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Organic Chemistry I Drill (CHEM 2210D) - 1st Module - Bonding

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A REVIEW OF GENERAL CHEMISTRY: ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

A STUDENT SHOULD BE ABLE TO:

1. Draw Lewis (electron dot and line) structural formulas for simple compounds and ions from molecular formulas. Correct structures should:
   - Have the skeleton arranged correctly.
   - Have the correct number of electrons.
   - Have an octet of electrons on second-row atoms. Some high-energy, reactive species have an atom with 6 or 7 valence electrons.
   - Show the correct formal and total charges, if any.

2. Define, recognize and give examples of constitutional isomers (same formula, different connectivity) for compounds having 6 carbons or fewer. Determine the Hydrogen Deficiency Index (HDI) and use HDI to solve problems.

3. Identify bonds as non-polar covalent, polar covalent or ionic, based on electronegativity of the atoms involved. Draw bond dipoles for polar covalent bonds. Determine whether molecules are polar or nonpolar.

4. Given a structure, predict the shape of the molecule and the approximate bond angles in it, and give the hybridization of central atoms.

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Atoms on Central At.</th>
<th>Lone Pairs</th>
<th>Steric No.</th>
<th>Hyb.</th>
<th>Bond Angle</th>
<th>Molecular Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>sp³</td>
<td>109.5°</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>NH₃</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>sp³</td>
<td>109.5°</td>
<td>trigonal pyramid</td>
</tr>
<tr>
<td>H₂O</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>sp³</td>
<td>109.5°</td>
<td>bent</td>
</tr>
<tr>
<td>BF₃</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>sp²</td>
<td>120°</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>HN=O</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>sp²</td>
<td>120°</td>
<td>bent</td>
</tr>
<tr>
<td>HC≡N</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>sp</td>
<td>180°</td>
<td>linear</td>
</tr>
</tbody>
</table>

5. Predict relative strengths and lengths of carbon-carbon bonds, and lengths of carbon-hydrogen bonds in hydrocarbons.

6. Distinguish between atomic orbitals (s, p, sp, sp², sp³) and molecular orbitals, including sigma and pi bonds. Given a structural formula, identify the bonds (sigma, pi) present, and indicate what atomic orbitals (s, p, sp, sp², sp³) are used to form them.

7. Determine how intermolecular forces and size/surface area (including branching) influence boiling point and solubility trends. The forces are: ionic, hydrogen bonds (in protic compounds with F, O, N), dipole-dipole interactions, and van der Waals/fleeting dipole-dipole interactions. Water solubility decreases with increased number of carbons, and increases with the number of polar groups.
To best prepare for this module, please work appropriate Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Draw Lewis structures for the following:
   a) C\(_3\)H\(_8\)  
   b) C\(_2\)H\(_5\)F  
   c) NH\(_3\)  
   d) CH\(_3\)\(^+\)  
   e) CH\(_3\)\(^-\)  
   f) OCN\(^-\)

1.2 Show the formal charges on all the atoms, other than hydrogens, of the following species. (The unshared electrons are shown.)
   a) \(\text{\dagger}\text{Cl} - \text{\dagger}\text{CH}_2 - \text{\dagger}\text{CH} - \text{\dagger}\text{NH}_2\)  
   b) \(\text{\dagger}\text{O} - \text{\dagger}\text{CH}_2 - \text{\dagger}\text{CH}_2 - \text{\dagger}\text{OH}\)

1.3 Show formal charges on all atoms, other than hydrogens, of the following compounds. (Unshared electrons are not shown; determine locations using the octet rule.)
   a) \(\text{\dagger}\text{N} - \text{\dagger}\text{C} - \text{\dagger}\text{O} - \text{\dagger}\text{H}_2\text{C} - \text{\dagger}\text{CH}_2\)
   b) \(\text{\dagger}\text{H}_3\text{B} - \text{\dagger}\text{OH}_2\)
   c) \(\text{\dagger}\text{C} - \text{\dagger}\text{CH}_3 - \text{\dagger}\text{CH}_3 - \text{\dagger}\text{O} - \text{\dagger}\text{H}\)

Overall charge: anion  neutral  cation

2.1 Draw two constitutional isomers for the molecular formulae given in parts (a) and (b).
   a) C\(_2\)H\(_7\)N  
   b) C\(_2\)H\(_4\)O

   c) Draw 4 constitutional isomers for C\(_4\)H\(_9\)Br. (There are two ways to arrange the carbons.)
2.2 Determine the relationship between the structures in each pair, choosing from: same compound, constitutional isomers, unrelated.

a) CH₃-CH₂-CH₂-Cl versus Cl-CH₂-CH₂-CH₃

b) CH₃-CH₂-CH₃ versus CH₂=CH-CH₃

c) H₃C-CH₂-CH₂-CH₃ versus CH₃-CH-CH₃

2.3 a) What is the HDI for a compound with two double bonds and zero rings?

b) What is the HDI for a compound with a triple bond and one ring?

c) What is the HDI for a compound with molecular formula C₄H₈? What are the possible structural features this molecule may have (e.g., how many pi bonds, rings)?

d) What is the HDI for a compound with molecular formula C₆H₁₀O? What are the possible structural features this molecule may have?

3.1 Draw bond dipoles for all polar covalent bonds. Show positive and negative charges for ionic bonds.

a) Cl-CH₃ 

b) LiCH₃

c) CH₃≡CNa

d) H-O-CH₃

e) H₃C-ONa

f) H₃C-C=O

3.2 a) For 3.1a, circle the atom that would attract an anion.

b) For 3.1d, circle the atom that would attract a proton.
3.3 Indicate directions of individual bond dipoles of the following compounds.

![Example diagram]

4.1. Provide hybridizations and approximate bond angles around the atoms that are in bold.

![Diagram with hybridization and bond angle annotations]

5.1 Which of the carbon-carbon bonds in the structure below is the shortest? Which is the longest? Which is the strongest?

![Structure diagram]

5.2 Which of the indicated carbon-hydrogen bonds in the structure below is the shortest? Which is the longest?

![Structure diagram with additional bonds]
6.1 Fill in the blanks for the following compound.

\[ \text{H}_2\text{C}=\text{C}=-\text{C}-\text{CH}_2-\text{CH}_2-\text{O}=\text{H} \]

1 2 3

a) The total number of sigma bonds in the compound is _____.
b) The total number of pi bonds is _____.
c) The total number of electrons in the pi orbitals is _____.
d) The total number of bonds formed by the overlap of two sp\(^3\) orbitals is _____.
e) Bond 1 is formed from the overlap of a(an) _____ orbital with a(an) _____ orbital.
f) Bond 2 is formed from the overlap of a(an) _____ orbital with a(an) _____ orbital.
g) Bond 3 is formed from the overlap of a(an) _____ orbital with a(an) _____ orbital.

7.1 Which of these compounds has the highest boiling point? Which has the lowest?

\[ \begin{array}{c}
\text{a) CH}_3\text{CH}_2\text{CH}_3 \\
\text{b) CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{c) CH}_3\text{CH}_2\text{CH}_2\text{Cl} \\
\text{d) CH}_3\text{CCH}_2\text{CH}_3
\end{array} \]

7.2 Which of the following compounds is most soluble in water? Which is the most soluble in hexanes (\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)?

\[ \begin{array}{c}
\text{a) CH}_3\text{CH}_2\text{Br} \\
\text{b) CH}_3\text{CH}_2\text{COH} \\
\text{c) CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{d) CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\end{array} \]

7.3 Arrange these compounds by water solubility, 1 = most water soluble.

\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{HO} \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{OH} & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{O} & \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{OH} & \quad \text{CH}_2
\end{align*}
SOLUTIONS TO SAMPLE PROBLEMS:

1.1

a) \[ \text{H-C-C-C-H} \]

b) \[ \text{H-C-C-F} \]

c) \[ \text{H-N-H} \]

d) \[ \text{H-C-H} \]

e) \[ \text{H-C-H} \]

1.2

Formal charges

a) \[ \text{C}^{0} \text{C}^{0} \text{N}^{-1} \text{C}^{1} \text{H}^{0} \]

b) \[ \text{C}^{0} \text{C}^{0} \text{O}^{+1} \text{H}^{0} \]

1.3

a) \[ \text{C}^{0} \text{N}^{0} \text{C}^{0} \text{H}^{-1} \]

b) \[ \text{B}^{0} \text{O}^{+1} \text{H}^{1} \]

c) \[ \text{C}^{0} \text{O}^{0} \text{C}^{0} \text{H}^{1} \]

2.1

a) \( \text{CH}_3\text{-CH}_2\text{-NH}_2 \) \( \text{CH}_3\text{-NH-CH}_3 \)

b) \( \text{CH}_3\text{-CH}=\text{O} \) \( \text{CH}_2=\text{CH-OH} \) (this isomer is much less stable)

c) \[ \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br} \]

d) \[ \text{CH}_3\text{-CH}_2\text{-CH}_3 \]

e) \[ \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br} \]

2.2

a) same 

b) unrelated (different formula) 

c) constitutional isomers

2.3

a) 2  
b) 3  
c) 1: 1 pi bond or 1 ring  
d) 2: 2 pi bonds (2 double or 1 triple bond) + 0 rings; or 1 pi bond + 1 ring; or 2 rings

3.1

a) \( \text{Cl-CH}_3 \)

b) \( \text{Li-CH}_3 \) or \( \text{Li}^{+}:\text{CH}_3 \)

c) \( \text{CH}_3\text{C}=\text{C}^{-}\text{Na} \)

These are resonance structures

d) \[ \text{H-O-CH}_3 \]

e) \[ \text{H}_3\text{C}^{--}\text{Na} \]

f) \[ \text{H}_3\text{C}^{--}\text{O}^{+} \]
3.2 electron poor C
\[
\begin{array}{c}
\text{Cl} \quad \text{C} \quad \text{CH}_3
\end{array}
\]
electron rich O
\[
\begin{array}{c}
\text{H} \quad \text{O} \quad \text{CH}_3
\end{array}
\]
a) b)

3.3 Bond dipoles:
a) Br \quad \text{C} \equiv \text{C} \quad \text{H} 
b) Br \quad \text{C} \equiv \text{C} \quad \text{H} 
c) \text{N} \quad \text{H} \quad \text{H} 
d) \text{H} \quad \text{C} \equiv \text{O}

4.1 Hybridizations and approximate bond angles:
\[
\begin{array}{cccc}
a) & \text{H} & \text{H} & \text{H} \\
& \text{sp}^2 & \text{sp}^2 & \text{sp} \\
& 120^\circ & 120^\circ & 180^\circ \\
b) & \text{CH}_2 \equiv \text{C} \equiv \text{CH} \quad \text{CH}_3 \\
& \text{sp}^2 & \text{sp} & \text{sp}^3 \\
& 120^\circ & 180^\circ & 109.5^\circ
\end{array}
\]

5.1 (a) is shortest; (d) is longest; (a) is strongest.
5.2 (d) is shortest; (c) is longest.

6.1
\[
\begin{array}{cccc}
\text{H} & \text{H} & \text{H} & \text{H} \\
\text{C} \equiv \text{C} & \text{C} \equiv \text{C} & \text{C} & \text{O} \\
\text{H} & \text{H} & \text{H} & \text{H}
\end{array}
\]
a) The total number of sigma bonds in the compound is 14.
b) The total number of pi bonds is 3.
c) The total number of electrons in the pi orbitals is 6.
d) The total number of bonds formed by the overlap of two sp
\[
\text{sp}^3
\]
orbitals is 2.
e) Bond 1 is formed from the overlap of a(an) sp
\[
\text{sp}^2
\]
orbital with a(an) sp orbital.
f) Bond 2 is formed from the overlap of a(an) sp orbital with a(an) sp
\[
\text{sp}^3
\]
orbital.
g) Bond 3 is formed from the overlap of a(an) sp
\[
\text{sp}^3
\]
orbital with a(an) s orbital.

7.1 (b) has highest BP; (a) has lowest.
7.2 (b) is most soluble in water. (d) is most soluble in hexanes.
7.3 Arrange these compounds by water solubility, 1 = most water soluble.
1. a) Calculate the HDI for C$_2$H$_6$O

   b) Draw two isomers having the molecular formula C$_2$H$_6$O.

2. Fill in the blanks: The three bonds in the carbon-carbon triple bond in H-C≡C-H are:
   a _______ bond formed from _______ orbitals
   a _______ bond formed from _______ orbitals
   a _______ bond formed from _______ orbitals

3. What is the formal charge on the indicated atoms?

4. Which of these is the most soluble in water?

5. Arrange these compounds based on boiling point. 1 = highest boiling

   CH$_3$CH$_2$Br   CH$_3$CH$_2$CH$_2$OH   CH$_3$CH$_2$CH$_2$CH$_3$   CH$_3$CH$_2$CH=O

6. Consider the molecule on the left. Give:
   a) the hybridization of C4 _______
   b) the hybridization of C3 _______
   c) the C2-C1-N bond angle _______
   d) the C2-C3-O bond angle _______
   e) the geometry of C5 _______
   f) The longest carbon-carbon bond in the molecule is between C ___ and C ___ (give numbers).

7. Draw CH$_2$=CF$_2$ in its approximate shape. Draw all bond dipoles.
1. Draw the Lewis structure of a molecule having the formula C₃H₄O

2. Draw the bond dipoles for:

3. Consider the molecule shown. What is:
   a) the hybridization of N5
   b) the hybridization of C2
   c) the C2-C3-C4 bond angle
   d) the geometry of C4
   e) the formal charge on N
   f) the formal charge on O

4. Give the information requested about the molecule CH₃—CH=CH₂.
   a) Which carbon-carbon bond is the longest?
   b) Which carbon-carbon bond is the strongest?
   c) Bond 2 is composed of a _____ bond made from head-to-head overlap of _____ orbitals and a _____ bond made from side-to-side overlap of _____ orbitals.

5. Calculate the HDI for:
   a) C₄H₆N
   b) C₆H₈Br₂
6. What is the relationship between the structures shown below? (Possible answers: same compound, constitutional isomers, unrelated molecules) Calculate the HDI of each molecule.

\[ \text{a) CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{and} \quad \text{b) CH}_2\text{Br-CHBr-CH}_3 \]

\[ \text{CH}_3-\text{CHBr-CH}_2\text{Br} \]

Multiple Choice:
7. Which of these molecules is most soluble in water?

a) CH\text{3CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}  \quad b) CH\text{3CH}_2\text{OH}  \quad c) CH\text{3CH}_2\text{Br}  \quad d) CH\text{3CH}_3

8. Which of these molecules has the lowest boiling point?

a) CH\text{3Li}  \quad b) CH\text{3CH}_3  \quad c) CH\text{3NH}_2  \quad d) CH\text{3CHBr}_2

9. Which of these molecules is linear? (Hint: draw a Lewis structure before you decide).

a) SO\text{2}  \quad b) SCO  \quad c) H\text{2O}_2  \quad d) H\text{2S}  \quad e) OF\text{2}

10. How many 2p atomic orbitals from boron must be mixed with a 2s atomic orbital to yield the bonding hybrid atomic orbitals in BF\text{3}? (Hint: What is the hybridization of B?)

a) 1  \quad b) 2  \quad c) 3  \quad d) 4  \quad e) 5