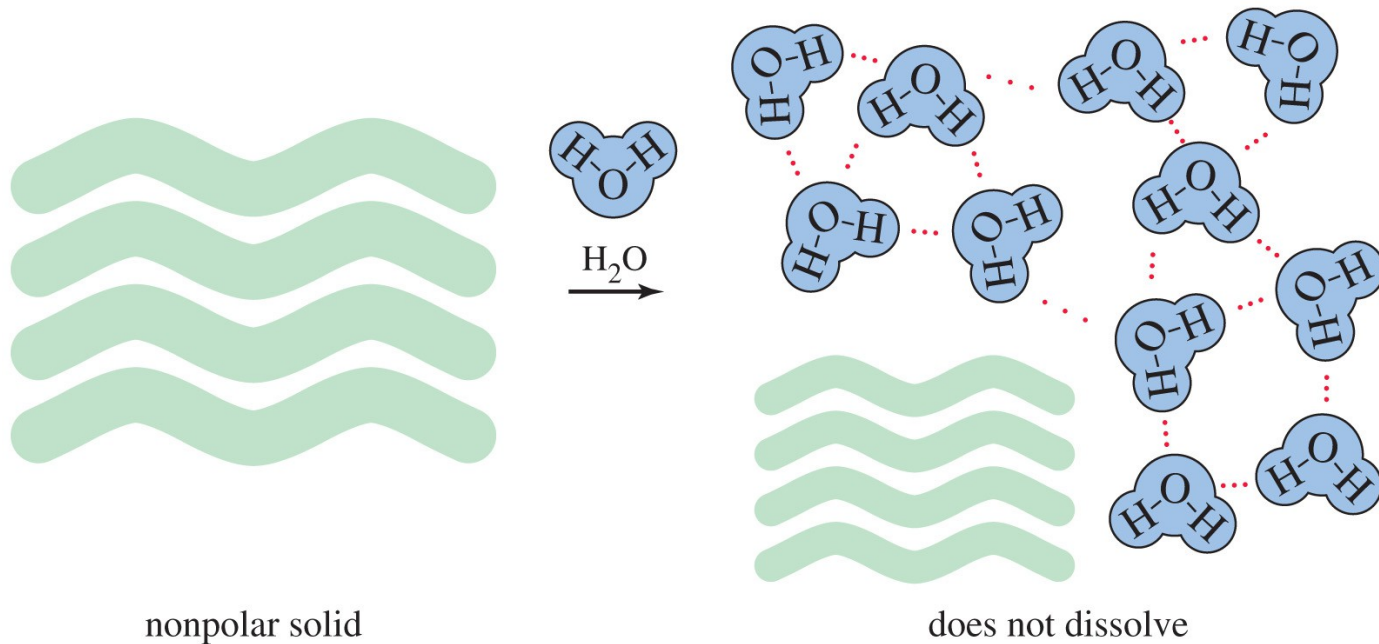
Nonpolar Solute with Nonpolar Solvent



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The weak intermolecular attractions of a nonpolar substance are overcome by the weak attractions for a nonpolar solvent. The nonpolar substance dissolves.

Nonpolar Solute with Polar Solvent



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If a nonpolar molecule were to dissolve in water, it would break up the hydrogen bonds between the water molecules. Therefore, nonpolar substances do not dissolve in water.

Classes of Compounds

- Classifications are based on **functional group**.
- Three broad classes:
 - Hydrocarbons
 - Compounds containing oxygen
 - Compounds containing nitrogen

Hydrocarbons

- Alkanes: Single bonds between the carbons; all carbons are sp^3 .
- Cycloalkanes: sp^3 carbons form a ring.
- Alkenes: Double bonds are present in the molecule; sp^2 carbons.
- Cycloalkenes: Double bond in a ring.
- Alkynes: Triple bonds are present; sp carbons
- Aromatic: Contain a benzene ring.