TOPIC 1. STRUCTURE AND BONDING
(Chapter 1)

These packages of notes are designed for use in conjunction with CHEM 2311 lectures. If you miss a lecture, get the completed notes from another student. Reading assignments (from Solomons) are given in the top right corner (S:#-#), along with relevant problems from the end of the chapter.

OBJECTIVES

1. Introduction to organic chemistry and review of terms
1. Describe distribution of electrons in organic molecules (atomic electronic configurations, Lewis structures, resonance)
2. Describe bonding C-C and C-H bonds in organic molecules (hybridization, overlap of atomic orbitals).
3. Describe molecular geometry.
YESTERDAY, TODAY AND TOMORROW

Yesterday

Pre-1820: “Vitalism” - belief that “natural compounds” possessed special properties, could not be made by man

1828: Wöhler: preparation of urea (organic) from ammonium cyanate (inorganic)

\[ \text{NH}_4^+ \text{OCN}^- \xrightarrow{\text{heat}} \text{CH}_3\text{N}_2\text{O} \]

1908: First production of a synthetic plastic, Bakelite

(1930s-50s: Commercialization of commodity plastics: nylon, polyester, PVC, polyethylene, polypropylene)

1928: Discovery of penicillin (1954: Celphalosporin)

1948: α-helix of protein structure determined

(1952: Determination of double helix structure of DNA)

1950s: Oral contraceptives

Today

**Major commodities** (annual US production) billion lb

| Ethylene  | 55 |
| Propylene | 32 |
| Dichloroethane | 22 |
| Urea      | 15 |
| Ethybenzene | 13 |
| Styrene   | 12 |
| Ethylene oxide | 9 |
| p-Xylene  | 8  |
| Cumene    | 8  |
| 1,3-Butadiene | 4 |
| Acrylonitrile | 3 |
| Benzene   | 2  |
| Aniline   | 2  |
| Isopropanol | 1 |
| o-Xylene  | 1  |
| 2-Ethylhexanol | 1 |

**Major US commodity Producers** (Annual Sales) billion$

| Dow | 28 |
| DuPont | 27 |
| BASF | 25 |
| Total | 18 |
| ExxonMobil | 16 |
| Shell Oil | 15 |
| BP Amoco | 13 |
| Degussa | 11 |
| Akzo Nobel | 9 |
| ICI Americas | 9 |
| SABIC | 8 |
| China Petroleum | 8 |
| Mitsui | 8 |
| General Electric | 7 |
| Huntsman | 7 |
| Union Carbide | 6 |
| Air Products | 5 |

**Major Pharmaceuticals**

Pristoc (Astra Pharm Inc., acid reflux)

Lipitor (Parke-Davis, high cholesterol)

Propecia (antibaldness)

AZT (Burroughs Wellcome, HIV)

Prozac (Fluoxetine) (Antidepressent, Llrl)

Viagra (Pfizer)

Zantac (Ranitidine) (Antulcer, Glaxo)

Claratin (Schering, allergies)

Amoxicillin (Antibiotic, SKII, Squibb)

Acetaminophen

**Recently**

Taxol (anticancer), C60-buckyball, nanoscience
Tomorrow

Better food:
- Nutrients
- Pesticides
- Fertilizers

Better health:
- Pharmaceuticals
- Biomedical engineered implants/replacements

Better environment:
- Cleaner processes

Better living….

…through responsible care and stewardship.

SOME BASIC STRUCTURAL FEATURES

Empirical Formula
- Ratio of atoms in a compound.

Molecular Formula
- Number of each atom in a molecule.

Valency
- Elements form a fixed number of bonds (H 1, O 2, N 3, C 4).

Structure
- Arrangement of atoms and bonds in a molecule.

Isomers
- Different compounds with the same molecular formula.

Constitutional isomers
- Compounds with the same formula, but with different connectivities of atoms.
A VERY GOOD PLACE TO START:
ELECTRONIC CONFIGURATION OF ATOMS

H  1s^1
He  1s^2
Li  1s^2, 2s^1
Be  1s^2, 2s^2
B  1s^2, 2s^2,2p^1  1s^2, 2s^1,2p_x^1
C  1s^2, 2s^2,2p^2  1s^2, 2s^1,2p_x^1,2p_y^1
N  1s^2, 2s^2,2p^3  1s^2, 2s^1,2p_x^1,2p_y^1,2p_z^1
O  1s^2, 2s^2,2p^4  1s^2, 2s^1,2p_x^2,2p_y^1,2p_z^1
F  1s^2, 2s^2,2p^5  1s^2, 2s^1,2p_x^2,2p_y^2,2p_z^1
Ne  1s^2, 2s^2,2p^6  1s^2, 2s^1,2p_x^2,2p_y^2,2p_z^2

BONDING: LEWIS STRUCTURES
AND FORMAL CHARGES

The Octet Rule
Atoms exchange or share electrons to complete the valence shell (adopt Noble gas electronic configuration)

Ionic Bonds
Atoms exchange electrons to form ions which are electrostatically attracted to one another.

Li + F → Li⁺ + F⁻

Ionic bonds are typically formed between atoms which are highly electronegative and highly electropositive.
**Covalent Bonds**
Atoms share valence shell electrons to form covalent bonds

\[
\begin{align*}
\text{C} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

Recommendation: ALWAYS explicitly show lone pairs of electrons

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**“Exceptions” to the Octet “Rule”**

Octet rule is the tendency to have eight valance electrons - only applies strictly to second row elements

\[
\begin{align*}
\text{BF}_3 & \quad \text{HO-SO}-\text{OH}
\end{align*}
\]
Formal Charge

\[ F = Z - \left( \frac{S}{2} \right) - U \]

Always show all formal charges in all structures!

Some Common Valencies

Not:
Constitutional Isomers
Given the common valencies of atoms (C=4, H=1), there might be a number of possible arrangements. These different structures are called constitutional isomers. Draw all the constitutional isomers with molecular formula \( \text{C}_4\text{H}_{10} \).

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Structure ⇒ Function

*Physical Properties of \( \text{C}_3\text{H}_8\text{O} \)*

- isopropyl alcohol  
  \((\text{CH}_3)_2\text{CHOH}\)
  - water-miscible
  - \( \text{bp} = 82^\circ\text{C} \)
- ethyl methyl ether  
  \( \text{CH}_3\text{CH}_2\text{OCH}_3 \)
  - water-insoluble
  - \( \text{bp} = 8^\circ\text{C} \)

*Reactivity of \( \text{C}_6\text{H}_{12} \)*

- 1-hexene  
  \( \downarrow \text{Br}_2 \)
  \( \text{C}_6\text{H}_{13}\text{Br} \)
  - no reaction
- cyclohexane  
  \( \downarrow \text{Br}_2 \)

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RESONANCE THEORY

e.g., Carbonate, CO$_3^{2-}$: A single Lewis structure does not accurately describe the structure of the carbonate dianion.

Molecules and ions that can be represented by more than one valid Lewis structure which differ only in the position of non-bonding electrons and double bonds exist as a hybrid of each contributing resonance structure.

Resonance structures ("contributors")

The hybrid is a combination (average) of all the contributing Lewis structures. It is more stable than the individual structures.
Problem: Which of the following are valid resonance structures?

Guidelines for Recognizing and Drawing Resonance Structures

- Individual resonance structures do not exist - the hybrid does. The energy of the actual molecule is lower than what might be predicted for any of the contributing structures.

- Resonance structures which possess features that impart stability contribute more to the hybrid structure. Stability is enhanced by:
  - Equivalent resonance structures contribute particular stability to the molecule
  - More bonds, stronger bonds
  - Complete valence shells (as opposed to incomplete valence shells)
  - Little (no) charge separation (separating charges costs energy!)
  - Negative charge on electronegative atoms (and vice versa)
Which structure in each pair is the more stable major contributor to the resonance hybrid? [Consider the factors that contribute to the stability/instability of each resonance structure]

\[
\begin{align*}
\text{H}_2\text{C} & \text{O} \text{CH}_3 \\
\text{H}_2\text{C} & \text{O} \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} & \text{O} \text{CH}_3 \\
\text{H}_2\text{C} & \text{O} \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{O} & = \text{C} = \text{N} \\
\text{O} & = \text{C} = \text{N}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} & \text{O} \text{CH}_3 \\
\text{H}_2\text{C} & \text{O} \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} & \text{O} \text{CH}_3 \\
\text{H}_2\text{C} & \text{O} \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{O} & = \text{C} = \text{N} \\
\text{O} & = \text{C} = \text{N}
\end{align*}
\]

**Problem:** Which of the following sets of curved arrows accurately represents resonance? [Draw the structures implied by the movement of electrons shown by the arrows, which of the species is a valid Lewis structure?]
Electrons are contained in atomic orbitals

Atomic orbitals overlap to form molecular orbitals

H 1s

E
Filling Orbitals
maximum of two $e^-$ per orbital
Aufbau Principle: $e^-$ fill lower energy orbitals
Pauli Principle: $e^-$ in same orbitals have different spins
Hund’s rule: degenerate orbitals are filled equally

Carbon:

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METHANE AND ETHANE:
sp$^3$ HYBRIDIZATION

e.g., methane, CH$_4$
methane, CH$_4$: gas (bp=-161 °C). Used as natural gas, for synthesis of other compounds.

$\text{s} + \text{sp}^3$ orbital overlap

e.g., ethane, C$_2$H$_6$

ALKENES: 
sp² HYBRIDIZATION

e.g., ethene (ethylene)

\[ \begin{align*}
1.34 \text{ Å} \\
146 \text{ kcal/mol}
\end{align*} \]

\[ \text{approx. 120°} \]

\[ \text{ethene (ethylene), C}_2\text{H}_4: \text{ gas (bp= -102 °C). Monomer for preparation of polyethylene, used for synthesis of ethylene oxide.} \]

\[ \text{LDPE} \]

\[ \text{HDPE} \]

\[ p + p \text{ orbital overlap} \]
Alkenes are thermally stable and do not undergo rotation around the C=C bond.

Constitutional and Geometric Isomers of Alkenes

*Geometric isomers* have the same connectivity of atoms, but different spatial arrangements.

<table>
<thead>
<tr>
<th></th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>bp/°C</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>mp/°C</td>
<td>-139</td>
<td>-104</td>
</tr>
</tbody>
</table>

\[ \text{Cl}_2\text{C}═\text{CH}_2 \quad \text{CICH}═\text{CHCl} \]
ALKYNES: sp HYBRIDIZATION

e.g., ethyne (acetylene)

ethyne (acetylene), C_2H_2: gas (bp = -81 °C). Used in oxy-acetylene welding torches, for manufacturing of acetic acid.
Comparing C-H Bond Lengths in Alkanes, Alkenes and Alkynes

C-H bond lengths

- 1.10 Å \(\text{Csp}^3 + \text{H1s}\)
- 1.08 Å \(\text{Csp}^2 + \text{H1s}\)
- 1.06 Å \(\text{Csp} + \text{H1s}\)

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

VSEPR Theory – *use to predict shape of molecules*

Pairs of valence e\(^-\) (in bonds and lone pairs) repel each other
BOND STRENGTHS

Orbital Energy Diagrams

Strong bonds are formed between atoms with similar size.
Long bonds are often weak.

Representative Bond Lengths and Strengths

<table>
<thead>
<tr>
<th>bond length</th>
<th>bond strength kcal/mol</th>
<th>bond strength kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-H</td>
<td>0.74</td>
<td>104</td>
</tr>
<tr>
<td>H-F</td>
<td>0.92</td>
<td>136</td>
</tr>
<tr>
<td>H-Cl</td>
<td>1.27</td>
<td>103</td>
</tr>
<tr>
<td>H-Br</td>
<td>1.41</td>
<td>87</td>
</tr>
<tr>
<td>H-I</td>
<td>1.61</td>
<td>71</td>
</tr>
<tr>
<td>H-O</td>
<td>0.97</td>
<td>110</td>
</tr>
<tr>
<td>H-C</td>
<td>1.10</td>
<td>99</td>
</tr>
<tr>
<td>C-C</td>
<td>1.55</td>
<td>88</td>
</tr>
<tr>
<td>C=C</td>
<td>1.33</td>
<td>152</td>
</tr>
<tr>
<td>C=O</td>
<td>1.20</td>
<td>200</td>
</tr>
<tr>
<td>C-F</td>
<td>1.43</td>
<td>80</td>
</tr>
<tr>
<td>C-Cl</td>
<td>1.77</td>
<td>79</td>
</tr>
<tr>
<td>C-Br</td>
<td>1.95</td>
<td>67</td>
</tr>
<tr>
<td>C-I</td>
<td>2.14</td>
<td>57</td>
</tr>
</tbody>
</table>

1 Å = 10⁻¹⁰ m = 100 pm
1 kcal = 4.18 kJ
REPRESENTING ORGANIC MOLECULES IN 2D AND 3D

e.g., Propane (C₃H₈)

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

dash condensed bond-line 3-D structure structure structure

line = bond
bond end, angles, nodes = carbon
Do not show H on C; do show H on other atoms
Assume C is tetravalent unless charges/electrons are shown

Remember you must always show heteroatoms and hydrogen atoms on heteroatoms. It is recommended that you always show lone pairs, however sometimes lone pairs are not shown. Even if lone pairs are not shown, you need to be able to identify when they are present (consider octet rule and presence of charges)
Problem. What is the molecular formula of each of the following compounds shown as bond-line structures?

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{H} \\
\text{O} & \quad \text{C}
\end{align*}
\]

\[\text{sp}^3 \text{ carbon atoms are tetrahedral: Practice drawing tetrahedra!}\]
You know a lot about organic structures!

Problem. Norethindrone, is a steroidal oral contraceptive. Identify the hybridization and geometry of each atom, and the length and overlap of atomic orbitals for each bond.

What is the empirical formula?
What is the molecular formula?
What is the molecular weight?

SUMMARY: MOLECULAR STRUCTURE CONCEPTS, MODELS, RULES AND THEORIES

Concept | Prediction
---|---
Valency/ Octet rule | Presence of lone pairs
Bonding | Covalent bonds between atoms of similar electronegativity
 | Ionic bonds between atoms of different electronegativity
VSEPR | Molecular geometry
Hybridization | Molecular geometry
Resonance | Charge distribution
ORGANIC CHEMISTRY
Some **GOLDEN** Rules

Molecular shape and electronic structure control reactivity
- orbitals
- formal charge
- hybridization
- non-bonding electrons
- VSEPR theory
- electronegativity

Opposites attract
+ ........ –

Molecules want to lower their potential energy
Always be on the lookout for reasons why a molecule or ion might be stable or unstable

Think mechanistically!

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**TOPIC 1 ON EXAM 1**

Types of Questions
- Identify formal charges, geometry (bond lengths, angles), hybridization.
- Draw and recognize resonance structures, constitutional isomers, atomic and molecular orbitals.
- *Do the problems in the book; they are great examples of the types of problems on the exam!*

Preparing for Exam 1
- Get up-to-date *NOW!*
- Work as many problems as possible. Do the problems first, then consult the solutions manual.
- Work in groups, discuss chemistry, teach and test each other.
- Do the “Learning Group Problem” at the end of the chapter.