

# Chapter 1

## Carbon Compounds and Chemical Bonds

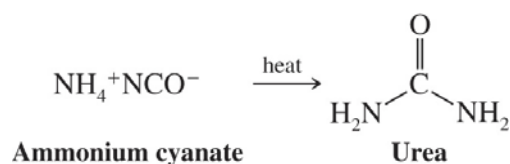
### ◆ Introduction

- Organic Chemistry

- The chemistry of the compounds of carbon
- The human body is largely composed of organic compounds
- Organic chemistry plays a central role in medicine, bioengineering etc.

- Vitalism

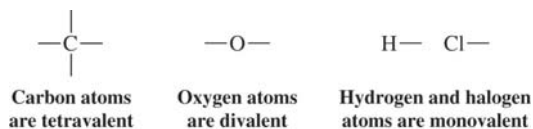
- It was originally thought organic compounds could be made only by living things by intervention of a "vital force"
- Fredrich Wöhler disproved vitalism in 1828 by making the organic compound urea from the inorganic salt ammonium cyanate by evaporation:



## ◆ Structural Theory

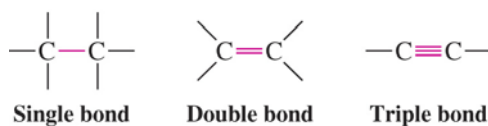
### ● Central Premises

→ Valency: atoms in organic compounds form a fixed number of bonds



→ Carbon can form one or more bonds to other carbons

#### Carbon-carbon bonds



Chapter 1

3

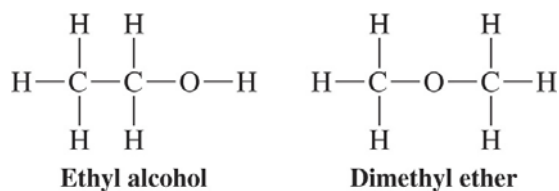
### ● Isomers

→ Isomers are different molecules with the same molecular formula

→ Many types of isomers exist

→ Example

- ⌘ Consider two compounds with molecular formula  $\text{C}_2\text{H}_6\text{O}$
- ⌘ These compounds cannot be distinguished based on molecular formula; however they have different structures
- ⌘ The two compounds differ in the *connectivity* of their atoms



Chapter 1

4

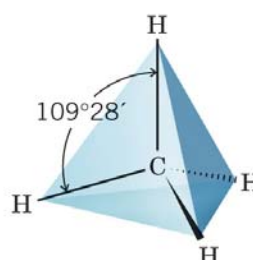
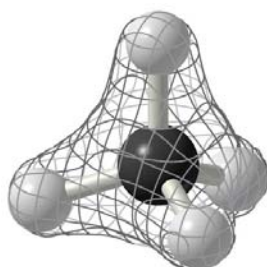
- **Constitutional Isomers**

- Constitutional isomers are one type of isomer
- They are different compounds that have the same molecular formula but different connectivity of atoms
- They often differ in physical properties (e.g. boiling point, melting point, density) and chemical properties

	Ethyl Alcohol $C_2H_6O$	Dimethyl Ether $C_2H_6O$
Boiling point ( $^{\circ}C$ )	78.5	-24.9
Melting point ( $^{\circ}C$ )	-117.3	-138

- **Three Dimensional Shape of Molecules**

- Virtually all molecules possess a 3-dimensional shape which is often not accurately represented by drawings
- It was proposed in 1874 by van't Hoff and le Bel that the four bonds around carbon were not all in a plane but rather in a tetrahedral arrangement *i.e.* the four C-H bonds point towards the corners of a regular tetrahedron



## ◆ Chemical Bonds: The Octet Rule

### ● Octet Rule

- Atoms form bonds to produce the electron configuration of a noble gas (because the electronic configuration of noble gases is particularly stable)
- For most atoms of interest this means achieving a valence shell configuration of 8 electrons corresponding to that of the nearest noble gas
- Atoms close to helium achieve a valence shell configuration of 2 electrons
- Atoms can form either ionic or covalent bonds to satisfy the octet rule

### ● Electronegativity

- Electronegativity is the ability of an atom to attract electrons
- It increases from left to right and from bottom to top in the periodic table (noble gases excluded)

⚠ Fluorine is the most electronegative atom and can stabilize excess electron density the best

Increasing electronegativity

			H 2.1				
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8						Br 2.8	

Increasing electronegativity

## ● Ionic Bonds

→ When ionic bonds are formed atoms gain or lose electrons to achieve the electronic configuration of the nearest noble gas

⌘ In the process the atoms become ionic

→ The resulting oppositely charged ions attract and form ionic bonds

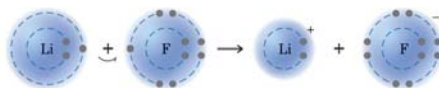
→ This generally happens between atoms of widely different electronegativities

→ Example

⌘ Lithium loses an electron (to have the configuration of helium) and becomes positively charged

⌘ Fluoride gains an electron (to have the configuration of neon) and becomes negatively charged

⌘ The positively charged lithium and the negatively charged fluoride form a strong ionic bond (actually in a crystalline lattice)



Chapter 1

9

## ● Covalent Bonds

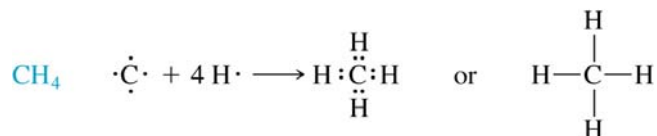
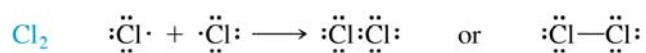
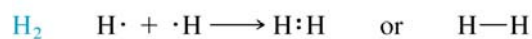
→ Covalent bonds occur between atoms of similar electronegativity (close to each other in the periodic table)

→ Atoms achieve octets by *sharing* of valence electrons

→ Molecules result from this covalent bonding

→ Valence electrons can be indicated by dots (electron-dot formula or Lewis structures) but this is time-consuming

→ The usual way to indicate the two electrons in a bond is to use a line (one line = two electrons)



Chapter 1

10

## ◆ Writing Lewis Structures

- Atoms bond by using their valence electrons
- The number of valence electrons is equal to the group number of the atom
  - ⌘ Carbon is in group 4A and has 4 valence electrons
  - ⌘ Hydrogen is in group 1A and has 1 valence electron
  - ⌘ Oxygen is in group 6A and has 6 valence electrons
  - ⌘ Nitrogen is in group 5A and has 5 valence electrons
- To construct molecules the atoms are assembled with the correct number of valence electrons
- If the molecule is an ion, electrons are added or subtracted to give it the proper charge
- The structure is written to satisfy the octet rule for each atom and to give the correct charge
- If necessary, multiple bonds can be used to satisfy the octet rule for each atom

Chapter 1

11

### ● Example

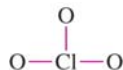
→ Write the Lewis structure for the chlorate ion ( $\text{ClO}_3^-$ )

- ⌘ The total number of valence electrons including the electron for the negative charge is calculated

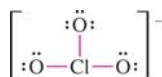
$$7 + 3(6) + 1 = 26$$



- ⌘ Three pairs of electrons are used to bond the chlorine to the oxygens



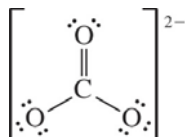
- ⌘ The remaining 20 electrons are added to give each atom an octet



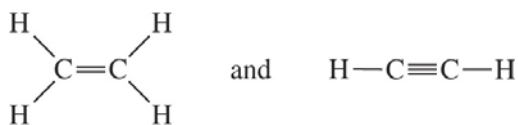
Chapter 1

12

→ The carbonate ion with 24 valence electrons and two negative charges must incorporate a double bond to satisfy the octet rule for every atom



→ The organic molecules ethene (C<sub>2</sub>H<sub>4</sub>) and ethyne (C<sub>2</sub>H<sub>2</sub>) must also use multiple bonds to satisfy the octet rule for each atom



Chapter 1

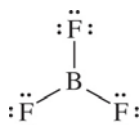
13

### ◆ Exceptions to the Octet Rule

→ The octet rule applies only to atoms in the second row of the periodic table (C, O, N, F) which are limited to valence electrons in the 2s and 2p orbitals

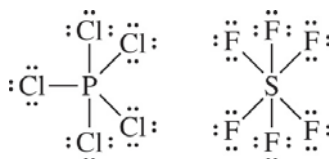
→ In second row elements *fewer* electrons are possible

→ Example: BF<sub>3</sub>



→ In higher rows other orbitals are accessible and more than 8 electrons around an atom are possible

→ Example: PCl<sub>5</sub> and SF<sub>6</sub>



Chapter 1

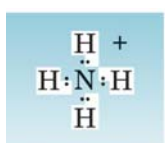
14

## ◆ Formal charge

- A formal charge is a positive or negative charge on an individual atom
- The sum of formal charges on individual atoms is the total charge of the molecule or ion
- The formal charge is calculated by subtracting the assigned electrons on the atom in the molecule from the electrons in the neutral atom
- Electrons in bonds are evenly split between the two atoms; one to each atom
- Lone pair electrons belong to the atom itself

## ● Examples

→ Ammonium ion ( $\text{NH}_4^+$ )

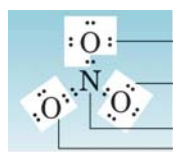


For hydrogen: valence electrons of free atom = 1  
 subtract assigned electrons =  $\frac{-1}{0}$   
 Formal charge =  $\frac{-1}{0}$

For nitrogen: valence electrons of free atom = 5  
 subtract assigned electrons =  $\frac{-4}{+1}$   
 Formal charge =  $\frac{-4}{+1}$

Charge on ion =  $4(0) + 1 = +1$

## ● Nitrate ion ( $\text{NO}_3^-$ )



Formal charge =  $6 - 7 = -1$

Formal charge =  $5 - 4 = +1$















Formal charge =  $6 - 6 = 0$

Charge on ion =  $2(-1) + 1 + 0 = -1$



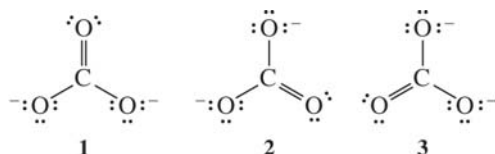
- An atom will always have the same formal charge depending on how many bonds and lone pairs it has regardless of which particular molecule it is in
- For example a singly bonded oxygen with 3 lone pairs will always have a negative charge and an oxygen with three bonds and one lone pair will always have a positive charge
- Knowing these forms of each atom is invaluable in drawing Lewis structures correctly and rapidly (See table next page)

### ◆ A Summary of Formal Charges

Group	Formal Charge of +1	Formal Charge of 0	Formal Charge of -1
3A			
4A			
5A			
6A			
7A			

## ◆ Resonance

- Often a single Lewis structure does not accurately represent the true structure of a molecule
- The real carbonate ion is not represented by any of the structures 1, 2 or 3



- Experimentally carbonate is known not to have two carbon-oxygen single bonds and one double bond; all bonds are equal in length and the charge is spread equally over all three oxygens

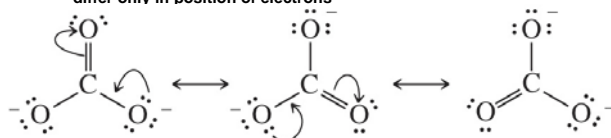
- The real carbonate ion can be represented by a drawing in which partial double bonds to the oxygens are shown and partial negative charge exists on each oxygen
- The real structure is a resonance hybrid or mixture of all three Lewis structures
- Double headed arrows are used to show that the three Lewis structures are resonance contributors to the true structure

† The use of equilibrium arrows is incorrect since the three structures do not equilibrate; the true structure is a hybrid (average) of all three Lewis structures



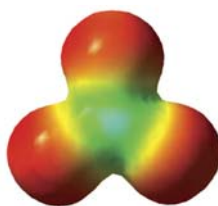
→ One resonance contributor is converted to another by the use of curved arrows which show the movement of electrons

⌘ The use of these arrows serves as a bookkeeping device to assure all structures differ only in position of electrons



→ A calculated electrostatic potential map of carbonate clearly shows the electron density is spread equally among the three oxygens

⌘ Areas which are red are more negatively charged; areas of blue have relatively less electron density



Chapter 1

21

● **Rules for Resonance:**

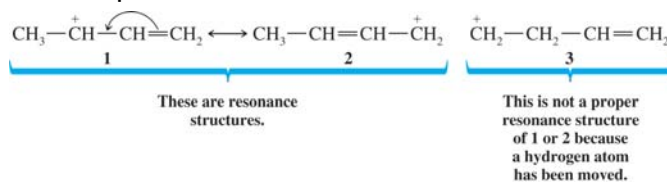
→ Individual resonance structures exist only on paper

⌘ The real molecule is a hybrid (average) of all contributing forms  
⌘ Resonance forms are indicated by the use of double-headed arrows

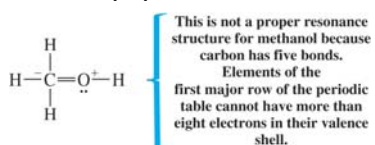
→ Only electrons are allowed to move between resonance structures

⌘ The position of nuclei must remain the same  
⌘ Only electrons in multiple bonds and nonbonding electrons can be moved

→ Example: 3 is not a resonance form because an atom has moved



→ All structures must be proper Lewis structures



Chapter 1

22

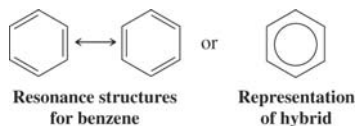
→ The energy of the actual molecule is lower than the energy of any single contributing form

¶ The lowering of energy is called resonance stabilization

→ Equivalent resonance forms make equal contributions to the structure of the real molecule

¶ Structures with equivalent resonance forms tend to be greatly stabilized

¶ Example: The two resonance forms of benzene contribute equally and greatly stabilize it



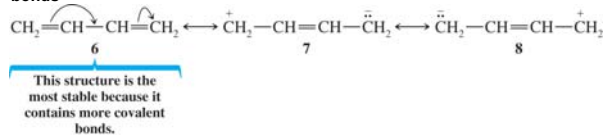
→ Unequal resonance structures contribute based on their relative stabilities

¶ More stable resonance forms contribute more to the structure of the real molecule

### ● Rules to Assign Relative Importance of Resonance Forms

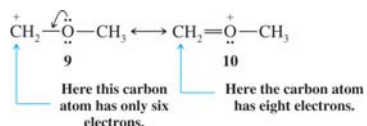
→ A resonance form with more covalent bonds is more important than one with less

¶ Example: 6 is more stable and more important because it has more total covalent bonds



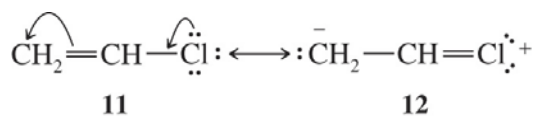
→ Resonance forms in which all atoms have a complete valence shell of electrons are more important

¶ Example: 10 is more important because all atoms (except hydrogen) have complete octets



→ Resonance forms with separation of charge are less important

- ⌘ Separation of charge cost energy and results in a less stable resonance contributor
- ⌘ Example: 12 is less important because it has charge separation

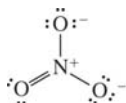


→ Forms with negative charge on highly electronegative atoms are more important

- ⌘ Those with positive charge on less electronegative atoms are also more important

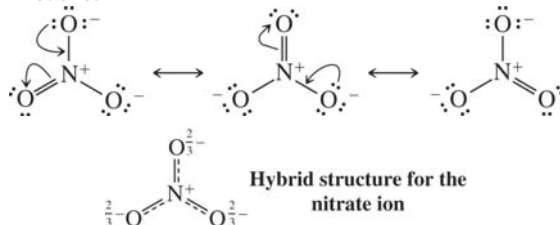
● Example

→ The nitrate ion is known to have all three nitrogen-oxygen bond lengths the same and the negative charge spread over all three atoms equally



→ Resonance theory can be used to produce three equivalent resonance forms

- ⌘ Curved arrows show the movement of electrons between forms
- ⌘ When these forms are hybridized (averaged) the true structure of the nitrate ion is obtained

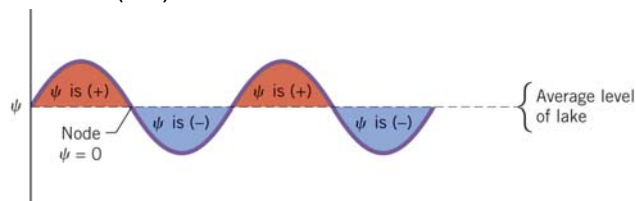


## ◆ Quantum Mechanics

- A mathematical description of bonding that takes into account the wave nature of electrons
- A wave equation is solved to yield a series of wave functions for the atom
- The wave functions  $\psi$  describe a series of states with different energies for each electron
- Wave Equations are used to calculate:
  - ⌘ The energy associated with the state of the electron
  - ⌘ The probability of finding the electron in a particular state

### → Phase sign: Wave equations, when solved, may be positive, negative or zero

- ⌘ In analogy to a wave in a lake, when the wave is above the average lake level, the sign is positive ( $\psi = +$ ); when it is below the lake level it is negative ( $\psi = -$ )
- ⌘ When the wave is exactly at average lake level it has a sign of 0 and this is called a node ( $\psi = 0$ )

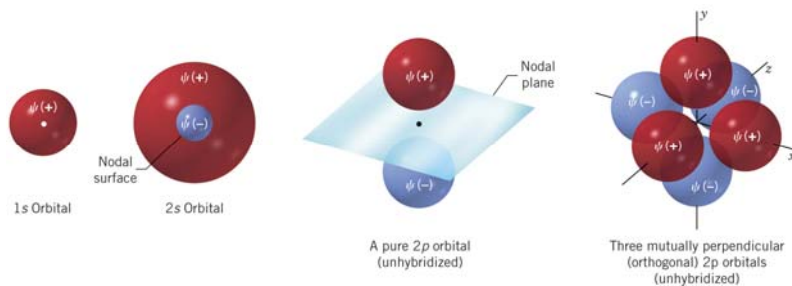


### → Wave equations can reinforce each other if they have the same sign or interfere with each other if they have different signs

## ◆ Atomic Orbitals (AOs)

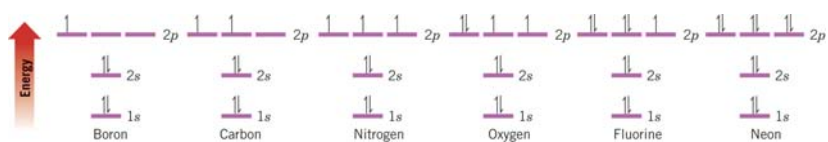
- The physical reality of  $\Psi$  is that when squared ( $\Psi^2$ ) it gives the probability of finding an electron in a particular location in space
- Plots of  $\Psi^2$  in three dimensions generate the shape of *s*, *p*, *d* and *f* orbitals
- Only *s* and *p* orbitals are very important in organic chemistry
- Orbital: a region in space where the probability of finding an electron is large
  - ↳ The typical representation of orbitals are those volumes which contain the electron 90-95% of the time

- 1*s* and 2*s* orbitals are spheres centered around the nucleus
  - ↳ Each orbital can accommodate 2 electrons
  - ↳ The 2*s* orbital is higher in energy and contains a nodal surface ( $\Psi = 0$ ) in its center
- Each 2*p* orbital has two nearly touching spheres (or lobes)
  - ↳ One sphere has a positive phase sign and the other a negative phase sign; a nodal plane separates the spheres
- There are three 2*p* orbitals which are perpendicular (orthogonal) to each other
  - ↳ Each *p* orbital can accommodate 2 electrons for a total of 6 electrons
  - ↳ All three *p* orbitals are degenerate (equal in energy)
- The 2*p* orbitals are higher in energy than the 1*s* or 2*s*



- The sign of the wave function *does not* indicate a greater or lesser probability of finding an electron in that location
- The greater the number of nodes in an orbital the higher its energy
  - ↳ 2s and 2p orbitals each have one node and are higher in energy than the 1s orbital which has no nodes

- Atoms can be assigned electronic configuration using the following rules:
  - Aufbau Principle: The lowest energy orbitals are filled first
  - Pauli Exclusion Principle: A maximum of two spin paired electrons may be placed in each orbital
  - Hund's Rule: One electron is added to each degenerate (equal energy orbital) before a second electron is added
- Electronic Configurations of Some Second Row Elements

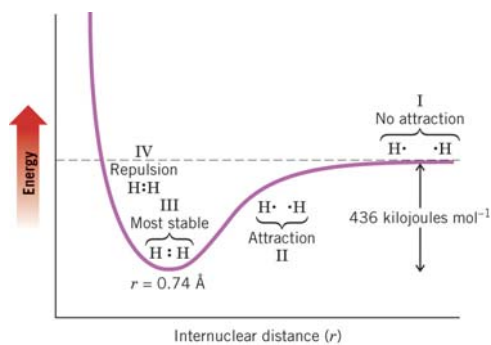




## ◆ Molecular Orbitals (MOs)

→ A simple model of bonding is illustrated by forming molecular H<sub>2</sub> from H atoms and varying distance:

- ⌘ Region I: The total energy of two isolated atoms
- ⌘ Region II: The nucleus of one atom starts attracting the electrons of the other; the energy of the system is lowered
- ⌘ Region III: at 0.74 Å the attraction of electrons and nuclei exactly balances repulsion of the two nuclei; this is the bond length of H<sub>2</sub>
- ⌘ Region IV: energy of system rises as the repulsion of the two nuclei predominates



Chapter 1

33

→ This simple model of bonding does not take into account the fact that electrons are not stationary but constantly moving around

- ⌘ Heisenberg uncertainty principle: the position and momentum of an electron cannot simultaneously be known

→ Quantum mechanics solves this problem by talking about the probability ( $\Psi^2$ ) of finding an electron at a certain location in space

→ As two atoms approach each other their atomic orbitals (AOs) overlap to become molecular orbitals (MOs)

→ The wave functions of the AOs are combined to yield the new wave functions of the MOs

→ The number of MOs that result must always equal the number of AOs used

Chapter 1

34

- **Example: H<sub>2</sub> molecule**

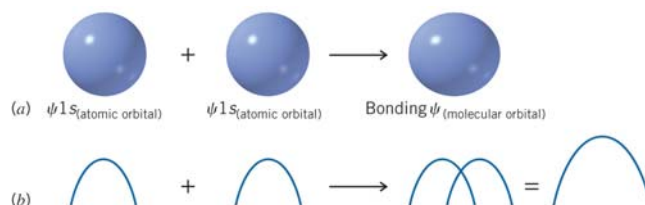
- As the hydrogen atoms approach each other their 1s orbitals ( $\psi_{1s}$ ) begin to overlap
- The MOs that form encompass both nuclei
- The electrons are not restricted to the vicinity of one nucleus or another
- Each MO has a maximum of 2 spin-paired electrons
- Addition of wave functions of the two atoms leads to a *bonding molecular orbital*
- Subtraction of wave functions of the two atoms leads to an *anti-bonding molecular orbital*
- The mathematic operation by which wave functions are added or subtracted is called the linear combination of atomic orbitals (LCAO)

Chapter 1

35

- **Bonding Molecular Orbitals ( $\Psi_{\text{molec}}$ )**

- AOs combine by addition (the AOs of the same phase sign overlap)
- The wave functions reinforce
- The value of  $\Psi$  increases between the two nuclei
- The value of  $\Psi^2$  (electron probability density) in the region between the two nuclei increases
- The two electrons between the nuclei serve to attract the nuclei towards each other
- This is the ground state (lowest energy state) of the MO



Chapter 1

36

- **Antibonding molecular orbital ( $\Psi^*_{\text{molec}}$ )**

- Formed by interaction of AOs with opposite phase signs

- Wave functions interfere and a node is produced ( $\Psi = 0$ )

- In the region between the two nuclei

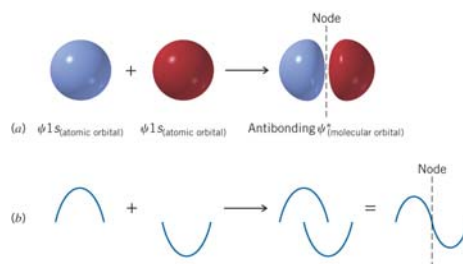
- ⌘ A node is produced

- ⌘ On either side of the node  $\Psi$  is small

- ⌘  $\Psi^2$  (electron probability density) is small

- Electrons in the antibonding orbital avoid the region between the two nuclei

- Repulsive forces between the nuclei predominate and electrons in antibonding orbitals make nuclei fly apart



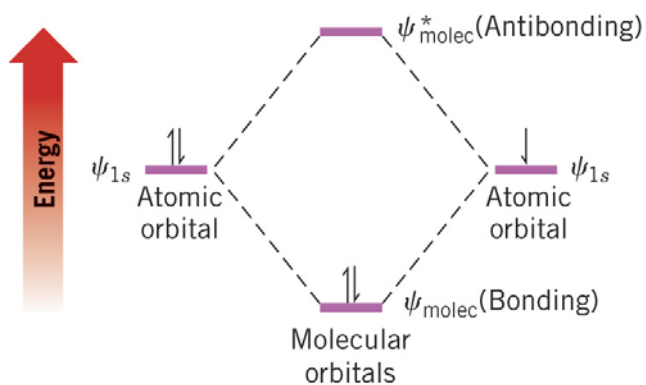
Chapter 1

37

- The energy of electrons in the bonding orbitals is substantially less than the energy of electrons in the individual atoms

- ⌘ The energy of electrons in the antibonding orbitals is substantially more

- In the ground state of the hydrogen molecule electrons occupy the lower energy bonding orbital only

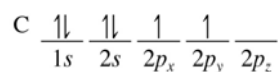


Chapter 1

38

### ◆ The Structure of Methane and Ethane: $sp^3$ Hybridization

→ The structure of methane with its four identical tetrahedral bonds cannot be adequately explained using the electronic configuration of carbon



Ground state of a carbon atom

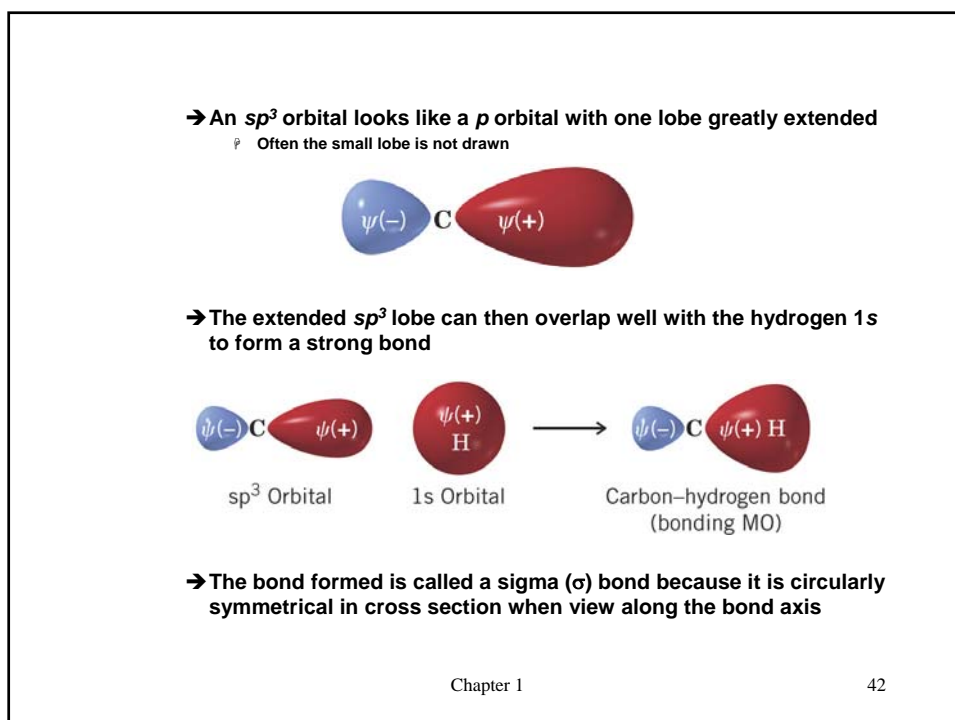
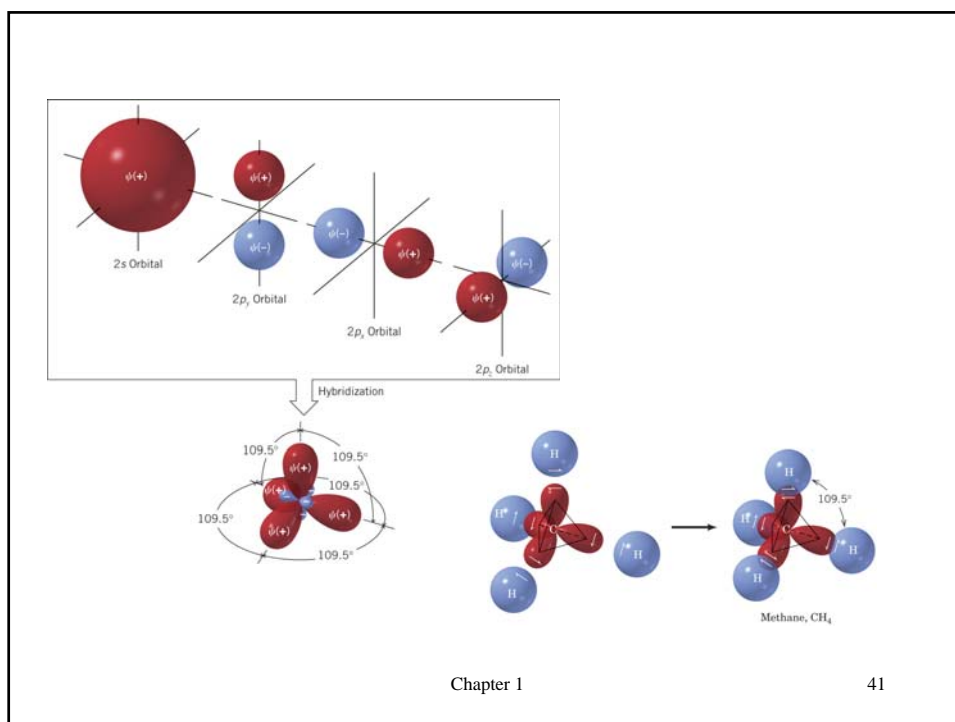
- Hybridization of the valence orbitals (2s and 2p) provides four new identical orbitals which can be used for the bonding in methane
- *Orbital hybridization* is a mathematical combination of the 2s and 2p wave functions to obtain wave functions for the new orbitals

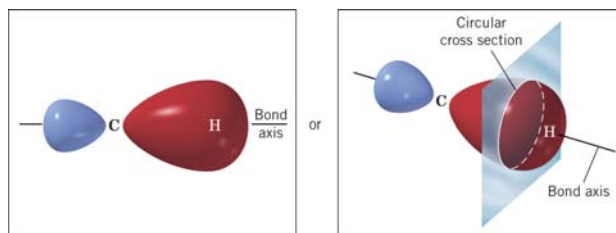
→ When one 2s orbital and three 2p orbitals are hybridized four new and identical  $sp^3$  orbitals are obtained

- ⌘ When four orbitals are hybridized, four orbitals must result
- ⌘ Each new orbital has one part s character and 3 parts p character
- ⌘ The four identical orbitals are oriented in a tetrahedral arrangement
- ⌘ The antibonding orbitals are not derived in the following diagram

→ The four  $sp^3$  orbitals are then combined with the 1s orbitals of four hydrogens to give the molecular orbitals of methane

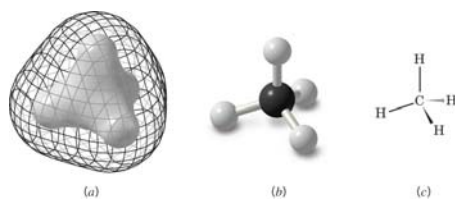
→ Each new molecular orbital can accommodate 2 electrons





→ A variety of representations of methane show its tetrahedral nature and electron distribution

⌘ a. calculated electron density surface b. ball-and-stick model c. a typical 3-dimensional drawing



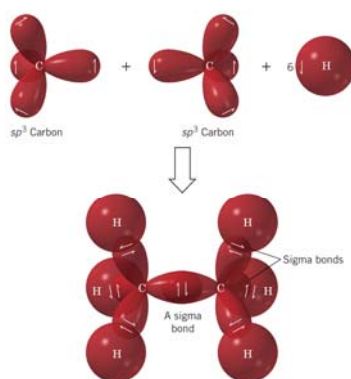
Chapter 1

43

### ● Ethane ( $C_2H_6$ )

→ The carbon-carbon bond is made from overlap of two  $sp^3$  orbitals to form a  $\sigma$  bond

→ The molecule is approximately tetrahedral around each carbon

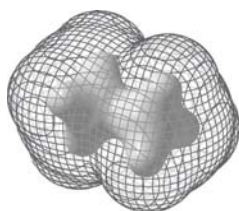


Chapter 1

44

→ The representations of ethane show the tetrahedral arrangement around each carbon

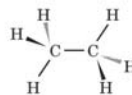
- ⌘ a. calculated electron density surface
- ⌘ b. ball-and-stick model
- ⌘ c. typical 3-dimensional drawing



(a)



(b)



(c)

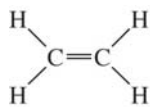
→ Generally there is relatively free rotation about  $\sigma$  bonds

- ⌘ Very little energy (13-26 kcal/mol) is required to rotate around the carbon-carbon bond of ethane

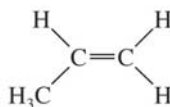
## ◆ The Structure of Ethene (Ethylene) : $sp^2$ Hybridization

→ Ethene ( $C_2H_4$ ) contains a carbon-carbon double bond and is in the class of organic compounds called *alkenes*

- ⌘ Another example of the alkenes is propene



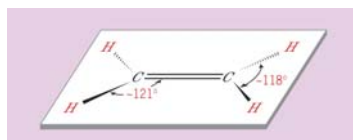
Ethene



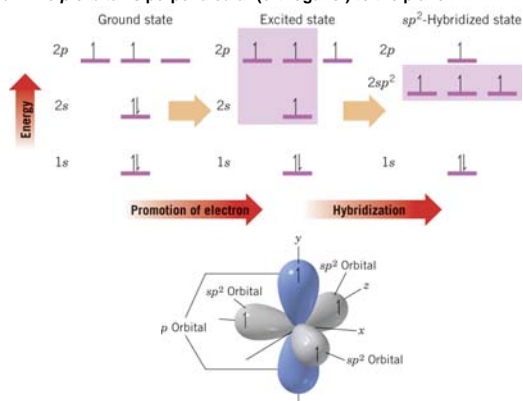
Propene

→ The geometry around each carbon is called *trigonal planar*

- ⌘ All atoms directly connected to each carbon are in a plane
- ⌘ The bonds point towards the corners of a regular triangle
- ⌘ The bond angles are approximately  $120^\circ$

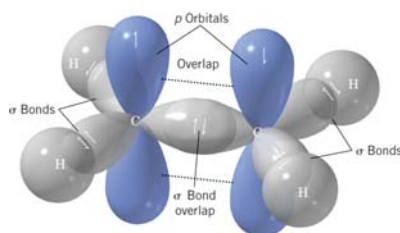


- There are three  $\sigma$  bonds around each carbon of ethene and these are formed by using  $sp^2$  hybridized orbitals
- The three  $sp^2$  hybridized orbitals come from mixing one s and two p orbitals
  - ⌘ One p orbital is left unhybridized
- The  $sp^2$  orbitals are arranged in a trigonal planar arrangement
  - ⌘ The p orbital is perpendicular (orthogonal) to the plane



47

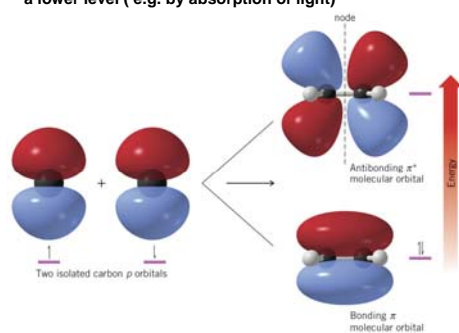
- Overlap of  $sp^2$  orbitals in ethylene results in formation of a  $\sigma$  framework
  - ⌘ One  $sp^2$  orbital on each carbon overlaps to form a carbon-carbon  $\sigma$  bond; the remaining  $sp^2$  orbitals form bonds to hydrogen
- The leftover p orbitals on each carbon overlap to form a bonding  $\pi$  bond between the two carbons
- A  $\pi$  bond results from overlap of p orbitals above and below the plane of the  $\sigma$  bond
  - ⌘ It has a nodal plane passing through the two bonded nuclei and between the two lobes of the  $\pi$  molecular orbital



48



- The bonding  $\pi$  orbital results from overlap of  $p$  orbital lobes of the same sign
- The antibonding  $\pi^*$  orbital results from overlap of  $p$  orbital lobes of opposite sign
  - ⌘ The antibonding orbital has one node connecting the two nuclei and another node between the two carbons
- The bonding  $\pi$  orbital is lower in energy than the antibonding orbital
  - ⌘ In the ground state two spin paired electrons are in the bonding orbital
  - ⌘ The antibonding  $\pi^*$  orbital can be occupied if an electron becomes promoted from a lower level (e.g. by absorption of light)



49

- The  $\sigma$  orbital is lower in energy than the  $\pi$  orbital
  - ⌘ The ground state electronic configuration of ethene is shown



Chapter 1

50

## ◆ Restricted Rotation and the Double Bond

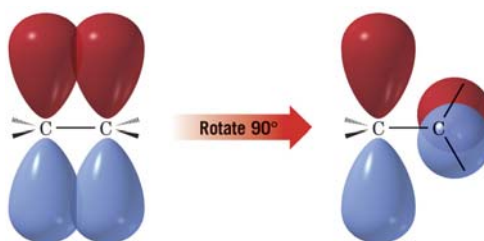
→ There is a large energy barrier to rotation (about 264 kJ/mol) around the double bond

⌘ This corresponds to the strength of a  $\pi$  bond

⌘ The rotational barrier of a carbon-carbon single bond is 13-26 kJ/mol

→ This rotational barrier results because the  $p$  orbitals must be well aligned for maximum overlap and formation of the  $\pi$  bond

→ Rotation of the  $p$  orbitals  $90^\circ$  totally breaks the  $\pi$  bond



Chapter 1

51

## ● Cis-trans isomers

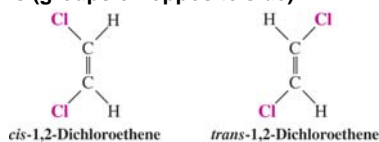
→ Cis-trans isomers are the result of restricted rotation about double bonds

→ These isomers have the same connectivity of atoms and differ only in the arrangement of atoms in space

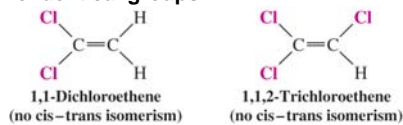
⌘ This puts them in the broader class of stereoisomers

→ The molecules below do not *superpose* on each other

→ One molecule is designated *cis* (groups on same side) and the other is *trans* (groups on opposite side)



→ Cis-trans isomerism is not possible if one carbon of the double bond has two identical groups



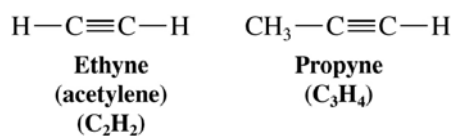
Chapter 1

52

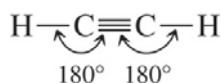
## ◆ The Structure of Ethyne (Acetylene): $sp$ Hybridization

→ Ethyne (acetylene) is a member of a group of compounds called alkynes which all have carbon-carbon triple bonds

⌘ Propyne is another typical alkyne



→ The arrangement of atoms around each carbon is linear with bond angles  $180^\circ$



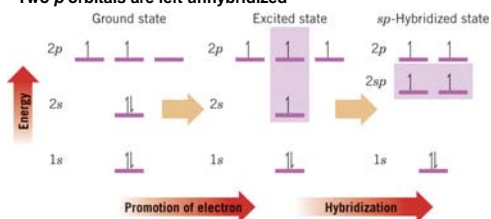
Chapter 1

53

→ The carbon in ethyne is  $sp$  hybridized

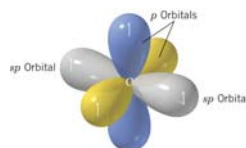
⌘ One  $s$  and one  $p$  orbital are mixed to form two  $sp$  orbitals

⌘ Two  $p$  orbitals are left unhybridized



→ The two  $sp$  orbitals are oriented  $180^\circ$  relative to each other around the carbon nucleus

⌘ The two  $p$  orbitals are perpendicular to the axis that passes through the center of the  $sp$  orbitals



Chapter 1

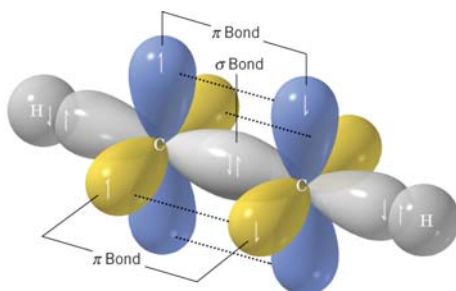
54

→ In ethyne the  $sp$  orbitals on the two carbons overlap to form a  $\sigma$  bond

↳ The remaining  $sp$  orbitals overlap with hydrogen  $1s$  orbitals

→ The  $p$  orbitals on each carbon overlap to form two  $\pi$  bonds

→ The triple bond consists of one  $\sigma$  and two  $\pi$  bonds

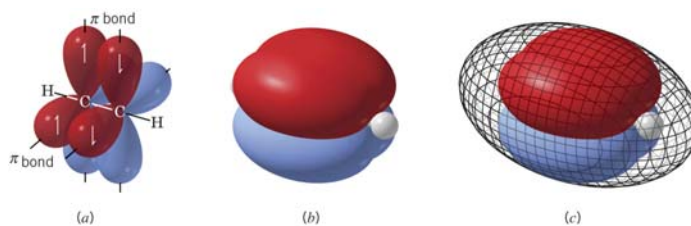


Chapter 1

55

→ Depictions of ethyne show that the electron density around the carbon-carbon bond has circular symmetry

↳ Even if rotation around the carbon-carbon bond occurred, a different compound would not result



Chapter 1

56

## ● Bond Lengths of Ethyne, Ethene and Ethane

→ The carbon-carbon bond length is shorter as more bonds hold the carbons together

⌘ With more electron density between the carbons, there is more "glue" to hold the nuclei of the carbons together

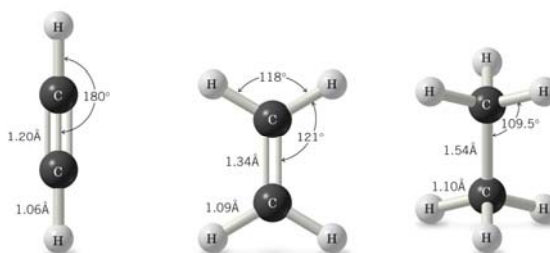
→ The carbon-hydrogen bond lengths also get shorter with more s character of the bond

⌘ 2s orbitals are held more closely to the nucleus than 2p orbitals

⌘ A hybridized orbital with more percent s character is held more closely to the nucleus than an orbital with less s character

⌘ The sp orbital of ethyne has 50% s character and its C-H bond is shorter

⌘ The sp<sup>3</sup> orbital of ethane has only 25% s character and its C-H bond is longer

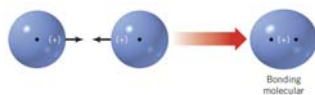


Chapter 1

57

## ◆ Summary of Concepts from Quantum Mechanics

- **Atomic Orbital (AO):** region in space around a nucleus where there is a high probability of finding an electron
- **Molecular Orbital (MO):** results from overlap of atomic orbitals
- **Bonding Orbitals:** when AOs of same sign overlap



- **Antibonding Orbitals:** when AOs of opposite sign overlap



- **The energy of electrons in a bonding orbital is less than the energy of the individual atoms**

⌘ The energy of electrons in an antibonding orbitals is more

Chapter 1

58

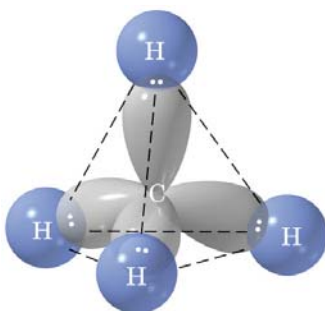
- The number of molecular orbitals formed equals the number of the atomic orbitals used
- Hybridized orbitals are obtained by mixing the wave functions of different types of orbitals
  - Four  $sp^3$  orbitals are obtained from mixing one  $s$  and three  $p$  orbitals
    - ⌘ The geometry of the four orbitals is tetrahedral
    - ⌘ This is the hybridization used in the carbon of methane
  - Three  $sp^2$  orbitals are obtained from mixing one  $s$  and two  $p$  orbitals
    - ⌘ The geometry of the three orbitals is trigonal planar
    - ⌘ The left over  $p$  orbital is used to make a  $\pi$  bond
    - ⌘ This is the hybridization used in the carbons of ethene
  - Two  $sp$  orbitals are obtained from mixing one  $s$  and one  $p$  orbital
    - ⌘ The geometry of the two orbitals is linear
    - ⌘ The two leftover  $p$  orbitals are used to make two  $\pi$  bonds
    - ⌘ This is the hybridization used in the carbons of ethyne
  - Sigma ( $\sigma$ ) bonds have circular symmetry when viewed along the bond axis
  - Pi ( $\pi$ ) bonds result from sideways overlap of two  $p$  orbitals

### ◆ Molecular Geometry: The Valence Shell Electron Pair Repulsion (VSEPR) Model

- This is a simple theory to predict the geometry of molecules
- All sets of valence electrons are considered including:
  - ⌘ Bonding pairs involved in single or multiple bonds
  - ⌘ Non-bonding pairs which are unshared
- Electron pairs repel each other and tend to be as far apart as possible from each other
- Non-bonding electron pairs tend to repel other electrons more than bonding pairs do (*i.e.* they are “larger”)
- The geometry of the molecule is determined by the number of sets of electrons by using geometrical principles

- **Methane**

- The valence shell of methane contains four pairs or sets of electrons
- To be as far apart from each other as possible they adopt a tetrahedral arrangement (bond angle  $109.5^\circ$ )
- The molecule methane is therefore tetrahedral

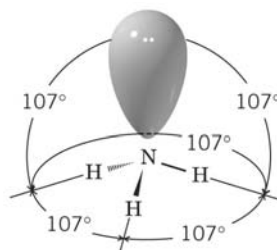
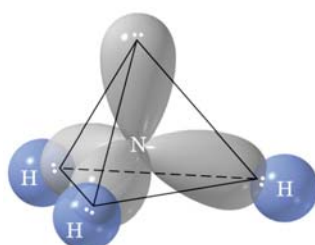


Chapter 1

61

- **Ammonia**

- When the bonding and nonbonding electrons are considered there are 4 sets of electrons
- The molecule is essentially tetrahedral but the actual shape of the bonded atoms is considered to be trigonal planar
- The bond angles are about  $107^\circ$  and not  $109.5^\circ$  because the non-bonding electrons in effect are larger and compress the nitrogen-hydrogen bond

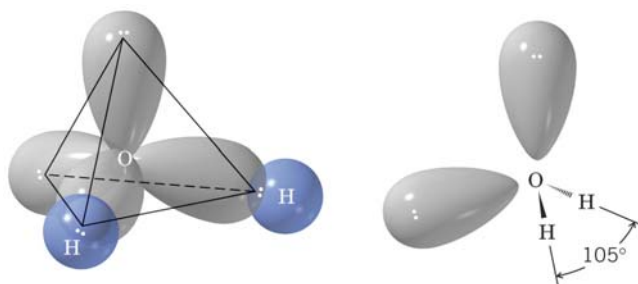


Chapter 1

62

- **Water**

- There are four sets of electrons including 2 bonding pairs and 2 non-bonding pairs
- Again the geometry is essentially tetrahedral but the actual shape of the atoms is considered to be an angular arrangement
- The bond angle is about  $105^\circ$  because the two “larger” nonbonding pairs compress the electrons in the oxygen-hydrogen bonds



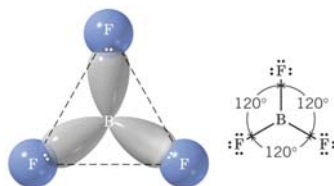
Chapter 1

63

- **Boron Trifluoride**

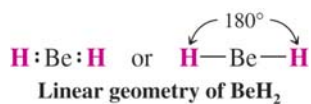
- Three sets of bonding electrons are farthest apart in a trigonal planar arrangement (bond angle  $120^\circ$ )

¶ The three fluorides lie at the corners of an equilateral triangle



- **Beryllium Hydride**

- Two sets of bonding electrons are farthest apart in a linear arrangement (bond angles  $180^\circ$ )



Chapter 1

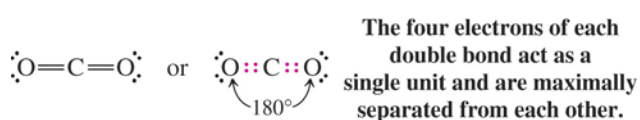
64



- **Carbon Dioxide**

→ There are only two sets of electrons around the central carbon and so the molecule is linear (bond angle 180°)

‡ Electrons in multiple bonds are considered as one set of electrons in total



→ A summary of the results also includes the geometry of other simple molecules

Number of Electron Pairs at Central Atom			Hybridization State of Central Atom	Shape of Molecule or Ion*	Examples
Bonding	Nonbonding	Total			
2	0	2	$sp$	Linear	$\text{BeH}_2$
3	0	3	$sp^2$	Trigonal planar	$\text{BF}_3$ , $\text{CH}_3^+$
4	0	4	$sp^3$	Tetrahedral	$\text{CH}_4$ , $\text{NH}_4^+$
3	1	4	$\sim sp^3$	Trigonal pyramidal	$\text{NH}_3$ , $\text{CH}_3^-$
2	2	4	$\sim sp^3$	Angular	$\text{H}_2\text{O}$

\*Referring to positions of atoms and excluding nonbonding pairs.

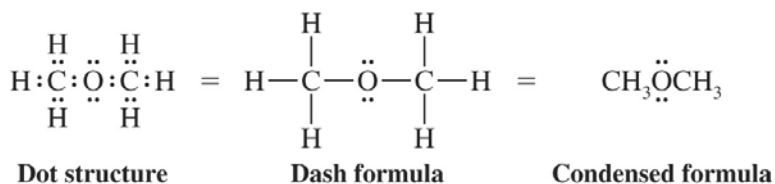
Chapter 1

65

- ◆ **Representations of Structural Formulas**

→ Dot formulas are more cumbersome to draw than dash formulas and condensed formulas

→ Lone-pair electrons are often (but not always) drawn in, especially when they are crucial to the chemistry being discussed



Chapter 1

66

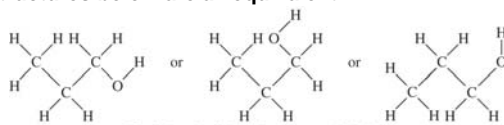
- **Dash formulas**

- Each dash represents a pair of electrons

- This type of representation is meant to emphasize connectivity and does not represent the 3-dimensional nature of the molecule

- ⌘ The dash formulas of propyl alcohol appear to have 90° angles for carbons which actually have tetrahedral bond angles (109.5°)

- There is relatively free rotation around single bonds so the dash structures below are all equivalent

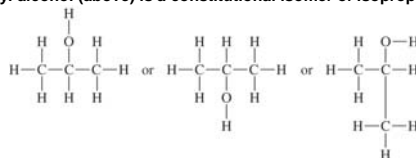


Equivalent dash formulas for propyl alcohol

- **Constitutional isomers**

- ⌘ Constitutional isomers have the same molecular formula but different connectivity

- ⌘ Propyl alcohol (above) is a constitutional isomer of isopropyl alcohol (below)



Equivalent dash formulas for isopropyl alcohol

Chapter 1

67

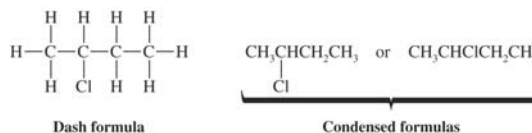
- **Condensed Structural Formulas**

- In these representations, some or all of the dash lines are omitted

- In partially condensed structures all hydrogens attached to an atom are simply written after it but some or all of the other bonds are explicitly shown

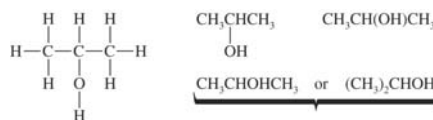
- In fully condensed structure all bonds are omitted and atoms attached to carbon are written immediately after it

- For emphasis, branching groups are often written using vertical lines to connect them to the main chain



Dash formula

Condensed formulas



Dash formula

Condensed formulas

Chapter 1

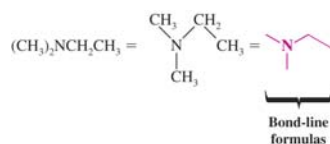
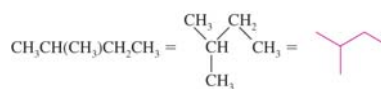
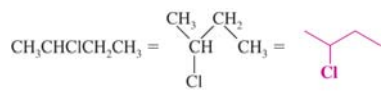
68

- **Bond-Line Formulas**

→ A further simplification of drawing organic molecules is to completely omit all carbons and hydrogens and only show heteroatoms (e.g. O, Cl, N) explicitly

→ Each intersection or end of line in a zig-zag represents a carbon with the appropriate amount of hydrogens

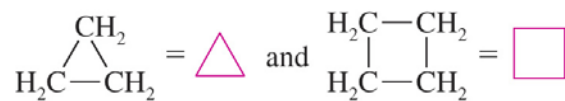
⚠ Heteroatoms with attached hydrogens must be drawn in explicitly



Chapter 1

69

→ Cyclic compounds are condensed using a drawing of the corresponding polygon



→ Multiple bonds are indicated by using the appropriate number of lines connecting the atoms



Chapter 1

70

- **Three-Dimensional Formulas**

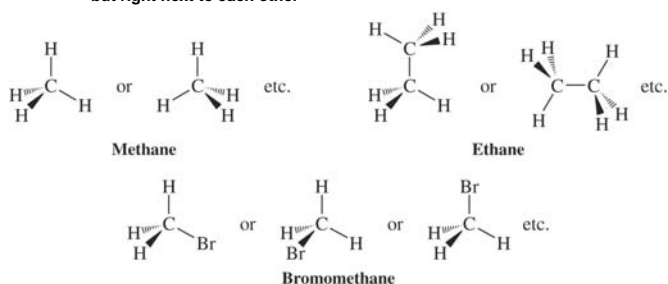
- Since virtually all organic molecules have a 3-dimensional shape it is often important to be able to convey their shape

- The conventions for this are:

- ⌘ Bonds that lie in the plane of the paper are indicated by a simple line
    - ⌘ Bonds that come forward out of the plane of the paper are indicated by a solid wedge
    - ⌘ Bonds that go back out of the plane of the paper are indicated by a dashed wedge

- Generally to represent a tetrahedral atom:

- ⌘ Two of the bonds are drawn in the plane of the paper about 109° apart
    - ⌘ The other two bonds are drawn in the opposite direction to the in-plane bonds but right next to each other



Chapter 1

71

- Trigonal planar arrangements of atoms can be drawn in 3-dimensions in the plane of the paper

- ⌘ Bond angles should be approximately 120°
    - ⌘ These can also be drawn side-on with the central bond in the plane of the paper, one bond forward and one bond back

- Linear arrangements of atoms are always best drawn in the plane of the paper

Chapter 1

72