1. Basic Concepts & Functional Groups
Broadly, there are three types of chemical bonding: **ionic**, **covalent**, and **metallic**:

<table>
<thead>
<tr>
<th>Bonding Type</th>
<th>Model</th>
<th>Nature of (Electrostatic) Attraction</th>
<th>Strength</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic bonding</td>
<td><img src="image" alt="Ionic Bonding" /></td>
<td>Attraction between positive and negative ions</td>
<td>Extremely strong (400–4000 kJ mol⁻¹)</td>
<td>NaCl</td>
</tr>
<tr>
<td>Covalent bonding</td>
<td><img src="image" alt="Covalent Bonding" /></td>
<td>Attraction between nuclei and shared electron pair</td>
<td>Very strong (150–1100 kJ mol⁻¹)</td>
<td>H–H</td>
</tr>
<tr>
<td>Metallic bonding</td>
<td><img src="image" alt="Metallic Bonding" /></td>
<td>Attraction between cations and delocalised electrons</td>
<td>Strong to very strong (75–1000 kJ mol⁻¹)</td>
<td>Na</td>
</tr>
</tbody>
</table>

In organic chemistry, we are concerned almost exclusively with covalent compounds, but charged organic molecules (anions or cations) can of course form ionic lattices in the solid phase.

Carbon is a unique element because it forms strong covalent bonds to itself, but also to hydrogen and other elements, enabling an essentially infinite variation of molecular structures.
### Intermolecular Forces: The interactions between molecules/ions

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Model</th>
<th>Nature of (electrostatic) attraction</th>
<th>Strength</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-dipole</td>
<td><img src="image" alt="Model" /></td>
<td>attraction between ion and permanent dipole</td>
<td>highly variable (40–600 kJ mol(^{-1}))</td>
<td>Na – O – H</td>
</tr>
<tr>
<td>Hydrogen bonding</td>
<td><img src="image" alt="Model" /></td>
<td>special type of dipole-dipole interaction between an acidic hydrogen (δ+) and a lone pair (δ−)</td>
<td>medium (10–40 kJ mol(^{-1}))</td>
<td>H – O – H – O</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td><img src="image" alt="Model" /></td>
<td>attraction between permanent dipoles</td>
<td>medium (5–25 kJ mol(^{-1}))</td>
<td>O – O – O</td>
</tr>
<tr>
<td>Ion-induced dipole</td>
<td><img src="image" alt="Model" /></td>
<td>attraction between ion and induced dipole</td>
<td>weak (3–15 kJ mol(^{-1}))</td>
<td>Na – ion</td>
</tr>
<tr>
<td>Dipole-induced dipole</td>
<td><img src="image" alt="Model" /></td>
<td>attraction between permanent dipole and induced dipole</td>
<td>weak (2–10 kJ mol(^{-1}))</td>
<td>Cl – H – Cl</td>
</tr>
<tr>
<td>Dispersion (London) forces</td>
<td><img src="image" alt="Model" /></td>
<td>attraction between random dipole and induced dipole</td>
<td>extremely weak (0.05–40 kJ mol(^{-1}))</td>
<td>I – I – I – I – I</td>
</tr>
</tbody>
</table>
Lewis Structures: Drawing organic molecules using lines to represent covalent bonds

- In 1916, Gilbert Lewis first proposed that covalent bonds consist of two electrons shared between two atoms (2c-2e bonding) and he also formulated the octet rule for second-row elements.
- You will already be familiar with Lewis dot diagrams for covalent bonding in simple molecules.

\[
\begin{align*}
4 \text{H}^+ + \text{C}^- & \rightarrow \text{H} - \text{C} - \text{H}^+ \\
(1s^1) \quad (2s^2, 2p^2) & \rightarrow \text{C has 8 valence electrons} \\
& \quad \text{H has 2 valence electrons}
\end{align*}
\]

\[
\begin{align*}
3 \text{H}^+ + \text{N}^- & \rightarrow \text{H} - \text{N} - \text{H}^+ \\
(1s^1) \quad (2s^2, 2p^3) & \rightarrow \text{N has 8 valence electrons and one lone pair} \\
& \quad \text{H has 2 valence electrons}
\end{align*}
\]

\[
\begin{align*}
3 \text{H}^+ + \text{O}^- & \rightarrow \text{H} - \text{O} - \text{H}^+ \\
(1s^1) \quad (2s^2, 2p^4) & \rightarrow \text{O has 8 valence electrons and two lone pairs} \\
& \quad \text{H has 2 valence electrons}
\end{align*}
\]

- Organic molecules that are drawn with lines to represent (2c-2e) covalent bonds are termed Lewis structures.
- When drawing molecules, lone pairs are usually omitted, unless they are required for emphasis (e.g., when drawing a curly arrow).

Take-home message: Whenever chemists draw molecules using lines for covalent bonds, they are intrinsically using Lewis's theory of bonding [i.e., that each covalent bond involves two electrons between two atoms (centres) - a so-called 2c-2e (2-centre 2-electron) bond]. The resultant representations are called Lewis structures. You will later learn that this is described as "localised" bonding.
**Formal Charges:** An electron-counting tool, though may not be representative of the real charge distribution

- The **formal charge** is the charge assigned to each atom in a molecule, using the *formalism* that the electrons in the bonds are equally shared between atoms, regardless of electronegativity. Though not always realistic, it is a useful concept for electron-counting purposes.

  Formal charge on atom = valence electrons of element – (number of unshared valence electrons + no. of \( \pi \) and \( \sigma \) bonds)

- Organic chemists do not need to calculate the formal charge on atoms each time – they simply remember that whenever an atom has 8 valence electrons, and has one more bond than its neutral state, it will bear a formal positive charge. Conversely, if it has one less bond than its neutral state, it will bear a formal negative charge.*

- Note that formal charge and **real electrostatic charge** is not always the same. In the ammonium ion (\( \text{NH}_4^+ \)), for example, calculations show that most of the positive charge is situated on the hydrogens, and the nitrogen atom itself bears an excess of negative charge, due to its high electronegativity.

  Electrostatic potential maps show areas of high electron density (\( \delta^- \)) as red and areas of lower electron density (\( \delta^+ \)) as blue

**Take-home message:** For 8 valence electron atoms (e.g., C, N, O), formal charges can be quickly deduced by the number of bonds around the atom. Note that this is purely a formalism (for electron counting), and **real** electrostatic charge can sometimes be opposite!

*Note that elements beyond the 2\(^{\text{nd}}\) row, such as S and P, can deviate from this due to hypervalency (e.g., \( \text{SF}_4 \) and \( \text{PCl}_5 \) are neutral).
**Bond Polarity and the Inductive Effect**

- As we’ve just seen with NH₄⁺, the assumption of equal electron-sharing in a covalent bond (as invoked in formal charge calculations) is not accurate when the atoms involved differ in electronegativity (EN).

- When two bonded atoms differ in EN, the bonding electron density is shifted closer in space to the nucleus of the more EN atom, and the bond is said to be polar (i.e., it develops some percentage of ionic character).

- This phenomenon of a more electronegative atom/group exerting a 'pull' on the electron density in covalent bonds is called the **inductive effect** (I). A more EN atom/group exerts a −I effect, whereas a more electropositive atom/group exerts a +I effect.

- The **dipole moment** (\(\mu\)) is a quantitative measure of a molecule's overall polarity, and it is measured in units of Debye (D) (where 4.8 D corresponds to a proton and an electron separated by 1 Å). As a vector quantity, it is the vector sum of individual bond dipoles (and any lone pairs).

- Bond polarities and molecular dipoles can affect both **reactivity** (e.g., high basicity/nucleophilicity of MeLi at carbon) and **physical properties** (e.g., boiling point, solubility).

**Take-home message:** Bonds between atoms of different electronegativity are polarised towards the more electronegative atom/group, and this redistribution of bonding electron density is referred to as the inductive effect (I). The overall polarity of a molecule is quantified by its dipole moment, and this can affect both the chemical and physical properties of the compound.

**Bond Strengths:** Bond dissociation energy (BDE) quantifies how much energy is stored in a given covalent bond

- All organic reactions involve the cleavage of covalent bonds, so you need a good appreciation of which factors govern the strength of these bonds (e.g., there is a thermodynamic cost to breaking strong bonds and replacing them with weaker ones).
- There are four main factors that determine the strength of a covalent bond, in terms of its (homolytic) bond dissociation energy (BDE) (and this applies as much to \( \pi \) bonds as it does to \( \sigma \) bonds):

1. **Orbital overlap** – Better size matching of orbitals increases the overlap, so bonds between light and heavy elements are generally weaker. Orientation of orbitals is also important, and angle strain can reduce overlap (e.g., cyclopropane).

2. **Ionic contribution** – A larger difference in electronegativity (EN) between A and B gives a stronger bond (i.e., stronger electrostatic attraction holding the atoms together).

3. **Lone-pair repulsion** – Homonuclear and heteronuclear bonds between N, O, and F (e.g., O–O, N–O, O–F) are anomalously weak, due to lp-lp repulsion.

4. **Radical stability** – Because homolytic cleavage produces radicals, it is obvious that more stable radicals should require less energy input to form [see "Conjugation" lectures]. However, it is worth noting that the above effects often have a larger absolute influence on the BDE.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Elements</th>
<th>BDE (kJ/mol)</th>
<th>Relative BDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>C–Sn</td>
<td></td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>C–C</td>
<td></td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>C–H</td>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>O–H</td>
<td></td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td>F–H</td>
<td></td>
<td>1.37</td>
<td>1.37</td>
</tr>
<tr>
<td>C–C</td>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>N–N</td>
<td></td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>O–O</td>
<td></td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>0.88</td>
<td>0.88</td>
</tr>
</tbody>
</table>

**Take-home message:** Quantifying covalent bond strengths is a critical part of understanding and rationalising chemical reactions, as both endergonic (bond cleavage) and exergonic (bond formation) contributions will factor in to the overall \( \Delta G^\circ \) (Gibbs energy) for a reaction.
The Shapes of Organic Molecules and How to Draw Them

Molecular shapes are principally determined by the number of ligands and/or lone pairs around each central atom.

1. Show bond angles
2. Remove C symbols
3. Blank-out H's

The valence shell electron pair repulsion (VSEPR) theory attributes these geometries to minimisation of electron-pair repulsions, but this explanation has no sound theoretical basis. We will soon learn that there is a much better explanation (i.e., orbital hybridisation).

So, at this level, you should always be drawing hydrocarbon structures as skeletal formulae.

Take-home message 1: Molecular shapes are determined by the number of ligands and/or lone pairs around each central atom.

Take-home message 2: Hydrocarbon backbones of organic molecules should be drawn as skeletal formulae without hydrogens.
Aliphatic versus Aromatic Compounds: The broadest way of categorising organic compounds

- **Aliphatic compounds** are those that do not contain aromatic rings, and representative examples are given below. They can be further subdivided into *acyclic* and *cyclic* molecules.

<table>
<thead>
<tr>
<th>alkanes</th>
<th>cycloalkanes</th>
<th>alkenes (olefins)</th>
<th>alkynes (acetylenes)</th>
<th>allenes (cumulenes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylbutane</td>
<td>cyclohexane</td>
<td>(Z)-3-methyl-2-hexene</td>
<td>5-methyl-2-hexyne</td>
<td>1,2-propadiene</td>
</tr>
</tbody>
</table>

- **Aromatic compounds** (*arenes*) are those that do contain aromatic rings, and representative examples are given below.

<table>
<thead>
<tr>
<th>benzene</th>
<th>toluene</th>
<th>naphthalene</th>
<th>anthracene</th>
<th>biphenyl</th>
<th>phenanthracene</th>
</tr>
</thead>
</table>

**Take-home message**: Organic compounds can be broadly categorised into aliphatic and aromatic compounds. As you will later see, this distinction exists because the chemistries of these two types of compounds are markedly different.
**Heterocyclic Compounds (Heterocycles):** Ubiquitous structural motifs in drugs, and key roles in biology (e.g., nucleic acids, proteins)

- **Heterocycles** are a class of cyclic molecules that contain one or more heteroatoms (almost exclusively O, N, and S). They are very important in Nature and also in pharmaceuticals/agrochemicals, and you eventually need to learn their names (but not just yet!).

**Take-home message:** Another major class of organic molecules is heterocycles – again divisible into aliphatic and aromatic categories. You won’t study these molecules in depth until Year 2, but they are of enormous significance in biology, and in man-made drugs.
**Tautomerism**: Molecular isomers that are rapidly interconverted by moving a hydrogen atom

- Some functional groups or aromatic heterocycles are able to exist in two isomeric forms, where the only difference between the two forms is the location of a hydrogen atom. This is a special type of isomerism called **tautomerism** and the isomers are called **tautomers**.

![Imidazoles](image1), ![Pyridones](image2), ![Hydroxypyridines](image3), ![Hydorphosphorus acid](image4)

- A common example of tautomerism is the interconversion of a ketone with its enol form, which is referred to as **keto-enol tautomerism**. For simple ketones, like cyclohexanone, the equilibrium lies strongly in favour of the carbonyl form (due to very high C=O bond strength).

- Keto-enol tautomerism does **not** proceed directly in a single step. It occurs stepwise by proton (H⁺) transfer to/from the solvent, and it is catalysed (accelerated) by acids or bases. You will cover this in more detail in the carbonyl chemistry course in the second semester.

<table>
<thead>
<tr>
<th>keto form (&gt;99.9%)</th>
<th>enol form (&lt;0.1%)</th>
</tr>
</thead>
</table>

![Keto-enol tautomerism](image5)

*(This is the acid-catalysed mechanism. You can have a go yourself at drawing the base-catalysed mechanism)*

![Not via...](image6)

*(1,3-H shifts are thermally forbidden by orbital symmetry rules - see Yr 2)*

**Take-home message**: Tautomerism is an important feature of some functional groups (e.g., enolisable ketones) and heteroaromatic compounds. It involves rapid migration of an atom/group (usually hydrogen) from one part of the molecule to another, and is reversible.
**Take-home message:** Organic chemists use the concept of oxidation levels rather than numerical oxidation states. You will need to recognise which oxidation level a molecule (or functional group) is at, in order to understand oxidation/reduction reactions.
**Functional Groups:** The alkene or alcohol oxidation level

- **Alcohols** and **ethers** are at the same oxidation level as alkenes - they can be interconverted without the need for oxidants/reductants.

  ![Chemical structures](image)

- **Thiols**, **thioethers** and **alkyl halides** are also at the same oxidation level as alkenes/alcohols, and are named in the same way.

  ![Chemical structures](image)

- **Amines** are also at the same oxidation level, and are classified according to the substituents on N and the α-C.

  ![Chemical structures](image)

**Take-home message**: Alcohols, ethers, amines, thiols, thioethers, and alkyl halides are all at the same oxidation level as alkenes (and also one another). Conversions between these functional groups do not require oxidants or reductants (i.e., redox-neutral).
**Functional Groups: The alkyne or carbonyl oxidation level**

- **Aldehydes** and **ketones** are at the same oxidation level as alkynes - they can be interconverted without the need for oxidants/reductants.

![Diagram showing interconversion of alkyne, enol, aldehyde, and ketone]

- Although **enols** (above) are usually far less stable than the carbonyl ('keto') tautomer, it is possible to switch the OH group to other heteroatom substituents and obtain stable compounds (you could call them **enol derivatives**).

![Diagram showing various enol derivatives]

- **Two electronegative atoms** (e.g., O, N, S, Hal) singly-bonded to the same carbon (1,1- or 'geminal') or on adjacent carbons (1,2- or 'vicinal') are also at the same oxidation level as alkynes, if you consider them as single functional group.

![Diagram showing various interaction products]

**Take-home message**: Aldehydes, ketones, enol derivatives, and _gem_ or _vic_-diols (or their derivatives) are all at the same oxidation level as alkynes (and also one another). Conversions between these functional groups do not require oxidants or reductants (i.e., redox-neutral).
**Functional Groups: The carboxylic acid oxidation level**

- **Carboxylic acids**, as well as **esters**, **acid anhydrides**, and **orthoesters**, are one oxidation level higher than alkynes/ketones/aldehydes.

- **Amides** and **nitriles** are at the same oxidation level. Indeed, it's possible to interconvert primary amides and nitriles by hydration and dehydration reactions. Amides are named in a similar fashion to amines (i.e., primary, secondary, tertiary).

- Other derivatives of carboxylic acids are also commonly encountered, such as **acyl chlorides** and **thioesters**. Again, these are at the same oxidation level as esters, amides, and nitriles.

**Take-home message**: Carboxylic acids, esters, acid anhydrides, orthoesters, amides, nitriles, acyl chlorides, and thioesters are all at the same oxidation level. Conversions between these functional groups do not require oxidants or reductants (i.e., redox-neutral).
Carbon dioxide in water forms small quantities of carbonic acid, which can be deprotonated once or twice to give bicarbonate and carbonate anions, respectively. **Organic carbonates** are effectively acetals of carbon dioxide (though they are not formed this way).

Other important molecules at the same oxidation level are the reagent **phosgene**, as well as **ureas** and **urethanes** (carbamates).

**Isocyanates** are a less commonly encountered, but still important, functional group. They are effectively imines of carbon dioxide (though they are not prepared this way) and they are highly reactive towards water or other nucleophiles.

**Take-home message**: The carbon dioxide oxidation level includes carbonates, ureas, urethanes (carbamates), phosgene (and its derivatives), and isocyanates.
Nitrogen-Based Functional Groups: There are lots, and you'll eventually need to be familiar with all of them

- Organonitrogen chemistry is extremely diverse, and you will encounter all of the following functional groups during the Organic course. No need to memorise them just yet, so just use this page as a handy reference (but note that it's not comprehensive!).

![Diagram of nitrogen-based functional groups]

- primary amine
- secondary amine
- tertiary amine
- amide anion
- amine N-oxide
- ammonium salt
- aniline
- imine
- enamine
- amide
- imide
- imidate
- amidine
- urethane (carbamate)
- isocyanate
- urea
- carbodiimide
- guanidine
- hydroxylamine
- hydrazine
- oxime
- nitroso
- nitro
- hydrazone
- azo
- nitrile
- isocyanide (isonitrile)
- diazonium
- diazo
- azide
An Aside: Cutting-Edge Research on Amines @ Bath (just for interest)

- Prof. Jonathan Williams (who sadly passed away in 2019) pioneered the concept of catalytic "hydrogen-borrowing" for amine synthesis directly from alcohols (see right; M = transition metal).

- A simple, powerful method for determining the enantiopurity of chiral amines was developed by Prof. Steve Bull and Prof. Tony James, using imine formation and Lewis acid-base reactivity.

- A new method for forming C-C bonds adjacent to primary amino groups was devised by Dr Alex Cresswell, using a technique called visible-light photoredox catalysis (see right). The reaction uses azide ion (N₃⁻) as a co-catalyst, and proceeds via radical intermediates (PC = photocatalyst).

"A simple protocol for NMR analysis of the enantiomeric purity of primary amines" Org. Lett. 2006, 8, 609 (Bull, James et al.)

"His research on developing new catalytic processes in organic chemistry was world-leading"
Sulfur-Based Functional Groups

- The chemistry of organosulfur compounds is very rich and diverse, and sulfur features heavily in both biology and synthetic chemistry.
- One of the defining features of organosulfur chemistry is the wide range of (formal) oxidation states that sulfur can adopt (−2 to +6).
- A logical way of classifying organosulfur compounds is by the number of oxygen atoms (or other electronegative atoms) attached to S, and the number of S=O groups.

![Diagram of sulfur-based functional groups]

- Note the highlighting of a sulfur-based lone pair on sulfoxides and related compounds. We often don’t draw this in, so sulfenyl groups can be misleadingly drawn as if they are trigonal planar (like C=O groups).

other important sulfur-based FGs

- thioester
- episulfide
- disulfide
- sulfonium salt
- sulfoxide
- sulfone
- sulfenic acid
- sulfinic acid
- sulfinate ester
- sulfite ester

nomenclature (prefixes)

- sulfenyl group
- sulfinyl group
- sulfonyl group

[Note: e → i → o is same as order in alphabet!]
Phosphorus-Based Functional Groups

Organophosphorus compounds (which exist in +3 and +5 oxidation states) are also important in biology and in synthetic chemistry.
**Naming Organic Molecules: IUPAC nomenclature for systematic naming of organic compounds**

- In 1949, the International Union of Pure and Applied Chemistry (IUPAC) formulated a set of rules for systematically naming organic compounds, and these rules are now used by all chemists to name organic compounds.* The **IUPAC name** of an organic compound can be factorised into several fields:

  - **Root** - Identify the longest continuous carbon chain (ensuring that it features the principle FG - see below). This will form the root (**2nd field**) of the name, and is based on alkane nomenclature that you are already familiar with (e.g., "but" for C₄, "hex" for C₆, etc.).

  - **Principle FG** - Identify the highest priority FG (see next slide). The suffix for this FG will form the end (**4th field**) of the name.

  - **Other FGs** - If lower priority FGs are present (see next slide), their prefixes are included in the **1st field**.

    - Exceptions are double and triple bonds, for which the suffixes "en" and "yn" are used (**3rd field**).

    - If there are multiple FGs of the same type, add a modifier before the prefix/suffix to denote the number (i.e., "di-", "tri-", "tetra-", etc.)

---

*Note that **trivial names** are still used for many simple organic molecules (e.g., acetone, acetic acid, toluene, chloroform, formaldehyde, acetylene...)*
The priorities of various functional groups, along with their prefixes and suffixes, are given below.

The table is continued on the next slide...

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Name</th>
<th>Formula</th>
<th>Prefix</th>
<th>Suffix</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Carboxylic acid" /></td>
<td>carboxylic acid</td>
<td>−CO₂H</td>
<td>carboxy-</td>
<td>-oic acid</td>
<td>propanoic acid</td>
</tr>
<tr>
<td><img src="image" alt="Ester" /></td>
<td>ester</td>
<td>−CO₂R</td>
<td>R-oxycarbonyl-</td>
<td>-R-oate</td>
<td>methyl ethanote</td>
</tr>
<tr>
<td><img src="image" alt="Acyl chloride" /></td>
<td>acyl chloride</td>
<td>−COCl</td>
<td>halocarbonyl-</td>
<td>-yl chloride</td>
<td>benzoyl chloride</td>
</tr>
<tr>
<td><img src="image" alt="Amide" /></td>
<td>amide</td>
<td>−CONR₂</td>
<td>carbamoyl-</td>
<td>-amide</td>
<td>butanamide</td>
</tr>
<tr>
<td><img src="image" alt="Nitrile" /></td>
<td>nitrile</td>
<td>−CN</td>
<td>cyano-</td>
<td>-nitrile</td>
<td>propanonitrile</td>
</tr>
<tr>
<td><img src="image" alt="Aldehyde" /></td>
<td>aldehyde</td>
<td>−CHO</td>
<td>formyl-</td>
<td>-al</td>
<td>butanal</td>
</tr>
<tr>
<td><img src="image" alt="Ketone" /></td>
<td>ketone</td>
<td>=O</td>
<td>oxo-</td>
<td>-one</td>
<td>2-propanone</td>
</tr>
<tr>
<td><img src="image" alt="Alcohol" /></td>
<td>alcohol</td>
<td>−OH</td>
<td>hydroxyl-</td>
<td>-ol</td>
<td>ethanol</td>
</tr>
<tr>
<td><img src="image" alt="Thiol" /></td>
<td>thiol</td>
<td>−SH</td>
<td>sulfanyl-</td>
<td>-thiol</td>
<td>methanethiol</td>
</tr>
<tr>
<td><img src="image" alt="Amine" /></td>
<td>amine</td>
<td>−NR₂</td>
<td>amino-</td>
<td>-amine</td>
<td>methylamine</td>
</tr>
<tr>
<td>Functional group</td>
<td>Name</td>
<td>Formula</td>
<td>Prefix</td>
<td>Suffix</td>
<td>Example</td>
</tr>
<tr>
<td>------------------</td>
<td>------------</td>
<td>---------</td>
<td>---------</td>
<td>--------</td>
<td>-----------------</td>
</tr>
<tr>
<td>benzene</td>
<td>arene</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>chlorobenzene</td>
</tr>
<tr>
<td>C= C= C=</td>
<td>alkene</td>
<td>–</td>
<td>alkenyl-</td>
<td>–ene</td>
<td>hex-2-ene</td>
</tr>
<tr>
<td>C≡ C≡</td>
<td>alkyne</td>
<td>–</td>
<td>alkynyl-</td>
<td>–yne</td>
<td>propyne</td>
</tr>
<tr>
<td>–</td>
<td>alkane</td>
<td>–</td>
<td>alkyl-</td>
<td>–ane</td>
<td>butane</td>
</tr>
<tr>
<td>OR</td>
<td>ether</td>
<td>–OR</td>
<td>alkoxy-</td>
<td>–</td>
<td>methoxymethane</td>
</tr>
<tr>
<td>Hal</td>
<td>alkyl halide</td>
<td>–Hal</td>
<td>halo-</td>
<td>–</td>
<td>2-bromopropane</td>
</tr>
<tr>
<td>NO_2</td>
<td>nitro compound</td>
<td>–NO_2</td>
<td>nitro-</td>
<td>–</td>
<td>nitromethane</td>
</tr>
<tr>
<td>N_3</td>
<td>azide</td>
<td>–N_3</td>
<td>azido-</td>
<td>–</td>
<td>azidomethane</td>
</tr>
</tbody>
</table>
4. **Side-Chains** - Identify any side-chains (i.e., carbon chains branched off from the main chain) and apply the necessary prefixes (e.g., methyl, propyl) in the 1st field. If there is more than one of the same type of side-chain, add a "di-" or "tri-" (etc.) modifier before it.

In the example above, there is a methyl group branching off the main chain, so the "methyl" prefix would be applied in the 1st field.

Next, arrange the prefixes for the different substituents (FGs, side-chains) in alphabetical order, ignoring any "di-" or "tri-" (etc.) modifiers for multiples of the same type of substituent (e.g., "ethyl" would come before "dihydroxy" or "dimethyl", as the "e" in "ethyl" precedes the "h" in "hydroxy" and the "m" in "dimethyl" alphabetically). Exceptions to the latter rule would include substituents that have "di-" or "tri-" (etc.) as an intrinsic part of the substituent name (e.g., a "trifluoromethyl" substituent would count as "t").

5. **Locants** - Number the carbon atoms in the main chain and assign locants (number positions) to all FGs and side-chains, choosing the locants so that their numerical values are as low as possible (or rather that their numerical sum is as low as possible).

Locants are positioned immediately before the associated prefix/suffix and are separated from it by a hyphen. A hyphen is also used before a locant, unless it is at the very beginning of the compound name or is grouped together with other locants, in which case the locants are separated from one another by commas (e.g., butyne-1,4-diol).

Additionally:
- If there are several substituents of the same type, either prefixed or suffixed, the locants are ordered numerically (e.g., ethane-1,2-diol rather than ethane-2,1-diol).
- If there are several identical substituents attached to the same carbon of the main chain, the locant is repeated as necessary (e.g., 2,2,3-trimethylheptane).
- The N locant for amines/amides comes before "1" [e.g., CH₃CH(CH₃)CH₂NH(CH₃) is N₂-dimethylpropanamine].
- If the FG can only ever be at the end of a chain (e.g., carboxylic acid, aldehyde, nitrile), it does not need a locant.
6. **Multiple Bond Index** - Lastly, we deal with the multiple bond index (3\textsuperscript{rd} field).

Identify any double/triple bonds and number them with the number of the carbon atom at the head of the bond (i.e., the carbon atom with the lower number). For example, a double bond between carbon atoms 3 and 4 is numbered as "3-ene".

For more than one of any multiple bond type, apply the usual "di-" or "tri-" (etc.) modifiers. If both types of bonds exist, then use "ene" before "yne" [e.g., (E)-pent-2-en-4-ynoic acid].

If all the C–C bonds are single, use "ane", without any numbers or prefixes. If there is a principal FG forming the very end of the compound name (4\textsuperscript{th} field), the "e" at the end of "ane", "ene" or "yne" is dropped, and they become "an", "en" or "yn" instead.

7. **Stereodescriptors** - Although we will not deal with stereochemical descriptors here (see later lectures), such descriptors appear in parentheses at the very start of the name (before the 1\textsuperscript{st} field) and are written in italics. A hyphen is used immediately after the parentheses to connect to the rest of the compound name. When multiple stereodescriptors are used, they are bundled together in the same set of parentheses and are separated by commas [e.g., (S,Z)-2-(N,N-dibenzylamino)octadec-3-en-1-ol].

- These rules are complex (and this is the abridged version!) so it's really not necessary to commit them all to memory. Most chemical drawing software packages (e.g., Chemdraw) have algorithms to name molecular structures, so it's rarely necessary to name molecules yourself, except in the simplest cases.

- Drawings are much more informative than complex chemical names, so you should use structures wherever possible.

- Perhaps the most useful skill is working backwards from a name to a structure, rather than what we've done in the example above.
Common Organic Substituents: Prefixes and shorthand symbols

Below is a collection of common organic groups, with their corresponding prefixes. Note that many of these prefixes derive from trivial names (non-IUPAC) but are still in widespread use. Some of these groups have shorthand symbols (e.g., Bn) that you need to learn.

- methyl (Me)
- ethyl (Et)
- propyl (Pr)
- isopropyl (i-Pr)
- butyl (Bu)
- isobutyl (i-Bu)
- sec-butyl (s-Bu)
- tert-butyl (t-Bu)
- phenyl (Ph) [or "aryl" (Ar) if substituted]
- p-tolyl (or "4-tolyl") (Tol)
- benzyl (Bn)
- vinyl
- allyl
- crotyl
- prenyl
- cinnamyl
- alkynyl
- propargyl

common sulfonyl and sulfonyloxy substituents

- formyl
- acetyl (Ac)
- benzoyl (Bz)

Note that "R" is often used as a wildcard symbol for any organic substituent (organyl group), and "X" is often used for any halogen.
**Substituent versus Salt Nomenclature:** "Iodomethane" or "methyl iodide", for example?

- **Substituent nomenclature** takes a parent compound and identifies substituents that replace hydrogens on it with either prefixes (e.g., chloro-, phenyl-) or suffixes (e.g., -ol, -one). This system can be based on trivial names for the parent compound (e.g., chloroacetone) or on IUPAC names. Such names are **one word**, except for certain FGs (notably acid derivatives like esters and acid chlorides) which retain their historical two-word salt names.

- **Salt nomenclature** was adopted from inorganic chemistry. In such names, the "cation" and the "anion" are always **separate words**: first the "cation" (generally ending in "yl" or "ene"), then the anion (e.g., butyl bromide, allyl iodide). If the last word ends in "ate" or "ide" you are using salt nomenclature, and your name will be at least two words.

<table>
<thead>
<tr>
<th>substituent nomenclature (one word)</th>
<th>salt nomenclature (two words)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trimethylchlorosilane</td>
<td>trimethylsilyl chloride</td>
</tr>
<tr>
<td>tributy lstannane</td>
<td>tributylstannyl hydride</td>
</tr>
<tr>
<td>iodobenzene</td>
<td>phenyl iodide</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>methylene chloride</td>
</tr>
<tr>
<td>1,2-dibromoethane</td>
<td>ethylene dibromide</td>
</tr>
<tr>
<td>2-propen-1-ol</td>
<td>allyl alcohol (alcohol = hydroxide)</td>
</tr>
<tr>
<td>1,2-oxidopropane</td>
<td>propylene oxide</td>
</tr>
<tr>
<td>1-azidopropane</td>
<td>propyl azide</td>
</tr>
</tbody>
</table>

- You should avoid using salt nomenclature for organic compounds that are not ethers, actual salts, or derivatives of acids, if convenient substituent names are available. However, many salt names are so firmly entrenched and convenient that they continue to be used [e.g., "allyl chloride" instead of "1-chloro-2-propene", or "benzyl bromide" instead of "(bromomethyl)benzene"].
**Amine** is considered a variant of "ammonia" (analogous to "phosphine"). Thus, amine names use substituent nomenclature, and are always one word.

**Ether** names, on the other hand, are adapted from salt nomenclature (ether = oxide), and each organyl group is a separate word. (I guess you can't expect a system developed by thousands of chemists over 150 years to be totally consistent!).

**Sulfide, selenide, alcohol, mercaptan, sulfoxide, sulfone, ketone**, etc. are also treated as salt names, since none of these words describes a specific compound.

<table>
<thead>
<tr>
<th>substituent nomenclature (one word)</th>
<th>salt nomenclature (two words)</th>
</tr>
</thead>
<tbody>
<tr>
<td>triethylamine</td>
<td>methyl alcohol (alcohol = hydroxide)</td>
</tr>
<tr>
<td>triphenylphosphine</td>
<td>dimethyl ether (ether = oxide)</td>
</tr>
<tr>
<td>ethyldimethylamine</td>
<td>methyl phenyl ether</td>
</tr>
<tr>
<td>methanol</td>
<td>phenyl mercaptan (mercaptan = hydrosulfide)</td>
</tr>
<tr>
<td>methoxyethane</td>
<td>methyl phenyl sulfone</td>
</tr>
<tr>
<td>methoxybenzene</td>
<td></td>
</tr>
<tr>
<td>benzenethiol</td>
<td></td>
</tr>
<tr>
<td>(methylsulfonyl)benzene</td>
<td></td>
</tr>
</tbody>
</table>

**Carboxylic acid derivatives** (as well as derivatives of other families of acids, such as sulfonic, carbonic, phosphonic, etc.) are named as salts. Note that the acids themselves are written as two words (e.g., acetic acid, propanoic acid, methanesulfonic acid).

Besides "formic" (C\(_1\)) and "acetic" (C\(_2\)), many carboxylic acids have trivial (non-IUPAC) names in common use, such as "propionic" (C\(_3\)), "butyric" (C\(_4\)), "valeric" (C\(_5\)), "caproic" (C\(_6\)), "pivalic", "phthalic", "succinic", "fumaric", "maleic", "lactic", "citric", etc.

These non-IUPAC names for acids can extend to the corresponding aldehydes (e.g., "valeraldehyde" for pentanal, "pivaldehyde" for trimethylacetaldehyde).

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**Take-home message:** If the last part of the compound name is an actual compound (e.g., methane, benzene, stannane, phosphine) then you are using substituent nomenclature, and the name will be one word. If the last part is not (e.g., acetate, chloride, ketone, sulfide, ether, sulfoxide) then you are using salt nomenclature, and the name will always be two or more words.
### Nomenclature of Ions and Reactive Intermediates

- **onium ion**
  - carbonium ion: $R_5C^+$
  - carbenium ion: $R_5C^+$
  - halonium ion: $R_2X^+$
  - ammonium ion: $R_4N^+$
  - nitrenium ion: $R_3N^+$
  - halenium ion: $RX^+$
- **neutral molecule**
  - carbon molecule: $R_4C$
  - halide: $R_2X$
  - alkoxide: $RO$ (8-O-1)
- **anion**
  - carbanion: $R_3C^-$
  - amide anion: $R_2N^-$
  - oxide anion: $RO^-$
- **radical**
  - carbon radical: $R_3C^-$
  - aminyl radical: $R_2N^-$
  - oxyl radical: $RO^-$
- **-enium ion**
  - carbenium ion: $R_5C^+$
  - nitrenium ion: $R_3N^+$
  - halenium ion: $RX^+$
- **-ene**
  - carbene: $R_2C^-$
  - nitrene: $RN$ (6-N-1)
  - oxene: $:O:$ (6-O-0)

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You'll also need to familiarise yourselves with the nomenclature for **ions and reactive intermediates**, and their relationship to stable molecules.

The blue arrows depict the structural or electronic relationships between each different species; in each case (from the bottom upwards) adding an organyl cation, $R^+$ (or $H^+$), or an electron, $e^-$. The information given in brackets is called an N-X-L descriptor. This designates the bonding about any atom (X) in terms of its number of valence electrons (N) and the number of ligands (L) directly bonded to it.

"Carbocation" is frequently used as a synonym of "carbenium ion", although the strict IUPAC definition of "carbocation" is inclusive of both carbenium and carbonium ions. Confusingly, in older literature (pre-1972), the name "carbonium ion" was used for what is today called a "carbenium ion"!
Revision Checklist

Revised?

☐ Types of bonding (covalent, ionic, metallic)

☐ Intermolecular interactions (with a qualitative appreciation of the relative magnitudes of interaction)

☐ Lewis structures and the concept of 2-centre 2-electron (2c-2e) bonds (i.e., "localised" bonds represented by lines between atoms)

☐ Formal charges (noting that real electrostatic charge on central atoms can be opposite in sign, as in 'onium' ions of N and O)

☐ Bond polarity and the inductive effect

☐ Bond strengths (including an appreciation of factors influencing it, with radical stability being addressed in the "Conjugation" lectures)

☐ Molecular shapes and conventions for drawing organic molecules (zig-zag skeletons with C symbols and non-FG hydrogens omitted)

☐ Aliphatic compounds (i.e., alkanes, alkenes, alkynes, and allenes) versus aromatic compounds (arenes) as a broad classification

☐ Heterocycles (no need to memorise all of the names/structures at this stage - just appreciate that they're very important!)

☐ Tautomerism (noting that keto-enol tautomerisation is usually heavily biased towards the carbonyl form, and proceeds stepwise)

☐ Oxidation levels of organic compounds (i.e., removal/addition of either oxygen atoms or the elements of H₂)

☐ Functional groups (no need to memorise all the nitrogen, sulfur, and phosphorus FGs at this stage, but some key ones to learn)

☐ Naming organic compounds (including learning the trivial names and shorthand symbols of common organic groups)

☐ Nomenclature for ions and reactive intermediates