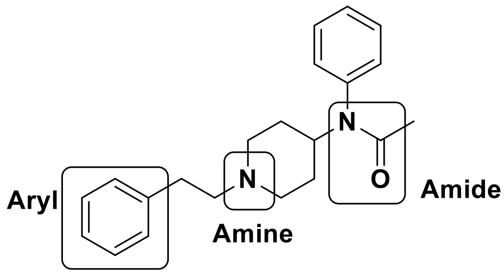
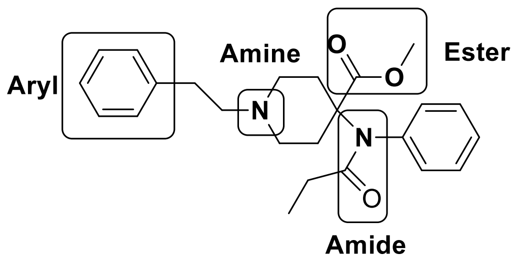
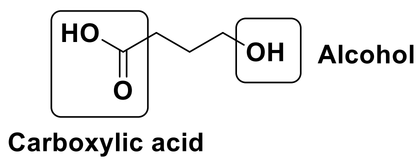
Examples for functional groups



Fentanyl



Carfentanil



Formal Charge

- Convention to keep track of charges
- ∑ (sum of) of formal charges on all atoms in a molecule = the overall charge on the molecule

Rules for calculating formal charge

- Add the number of protons (the atomic number) in the nucleus
- Subtract the number of inner shell electrons
- Subtract the number of unshared electrons
- Subtract ½ of the number of shared outer shell electrons

Examples:

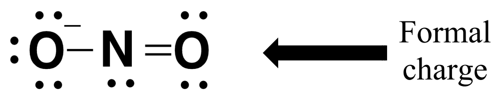
1. **$NaNO_2$ (sodium nitrite;** food preservative**)**
   Nitrite anion

Single bonded oxygen:

+8 (number of protons)
-2 (1s electrons)
-6 (unshared electrons)
½ x 2 = -1 (1/2 of shared electrons)
-1

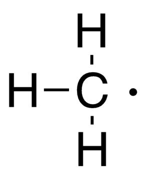
Central N:

+7 (number of protons)
-2 (1s e^-)
-2 (unshared e^-)
-3 (1/2 shared e^-)



Overall charge on the nitrite anion is = **-1**

2. **Methyl radical (sp^3, tetrahedral)**



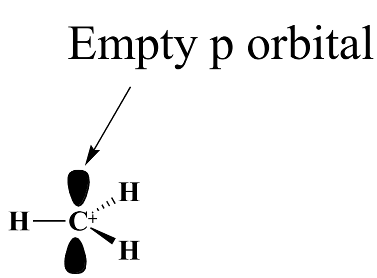
Formal Charge on Carbon
+6 (number of protons)
-2 (1s electrons)
-1 (unshared electrons)
½ x 6 = -3 (1/2 of shared electrons)
0

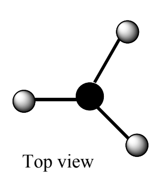
Overall charge on the methyl anion is = **0**
Very unstable since it doesn't have an inert gas configuration

3. **Methyl cation (carbocation, sp^2, planar)**
    - (sp^2 hybridized carbon, planar shape)
    - can be reactive intermediate in principle

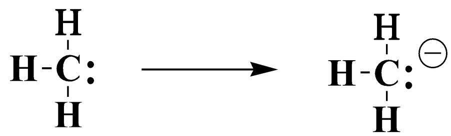
Formal Charge on Carbon
+6 (number of protons)
-2 (1s electrons)
0 (unshared electrons)
½ x 6 = -3 (1/2 of shared electrons)
+1

Overall charge on the methyl anion is = **+1**





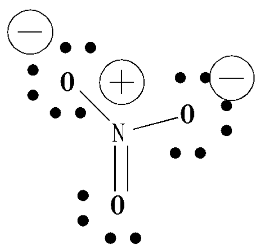
4. **Methyl anion (sp^3, tetrahedral)**



Formal Charge on Carbon
+6 (number of protons)
-2 (1s electrons)
-2 (unshared electrons)
½ x 6 = -3 (1/2 of shared electrons)
-1

Overall charge on the methyl anion is = **-1**

5. **Sodium Nitrate ($NaNO_3$)**

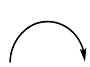


Formal Charge on Nitrogen
+7 (number of protons)
-2 (1s electrons)
0 (unshared electrons)
½ x 8 = -4 (1/2 of shared electrons)
+1

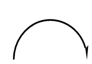
Formal charge on Oxygen
+8 (number of protons)
-2 inner electrons
-6 unshared electrons
-1/2 x 2 = -1 (1/2 of shared electrons)
→ **-1**

Resonance Structures: Different drawings (or pictures) of the same molecule made by moving electrons but not atoms

- Move the electrons, keeping the position of the atoms the same
- Good resonance structures:
    - Maintain inert gas configuration around each atom
    - Avoid the separation of charges
- Avoid like-charges on adjacent atoms
- Double-headed arrow (⟷) is used to indicate resonance forms. Fish Hook and double-headed arrows are used to show electron movement



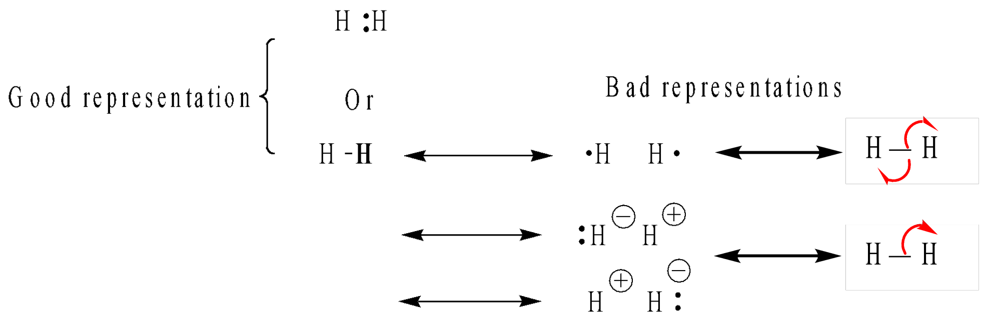
Double Headed Arrow
Show movement of $2e^-$



Fish Hook Arrow
Show movement of $1e^-$

Examples

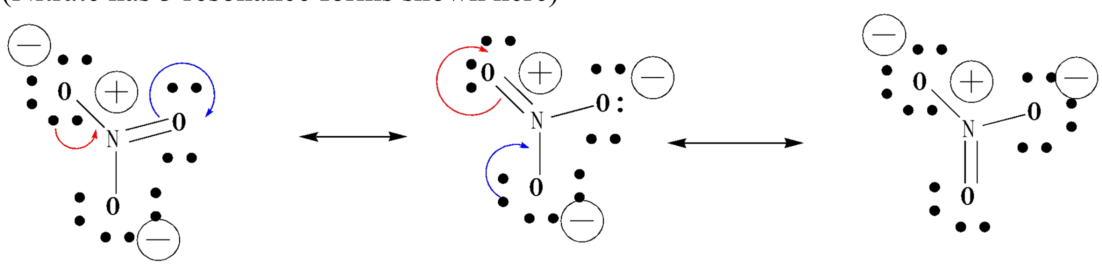
1. Hydrogen gas, H_2



In the bad representations, non- inert gas configuration and extra charges have been created

2. Sodium Nitrate, $NaNO_3$, Na^+ NO_3^-

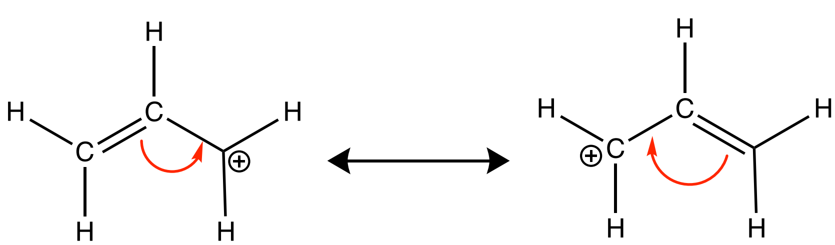
(Nitrate has 3 resonance forms shown here)



No inert gas configuration disrupted
No extra charge created

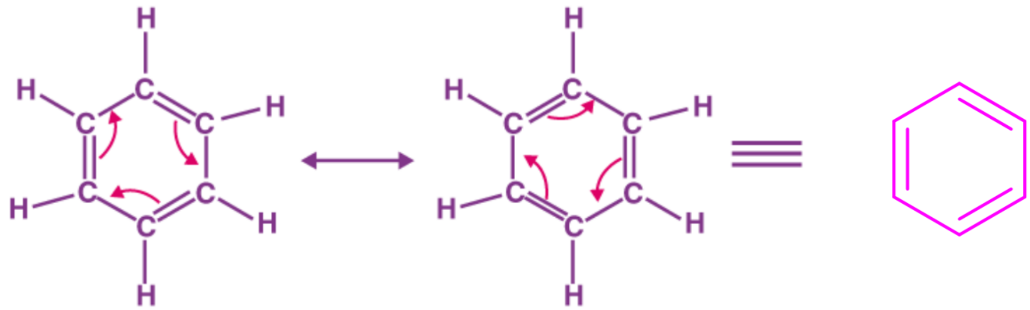
- The O atoms contain partial single and double bond characteristics (each O has -2/3 charge)

3. Allyl Cation

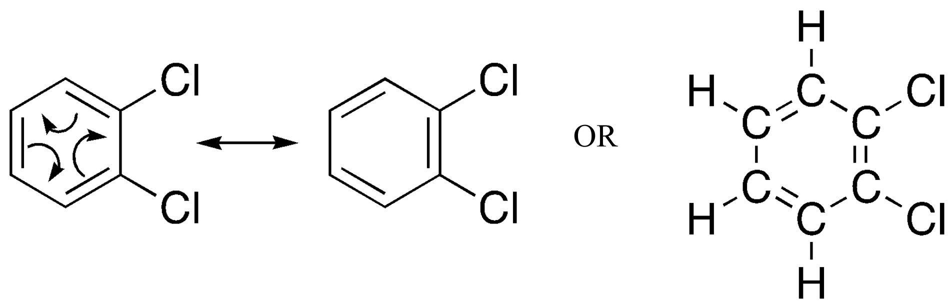


-electrons are delocalized between the two carbons on both side of the central C and C atoms has -1/2 charge and contains partial double and single bond character.

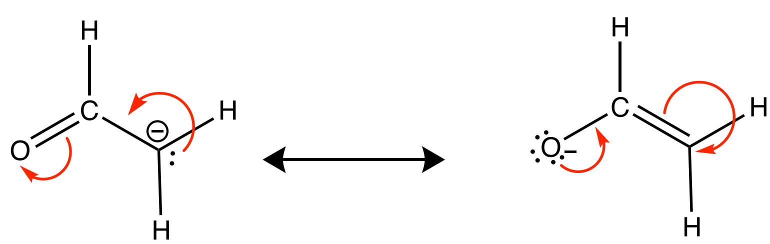
4. Benzene, $C_6H_6 = \Phi$



4. 1,2-Dichlorobenzene

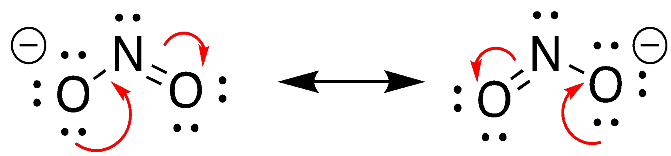


5. Keto-Enol



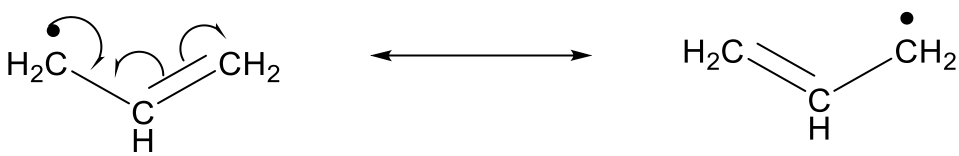
Ketone **Enolate**

6. Sodium Nitrite, $NaNO_2$



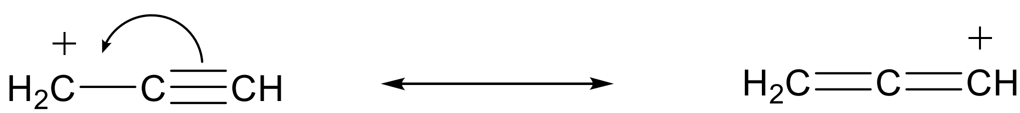
Nitrite anion is reactive in both O atoms. Electrons are delocalized in more than one atom – both O atoms has -1/2 charge and contains partial double and single bond character.

7. **Allyl Radical**



The radical is relatively stable due to resonance.

8. **Propyne cation**



Intermolecular Forces: forces present between molecules, governed by electronegativity

- Attractive intermolecular forces:
  - i) **Hydrogen bonding** – strongest on per atom basis (e.g. base recognition in forming DNA helix) (also in RNA)
    - *Linus Pauling - development of H bonding*
  - ii) **Dipole-dipole interaction** (Intermediate strength)
  - iii) **London forces** (temporary dipole; hydrophobic bonding) – weakest on per atom basis – distortion of inner shells.

Electronegativity:

- An atom's desire for electrons (negative charge).
- On the periodic table, electronegativity increases as you go from left to right (up to inert gases, which are not electronegative) and as you go from down to up
- Halogens (F, Cl, Br, I) are highly electronegative
  - o i.e. Fluorine is the most electronegative atom (wants to gain the inert gas configuration of Ne) and is small (has few electrons)
- It influences acidity of H's attached, as well as the intermolecular forces between molecules.

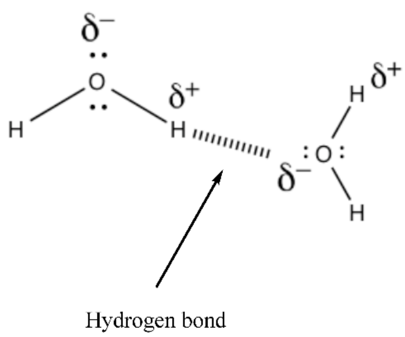
Hydrogen Bonding:

- Strongest intermolecular attractive force
- Need H directly attached to a very electronegative atom (N, O, F, Cl, Br, I)
    - Known as **donors**
- Very electronegative atom needs a lone pair of electrons (N, O, F, Cl, Br, I)
    - Known as **acceptors**

Examples:

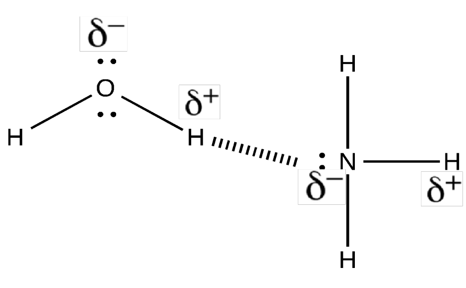
Methane: (CH_4) Incapable of hydrogen bonding, has a low boiling point because the intermolecular forces are weak.

H-O-H (water):



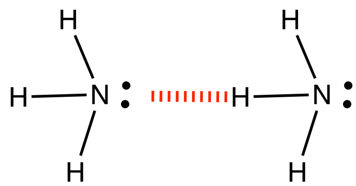
- Oxygen is electronegative and it is sp^3 hybridized
- The partial positive charge on H and the partial negative charge on O lead to their attraction
- Results in high boiling point (100 C) and high melting point by self-association
- HF, H_2O and NH_3 form hydrogen bonds

Water can form "temporary" bonds, resulting in a large number of intermolecular bonds.



- Water is a liquid at RT while ammonia is a gas
- Oxygen is more e-neg than nitrogen, so the protons on water have a higher positive partial charge than the protons on ammonia
- In an ammonia solution, water would be the hydrogen bond donor and ammonia would be the acceptor
- Water dissolves ammonia very well – up to 18M

Ammonia:
- both H-bond acceptor and donor
- H-bond is weaker than the H-bond of water because N is less electronegative than O
- BP: -33C (much higher than methane)

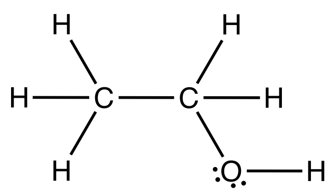


Acceptor (lone pair). Donor (H available)

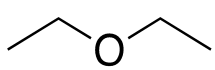
Ethanol

- both H-bond acceptor and donor

-BP: 78.5 ºC

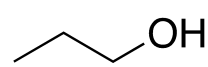


Hydrogen bonding in mixtures:



Diethyl Ether

- Cannot hydrogen bond to itself
  - Has no H directly attached to oxygen (No donor)
  - Can H-bond to water because it has an acceptor
- Has a low boiling point
- Will not dissolve in water very well (although a little bit will be dissolved)



n-Propanol
(1-Propanol)

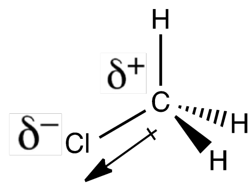
- Can hydrogen bond to itself
  - Has H directly attached to oxygen
- Has a high boiling points relative to its size due to hydrogen bonding
- Can dissolve in water very well

Dipole-Dipole Interactions:

Dipole drawing convention:

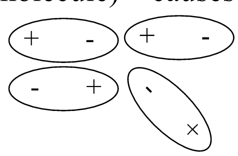
Partial positive charge is the "plus" end, partial negative charge is the arrow head.

Chloromethane, methyl chloride; CH_3Cl

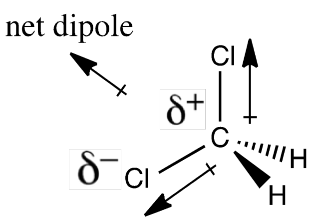


- H and C have similar electronegativity values (non-polar bond)
- Cl is very electronegative due to the fact that it only needs one electron to get inert gas configuration.
- Electron density is pulled toward the chlorine atom, creating a net dipole toward chlorine atom. A net dipole is the vector sum of individual bond dipoles.
- Has a higher MP and BP than methane

Dipoles in different molecules tend to line-up temporarily with each other (partial positive / negative charge on the molecule) – causes molecules to "stick" to each other



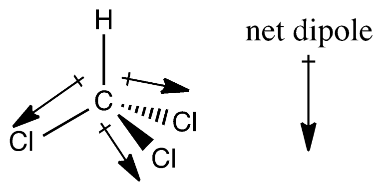
Dichloromethane, methylene chloride; CH_2Cl_2. (Methylene = CH_2 group)



- Liquid at room temperature BP 40 °C MP – 95 °C
- More polar than chloromethane
- Not miscible with water

Net dipole: overall vector sum of all the bond dipoles.

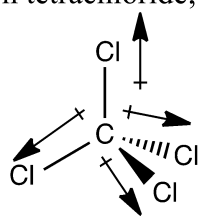
Trichloromethane, chloroform; $CHCl_3$



- More polar than methylene chloride BP 61 °C MP – 64 °C

- Higher than dichloromethane due to dipole dipole interaction

Tetrachloromethane, carbon tetrachloride; CCl_4 (toxic)



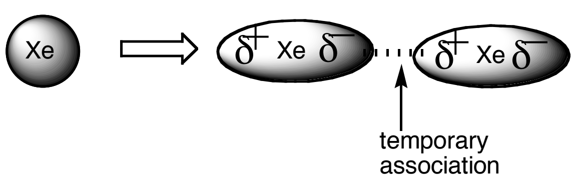
NO net dipole

- Non-polar molecule (net-zero dipole)
- Has temporary dipoles since chlorine is polarizable (see below), BP ~77 °C
- Historically used as a dry-cleaning fluid

London Forces:

- Also known as dispersion forces, temporary dipoles or Van der Waals forces (less good)
- Weakest attractive force
- Distortion of filled outer shell electrons
- Principal effect in hydrophobic interactions

Atoms	Boiling Point	
He	-269 °C	Small atom/ Low polarizability
Ne	-246 °C	↓
Ar	-186 °C	
Kr	-153 °C	
Xe	-108 °C	Large atom/ High polarizability



- The larger the atom (expanded electron density), the easier the formation of temporary dipoles.

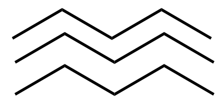
Steric effect: interaction of a filled shell of electrons. Causes repulsion.

This is the reason why CH_4 associates with CH_4, due to London forces

C_5H_{12} hydrophobic bonding:

$$H_3C-CH_2-CH_2\cdot CH_2-CH_3$$

n-pentane
n= Normal=straight



Hydrophobic bonding

n-Pentane has a boiling point of 35 ºC; therefore, it is a liquid at room temperature - why is it a liquid? Because its temporary dipoles – it is not miscible in water – water would rather hydrogen bond to itself – like dissolves like.