

1. Bonding & Shapes of Molecules (text 1.1 – 1.8)

Most of this section's material is from first-year chem. It is being reviewed because a thorough understanding of it is absolutely necessary before continuing on in organic chemistry.

A. Electronic Structure of Atoms

- The bonding behaviour of atoms depends *entirely* on electron configuration, revealed by an atom's location on the *Organic Chemist's Periodic Table*.

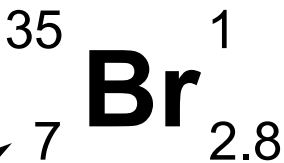
$\begin{smallmatrix} 1 & \text{H}^1 \\ 1 & 2.2 \end{smallmatrix}$						
$\begin{smallmatrix} 3 & \text{Li}^1 \\ 1 & 1.0 \end{smallmatrix}$	$\begin{smallmatrix} 5 & \text{B}^3 \\ 3 & 2.0 \end{smallmatrix}$	$\begin{smallmatrix} 6 & \text{C}^4 \\ 4 & 2.5 \end{smallmatrix}$	$\begin{smallmatrix} 7 & \text{N}^3 \\ 5 & 3.0 \end{smallmatrix}$	$\begin{smallmatrix} 8 & \text{O}^2 \\ 6 & 3.5 \end{smallmatrix}$	$\begin{smallmatrix} 9 & \text{F}^1 \\ 7 & 4.0 \end{smallmatrix}$	
$\begin{smallmatrix} 11 & \text{Na}^1 \\ 1 & 0.9 \end{smallmatrix}$	$\begin{smallmatrix} 12 & \text{Mg}^2 \\ 2 & 1.2 \end{smallmatrix}$	$\begin{smallmatrix} 13 & \text{Al}^3 \\ 3 & 1.5 \end{smallmatrix}$	$\begin{smallmatrix} 14 & \text{Si}^4 \\ 4 & 1.8 \end{smallmatrix}$	$\begin{smallmatrix} 15 & \text{P}^3 \\ 5 & 2.1 \end{smallmatrix}$	$\begin{smallmatrix} 16 & \text{S}^2 \\ 6 & 2.5 \end{smallmatrix}$	$\begin{smallmatrix} 17 & \text{Cl}^1 \\ 7 & 3.1 \end{smallmatrix}$
$\begin{smallmatrix} 19 & \text{K}^1 \\ 1 & 0.8 \end{smallmatrix}$						$\begin{smallmatrix} 35 & \text{Br}^1 \\ 7 & 2.8 \end{smallmatrix}$
						$\begin{smallmatrix} 53 & \text{I}^1 \\ 7 & 2.5 \end{smallmatrix}$

Atomic number = #
of electrons

Valence = # of
unpaired electrons
in valence shell

Group number = #
of outer-shell electrons

Electronegativity



- Recall: four *quantum numbers* used to identify electrons

1. Principal Quantum Number (n)

where n = any integer greater than zero (e.g. 1, 2, 3, 4...).

- As the level n increases, so does the energy of the electron and its distance from the nucleus.
- Within each n level are sublevels designated ℓ .

2. Orbital Quantum Number (ℓ)

where ℓ = any integer between 0 and $(n - 1)$.

- For example, if $n = 2$, then $\ell = 0$ or 1.
- ℓ determines the *shape* of the electron cloud, named:

$\ell = 0 \rightarrow s$ electrons	$\ell = 1 \rightarrow p$ electrons
$\ell = 2 \rightarrow d$ electrons	$\ell = 3 \rightarrow f$ electrons

3. Magnetic Quantum Number (m_ℓ)

where m_ℓ = any integer between $-\ell$ through 0 to $+\ell$.

- Thus, if $\ell = 1$ (p electron), then $m_\ell = -1, 0$, or $+1$.
- m_ℓ represents the electron's *magnetic moment*

4. Spin Quantum Number (m_s)

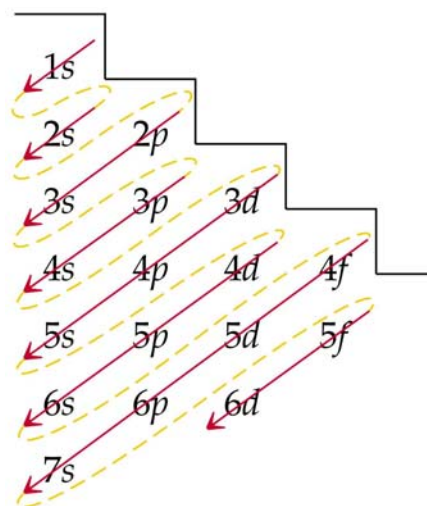
where $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ regardless of other quantum numbers.

- When electrons come together, their *spins* may be the same (both $+$ or both $-$) or opposite (one $+$ and one $-$). These are respectively called *parallel spins* or *opposite spins*, and are denoted by arrows pointing up or down.

$\uparrow \uparrow$ (parallel, not allowed) $\uparrow \downarrow$ (opposite, allowed)

- Ground state electron configuration

- The lowest energy state for electrons in an atom is determined by placing electrons *in pairs* into atomic orbitals.
- 3d and 4s are close in energy.
- This filling-order gives the correct electronic configuration for all atoms normally seen in organic chemistry.



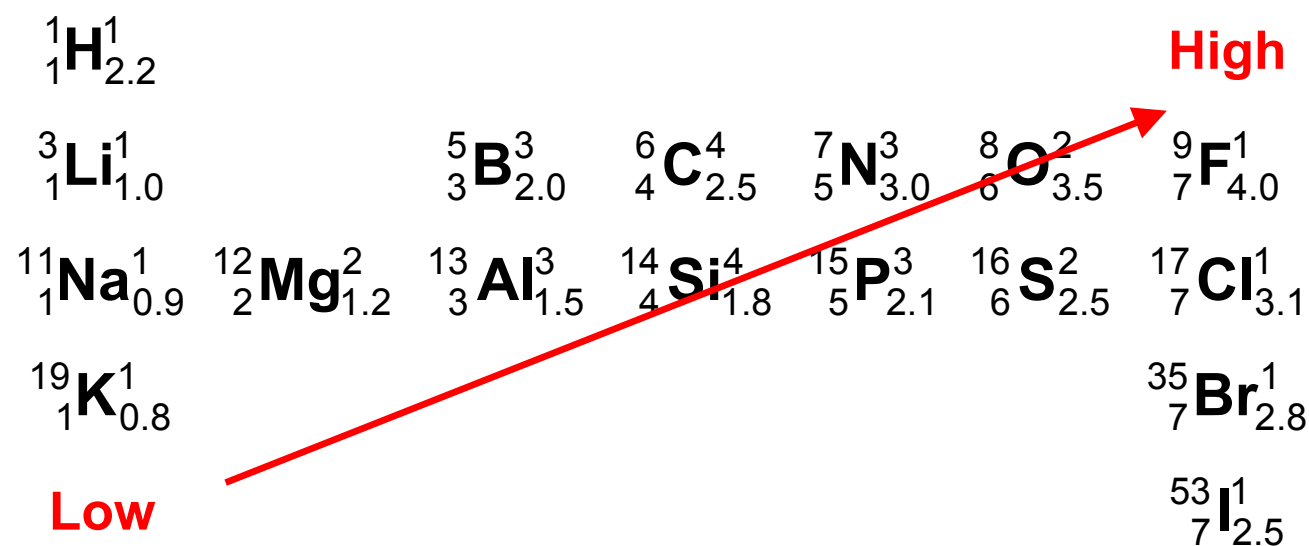
- *E.g.* $^{17}\text{Cl} =$
- The valence shell electron structure, called the **Lewis structure**, can be easily drawn for the first 18 elements of the periodic table (highest configuration $1s^2 2s^2 2p^6 3s^2 3p^6$).

Valence Shell Electron Configuration							
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
H •							He ••
Li •	Be ••	•B••	•C••	•N••	•O••	•F••	•Ne••
Na •	Mg ••	•Al••	•Si••	•P••	•S••	•Cl••	•Ar••

- For elements in groups IIA, IIIA, and IVA, the paired electrons become unpaired before forming bonds, so the valence is the total number of valence electrons (*e.g.* C = 4, Mg = 2, etc.).

B. Ionic, Covalent, and Polar Bonding

- **Electronegativity** reflects an atom's ability to attract a pair of electrons to itself. Be sure to know the general trend (this is enough for exams; actual values are not provided).



- Electronegativity differences account for the characteristics of three main types of bonds:

1. Ionic Bonds

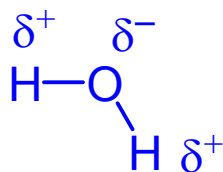
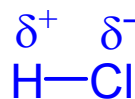
are from the *complete* transfer of an electron from the less- to the more-electronegative atom. e.g. Na^+Cl^-

- This *complete* transfer occurs when the electronegativity difference between bonded atoms is > 1.9 , which corresponds to bonds between atoms > 3 groups apart.
- This 1.9 is not a hard and fast rule. If the electronegativity difference is large, the bond will be very polar or ionic.

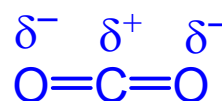
2. Polar Bonds (Polar Covalent Bonds)

are from the *unequal sharing* of electrons between unlike atoms with electronegativity differences < 1.9 , but > 0.5 .

- This corresponds to < 3 groups apart in the periodic table.
- Denoted by δ^+ and δ^- , meaning slight positive and slight negative charges, respectively.
- Molecules with polar bonds are usually also polar molecules, but sometimes the dipoles of polar bonds cancel out, so the molecule itself is non-polar.



polar



non-polar

- This means that the 3D structure of a molecule needs to be known before its overall polarity can be recognized; structure will be covered in more detail later.

3. Covalent Bonds

result from the *equal sharing* of electrons between atoms

- This occurs when with electronegativity difference < 0.5 , for example C-C, C-H, Cl-Cl.
- All three bond types are found in organic compounds!

C. Bond Cleavage

- All bonds can be broken (by heat, light, x-rays, etc.) into separate fragments. These fragments can be either:

1. Ions (cations and/or anions)

where the shared electron *pair* is transferred to one atom, usually the more-electronegative atom.

- This is often referred to as *heterolytic cleavage*, and because it involves the formation of ions, *ionization*



2. Radicals (neutral species with one unpaired electron)

where one electron of the bond goes to each atom.

- This is often referred to as *homolytic cleavage*



D. Drawing Lewis Structures

- Summary of method used in Chem 1050...
 - i. Analyse the molecular formula to determine which atoms are bonded to which.
 - ii. Write out the central atom in its normal Lewis structure (p. 1-4).
 - iii. Attach each atom bonded to the central one, one-by-one, where each attached atom begins in its normal structure and you:
 - a. Attach each atom by a single bond using unpaired electrons in each of the bonded atoms.
 - b. If necessary, break apart an electron pair on the central atom to form bonds to the attached atom.
 - c. Attach remaining unpaired electrons on the bonded atoms to form double or triple bonds.
 - iv. Add one electron for each negative charge, or subtract one for each positive charge. Always add or remove electrons that will result in filled valence shells.
 - v. Assign *formal charges* to the atoms that bear them.
 - vi. Repeat the process for each atom in the molecule.
 - vii. Remember, atoms in the first full row of the periodic table (e.g. C, N, O) cannot have more than an octet of electrons. However, P can have 10, and S can have 12.



E. Formal Charge

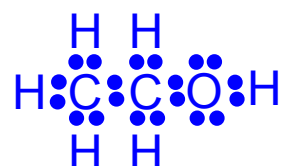
- An atom in a molecule is assigned a *formal charge* if the number of electrons “belonging to” that atom differs from the number around it in its *neutral, atomic state*.
- Belonging to = all non-bonded pairs + one electron per covalent bond. e.g. ${}^8\text{O} = 1s^2 2s^2 2p^4 = 6$ valence e^-

Species	Structure	Charge on O	Electrons belonging to O
atomic O	$\cdot\ddot{\text{O}}\cdot$	none	6
H ₂ O	$\text{H}\ddot{\text{O}}\text{H}$	none	6
H ₃ O ⁺	$\text{H}\ddot{\text{O}}^+\text{H}_2$	+1	
CH ₃ O ⁻	$\text{H}_3\text{C}\ddot{\text{O}}^-$		7

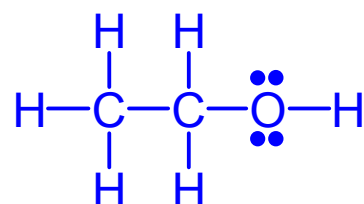
F. Structural Formulas

- Recall the different methods used to show (imply) the locations of electrons and bonds in molecules. The conventions are shown below for ethanol.

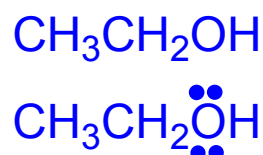
Full Lewis dot structure
(all valence electrons shown)



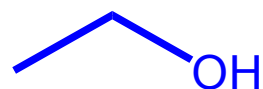
Lewis structure, with covalent bonds represented as lines.



Covalent bonds omitted, but assumed. With or without non-bonding pairs. Used for simple molecules.



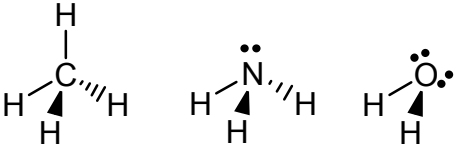
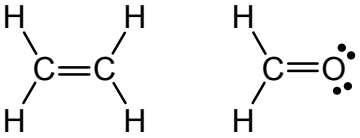

C-C bonds shown only by a line.
H atoms bonded to C not shown
(implied).



- These diagrams *only show the bonding sequences* and are not designed or intended to show actual 3D structure. Line diagrams are often used for large molecules.

G. Molecular Shapes

- The basic shapes of organic molecules are well-predicted by VSEPR theory (Table 1.8 in the textbook).

Regions of e ⁻ density around central atom	Predicted shape of electrons	Angles	Examples
4	tetrahedral	109.5°	
3	trigonal planar	120°	
2	linear	180°	

- Lone pairs of electrons exert a greater repulsive force than pairs in bonds, causing a reduction in bond angles.
- Double and triple bonds act as single bonds (a single region of electron density) in VSEPR theory



- By applying VSEPR shapes to all bonded sites in a molecule, the correct shape of nearly every organic molecule can be predicted and drawn in 3D.

- The dot-line-wedge symbolism is the most common way of depicting three-dimensional structures:

Line: represents a bond
in the plane of the paper



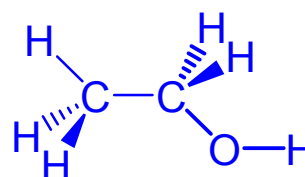
Dotted line: represents a bond directed
behind the plane of the paper



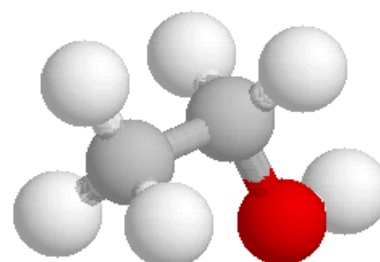
Wedged line: represents a bond directed
in front of the plane of the paper



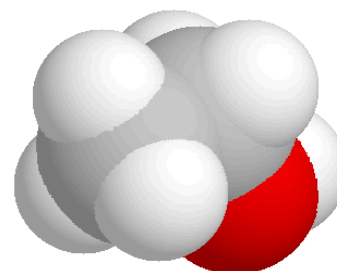
- The 3D structure of ethanol is therefore represented as:



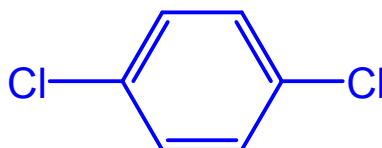
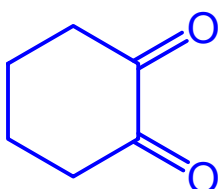
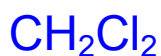
- The best 3D representation of ethanol is given by molecular models, or drawn as ball and stick models.
 - C = grey, H = white, O = red



- If one wishes to get an idea of the molecule in which its electronic field is indicated by spheres representing the outermost filled electronic orbitals, a *space-filling* model is used.



- Using our knowledge of polar bonds and molecular shapes, we can determine if molecules with polar bonds are either polar or non-polar. Those that are non-polar have no net dipole moment.



Summary:

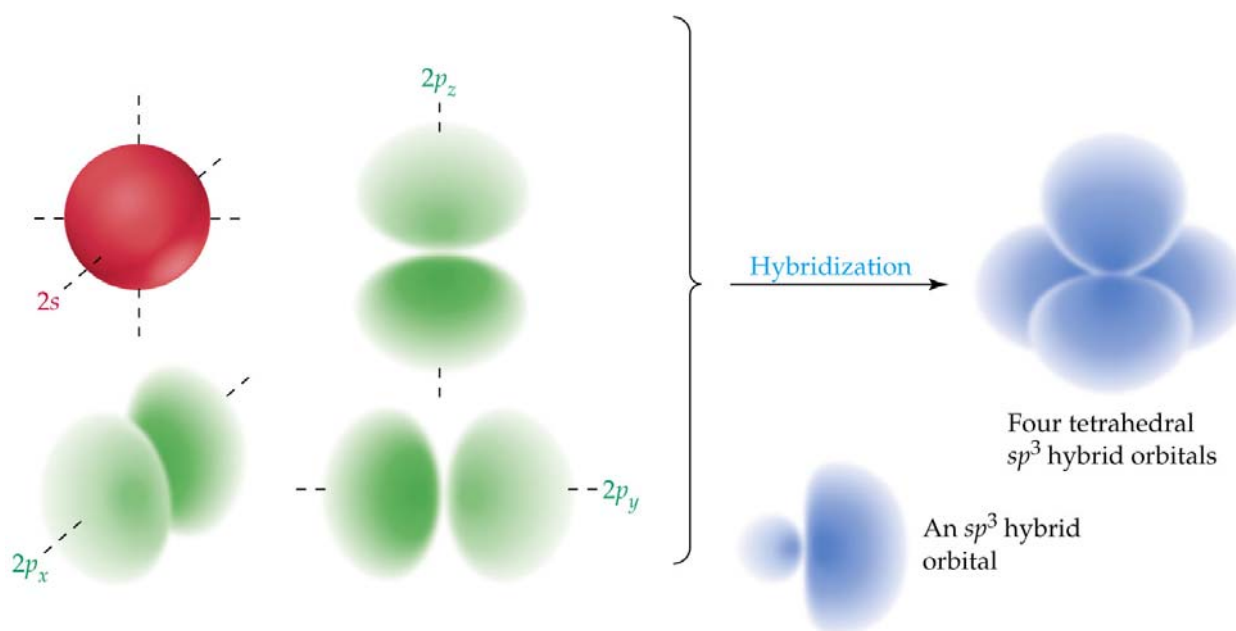
- Textbook pages covered: Chapter 1, 1-20
- Suggested text problems: 20, 22, 25, 26, 30, 32, 38, 41
 - If, after study, you have any difficulties with these, try the related in-chapter practice problems
- Questions from previous midterm tests:
 - 2005: 1 and 3
 - 2006: 1, 2, and 4
 - 2007: 2
 - 2008: 1

H. Hybridization

- Prior to bonding, non-hydrogen elements will “hybridize” their valence-shell atomic orbitals.

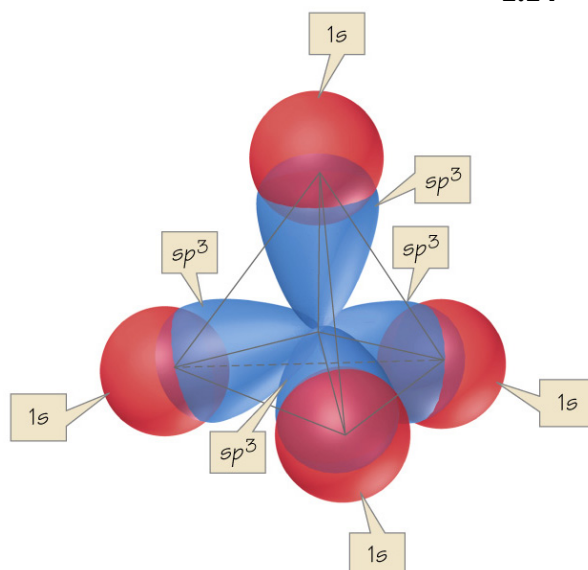
1. sp^3 hybridization

- One s + three p = four sp^3 hybrid atomic orbitals
- Electronic arrangement = 109.5° apart (tetrahedral)
- There are no leftover p orbitals



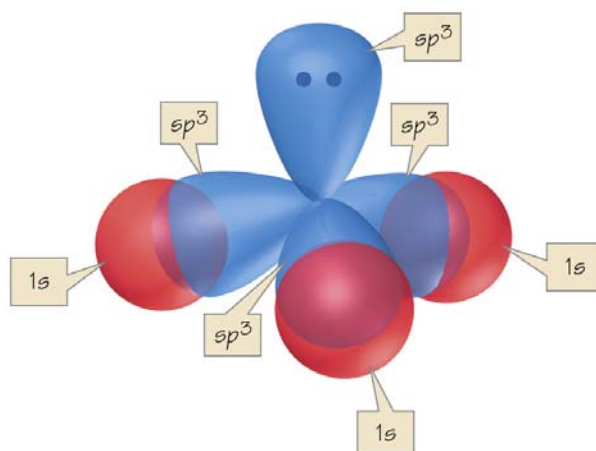
- The electronic arrangement is always tetrahedral, but the molecular shape may differ if there are non-bonding pairs.

- CH_4 is the best example of sp^3 hybridization. Each new hybrid orbital around the C contains one electron.
- After each pairs up with one electron from H, the orbitals each contain an electron pair.



- The single bond formed by the *direct, head-on overlap* of orbitals is a **sigma bond (σ)**.
- Hybrid orbitals can also have non-bonding pairs, for example, in ammonia and water. These also have tetrahedral electronic arrangements and are sp^3 .

- NH_3 , which has a tetrahedral electronic arrangement, contains three σ bonds. Its shape is trigonal pyramidal.



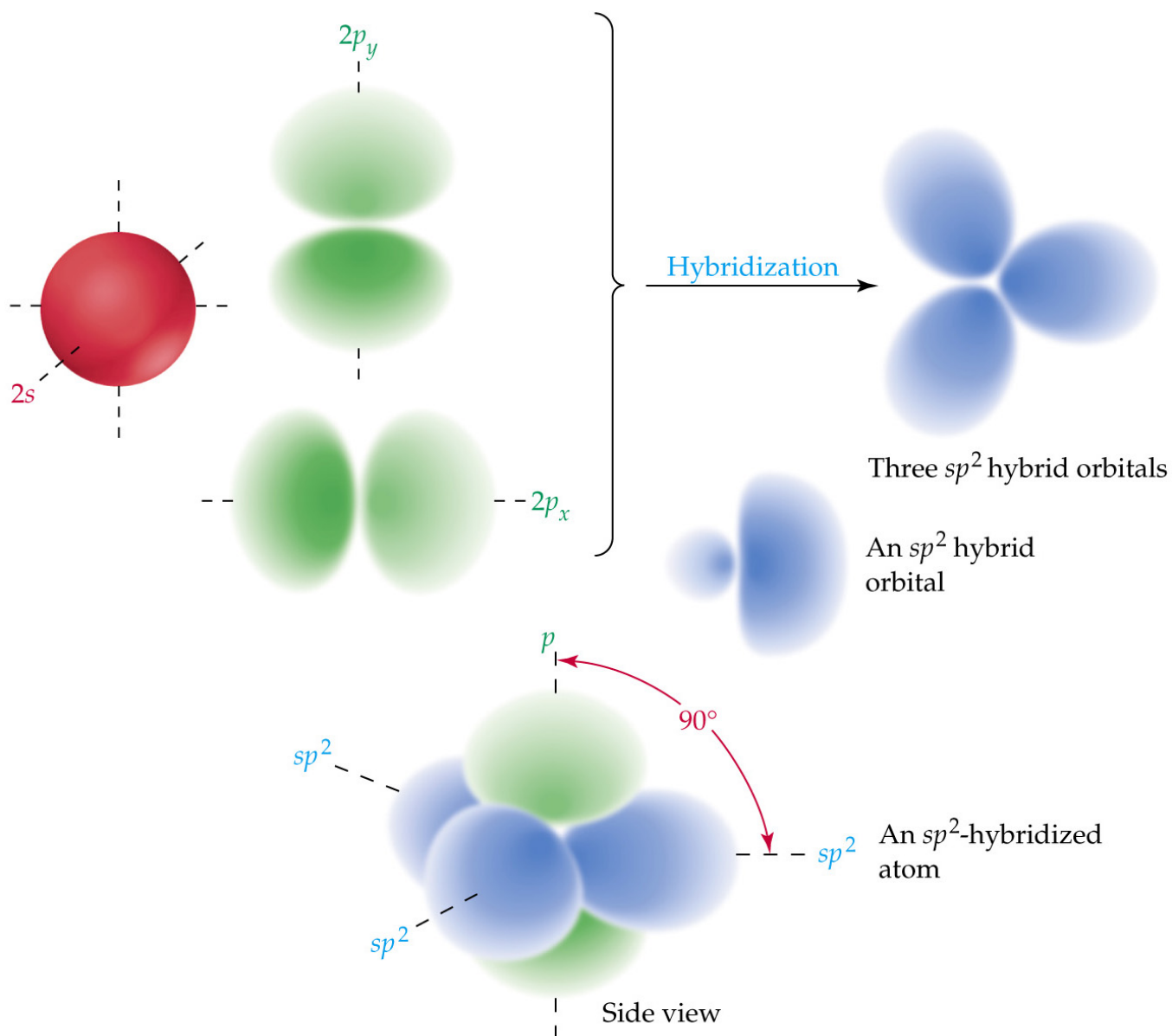
- sp^3 hybridization is just one possibility. Five major hybridization types form the VSEPR structures, and these types are summarized in the next table.
- Note the relationship between hybridization, the number of regions of electron density, and the shape of the electronic arrangement.

Regions of e^- density	Atomic orbitals	Hybrid orbitals	Electronic arrangement
2	one s, one p	two sp	linear
3	one s, two p	three sp^2	trigonal planar
4	one s, three p	four sp^3	tetrahedral
5	one s, three p , one d	five sp^3d	trigonal bipyramidal
6	one s, three p , one d	six sp^3d^2	octahedral

- *Regions of electron density*: a non-bonding pair, a single bond, or a multiple bond each constitutes one region.
- *Electronic arrangement* may not equate to molecular shape if there is one or more non-bonding pair present.

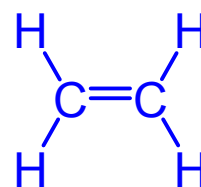
2. sp^2 hybridization

- One s + two p = three sp^2 orbitals 120° apart

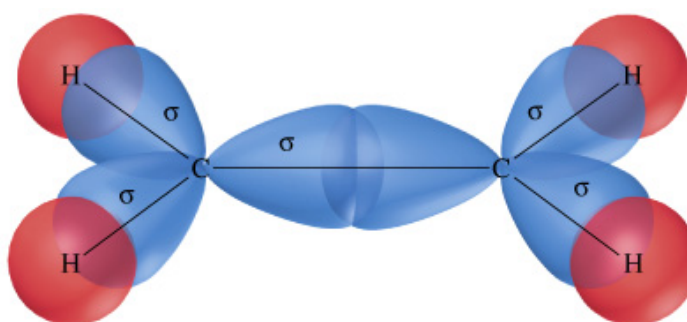


- There is one leftover p orbital remaining, since we started with three p orbitals and used just two of them. This remaining orbital is perpendicular to the trigonal plane.

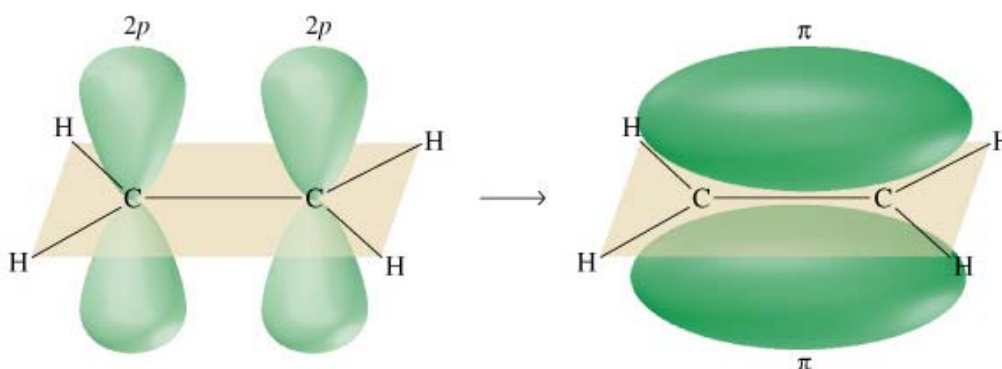
- Consider ethene. Each carbon has three regions of electron density (sp^2 hybridized).
- The σ bonds are formed by the direct overlap of sp^2 orbitals, which result in single bonds.
- Where do double bonds come from?



- The first bond in the double bond comes from a single bond caused by direct overlap (*i.e.* a σ bond)

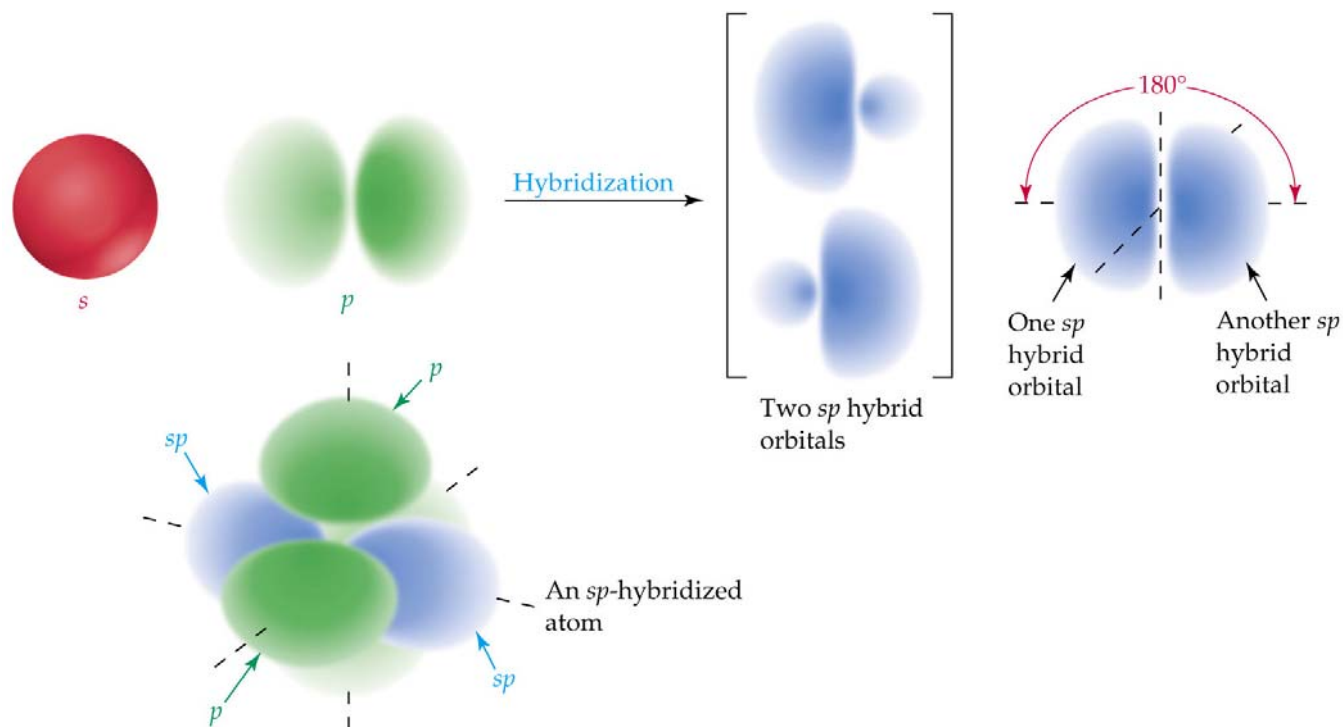


- The second bond comes from the *sideways overlap* of the leftover p orbitals to give a π bond. The π bond is 90° to the plane defined by the trigonal σ bonds.
- Due to the sideways overlap, π bonds cannot rotate.

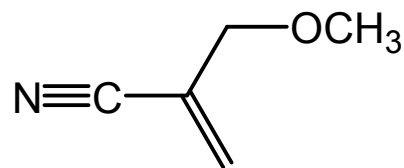


3. *sp* hybridization

- One *s* + one *p* = two *sp* orbitals 180° apart.



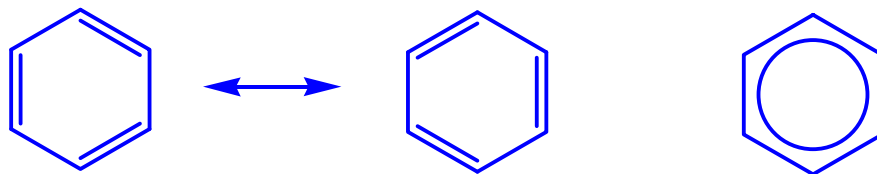
- Since only one *p* orbital is used, there must be two *p* orbitals remaining. These leftover orbitals are used to form π -bonds with adjacent atoms.
- The two *p* are 90° to each other and to the *sp* hybrids.
- As predicted by VSEPR theory, the geometry of such molecules is linear (recall CO₂, BeCl₂, and acetylene).
- Example: label the hybridization and give the approximate bond angles for C, N, and O in this molecule.



I. Resonance Structures

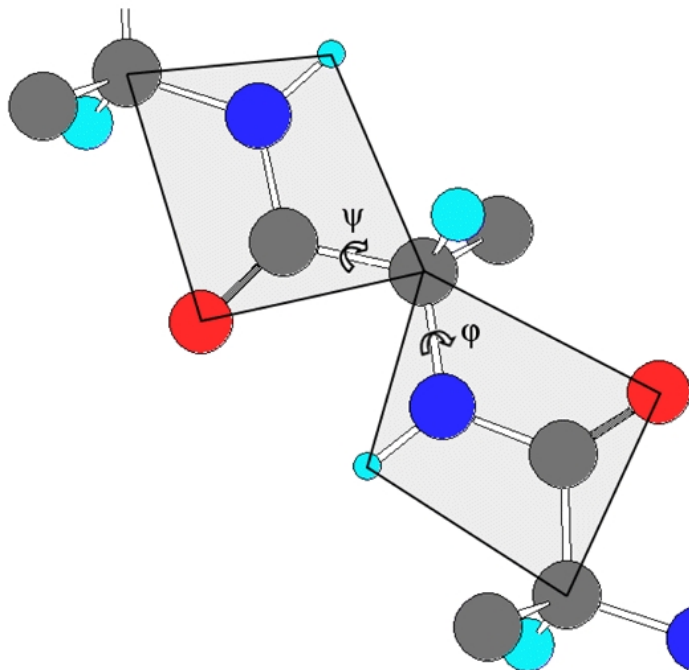
- We can often draw multiple Lewis structures that differ only in the positions of the electrons. Such structures are called **resonance structures (contributing structures)**.
- For example, nitrate ion (NO_3^-) can be drawn in 3 energetically equivalent Lewis structures.
- These differ *only* in the positions of the electrons, *not* atoms. In each of these structures, the double bond and the formal negative charges reside on different atoms.
- Which one of these three is the actual structure of nitrate? Not one of them is correct by itself. Each one “contributes” to the actual electronic structure, the **resonance hybrid**.
- The arrow \longleftrightarrow is used exclusively to indicate resonance. It is not an equilibrium arrow, because the structures are not distinct species that are in equilibrium.

- The best example of resonance is benzene. All six carbon-carbon bonds are identical.

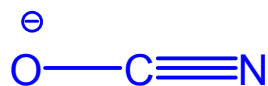
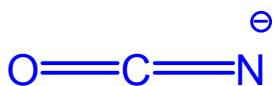


- Another example is the acetate ion, CH_3COO^- . In the actual structure, the resonance hybrid, both O atoms have partial negative charge and the CO bonds are identical.
- A less-obvious example is the amide functional group, where the N is sufficiently low enough in electronegativity to donate to the carbonyl group. In this case, the two resonance structures differ in energy.

- **Important:** When assigning hybridization, it is necessary to consider resonance and examine the resonance hybrid.
 - Carboxylate (such as acetate) oxygens are both sp^2
 - Amide nitrogen is sp^2 – conveys important properties to the amide (peptide) backbone of proteins



- In general, the existence of resonance is indicative of *increased stability*. Stabilization is greatest in molecules that have energetically equivalent resonance structures, as in the previous examples. However, molecules and ions can be stabilized, but to a lesser extent, by *non-equivalent contributing structures*.



- Electron movements needed to convert one resonance form to another are shown by curved arrows. Each curved arrow depicts the movement of an electron *pair* from its existing location to a new location.

J. Arrow Formalism in Organic Chemistry

1. Curved arrows

depict the movement of a *pair* of electrons, either from one resonance form to another, or for a chemical reaction.

2. Fishhooks

depict the movement of *single* electrons and are used for reactions which form, change, or destroy radicals.

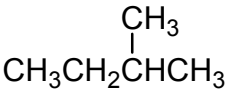
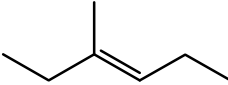

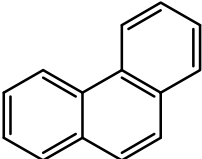
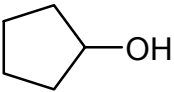
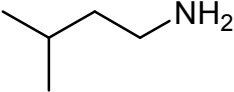
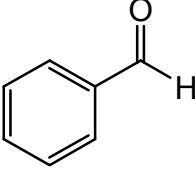
3. Straight arrows (regular or double-fishhook)

are used to show reactions (\longrightarrow) or equilibria (\rightleftharpoons).

4. Double-headed arrows (\longleftrightarrow)

are used to show resonance, and only resonance!

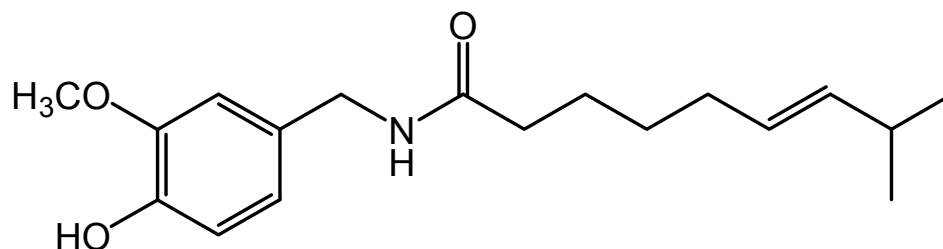
K. Functional Groups

Name	General formula	Main reaction	Example
alkane	R_3C-H C_nH_{2n+2}	combustion	
alkene	$R_2C=CR_2$ C_nH_{2n}	addition	
alkyne	$RC\equiv CR$ C_nH_{2n-2}	addition	$HC\equiv CCH(CH_3)_2$
aromatic compounds	contain 	substitution	
alcohol	$R-OH$	oxidation	
ether	$R-O-R$	combustion	$CH_3CH_2OCH_3$
amine	$R-NH_2$	basicity	
aldehyde	$\begin{array}{c} O \\ \\ RCH \end{array}$	oxidation	
ketone	$\begin{array}{c} O \\ \\ RCR \end{array}$	reduction	$CH_3\overset{\overset{O}{ }}{C}CH_3$
carboxylic acid	$\begin{array}{c} O \\ \\ RCOH \end{array}$	acidity	$CH_3\overset{\overset{O}{ }}{C}OH$
ester	$\begin{array}{c} O \\ \\ RCOR \end{array}$	hydrolysis	$CH_3CH_2\overset{\overset{O}{ }}{C}OCH_3$
amide	$\begin{array}{c} O \\ \\ RCNR_2 \end{array}$	hydrolysis	$CH_3\overset{\overset{O}{ }}{C}NHCH_3$

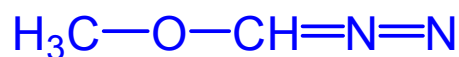
In all functional groups listed above, R = any chain of carbon atoms, or sometimes, an H atom, if H does not result in a different functional group.

- Recall that functional groups are groupings of atoms that convey specific patterns of reactivity to organic molecules. No matter how small or large, the functional groups in that molecule will undergo their characteristic reactions.
- Amines are frequently categorized depending on the number of alkyl groups (C chains, R) bonded to the N.
 - Primary (1°) amine Secondary (2°) amine
 - Tertiary (3°) amine Quaternary (4°) amine
- Carbon atoms of alkyl groups are categorized based on the number of carbons bonded to it.
- Alcohols are categorized depending on the number of alkyl groups bonded to the carbon bearing the OH
 - 1° alcohol 2° alcohol 3° alcohol

- Example: Label all functional groups in capsaicin, the molecule that gives peppers and paprika their hot taste.

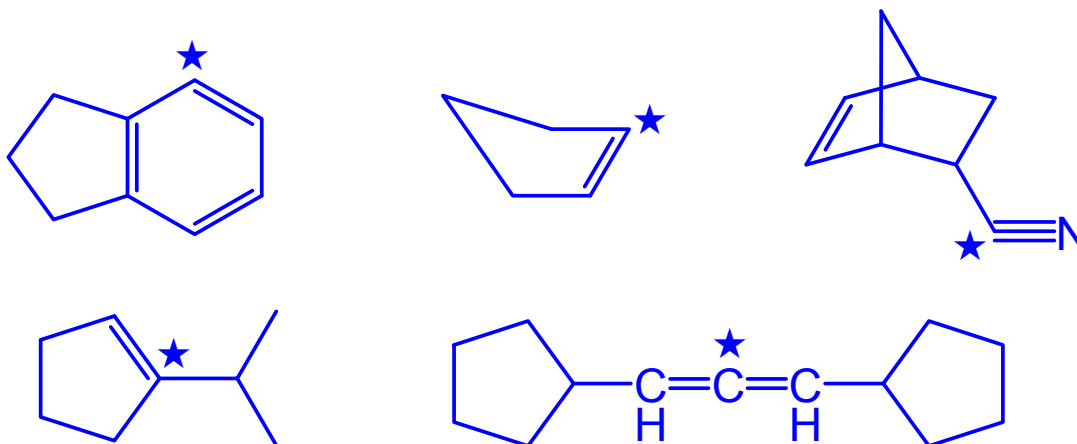


- Summary
 - Textbook pages covered: Chapter 1, 20-34
 - Text problems: 47, 49, 50, 52, 54, 55, 58, 62
 - Old midterm exams
2005: 4, 5; 2006: 3, 5, 6; 2007: 1, 3-6; 2008: 2-6
- Past test questions
 - Assuming filled valence shells for each atom, what is the overall charge on the molecule shown?

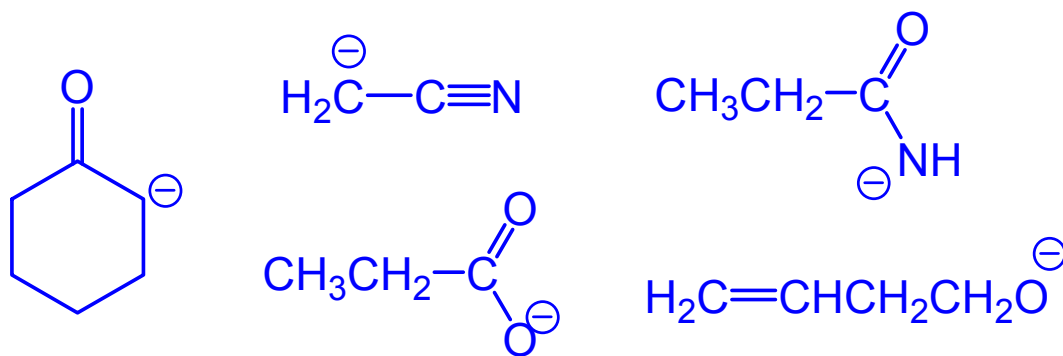


- A) -2 B) -1 C) 0 D) +1 E) +2

- In which two of the following is the atom marked with an asterisk not sp^2 -hybridized?



- Which one of the following anions is not stabilized by resonance?



MCAT Questions

While this is not an MCAT course, sample questions from MCAT exams are provided for study purposes. They will not be discussed in class, but answers will be posted online.

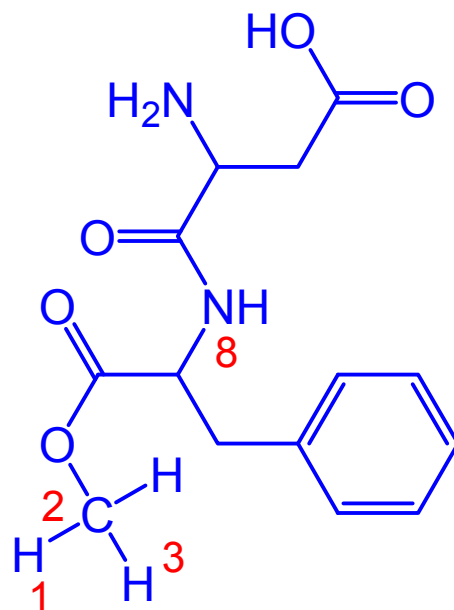
- What determines the polarity of a covalent bond?
 - A) Difference in atomic size
 - B) Difference in electronegativity
 - C) Difference in the total number of protons
 - D) Difference in the number of total valence electrons
- Refer to the structure of aspartame (right), an artificial sweetener, to answer the next two questions.

The hybridization of N8 is:

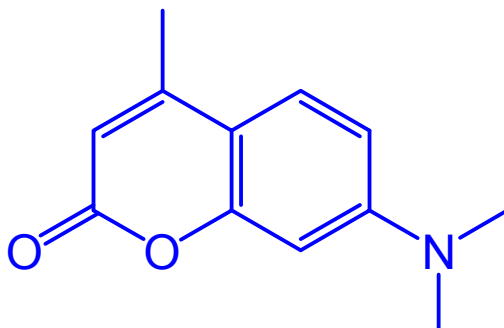
- A) sp B) sp^2 C) sp^3 D) sp^3d

The bond angle formed by H1, C2, and H2 is

- A) 180° B) 120° C) 109° D) 90°



- A brightener that is used on wool and nylon fabrics is 7-dimethylamino-4-methylcoumarin. What functional groups are present in this brightener?



- A) Aromatic ring, alkene, ketone, ether, and amide
- B) Aromatic ring, cycloalkene, ketone, and ether
- C) Aromatic ring, cycloalkene, ester, and amine
- D) Aromatic ring, cycloalkene, ester, and amide