2.2 Polar Covalent Bonds: Dipole Moments

Molecules as a whole are often polar

- Molecular polarity results from the vector summation of all individual bond polarities and lone-pair contributions in the molecule
- Strongly polar substances are soluble in polar solvents like water

**Dipole moment** ($\mu$)

- Magnitude of charge $Q$ at either end of molecular dipole times distance $r$ between charges
  \[ \mu = Qr \] (in debyes (D))
  \[ 1 \text{ D} = 3.336 \times 10^{-30} \text{ coulomb meter (C m)} \]
- A measure of the net polarity of a molecule
- Arises when the centers of mass of positive and negative charges within a molecule do not coincide

### Polar Covalent Bonds: Dipole Moments

**TABLE 2.1** Dipole Moments of Some Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dipole moment (D)</th>
<th>Compound</th>
<th>Dipole moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>9.00</td>
<td>NH$_3$</td>
<td>1.47</td>
</tr>
<tr>
<td>CH$_3$O</td>
<td>2.33</td>
<td>CH$_3$NH$_2$</td>
<td>1.31</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>1.87</td>
<td>CO$_2$</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.85</td>
<td>CH$_3$</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>1.79</td>
<td>CH$_3$CH$_2$</td>
<td>0</td>
</tr>
<tr>
<td>CH$_2$=CH</td>
<td>1.79</td>
<td>Benzene</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$SH</td>
<td>1.52</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Polar Covalent Bonds: Dipole Moments

**Factors Affecting Dipole Moments**

- Lone-pair electrons on oxygen and nitrogen project out into space away from positively charged nuclei giving rise to a considerable charge separation and contributing to the dipole moment
- Symmetrical structures of molecules cause the individual bond polarities and lone-pair contributions to exactly cancel
Make a three-dimensional drawing of methylamine, \( \text{CH}_3\text{NH}_2 \), and show the direction of its dipole moment (\( \mu = 1.31 \))

**Worked Example 2.1**

**Predicting the Direction of a Dipole Moment**

2.3 Formal Charges

**Formal charge**
- The difference in the number of electrons owned by an atom in a molecule and by the same atom in its elemental state
- Formal charges do not imply the presence of actual ionic charges
- Device for electron “bookkeeping”
- Assigned to specific atoms within a molecule
  - Dimethyl sulfoxide \( \text{CH}_3\text{SOCH}_3 \)
  - Sulfur atom has three bonds rather than the usual two and has a formal positive charge
  - Oxygen atom has one bond rather than the usual two and has a formal negative charge

**Formal Charges**

**Formal Charge Determination**

An isolated carbon atom owns 4 valence electrons. This carbon atom also owns 8 valence electrons.

An isolated nitrogen atom owns 5 valence electrons. This nitrogen atom also owns 8 valence electrons.
2.4 Resonance

Two different ways to draw the acetate ion

- Double bond placement
  - Neither structure correct by itself
  - True structure is intermediate between the two
  - Two structures are known as resonance forms
Resonance forms

- Individual line-bond structures of a molecule or ion that differ only in the placement of \( \pi \) and nonbonding valence electrons
- Indicated by "\( \longrightarrow \)"
- Resonance forms contribute to a single, unchanging structure that is the resonance hybrid of the individual forms and exhibits the characteristics of all contributors

Resonance

Benzene has two equivalent resonance forms

- The true structure of benzene is a hybrid of the two individual forms, and all six carbon-carbon bonds are equivalent
- Symmetrical distribution of electrons is evident in an electrostatic potential map of benzene

2.5 Rules for Resonance Forms

Rule 1 – Individual resonance forms are imaginary, not real
- Real structure is a composite

Rule 2 – Resonance forms differ only in the placement of their \( \pi \) or nonbonding electrons

The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of a C=O double bond.

Simultaneously, two electrons from the C=O double bond move onto the bottom oxygen atom to become a lone pair.

The new resonance form has a double bond here...

and has a lone pair of electrons here.
Electrons in double bonds of benzene move
Electron movement is indicated by curved arrow formalism
Curved arrows indicate electron flow, not the movement of atoms
A curved arrow indicates that a pair of electrons moves from the atom or bond at the tail of the arrow to the atom or bond at the head of the arrow

Rules for Resonance Forms

Rule 3 – Different resonance forms of a substrate do not have to be equivalent

Rules for Resonance Forms

Rule 4 – Resonance forms obey normal rules of valency (follow the octet rule)

Rule 5 – The resonance hybrid is more stable than any individual resonance form

• Resonance leads to stability
In general any three-atom grouping with a \( p \) orbital on each atom has two resonance forms:

- The atoms X, Y, and Z in the general structure might be C, N, O, P, or S.
- The asterisk (*) on atom Z for the resonance form on the left might mean that the \( p \) orbital is:
  - Vacant
  - Contains a single electron
  - Contains a lone pair of electrons

### 2.6 Drawing Resonance Forms

**Reaction of pentane-2,4-dione with a base**

- \( \text{H}^+ \) is removed
- An anion is formed

**Resonance of the anion product:**

**Worked Example 2.2**

**Drawing Resonance Forms of an Anion**

Draw three resonance forms for the carbonate ion, \( \text{CO}_3^{2-} \).
Draw three resonance forms for the pentadienyl radical. A radical is a substance that contains a single, unpaired electron in one of its orbitals, denoted by a dot (•).

Unpaired electron

Pentadienyl radical