Molecular Geometry and Hybrid Orbitals

Molecular Geometry

Why Should I Care About Molecular Geometry?
Molecular geometry (shape) influences...

- **Physical properties:**
  - Pentane (bp 36°C)
  - 2,2-Dimethylpropane (bp 10°C)

- **Chemical properties:**
  - \((\text{CH}_3)_3\text{C-Br} + \text{HO}^- \rightarrow (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{Br}^-\)
  - \(\text{H}_3\text{C-Br} + \text{HO}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-\)

- **Biological properties:** Enzyme specificity
Molecular Geometry

How Do We Determine Molecular Shape?
• Empirically (spectroscopy, etc)
• Predict via theory

Example: \( \text{CH}_3\text{OH} \) Lewis structure implies planarity
But other geometries can be conceived
So what is the real structure of this molecule?

• Bonds vibrating, bending, etc.
• By ‘geometry’ we usually mean ‘most common’ geometry
• Most common geometry = geometry with lowest energy

What Controls Molecular Geometry?
Most common geometry = geometry with lowest energy

Lowest energy results from...
...minimizing electron repulsion (nonbonded interactions; van der Waals repulsions)
...resonance, conjugation, and aromaticity

How does the molecule minimize electron repulsion?
• Moving electron clouds (electron groups) away from each other
• Electron groups = Atoms
  Groups of atoms
  Lone pairs
• Valence Shell Electron Pair Repulsion theory (VSEPR)
**Molecular Geometry Survey**
Best geometry = largest distance between electron groups

<table>
<thead>
<tr>
<th>Composition</th>
<th>Geometries</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>Linear</td>
<td>$\begin{align*} &amp; A - H \ &amp; H - H \end{align*}$</td>
</tr>
<tr>
<td>AB$_2$</td>
<td>Linear</td>
<td>$\begin{align*} &amp; H - A - H \ &amp; C - C \end{align*}$</td>
</tr>
<tr>
<td></td>
<td>Bent</td>
<td>$\begin{align*} &amp; H - A - B \ &amp; C - C \end{align*}$</td>
</tr>
<tr>
<td>AB$_3$</td>
<td>T-shape</td>
<td>$\begin{align*} &amp; H - A - H \ &amp; H - H \end{align*}$</td>
</tr>
<tr>
<td></td>
<td>Trigonal planar</td>
<td>$\begin{align*} &amp; H - H \end{align*}$</td>
</tr>
<tr>
<td>AB$_4$</td>
<td>Square planar</td>
<td>$\begin{align*} &amp; H - A - B \ &amp; H - H \end{align*}$</td>
</tr>
<tr>
<td></td>
<td>Tetrahedral</td>
<td>$\begin{align*} &amp; H - H \end{align*}$</td>
</tr>
<tr>
<td></td>
<td>Receding back</td>
<td>$\begin{align*} &amp; H - H \end{align*}$</td>
</tr>
<tr>
<td>AB$_5$</td>
<td>Trigonal bipyramid</td>
<td>$\begin{align*} &amp; C - C - C - C - C \end{align*}$</td>
</tr>
</tbody>
</table>

Explore and verify molecular geometry examples with molecular models.
Bond Angles

Best geometry = largest distance between electron groups

Are bond angles always equal?
• Bond angles controlled by magnitude of electron group repulsions

![Diagrams showing electron group repulsions equal and unequal]

Electron groups equal size
All H-C-H 109.5°

Electron group repulsions equal

Electron group repulsions unequal

H-N-H 107°
H-C-H < 109.5°

Which electron groups have greatest repulsion? (Which electron groups are largest?)

Approximate size ranking: H, F < lone pair, Cl, Br, I < all groups of atoms

Bond Angles

In general...
• Two electron groups = linear
• Three electron groups = trigonal planar or distorted trigonal planar
• Four electron groups = tetrahedron or distorted tetrahedron

Warning! Atomic geometry may also be influenced by...
...resonance (covered in Chem 30A)
...conjugation
...aromaticity

Not a consideration in Chem 30A

Example:

Four attachments
Trigonal planar due to resonance
Molecular Geometry and Orbitals

Covalent bonds formed by overlap of orbitals

- Example: Two H 1s orbitals (spheres) overlap to form H-H bond

\[
\text{Hydrogen atoms} \quad \rightarrow \quad \text{Hydrogen molecule}
\]

Therefore this orbital combination incorrect

Verify with your model kit
Molecular Geometry and Orbitals

Solution (Linus Pauling, 1931)

- Combine s, p_x, p_y, and p_z orbitals to form correct # of bonds with correct geometry
- Combinations = **hybrid orbitals**

Hybridization scheme for atom with four electron groups

- CH₄ geometry = tetrahedral; need four bonds and four hybrid orbitals
- Orbital conservation: four hybrid orbitals come from four atomic orbitals
  - \( C \text{ sp}^3 + H \text{ 1s} \rightarrow C-H \sigma \) bond

Hybridization scheme for atom with three electron groups

- Carbon = trigonal planar; need three bonds and three hybrid orbitals
- Three hybrid orbitals come from three atomic orbitals:
  \[
  s + p_x + p_y + p_z \rightarrow \text{sp}^2 + \text{sp}^2 + \text{sp}^2 + p_z
  \]

Example:

- Top view without \( p_z \)
- Top view with \( p_z \)
- Side view
Molecular Geometry and Orbitals

Combine orbitals to build

\[ \text{C-H } \sigma \text{ bond} \]

\[ \text{C-C } \pi \text{ bond} \]

Explore and verify with molecular models

Molecular Geometry and Orbitals

Hybridization scheme for atom with two electron groups

Example: \( \text{H} \text{C} \equiv \text{C} \text{H} \)

- Carbon = linear; need two bonds and two hybrid orbitals
- Two hybrid orbitals come from two atomic orbitals:

\[ s + p_x + p_y + p_z \rightarrow sp + sp + p_y + p_z \]

Mixed Not used

Top view without \( p_y \)

Top view with \( p_y \)

Side view without \( p_y \)

Side view with \( p_y \)
Molecular Geometry and Orbitals

Combine orbitals to build

\[
\begin{align*}
C\ sp + H\ 1s & \rightarrow C-H\ \sigma\ bond \\
C\ sp + C\ sp & \rightarrow \\
C\ p_y + C\ p_y & \rightarrow \\
C\ p_z + C\ p_z & \rightarrow
\end{align*}
\]

Side view

\(p_y - p_y\ \pi\) bond not shown

C-H \(\sigma\) bond

Top view

\(p_z - p_z\ \pi\) bond not shown

C-C \(\pi\) bond

C-C \(\sigma\) bond

Explore and verify with molecular models

Molecular Geometry and Orbitals

A few final notes...

• Other double bonds (C=O, C=N) similar orbital arrangements to C=C

• Other triple bonds (C≡N) similar orbital arrangements to C≡C

• C, O, N almost always hybridized in organic molecules

Four electron groups

\(sp^3\)

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

Three electron groups

\(sp^2\)

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

Two electron groups

\(sp\)

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} = \text{N} \ 
\end{array}
\]