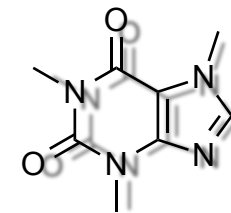


Chemistry 2500

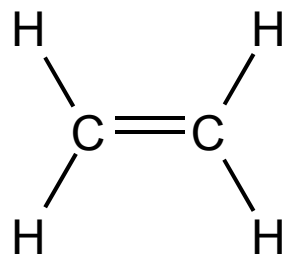
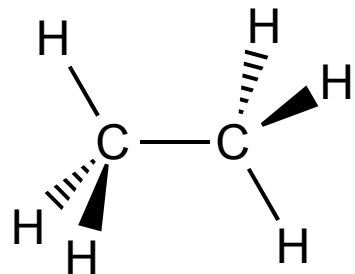
Chapter 1

Carbon and its Compounds

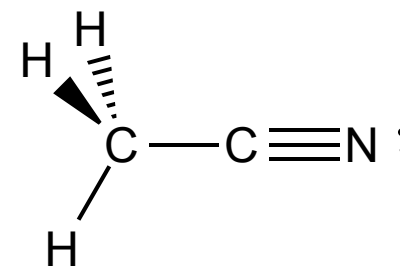
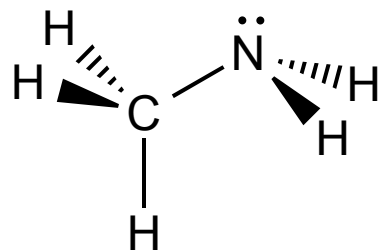
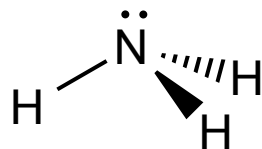
Carbon And Its Compounds – Lewis Structures



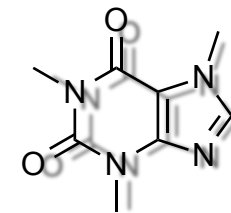
- Stable carbon-containing compounds have 4 bonds to carbon



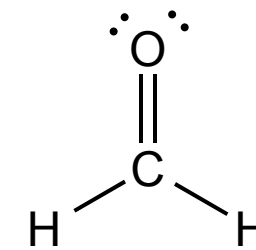
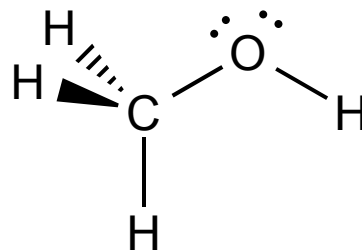
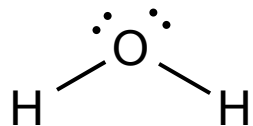
- 3 bonds to nitrogen



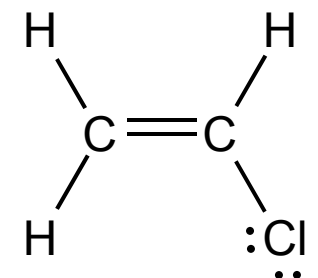
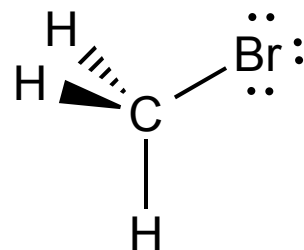
Carbon And Its Compounds – Lewis Structures



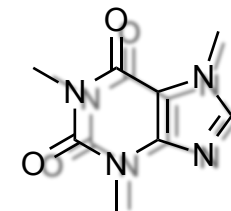
- 2 bonds to oxygen



- 1 bond to H, F, Cl, Br, I

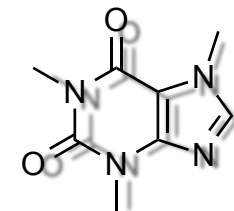


Developing Lewis Structures For Organic Compounds



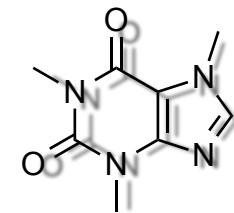
1. Draw the full structure of the molecules with the connectivity suggested by the formula such that all valences are met (octets for C, N, O, F, Cl, Br, I – **always**)
2. Always show all valence electrons (bonds *and* lone pairs).
 - a) Count the number of valence electrons in the entire molecule (each atom has the same number of valence electrons as its group number in the periodic table)
 - b) From the number in a), subtract the number of bonding electrons (2x the number of lines in your structure). Any electrons that are unpaired are added to atoms that lack a full octet (usually heteroatoms) as lone pairs.
 - c) Atoms still lacking octets are satisfied by using lone pairs from adjacent atoms to form multiple bonds.
3. Always show formal charges according to the following formula:
$$\text{F.C} = \# \text{ of valence electrons} - (\# \text{ of bonds to that atoms}) - (\# \text{ of lone pair electrons})$$
4. Formal charges of 0 is always better than charge separation.

Developing Lewis Structures For Organic Compounds

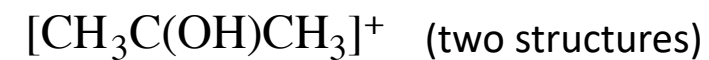


5. No charges on carbon if the molecule is neutral.
6. Never draw structures with adjacent like charges.
7. Do not place multiple charges on 1st and 2nd row atoms (-1 and +1 only)
8. When placing charges, - charges should be placed on the more electronegative atoms and + charges should be placed on the less electronegative atoms.
9. Avoid the formation of O-O when possible and the formation of halogen-heteroatom bonds. A heteroatom is any atom other than carbon and hydrogen.
10. In general:
 - H only needs 2 electrons (1 bond)
 - B and Al need only 6 electrons (3 bonds)
 - C, N, O, F can **NEVER** exceed 8 electrons (C may have less)
 - Atoms below the second row may have more than 8 electrons.

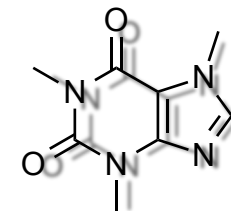
Lewis Structures



- Draw the following molecules as Lewis Structures.



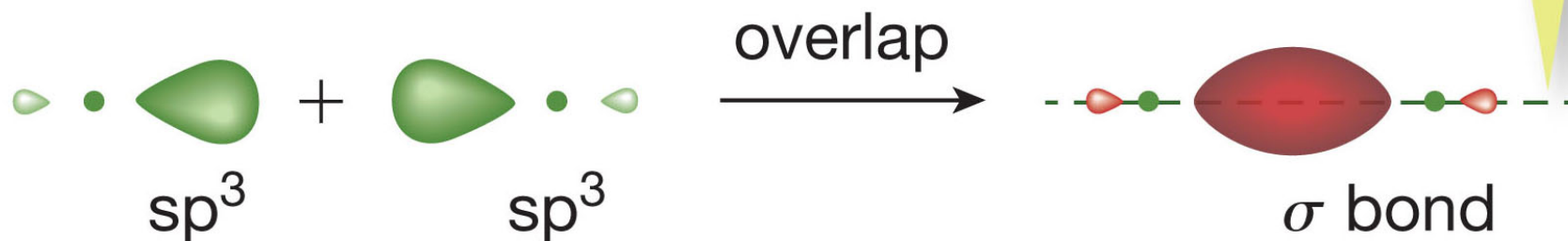
Covalent Bonding: Atomic Orbital Overlap



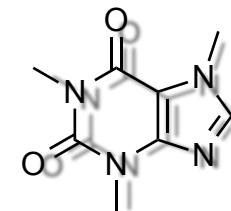
- Sigma (σ) bonds:



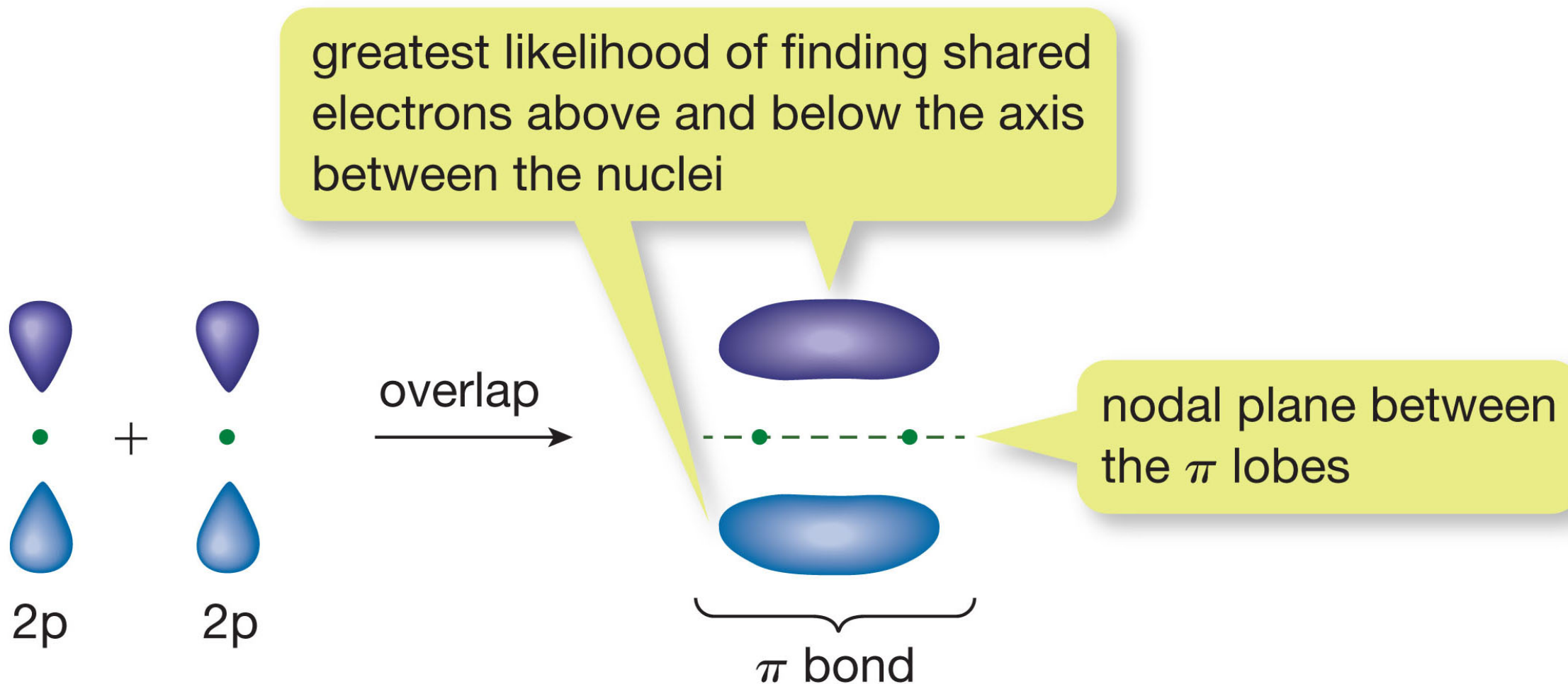
greatest likelihood of finding shared electrons along the axis between the nuclei



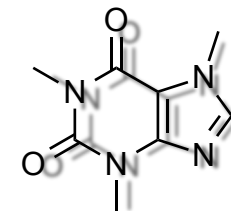
Covalent Bonding: Atomic Orbital Overlap



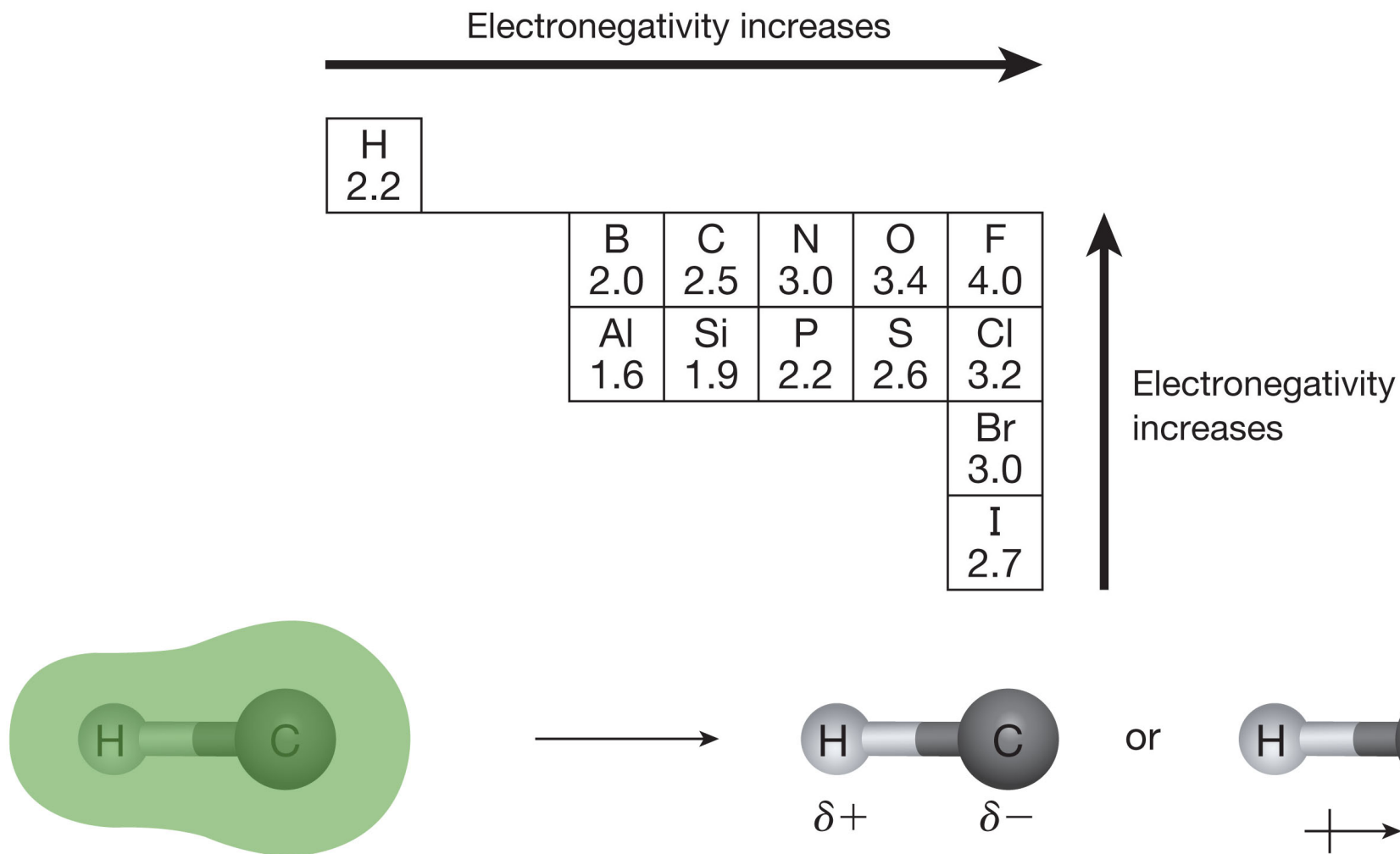
- Pi (π) bonds:



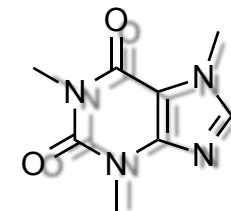
Dipoles



- Electronegativity differences between atoms accounts for bond dipoles.

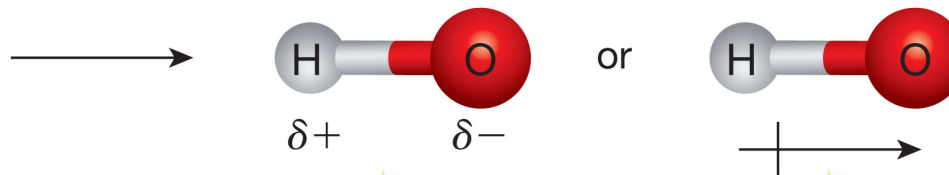
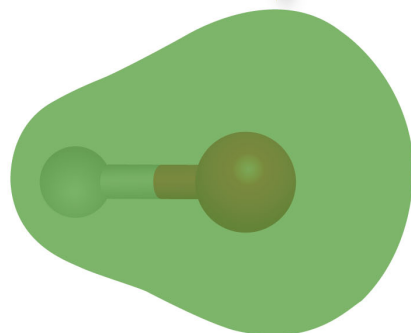


Dipoles



- Electronegativity differences between atoms accounts for bond dipoles.

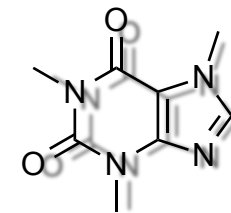
Oxygen is much more electronegative than hydrogen as seen in this electron density map. There is an unequal sharing of electrons between them, making the oxygen slightly negative and the hydrogen slightly positive. In this depiction, the size of the orbital lobe is used to depict the likelihood of finding electrons around each atom in the bond.



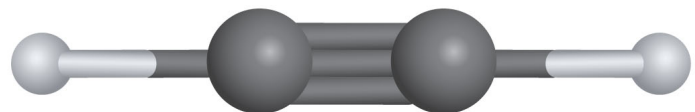
The dipole can be shown as a pair of partial charges ...

... or as a dipole arrow. The longer the arrow, the stronger the dipole.

The Shapes of Atoms - VSEPR

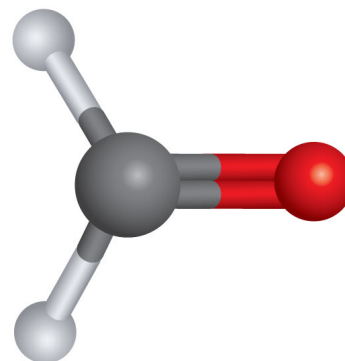
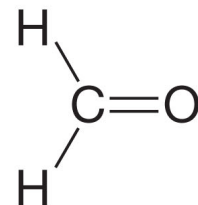


- Covalently bonded carbon atoms have 3 possible structural geometries:



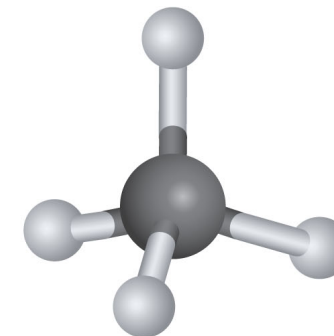
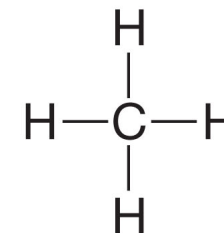
ethyne, C₂H₂

linear



formaldehyde, CH₂O

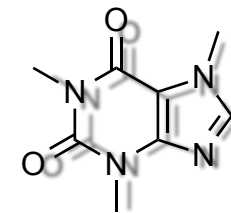
trigonal planar



methane, CH₄

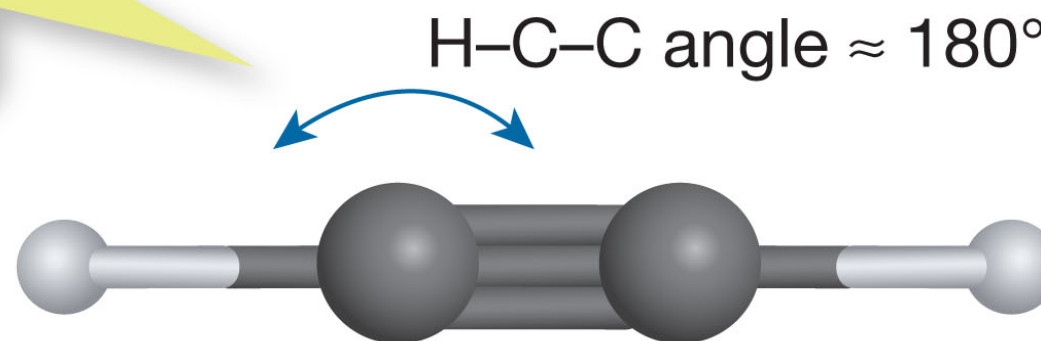
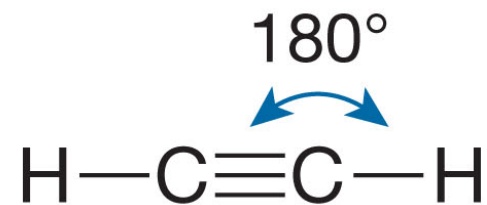
tetrahedral

Valence Shell Electron Pair Repulsion (VSEPR)

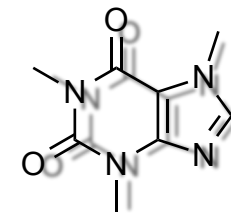


- Linear:

two groups of electrons spaced at maximum distance from each other produces a linear geometry

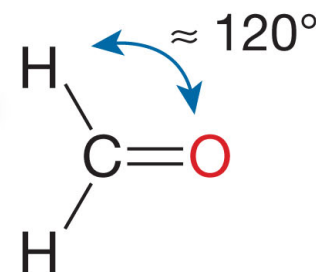


Valence Shell Electron Pair Repulsion (VSEPR)

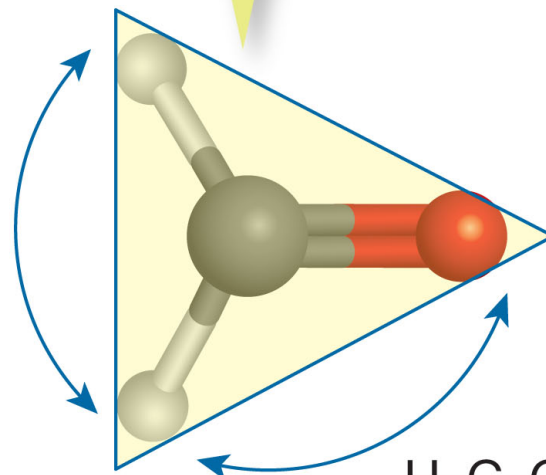


- Trigonal Planar:

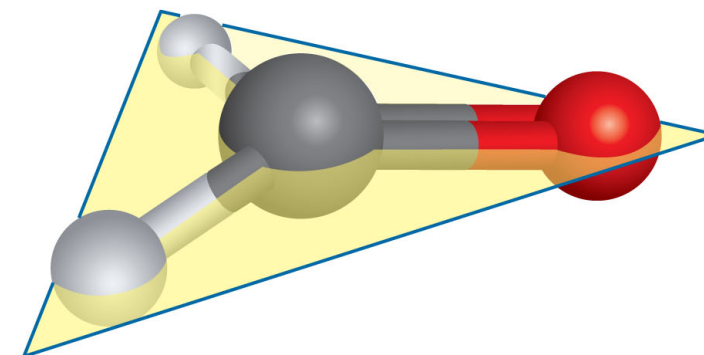
three groups of electrons spaced at maximum distance from each other produces a trigonal geometry



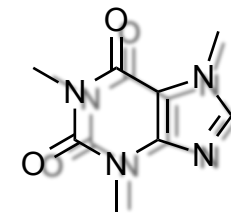
H-C-H angle $\approx 120^\circ$



H-C-O angle $\approx 120^\circ$

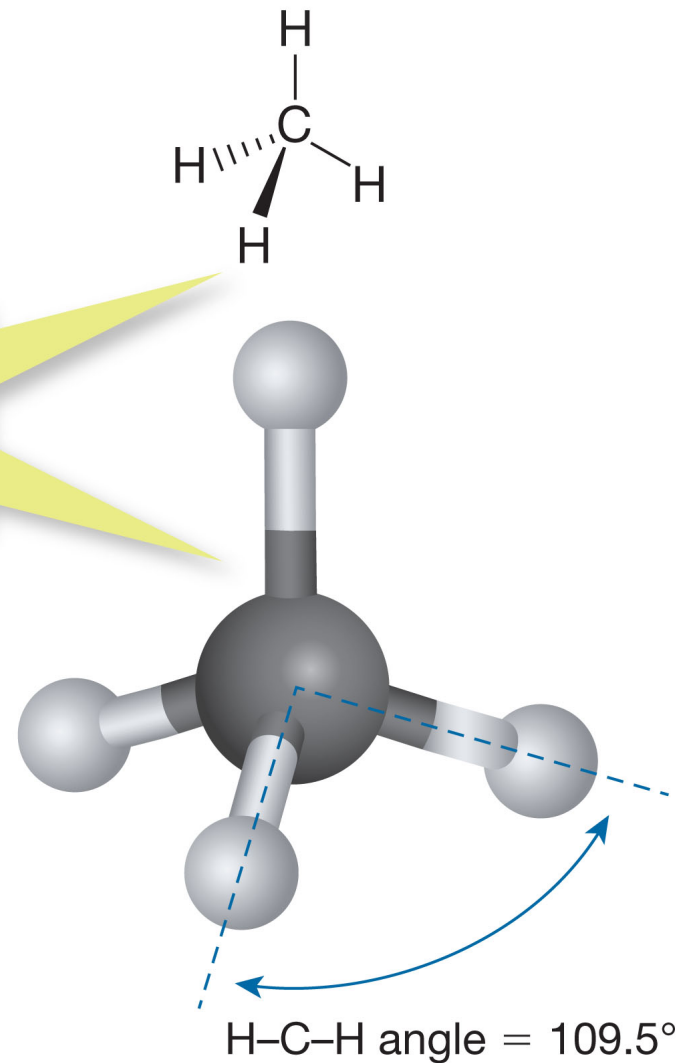


Valence Shell Electron Pair Repulsion (VSEPR)

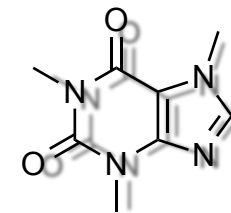


- Tetrahedral:

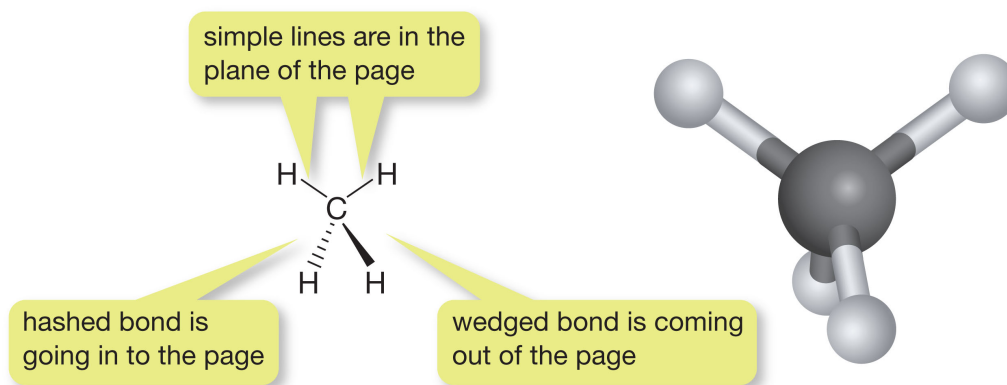
four groups of electrons spaced at maximum distance from each other produces a tetrahedral geometry



Tetrahedral geometry: Dashes/Wedges



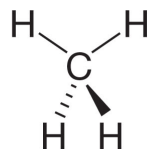
- Dashes/Wedges are used to depict the 3-D geometry of tetrahedral bonds



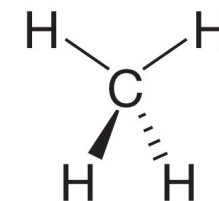
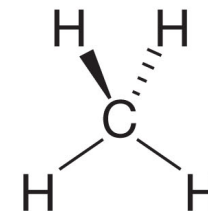
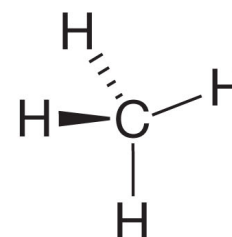
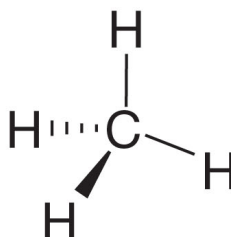
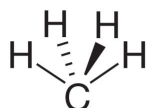
- Note: 2 bonds are drawn as simple lines in a 'V', while the dash/wedge, also in a 'V' are drawn on the opposite side of the simple lines:

tetrahedron ✓

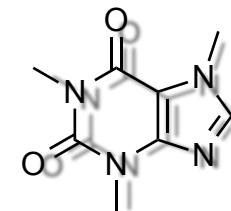
not a tetrahedron ✗



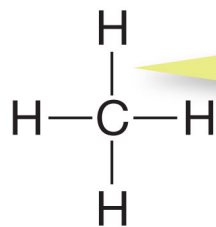
next to each other



Valence Bond (VB) Theory

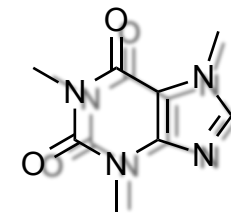


- Valence bond theory extends the idea that a bond involves the sharing of spin-paired electrons through the overlap of atomic orbitals between atoms.
- These are called *localized bonds*, and are confined to the region between the two participating atoms.
- Valence bond theory uses *hybrid orbitals* to describe and explain the observed geometries in organic molecules.
- Hybridization is not a physical process but a mathematical process.



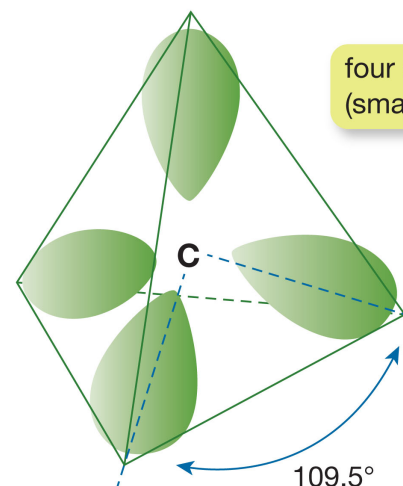
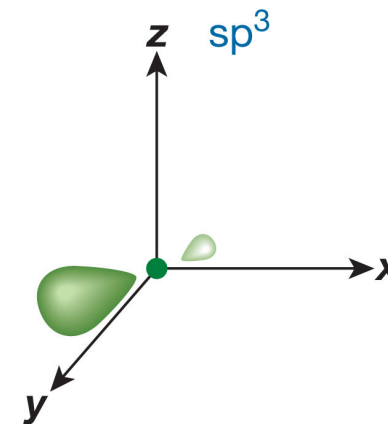
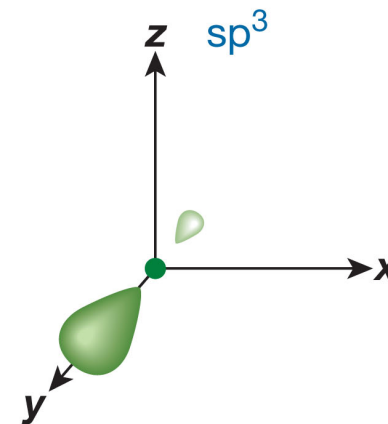
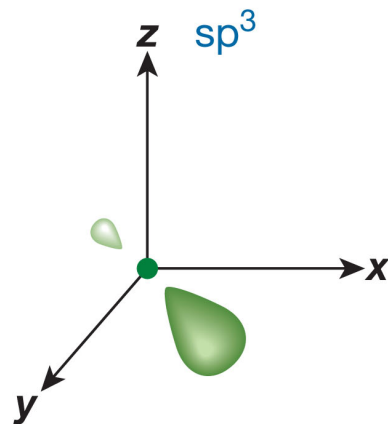
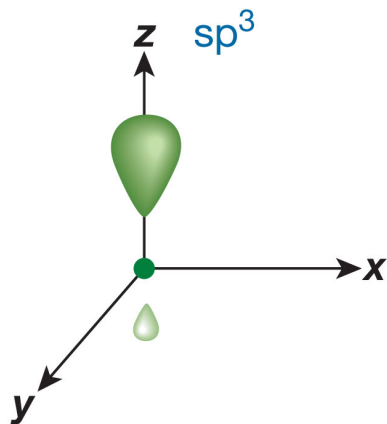
In valence bond terms, each line in a Lewis structure represents a localized bond in which the probability of finding the electron pair is confined to the regions between the atoms.

Valence Bond Theory



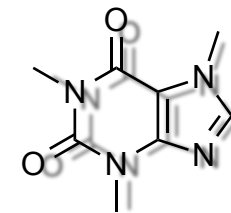
- Tetrahedral geometry requires sp^3 hybrids:

$$2s + 3\ 2p =$$

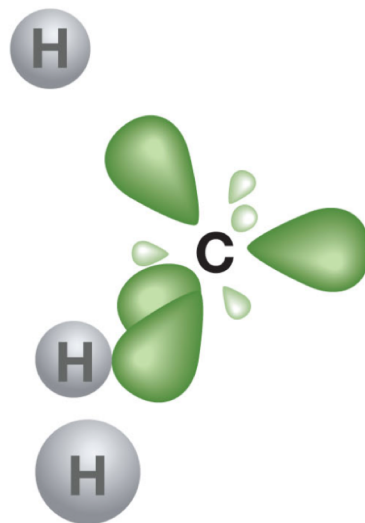
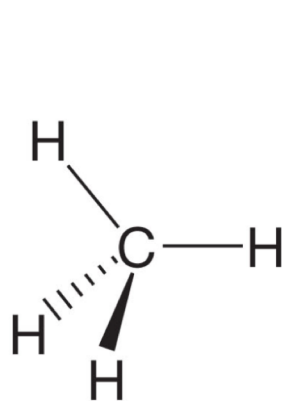


four sp^3 hybrid atomic orbitals
(small lobes not shown)

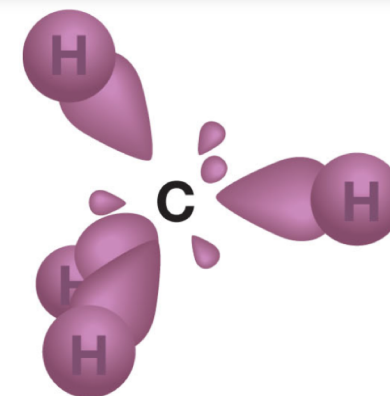
Valence Bond Theory



- Tetrahedral geometry requires sp^3 hybrids:

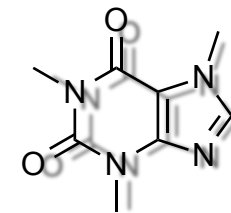


overlap orbitals

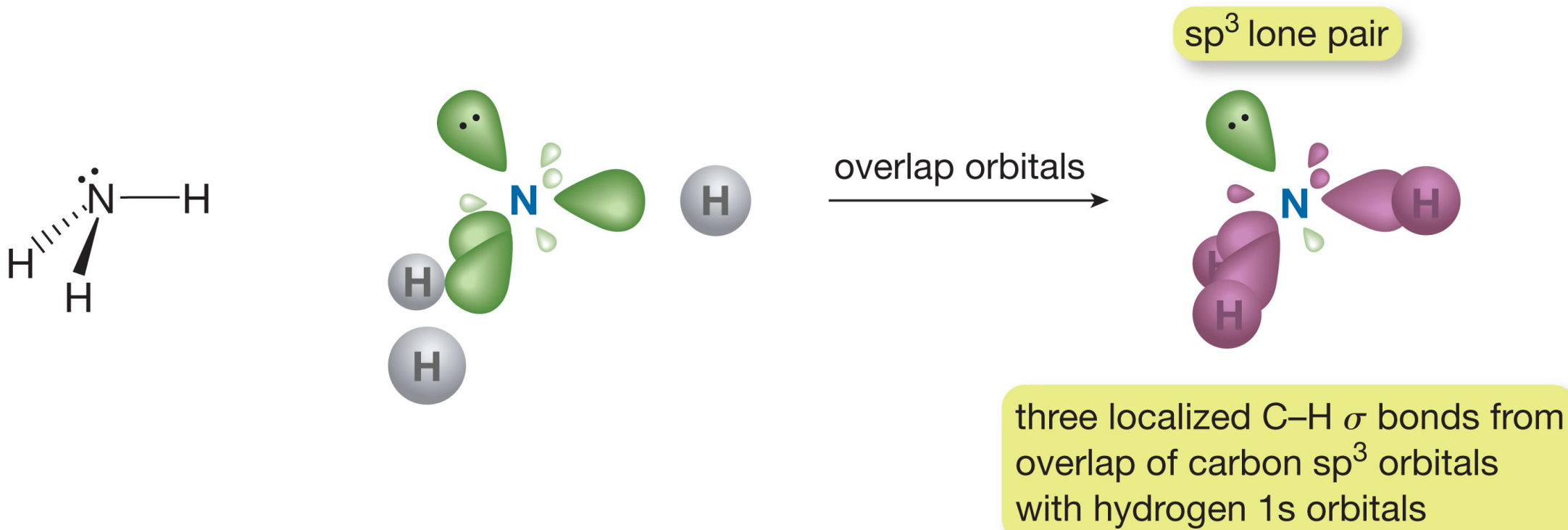


four localized C-H σ bonds from overlap of carbon sp^3 orbitals with hydrogen 1s orbitals

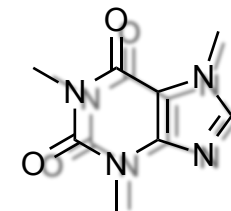
Valence Bond Theory



- Tetrahedral geometry requires sp^3 hybrids:

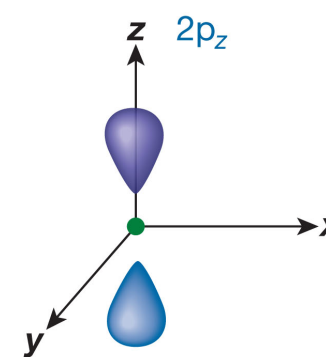
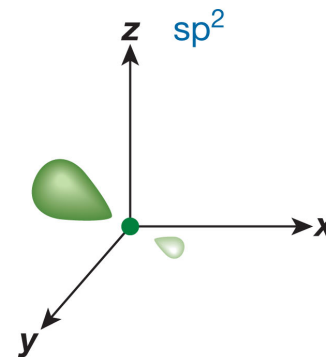
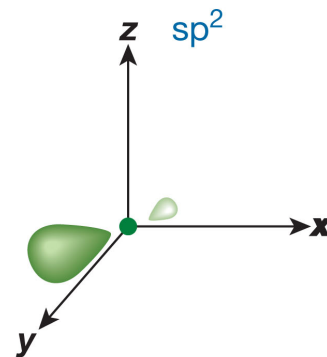
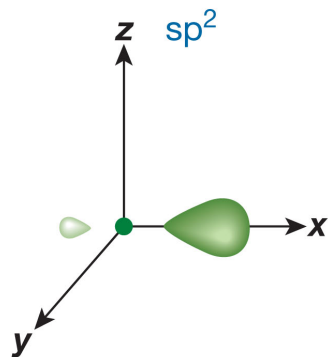


Valence Bond Theory



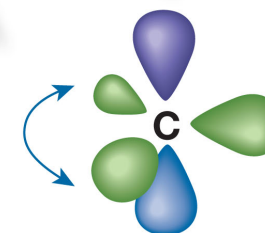
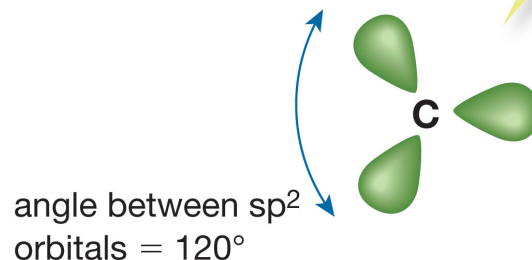
- Trigonal planar geometry requires sp^2 hybrids:

$$2s + 2\ 2p =$$

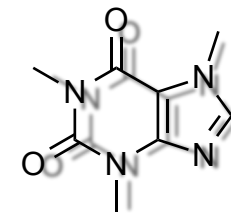


three sp^2 hybrid atomic orbitals
(small lobes not shown)

$2p_z$ orbital perpendicular to
the plane of the sp^2 hybrids

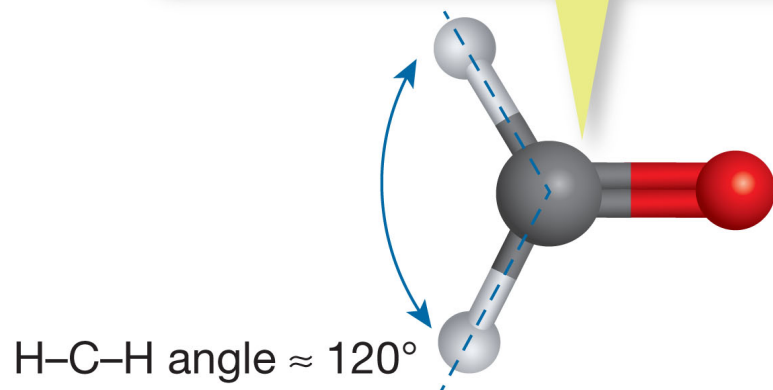


Valence Bond Theory

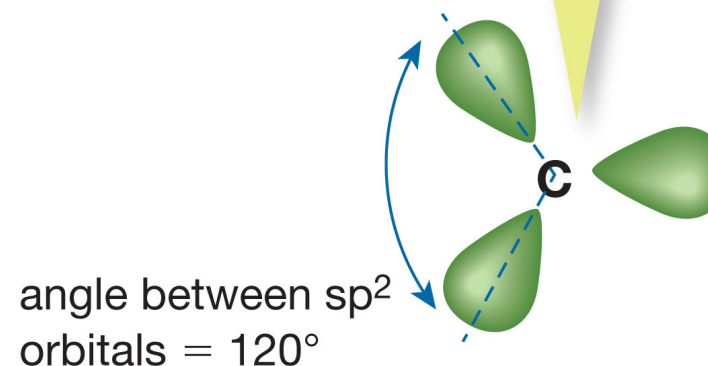


- Trigonal planar geometry requires sp^2 hybrids:

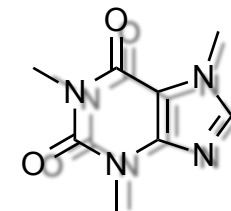
A carbon with a trigonal planar arrangement of three groups requires ...



... a trigonal planar arrangement of its orbitals: three sp^2 hybrid atomic orbitals.

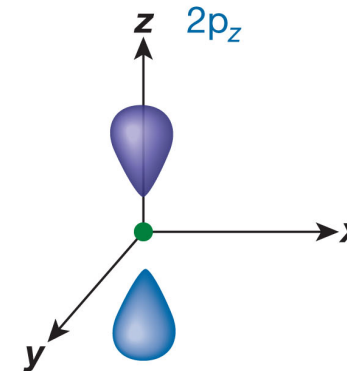
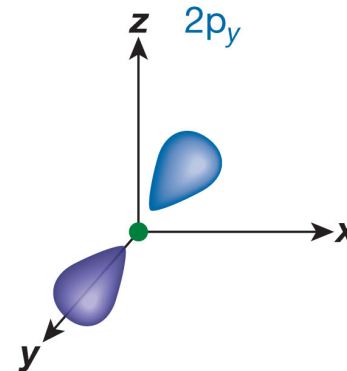
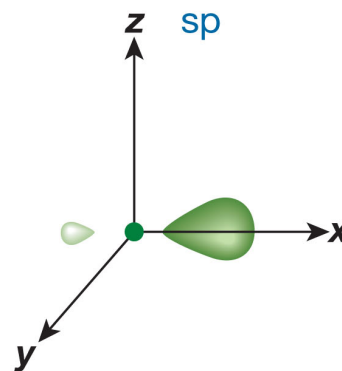
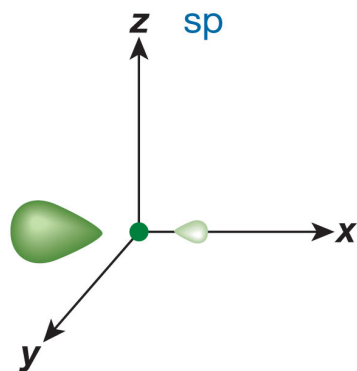


Valence Bond Theory

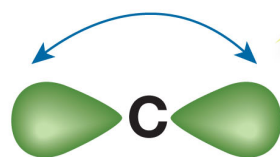


- Linear geometry requires sp hybrids:

$$2s + 1\ 2p =$$



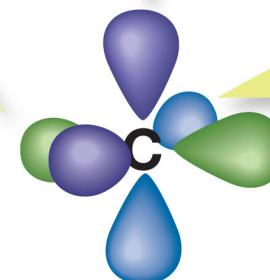
angle between sp
orbitals = 180°



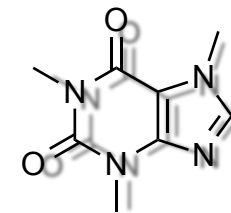
two sp hybrid atomic orbitals
(small lobes not shown)

$2p_z$ orbital perpendicular to
the sp hybrids

$2p_y$ orbital perpendicular
to the sp hybrids



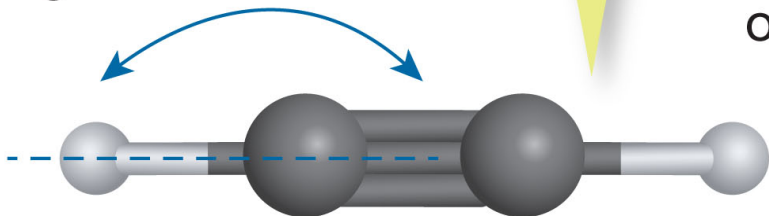
Valence Bond Theory



- Linear geometry requires sp hybrids:

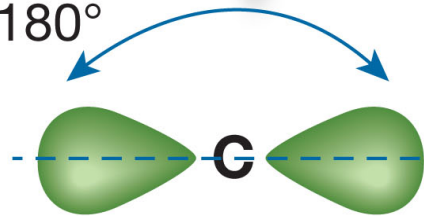
A carbon with a linear arrangement of two groups requires ...

H-C-C angle = 180°

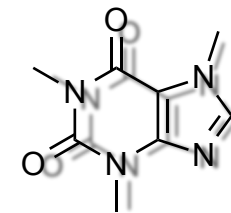


... a linear arrangement of its orbitals: two sp hybrid atomic orbitals.

angle between sp orbitals = 180°

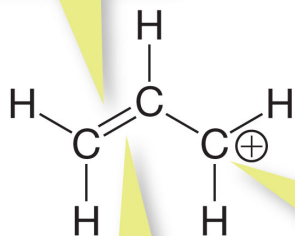


Resonance Structures



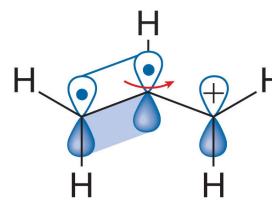
- Lewis structures are sometimes limiting in their ability to describe the bonding in a molecule, especially those that involve π bonds.
- Resonance structures are used to describe the delocalization of π electrons in a molecule.

σ bond from sp^2-sp^2 overlap

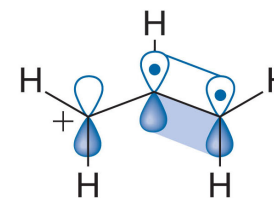


π bond from p-p overlap

carbon is surrounded by only three groups of electrons and must be sp^2 hybridized

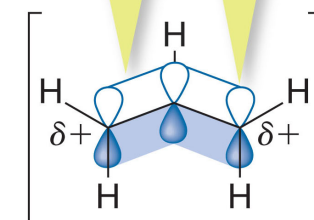


(a)



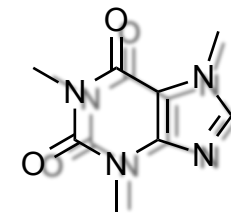
(b)

p orbital overlap is the same between all three carbons



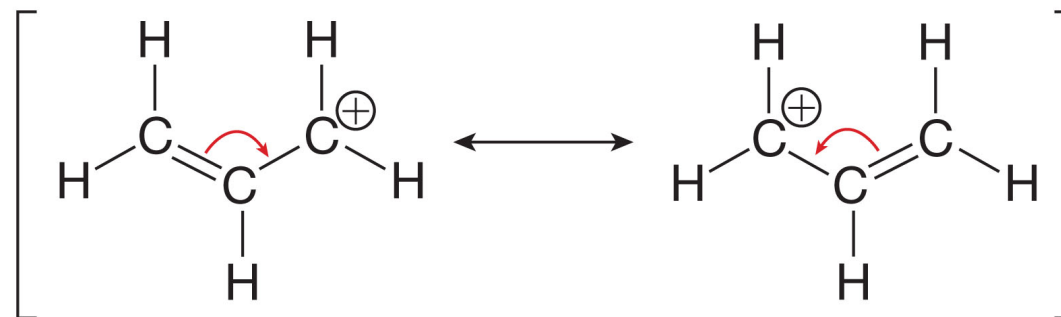
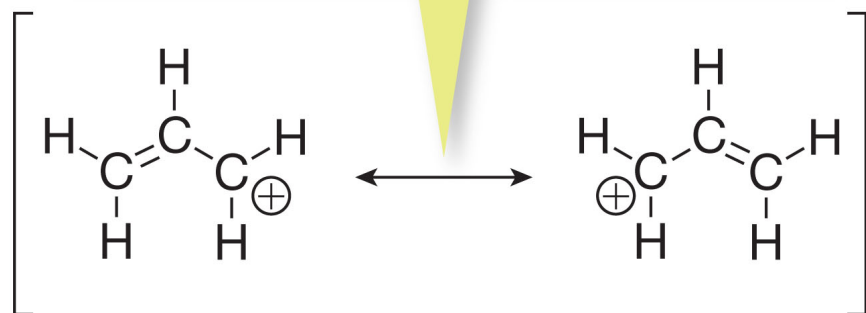
(c)

Resonance Structures

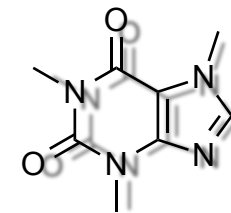


- It is of upmost importance to understand that resonance structures do NOT exist.
- The molecule does NOT flip-flop between resonance structures.
- The actual structure of the molecule is a weighted average of all resonance structures. All the resonance structures, blended together, provide a picture of the π bonding in the molecule.

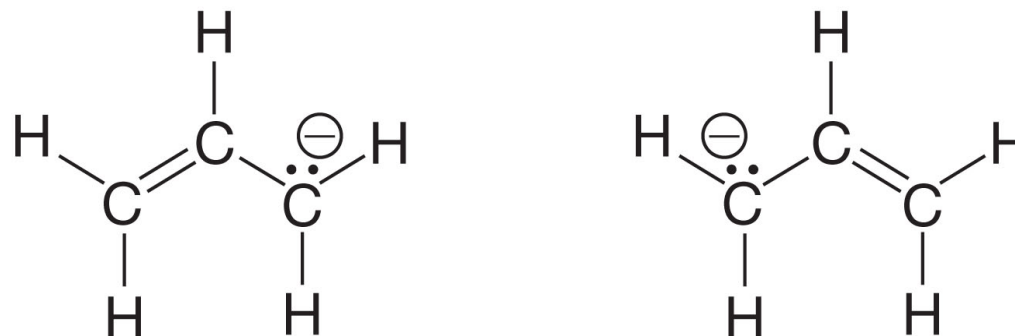
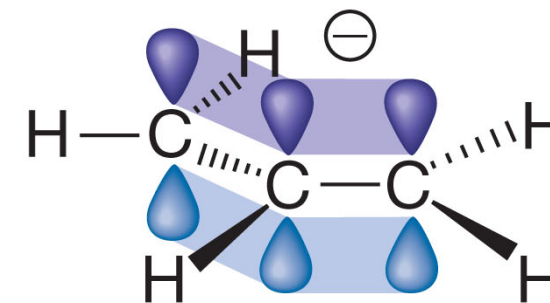
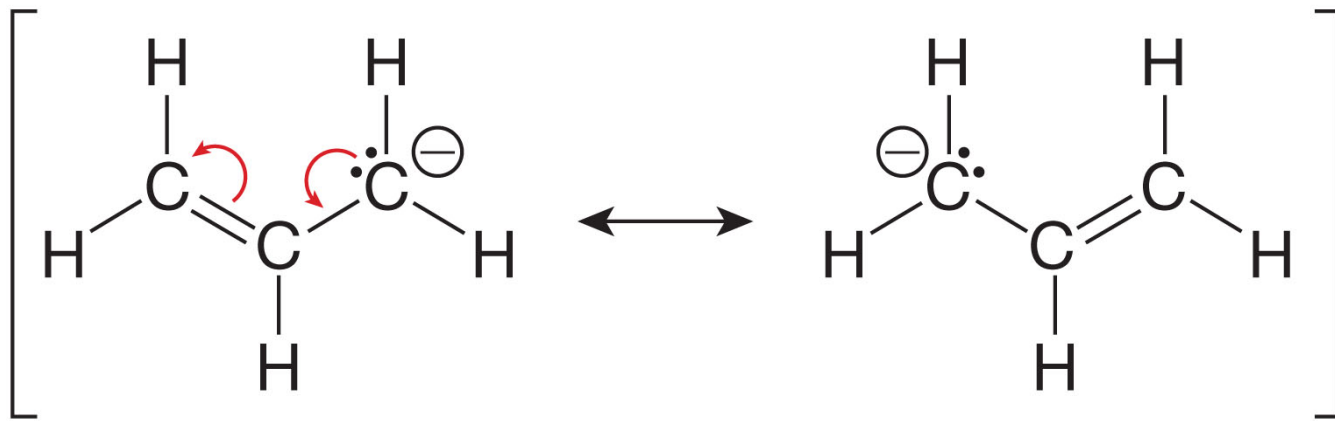
double-ended arrows are used to indicate and separate resonance forms



Resonance Forms

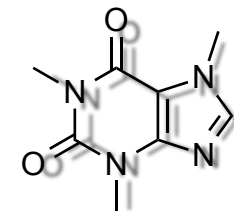


- What is the geometry of each carbon atom in the allyl anion?



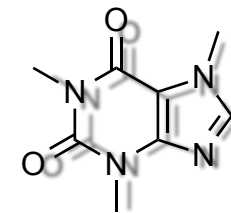
two equivalent Lewis structures

Molecular Orbital (MO) Theory

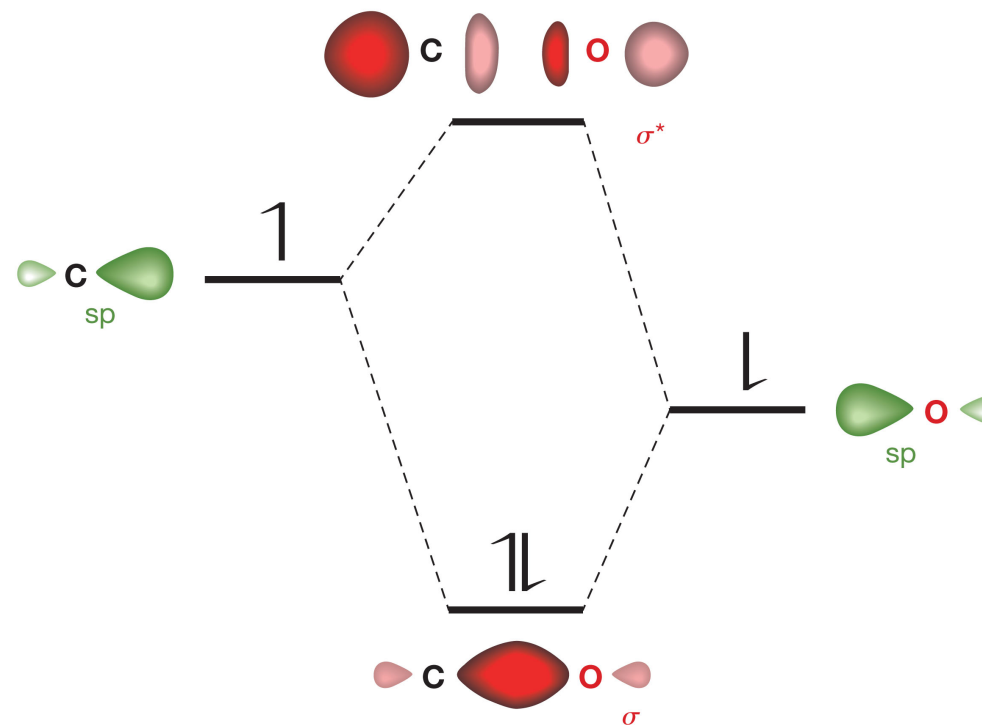


- Molecular orbital theory is another method of describing the bonding in organic molecules.
- Unlike the ‘localized’ approach of VB theory, molecule orbital theory extends the idea of bonding to the entire molecule.
- Atomic orbitals are mixed to create a set of molecular orbitals.
- Molecular orbitals describe the likelihood of finding electrons in the space around the molecule.

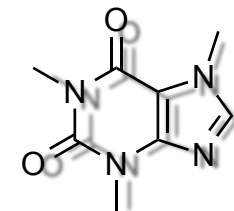
Molecular Orbital (MO) Theory



- Molecular orbitals that show continuous electron density between atoms are known as ***bonding molecular orbitals***.
- Molecular orbitals that show zero probability of finding an electron (node) between atoms are known as ***antibonding molecular orbitals***.

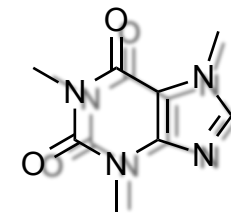


Condensed and Line Structures

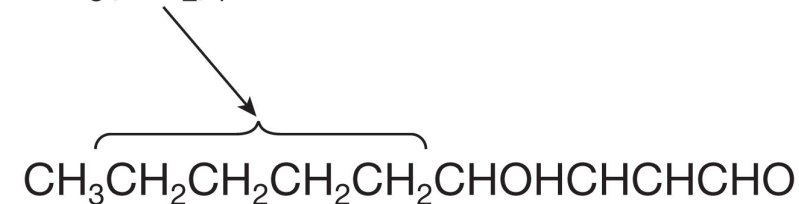
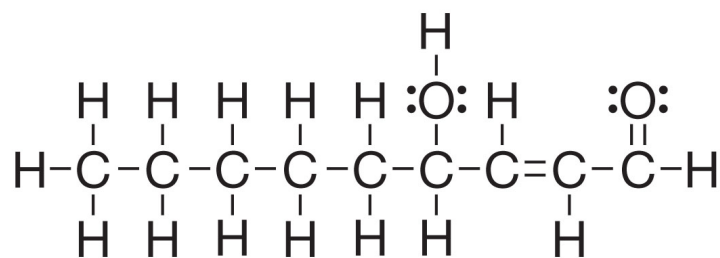


- While Lewis structures show you all the atoms in a molecule and their associated bonds and lone pairs, they do have drawbacks.
 - Lewis structures can be time consuming for larger molecules.
 - Lewis structures can quickly become cluttered, obscuring key features of structure and reactivity.
- Two shorthand drawing styles are used to work around these problems, namely *condensed structures* and *line structures*.

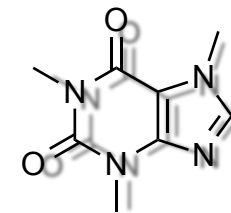
Condensed Structures



- Condensed structures eliminate certain bonds reducing the amount of clutter. Interpreting the structure is done with an understanding of the valence of each atom involved.
 - Carbon atoms followed by hydrogen atoms are assumed to be directly bonded
 - If the number of hydrogen atoms are less than the valence of carbon, then it is assumed that the next atom listed is bonded to carbon.
 - If multiple similar groups are attached to a carbon, these groups may be listed in parentheses.



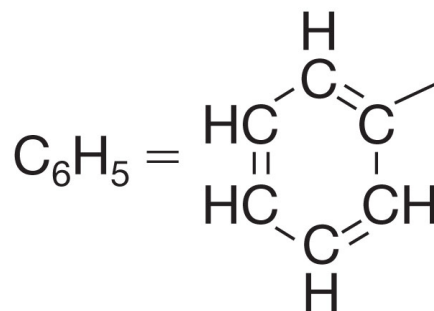
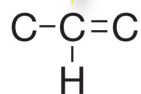
Condensed Structures



- If a structure cannot account for a full valence, there must be multiple bond connections.
- Some groups are common and have condensed abbreviations that must be recognized.
- It is useful to know the 'normal' number of bonds (valence) each atom forms



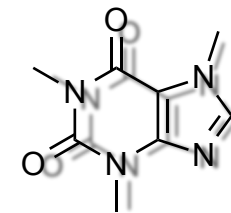
This carbon is connected to one hydrogen and two carbons. This does not give a full valence and so there must be additional bonds to fill the valence.



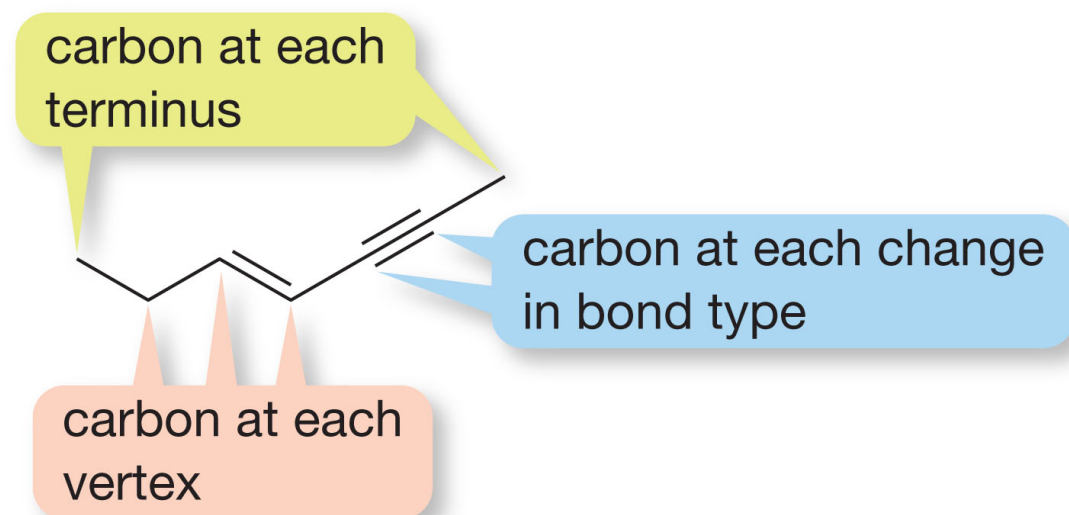
1					
H					
	3	4	3	2	1
	B	C	N	O	F
	Al	Si	P	S	Cl
					Br
					I

number of bonds to obtain a neutral structure

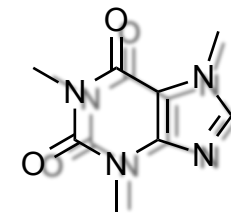
Line Structures



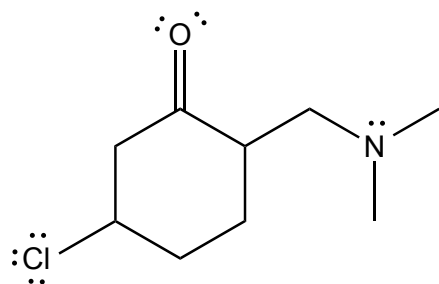
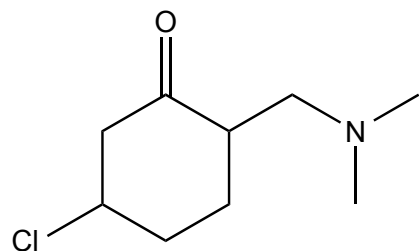
- Line structures are the preferred method of depicting organic molecules.
- Line structures are preferred because they are quick to draw, reduce the amount of clutter, and can emphasize the shapes and functional parts of molecules.
 - All bonds between atoms are drawn as solid lines in a zig-zag pattern.
 - Carbon atoms are generally not explicitly drawn; rather, each vertex, line terminus, and bond transition is understood to represent a carbon atom.



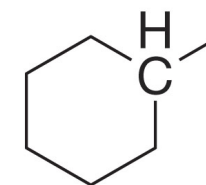
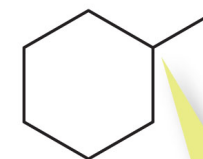
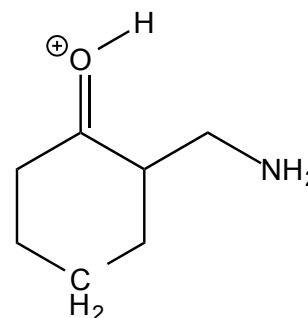
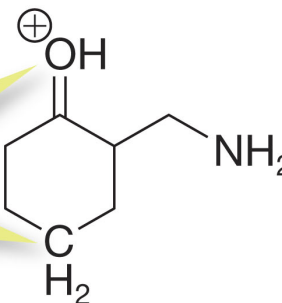
Line Structures



- All heteroatoms (atoms other than C and H) **are** always explicitly drawn.
- Hydrogen atoms are only drawn when attached to an explicitly drawn atom.
- The number of H atoms attached to carbon is implied from the valency of carbon.
- Lone pairs are often omitted in line structures but it is important to remember that they are there. For this reason, all line structures drawn by you must include lone pairs.

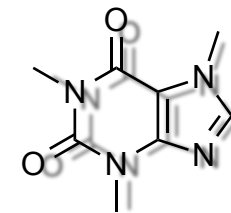


hydrogens are shown when attached to an explicitly drawn atom

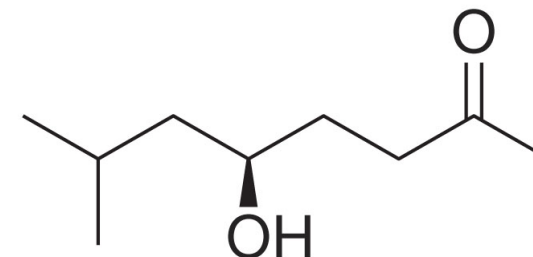
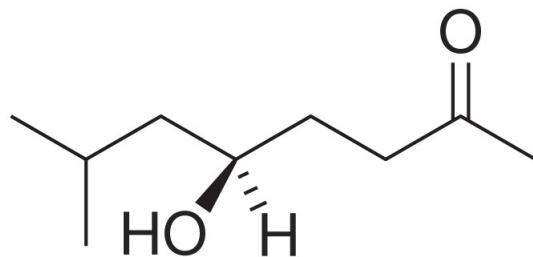


Three bonds are shown to this carbon. The fourth bond must be to a hydrogen.

Line Structures



- Dashes and wedges are used to convey the geometry at tetrahedral centres.
- Because hydrogen atoms attached to carbon atoms are often omitted in line structures, you may draw a structure that will have only a dash or a wedge, but not both.



- Draw line structures for the following Lewis Structures:

