

# Structure and Bonding

## Introduction

Organic chemistry is the study of carbon-based compounds. The immense diversity of organic molecules, which form the basis of all life, stems from carbon's unique ability to form four stable covalent bonds (tetravalency) and link together to form chains, rings, and complex frameworks. Understanding how atoms bond and the resulting molecular shape (structure) is the foundation for predicting a molecule's behavior.

## Learning Objectives

By the end of this module, you will be able to:

- Apply the concepts of organic structural theory to predict physical and chemical properties of organic compounds.
- Predict chemical reactivity of organic compounds.

## Key Concepts and Definitions

Term	Definition
<b>Covalent Bond</b>	A chemical bond formed by the sharing of electrons between atoms.
<b>Electronegativity</b>	Ability of an atom to attract shared electrons.
<b>Polar Covalent Bond</b>	Unequal sharing of electrons leading to partial charges.
<b>Hybridization</b>	Mixing of atomic orbitals (s, p) to form new hybrid orbitals (sp, sp <sup>2</sup> , sp <sup>3</sup> ).
<b>Resonance</b>	When a molecule can be represented by two or more valid Lewis structures.
<b>Lewis Structure</b>	Diagram that represents bonding and nonbonding electrons.
<b>Sigma (<math>\sigma</math>) Bond</b>	Strongest type of covalent bond formed by head-on orbital overlap.

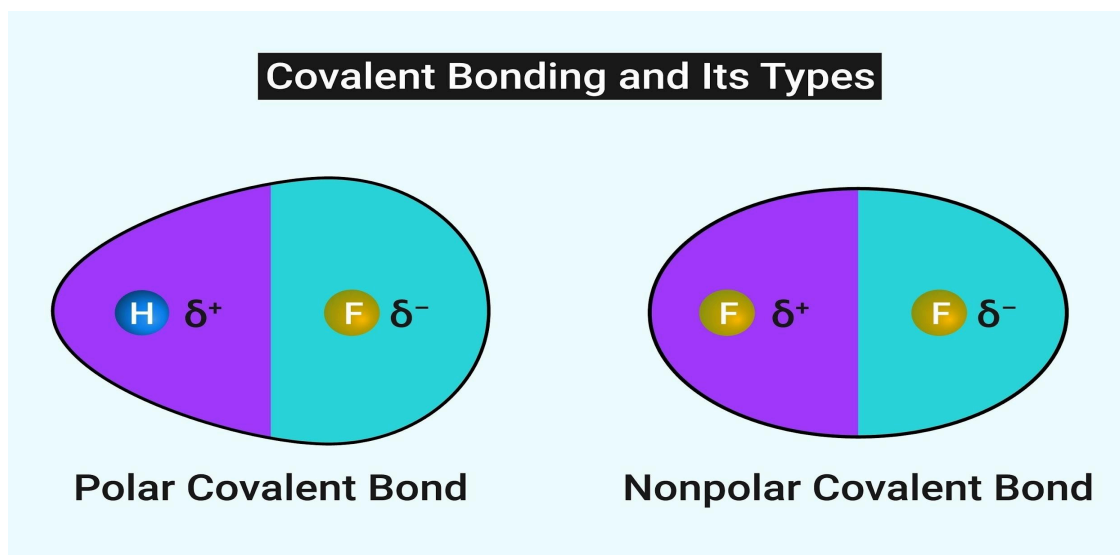
<b>Pi (<math>\pi</math>) Bond</b>	Weaker sideways overlap of unhybridized p orbitals; present in multiple bonds.
<b>Functional Groups</b>	Atom groups that determine the properties of organic molecules.
<b>Intermolecular Forces</b>	The attractive or repulsive forces that exist between neighboring molecules, which largely determine physical properties like boiling point.

## Detailed Discussion

### Covalent Bonding, Electronegativity, and Polarity

The majority of organic bonds are **covalent bonds**. When two atoms of different elements bond, the difference in their **electronegativity (EN)** determines the nature of the bond.

- **Nonpolar Covalent Bonds:** Bonds between atoms with very similar EN values, such as C-C or C-H, where electrons are shared essentially equally.
- **Polar Covalent Bonds:** Bonds between atoms with differing EN values, such as C-O, C-N, or C-Cl. The more electronegative atom attracts the electron density, gaining a **partial negative charge ( $\delta^-$ )**, and the less electronegative atom gains a **partial positive charge ( $\delta^+$ )**.



The polarity of bonds is critical: it creates electron-rich and electron-poor regions in a molecule, which are the sites of chemical reactivity

## Oxidation States in Organic Molecules

The oxidation state (or oxidation number) of carbon is a bookkeeping tool used to describe the degree of oxidation or reduction of a carbon atom in a molecule. In organic chemistry, oxidation states help predict reaction trends, especially in oxidation–reduction reactions.

Rules for assigning oxidation states to carbon:

- Each bond between carbon and a more electronegative atom (such as O, N, or halogens) increases carbon's oxidation state by +1.
- Each bond between carbon and hydrogen decreases carbon's oxidation state by –1.
- Carbon–carbon bonds contribute 0.

Example:

- In methane (CH<sub>4</sub>), carbon has four C–H bonds, giving it an oxidation state of –4.
- As carbon forms bonds with more electronegative atoms, its oxidation state increases.

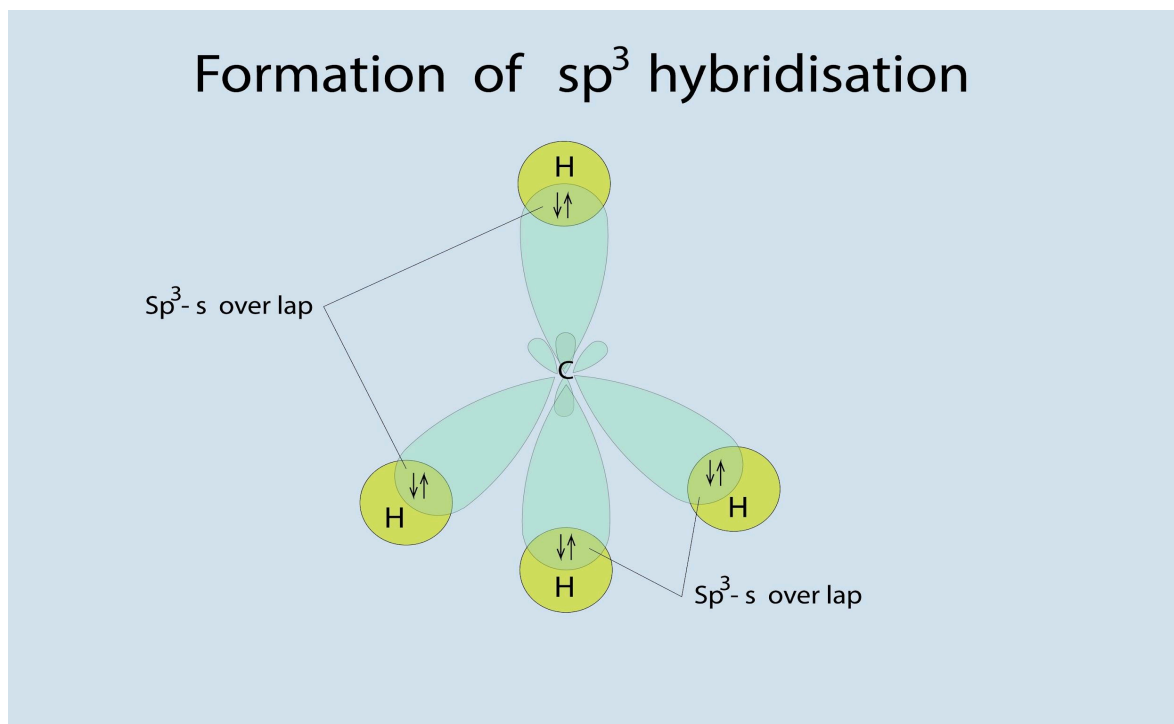
## Molecular Geometry and Hybridization

The three-dimensional shape of an organic molecule is defined by the arrangement of electron groups (bonds and lone pairs) around each atom, explained by **VSEPR Theory** and **orbital hybridization**. Carbon forms three main types of hybrid orbitals:

Hybridization	Bonding	Geometry	Bond Angle	Example
sp <sup>3</sup>	4 single bonds (σ)	Tetrahedral	109.5°	CH <sub>4</sub> (Methane)
sp <sup>2</sup>	1 double bond (1 σ, 1 π)	Trigonal Planar	120°	C <sub>2</sub> H <sub>4</sub> (Ethene)

sp	1 triple bond (1 $\sigma$ , 2 $\pi$ )	Linear	180°	C <sub>2</sub> H <sub>2</sub> (Ethyne)
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**Sigma ( $\sigma$ ) bonds** are formed by the direct, head-on overlap of orbitals. **Pi ( $\pi$ ) bonds** are formed by the sideways overlap of unhybridized  $p$  orbitals and are found only in double and triple bonds.



## Degree of Unsaturation (Index of Hydrogen Deficiency)

The degree of unsaturation indicates the total number of rings and  $\pi$  bonds present in a molecule. It provides insight into the structure of an organic compound before drawing its full Lewis structure.

**Formula:** Degree of Unsaturation =  $(2C + 2 - H + N - X) / 2$

**Where:**

- **C** = number of carbons
- **H** = number of hydrogens
- **N** = number of nitrogens
- **X** = number of halogens

Each degree of unsaturation corresponds to either one ring or one  $\pi$  bond.

## Predicting Physical Properties

The physical properties, like **boiling point (BP)**, **melting point (MP)**, and **solubility** are governed by the strength of the **Intermolecular Forces (IMFs)**, the attractions between neighboring molecules. To boil a liquid or melt a solid, these IMFs must be overcome.

IMF Type	Description & Strength	Molecules Affected	Effect on BP/MP
London Dispersion Forces (LDFs)	Weakest. Induced, temporary dipoles. Strength increases with molecular size and surface area.	All molecules (Only IMF in nonpolar molecules).	Low to moderate Increases with chain length or size.
Dipole-Dipole Interactions	Attraction between permanent partial charges of polar molecules.	Polar molecules (e.g., ketones, aldehydes).	Higher than nonpolar molecules of similar size.
Hydrogen Bonding (H- Bonding)	Strongest. Requires an H atom bonded directly to N, O, or F	Alcohols (R-OH), Amines (R-NH <sub>2</sub> ), Carboxylic Acids.	Highest; requires the most energy to break.

**Solubility** is predicted by the "like dissolves like" rule:

- **Polar/Ionic** compounds dissolve in **Polar** solvents (e.g., Methanol in Water).
- **Nonpolar** compounds dissolve in **Nonpolar** solvents (e.g., Hexane in Oil).

The presence of polar functional groups such as -OH, -NH<sub>2</sub>, and -COOH significantly increases water solubility due to hydrogen bonding. In contrast, nonpolar functional groups decrease solubility in water even if the molecule is small.

**Isomerism:** Isomers are compounds that have the same molecular formula but differ in the arrangement of atoms.

**Structural (Constitutional) Isomers:**

- Differ in the connectivity of atoms.
- May have different physical and chemical properties.

**Examples:**

- Chain isomerism (different carbon skeletons)
- Functional group isomerism (same formula, different functional groups)

Understanding isomerism is essential for predicting properties such as boiling point, reactivity, and stability.

## Acidity and Basicity in Organic Compounds

Many organic molecules can act as acids or bases. Acidity refers to the ability of a compound to donate a proton ( $\text{H}^+$ ), while basicity refers to the ability to accept a proton.

**Factors Affecting Acidity:**

- **Electronegativity:** More electronegative atoms stabilize negative charge better, increasing acidity.
- **Inductive Effect:** Electron-withdrawing groups stabilize conjugate bases and increase acidity.
- **Hybridization:** Acidity increases as the s-character of the orbital increases ( $\text{sp} > \text{sp}^2 > \text{sp}^3$ ).

**Factors Affecting Basicity:**

- **Availability of lone pairs:** More available lone pairs increase basicity.
- **Electronegativity:** Less electronegative atoms hold lone pairs less tightly and are more basic.
- **Resonance:** Delocalization of lone pairs lowers basicity.

These factors explain trends in acidity and basicity observed among alcohols, amines, carboxylic acids, and hydrocarbons.

## Predicting Chemical Reactivity

A molecule's structure provides two main ways to predict its chemical reactivity:

### 1. Functional Groups are the Centers of Reactivity:

- Functional groups are the sites where almost all chemical reactions occur. For example, the presence of an O-H group (an alcohol) predicts a molecule will undergo reactions characteristic of alcohols, regardless of the rest of the molecule's structure.

### 2. Electronic and Steric Factors:

- **Electronic Effects (Polarity): Polar bonds** are the main drivers of many reactions. The electron-poor ( $\delta^+$ ) atom is the site for attack by an electron-rich species, while the lone pairs or  $\pi$  bonds (electron-rich regions) are reactive sites for electron-poor species.
- **Bond Strength:** Molecules containing **weaker bonds** (like the  $\pi$  bond in a double bond) are generally more reactive than molecules that only have stronger  $\sigma$  bonds (like alkanes).
- **Steric Hindrance:** The physical bulk of surrounding groups can block access to a reaction site. More crowded groups can significantly **slow down** or prevent a reaction from occurring.

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