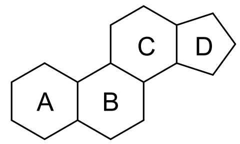
CHEM 261 January 17, 2023

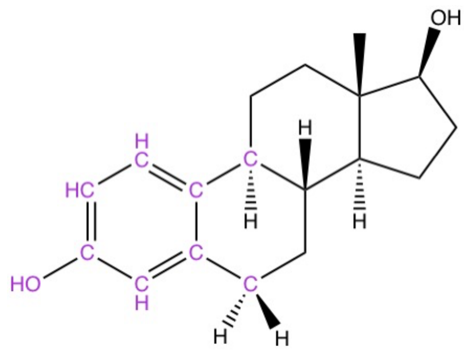
AS A REMINDER:

More examples for representation of molecules



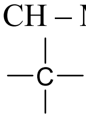
Steroid (C_{17})

1. **Estradiol**



Female hormone
All purple atoms are in the same plane

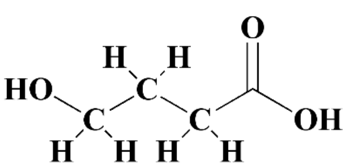
Types of C:
CH_3 – Methyl
CH_2 – Methylene
CH – Methine



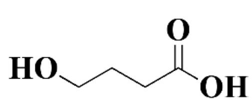
- Quaternary carbon

DRAWING CHEMICAL STRUCTURES

γ -Hydroxybutyric acid



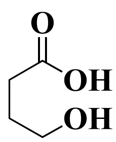
Open chain form

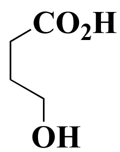


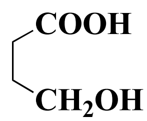
Bond line form

MF = $C_4H_8O_3$

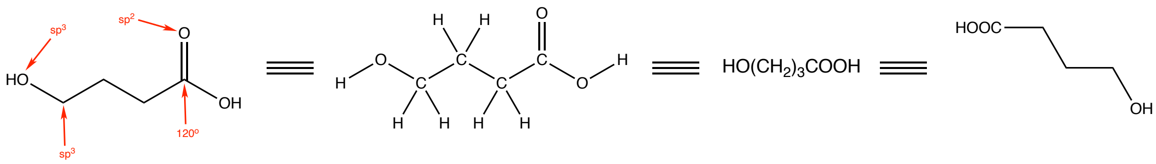
The above compound can also be represented in the following forms, resulting from the free rotation of single bonds (sigma).







Example:



Note: Single bonds, in general, have free rotation

Formal Charge

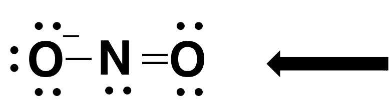
- Convention to keep track of charges
- ∑ (sum of) of formal charges on all atoms in a molecule = overall charge on molecule

Rules for calculating formal charge

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

Examples:

1. **Nitrite anion**



Formal charge

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

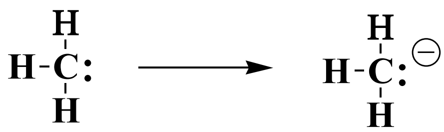
Single bonded oxygen:

+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^-)
= **0**

2. Methyl anion

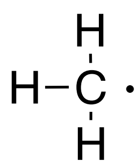


Formal Charge on Carbon

+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**

3. Methyl radical



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

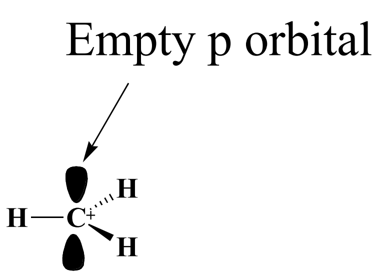
4. Methyl cation

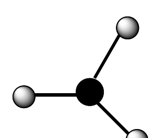
- (sp^2 hybridized carbon, planer shape)
- can be reactive intermediate in principle

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**





Top view

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 same
- Good resonance structures:
  - Maintain inert gas configuration around each atom
  - Avoid separation of charges
- Avoid like-charges on adjacent atoms
- Double headed arrow (⟷) is used indicate resonance forms

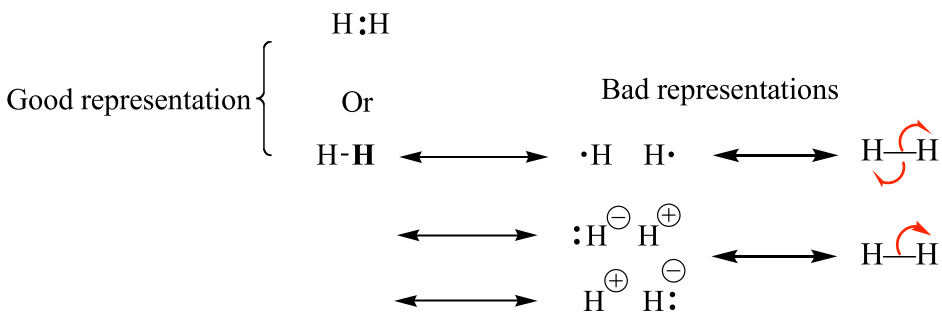
- Fish Hook and double headed arrows are used to show electron movement

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

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

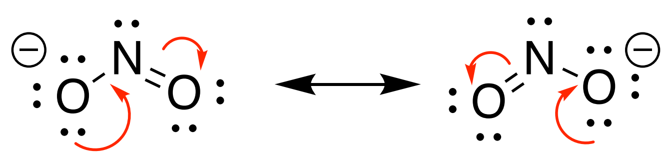
Examples

1. **Hydrogen gas, H_2**



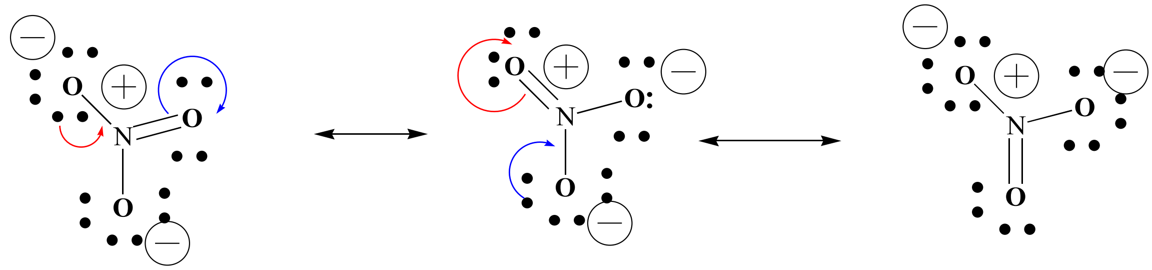
In the bad representations, non- inert gas configuration and extra charges have been created

2. **Sodium 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.

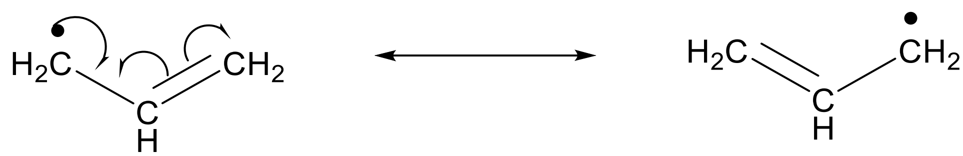
3. Sodium Nitrate, $NaNO_3$



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)

4. Allyl Radical

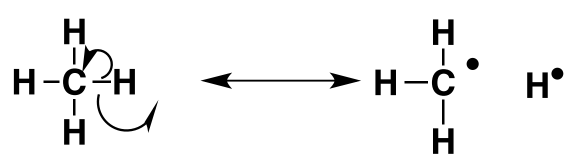


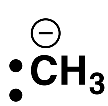
The radical is relatively stable due to resonance.

5. Propyne cation

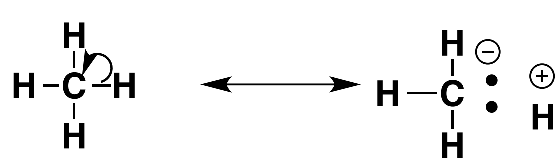
6. CH_4 Methane – below are **POOR** resonance structures – additional charges or unshared electrons (not inert gas configuration)

but methyl radical – can be reactive intermediate in principle



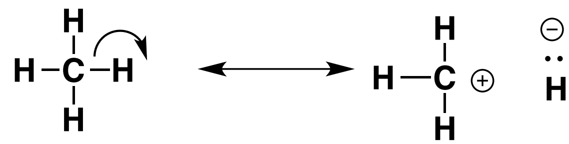


but methyl anion – can be a reactive intermediate in principle

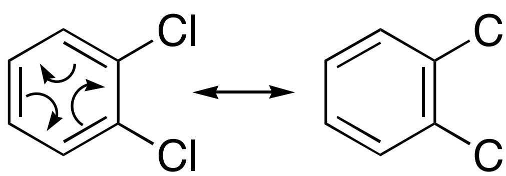


$\overset{\oplus}{CH_3}$

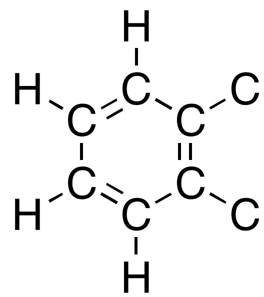
but methyl cation – can be a reactive intermediate in principle

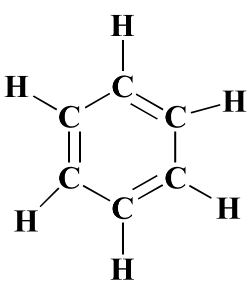


7. **1,2-Dichlorobenzene**



OR





BENZENE

Intermolecular Forces: (forces present between molecules)

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

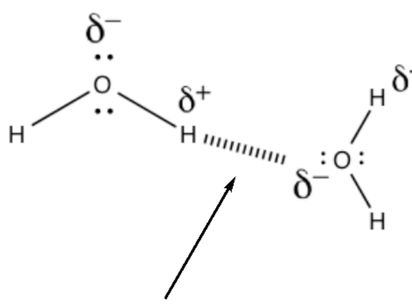
Electronegativity:

- 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
    - 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:

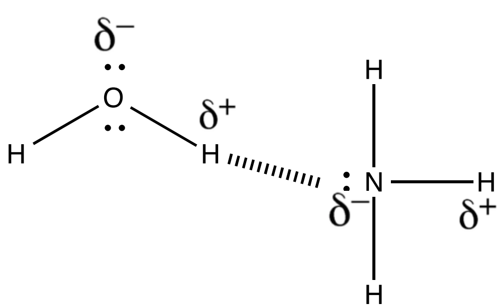
- Strongest intermolecular attractive force
- Need H directly attached to a very electronegative atom (N, O, F, Cl, Br, I)
    - Known as **<u>donors</u>**
- Very electronegative atom needs a lone pair of electrons (N, O, F, Cl, Br, I)
    - Known as **<u>acceptors</u>**

e.g. H-O-H (water)

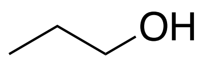


Hydrogen bond

- 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

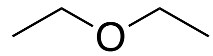


1. Water is a liquid at RT while ammonia is a gas
2. Oxygen is more e-neg than nitrogen, so the protons on water have a higher positive partial charge than the protons on ammonia
3. In an ammonia solution, water would be the hydrogen bond donor and ammonia would be the acceptor
4. Water dissolves ammonia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



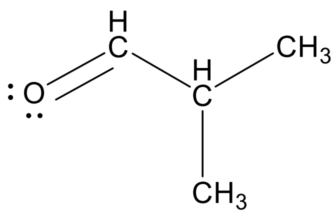
n-Propanol
(1-Propanol)

- 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



Diethyl Ether

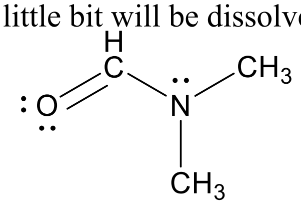
- Cannot hydrogen bond to itself
  - Has no H directly attached to oxygen (No donor)
  - Can H-bond to water because it has an acceptor
- Has a low boiling point
- Will not dissolve in water very well (although a little bit will be dissolved)



Isobutyraldehyde

Can't form H-bonds with itself (not a H-bond donor)
Lone pairs on O can form H-bonds with water (H-bond acceptor)
Poorly soluble in water

vs



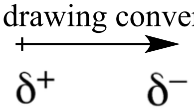
Dimethylformamide

Can't form H-bonds with itself (not a H-bond donor)
Lone pairs on O and N can form H-bonds with water (H-bond acceptor)
Infinitely soluble (miscible) in water

Note: The more H-bonds it can form, the more soluble it is in water

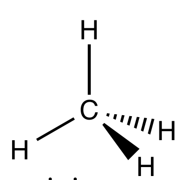
Dipole-Dipole Interactions:

Dipole drawing convention:



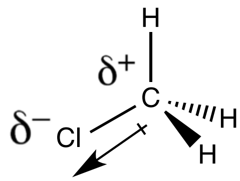
Partial positive charge is the "plus" end, partial negative charge is the arrow head

1. Methane; CH_4



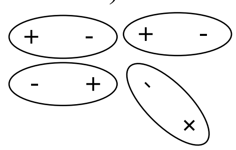
- C and H have ~same electronegativity
- Non-polar (net-zero ~dipole); gas at room temperature
- Low BP -164 ºC (this is relatively low compared to water at 100ºC)
- Low MP -182 ºC

2. Chloromethane, methyl chloride; CH_3Cl



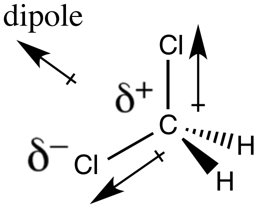
- H and C have similar electronegativity values (non-polar bond)
- Cl is very electronegative due to the fact that it only needs one electron to get inert gas configuration.
- Electron density is pulled toward the chlorine atom, creating a net dipole toward chlorine atom. A net dipole is the vector sum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



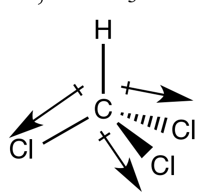
3. Dichloromethane, methylene chloride; CH_2Cl_2

net dipole

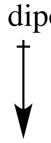


- Liquid at room temperature BP 40 ºC MP – 95 ºC
- More polar than chloromethane
- Not miscible with water

4. Trichloromethane, chloroform; $CHCl_3$

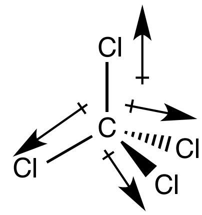


net dipole



- More polar than methylene chloride BP 61 ºC MP – 64 ºC
- Higher than dichloromethane due to dipole dipole interaction

5. Tetrachloromethane, carbon tetrachloride; CCl_4 (toxic)



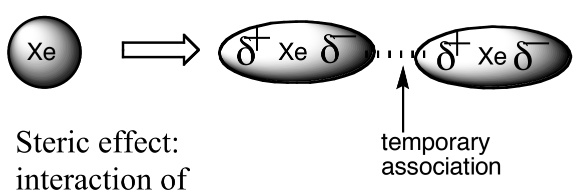
NO net dipole

- Non-polar molecule (net-zero dipole)
- Has temporary dipoles since chlorine is polarizable (see below), BP ~77
- 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



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

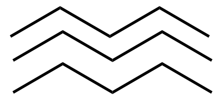
- The larger the atom (expanded electron density), the easier the formation of temporary dipoles.

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

C_5H_{12} hydrophobic bonding:

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

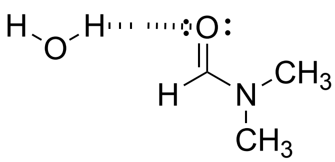
n-pentane
n= Normal=straight



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.

Example: DMF - dimethylformamide

donor acceptor



soluble in water