Chapter 2: The Nature of Bonds and Structure of Organic Molecules

Bonds and Polarity. Bond polarity is based on the difference of the electronegativity of each individual atom in a bond. For the hypothetical bond A-B, the extreme picture would be either ionic or covalent. In reality many bonds are somewhere in between.

\[ \text{covalent} \quad \text{A} \quad \text{B} \quad \text{ionic} \]

low EN difference \quad \text{large EN difference}

What is the definition of electronegativity?

What is a dipole? A dipole \( \mu \) is proportional to the charge \( x \) distance between them. The dipole moment is drawn as a crossed arrow with the direction going towards the positive end of the molecule. Here are some examples:
Ammonia :\( \text{NH}_3 \). On the left, there is the dipole arrow. Right, there is charge density picture with red indicating negative charge and blue indicating positive.

Here is \( \text{BFH}_2 \).

What is the difference between a non-polar, polar-covalent and ionic bond?
Non-polar covalent
Polar covalent
Ionic
Metals and Non-Metals
Metals tend to be electropositive – easy to lose electrons.
These have low EN values.

Non-metals (called main group elements) approach the most electronegative element F.
H is not really a metal. It is compatible with the main group elements. C is average for a non-metal.

<table>
<thead>
<tr>
<th>H</th>
<th>Electronegativity Values for Some Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.0</td>
</tr>
<tr>
<td>Be</td>
<td>1.5</td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
</tr>
<tr>
<td>C</td>
<td>2.5</td>
</tr>
<tr>
<td>N</td>
<td>3.1</td>
</tr>
<tr>
<td>O</td>
<td>3.5</td>
</tr>
<tr>
<td>F</td>
<td>4.1</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
</tr>
<tr>
<td>Mg</td>
<td>1.2</td>
</tr>
<tr>
<td>Al</td>
<td>1.5</td>
</tr>
<tr>
<td>Si</td>
<td>1.7</td>
</tr>
<tr>
<td>P</td>
<td>2.1</td>
</tr>
<tr>
<td>S</td>
<td>2.4</td>
</tr>
<tr>
<td>Cl</td>
<td>2.8</td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
</tr>
<tr>
<td>Ca</td>
<td>1.0</td>
</tr>
<tr>
<td>Ga</td>
<td>1.8</td>
</tr>
<tr>
<td>Ge</td>
<td>2.0</td>
</tr>
<tr>
<td>As</td>
<td>2.2</td>
</tr>
<tr>
<td>Se</td>
<td>2.5</td>
</tr>
<tr>
<td>Br</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table taken from Bill Reusch, [http://www.cem.msu.edu/~reusch/VirtualText/intro2.htm#strc2](http://www.cem.msu.edu/~reusch/VirtualText/intro2.htm#strc2)

Classify these fictitious bonds as non-polar or polar and if polar show the d+ and d-.

- Polar: A -- B  \(\text{EN}_A >> \text{EN}_B\)
- Polar: A -- B  \(\text{EN}_B >> \text{EN}_A\)
- Non-polar: A -- B  \(\text{EN}_A \sim \text{EN}_B\) (usually < .4-.5)

For some real bonds. Classify as non-polar or polar and if polar show the d+ and d-.

- C -- N  B -- H  Al -- H  C -- O  C -- F  Li -- H
- F -- F  B -- Cl  Li -- Al  Al -- O  B -- O  Li -- Li  C -- Li

Molecular Polarity and Intermolecular Forces
To understand the overall polarity of a molecule, the polarity of each bond and the arrangement of the bonds in the molecule have to be considered.
For a molecule with non-polar bonds, it’s easy to see that the molecule overall is non-polar. Consider these molecules:

- H\(\equiv\)C\(\equiv\)H
- C=C\(\equiv\)H
- H\(\equiv\)C\(\equiv\)H

How about molecules with polar bonds: Here the polar vectors must be added based on the shape. Here are some simple examples.

\[\delta^+ \quad \delta^-\]

\(\text{H--Cl}\)

\(\text{H--O}\)

\(\text{H--N}\)

\(\text{H--F}\)
Polar Covalent Bonds and Polar Molecules.

Just having polar bonds does not make the molecule polar. Consider these examples:

\[
\begin{align*}
&\text{O} \equiv \text{C} \equiv \text{O} \\
&\text{F} \quad \text{B} \quad \text{F} \\
&\text{Cl} \quad \text{C} \cdots \text{Cl}
\end{align*}
\]

Shape

**Intermolecular Forces:**

Just as there are attractions within molecules to hold the atoms together, there are forces between molecules that give the ensemble of molecules their physical properties:

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>Strong Forces</td>
<td>Weak Forces</td>
</tr>
<tr>
<td>Boiling point</td>
<td>Strong Forces</td>
<td>Weak Forces</td>
</tr>
</tbody>
</table>

There are 3 main classes of intermolecular forces:

- **Dipole-Dipole** (permanent)
- **H-Bonding:** The elements N, O, and F can share H’s between them. This is a very special force.
- **London, Van der Waals, or Dispersion** (induced dipole)

Relative magnitudes of forces

<table>
<thead>
<tr>
<th>Attractive Force</th>
<th>Covalent bonds</th>
<th>H-bonding</th>
<th>Dipole-dipole</th>
<th>London forces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>~100 kcal/mole</td>
<td>5-10 kcal/mole</td>
<td>&lt; 5 kcal/mole</td>
<td>&lt; 1 kcal/mole</td>
</tr>
</tbody>
</table>

See [http://www.chm.bris.ac.uk/webprojects2003/swinerd/forces/forces.htm](http://www.chm.bris.ac.uk/webprojects2003/swinerd/forces/forces.htm)
Shape and Size
Since the interactions between the two atoms or molecules depends on the surface area between the two bodies, the shape is important:

<table>
<thead>
<tr>
<th>Sphere – Sphere = small contact area</th>
<th>Rod—Rod = large contact area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neopentane (bp = 282.7 K)</td>
<td>( n )-Pentane (bp = 309.4 K)</td>
</tr>
</tbody>
</table>

Boiling Points (ºC) of Selected Elements and Compounds --Mass in ()

### Increasing Size

<table>
<thead>
<tr>
<th>Atomic</th>
<th>Ar (40) -186</th>
<th>Kr (83) -153</th>
<th>Xe (131) -109</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>CH(_4) (16) -161</td>
<td>(CH(_3))(_4)C (72) 9.5</td>
<td>(CH(_3))(_4)Si (88) 27</td>
</tr>
</tbody>
</table>

### Molecular Shape

| Spherical: CH\(_3\)(CH\(_2\))\(_2\)CH\(_3\) (72) 36 | (CH\(_3\))\(_2\)CCl\(_2\) (113) 69 | (CH\(_3\))\(_3\)CC(CH\(_3\))\(_3\) (114) 106 |
| Linear: CH\(_3\)(CH\(_2\))\(_2\)CH\(_3\) (72) | Cl(CH\(_3\))\(_3\)Cl (113) 121 | CH\(_3\)(CH\(_2\))\(_5\)CH\(_3\) (114) 126 |

### Molecular Polarity

| Non-polar: H\(_2\)C=CH\(_2\) (28) -104 | F\(_2\) (38) -188 | CH\(_3\)C=CH\(_3\) (54) -32 | CF\(_4\) (88) -130 |
| Polar: H\(_2\)C=O (30) -21 | CH\(_3\)CH=O (44) 20 | (CH\(_3\))\(_2\)N (59) 3.5 | (CH\(_3\))\(_2\)C=O (58) 56 |
| HC=N (27) 26 | CH\(_3\)C=N (41) 82 | (CH\(_2\))\(_3\)O (58) 50 | CH\(_3\)NO\(_2\) (61) 101 |

Table taken from Bill Reusch, [http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4](http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4)
**H-Bonds**  Boiling points of compounds containing N, O, F—H bonds compared to analogs.

![Graph showing boiling point vs molecular weight]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Mol. Wt.</th>
<th>Boiling Point</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyl ether</td>
<td>CH₃OCH₃</td>
<td>46</td>
<td>−24 ºC</td>
<td>−138 ºC</td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH₃CH₂OH</td>
<td>46</td>
<td>78 ºC</td>
<td>−130 ºC</td>
</tr>
<tr>
<td>Propanol</td>
<td>CH₃(CH₂)₂OH</td>
<td>60</td>
<td>98 ºC</td>
<td>−127 ºC</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>(CH₂CH₂)₂O</td>
<td>74</td>
<td>34 ºC</td>
<td>−116 ºC</td>
</tr>
<tr>
<td>propyl amine</td>
<td>CH₃(CH₂)₂NH₂</td>
<td>59</td>
<td>48 ºC</td>
<td>−83 ºC</td>
</tr>
<tr>
<td>Methylaminoethane</td>
<td>CH₃CH₂NHCH₃</td>
<td>59</td>
<td>37 ºC</td>
<td></td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>(CH₃)₃N</td>
<td>59</td>
<td>3 ºC</td>
<td>−117 ºC</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>HOCH₂CH₂OH</td>
<td>62</td>
<td>197 ºC</td>
<td>−13 ºC</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃CO₂H</td>
<td>60</td>
<td>118 ºC</td>
<td>17 ºC</td>
</tr>
<tr>
<td>ethylene diamine</td>
<td>H₂NCH₂CH₂NH₂</td>
<td>60</td>
<td>118 ºC</td>
<td>8.5 ºC</td>
</tr>
</tbody>
</table>

Table taken from Bill Reusch, [http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4](http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp4)

![Cutout of the H-bonding in ice – responsible for the interesting structure of snow flakes]
Solubility: In general like dissolves like. Polar with polar. Non-polar with non-polar.

http://www.cem.msu.edu/~reusch/VirtualText/physprop.htm#exp6

Predict solubilities of the following in water.

NaCl
HCl
CH₃(CH₂)₃CH₃ hexane
CH₂C₆H₅ toluene
CH₂Cl₂ Dichloromethane
CH₃CH₂OCH₂CH₃ Diethyl ether

What functional groups are exceptions?

Classifying Polarity in Bonds in terms of Valence Bond Models

Formal Charges

\[
\text{Formal Charge} = \frac{\text{Valence Electrons}}{\text{In Neutral Atom}} - \left( \frac{\text{Unshared Valence Electrons}}{2} + \frac{\text{Half of the Shared Electrons}}{2} \right)
\]

or Half of the Shared Electrons = # of bonds.

Here is the acid dissociation reaction of the following oxoacids. You must supply the formal charges. Make sure there is charge balance both on molecule and in the reaction.

Nitric Acid HNO₃ dissociates to make nitrate.

Sulfuric Acid H₂SO₄ dissociates to make hydrogensulfate.
Resonance

(1) Resonance repairs inadequacy of Lewis Structures.

Experimentally ozone and SO$_2$ is bent (bond angle 120°) and has equal length S--O bonds (143.2 pm). Resonance hybrids (the two structures) are always represented by a double headed arrow.

Draw the resonance structures for cyanate, CNO$^-$

Note formal charges.

What does this imply about the bond order of these molecules? Which structure is more important? Why?

(2) Resonance can be used to show molecular properties:

formaldehyde

Which structures are more important?

(3) Wacky resonance structures do not have much effect.

Which structures of azide, N$_3^-$ are important contributors? Which ones are not?
Resonance Summary

Resonance structures involve molecules with the same molecular structure and number of electrons. Resonance hybrids have different types of electronic localization.

The following factors are important in evaluating the contribution each of these canonical structures makes to the actual molecule.

1. The number of covalent bonds in a structure. (The greater the bonding, the more important and stable the contributing structure.)
2. Formal charge separation. (Other factors aside, charge separation decreases the stability and importance of the contributing structure.)
3. Electronegativity of charge bearing atoms and charge density. (High charge density is destabilizing. Positive charge is best accommodated on atoms of low electronegativity, and negative charge on high electronegative atoms.)

Based on [http://www.cem.msu.edu/~reusch/VirtualText/intro3.htm#strc7](http://www.cem.msu.edu/~reusch/VirtualText/intro3.htm#strc7)

Practice: For the compounds and ions listed below, write Lewis / Kekulé structures for as many reasonable canonical forms as you can.

Formic Acid \( \text{HCO}_2\text{H} \)

Formate Anion \( \text{HCO}_2^{-} \)

Nitromethane \( \text{CH}_3\text{NO}_2 \)

Methyl Nitrite \( \text{CH}_3\text{ON}=\text{O} \)

Diazomethane \( \text{CH}_2=\text{N}=\text{N} \)

Considering the resonance hybrid forms written here, which three of these compounds or ions will exhibit the greatest resonance stabilization?

Practice: Reconsider the resonance of \( \text{HNO}_3 \), \( \text{HNO}_2 \), and \( \text{H}_2\text{SO}_4 \) and their anions. Which is the best structure?
Acid/Base chemistry is based on acid dissociation: We talk about $K_a$ and $pK_a$.

\[ HA \xleftarrow{\text{H}^+} H^+ + A^- \]

$K_a = [H^+] [A^-]/[HA]$ in general products / reactants.

Why don't we talk about $pK_b$?

When is the ratio $> 1$?
When is the ratio $< 1$?

What about the $\Delta G$? Remember $\Delta G = -RT \ln K_a$.
When is the ratio $> 1$?
When is the ratio $< 1$?

Some acid reactions are very favorable. What do we call this kind of acid? ________________

Name the 6 main acids in this group? Are any organic acids?

The $K_a$ of a strong acid is $10^x$ Therefore, the $pK_a$ is positive or negative?

<table>
<thead>
<tr>
<th>pKa</th>
<th>Acidities of Some Common Hydrides</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>CH$_3$-H</td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
<tr>
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<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$pK_a$ of neutral hydrides above and selected charged compounds below.

NH$_4^+$ 9.24 | OH$^-$_1 1.74 | S-H$^{(1)}$ 15 (pK2) | Se-H$^{(2)}$ 11 (pK2)

[Link](http://www.cem.msu.edu/~reusch/VirtualText/suppmnt2.htm#top4)

The main X-H bonds in organic chemistry are C-H, N-H, O-H. Rank them in acidity:

Now let’s look at the acidity of H in respect to X-H bond. With respect to elements, what determines the acid strength? ________________.

Make sure that you understand this order and what the $pK_a$ means. C-H depends on the electronic state of C? How do we classify these hybrid states?

Of the three states above, rank them in order of acidity: (p.287)

Typical $pK_a$’s of these acids are approximately

CH$_4$ 50 | H$_2$C=CH$_2$ 45 | HC=CH 25

Now let’s review magnitudes. $10^x$

<table>
<thead>
<tr>
<th>Magnitude</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A photon of light is about $10^x$ m</td>
<td>The number of students in this OCHEM course is about $10^x$</td>
</tr>
<tr>
<td>A pore in a good water purifier is $10^x$ m</td>
<td>The thickness of McMurray is about $10^x$ pages</td>
</tr>
<tr>
<td>The thickness of this paper is about $10^x$ m</td>
<td>The federal deficit is about $10^x$</td>
</tr>
<tr>
<td>The length of a child is about $10^x$ m</td>
<td></td>
</tr>
</tbody>
</table>

|
Unlikely acids
Most C-H acids are extremely weak.

\[
\begin{align*}
R_3C(sp^3)^{-}H &\rightleftharpoons H^+ + R_3C(sp^3)^-; \quad Ka = \text{pKa}= \\
R_3C(sp^2)^{-}H &\rightleftharpoons H^+ + R_3C(sp^2)^-; \quad Ka = \text{pKa}= \\
R_3C(sp)^{-}H &\rightleftharpoons H^+ + R_3C(sp)^-; \quad Ka = \text{pKa}=
\end{align*}
\]

We explain this based on the stability of the anion. The C-H species are all about the same stability, but the anion products are stabilized differently.

\[
R-H \rightarrow R^{-}(sp^3) \rightarrow R^{-}(sp^2) \rightarrow R^{-}(sp)
\]

Unlikely acids

We explain this based on the stability of the anion. The C-H species are all about the same stability, but the anion products are stabilized differently.

\[
E \quad \text{ Ka } 10^{35}
\]

N-H acids,
What are some N-H acids?
pKa's of N-H:
pKa's of N'-H

O-H acids?
What are some O-H acids?
pKa's of O-H:
pKa's of O'-H

Equilibrium and predicting reaction
To calculate the extent of an acid base reaction is crucial.

Given \( pKa(\text{HCl}) = -5 \) and \( pKa(\text{H}_2\text{O}) = 16 \) and \( pKa(\text{NH}_3) = 33 \). \( pKa(\text{NH}_4^+) = 9 \). Note N-H can have more than one acid strength depending if N is neutral or positive. Write these reactions as ionization reactions.

\[
\begin{align*}
\text{HCl} &\rightleftharpoons \\
\text{H}_2\text{O} &\rightleftharpoons \\
\text{NH}_3 &\rightleftharpoons \\
\text{NH}_4^+ &\rightleftharpoons
\end{align*}
\]

Strategy: (1) Find the acid on left and conjugate acid (CA) on right. (2) The reaction proceeds towards the side with the highest pKa. (3) The magnitude of the \( Keq = 10^{+ (pKa1-pKa2)} \).

Left = -, Right = +. This can be derived algebraically. Anyway you want, you’re going to have to predict it.

Reactions.

\[
\text{HO}^- + \text{H-Cl} \rightleftharpoons \text{H-OH} + \text{Cl}^- 
\]

Which direction and what will be the magnitude of the \( Keq \)?

\[
(\text{Acetylene})\text{C-H} + \text{OH}^- \rightleftharpoons \text{H-OH} + \text{HCC}^- 
\]

Which direction will this reaction go and what will be the magnitude of the \( Keq \)?

\[
(\text{Acetylene})\text{C-H} + \text{NH}_2^- \rightleftharpoons \text{H-NH}_2 + \text{HCC}^- 
\]

Which direction will this reaction go and what will be the magnitude of the \( Keq \)?

Practice:
(1) Write the reaction of amide + ammonium and predict the direction.
(2) Given methanol \( \text{CH}_3\text{OH} \) pKa = 16 and water pKa = 16. Why can NaOH not completely deprotonate methanol?
(3) Hydride is a strong base, \( \text{H}^- \). What is the CA of hydride? That acid has a pKa of 38.
Extension to Organic Chemistry

Acid/Base Organic Chemistry

Acid = H⁺  
Electrophile = E⁺

Base => goes after H⁺  
Nucleophile => goes after Nucleus

Introduction to Arrow Pushing:
Always draw the arrows from LP or bonds towards nuclei.

- New bonds are formed whenever a pair of electrons in a bond or LP is pushed towards a new atom; the flow is from – to +.
- A bond is broken when the electrons are pushed away from an atom in the bond. In the worked examples above note which bonds are formed and which bonds are broken.
- Note that formal charges often develop from arrow pushing. Formal charge is either calculated or just reasoned: if an atom gains an electron, it becomes -1; if an atom loses an electron, it becomes +1.

Additional practice is available from:  http://www.abdn.ac.uk/curly-arrows/

Provide arrows. Identify the nucleophile and the electrophile.

- a. N2O₄ + H₂O → 2H₂O₄⁺
- b. C₆H₅NO₂ + Cl⁻ → C₆H₅NO₂⁻ + Cl⁻
- c. C₆H₅ + CH₃CO₂⁻ → C₆H₅CO₂⁻ + CH₃OH + Cl⁻
- d. H₂C(OH)₂ + NH₃ → H₂C(OH)₂⁻ + NH₄⁺
- e. H₂C(OH)₂ + Cl⁻ → H₂C(OH)₂⁻ + Cl⁻

Provide products:

- f. H₂C(=O)Cl
- g. C₆H₅NO₂ + H₂O → C₆H₅NO₂⁻ + H₂O
- h. H₂C(OH)₂ + Cl⁻ → H₂C(OH)₂⁻ + Cl⁻
- i. H₂C(OH)₂ + Cl⁻ → H₂C(OH)₂⁻ + Cl⁻
- j. C₆H₅NO₂ + H₂O → C₆H₅NO₂⁻ + H₂O
- k. C₆H₅NO₂ + H₂O → C₆H₅NO₂⁻ + H₂O
- l. C₆H₅NO₂ + H₂O → C₆H₅NO₂⁻ + H₂O