Chapter IV

Structural Effects

Generalities

Dipole Moment μ

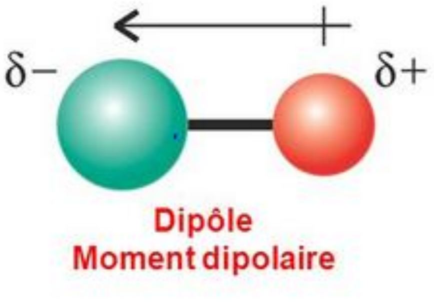
A dipole is defined as a system formed by two equal but opposite charges separated by a distance d. A dipole is characterized by its electric dipole moment μ, defined as:

$$\mu = q \times d$$

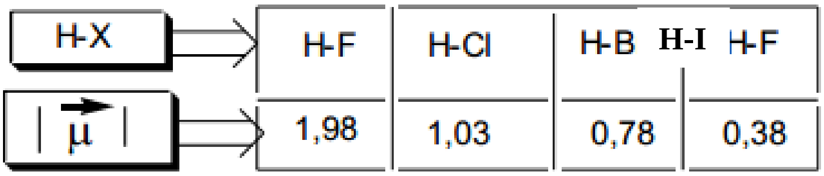
µ is expressed in coulomb meters (**C·m**). This quantity is often expressed in debye (**D**) with:

$$1\ \text{D} = 3{,}33.10^{-30}\ \text{C.m}$$

A polarized covalent bond can be considered as a dipole, which corresponds to a ***dipole moment*** (experimental data) represented by a vector **µ** direc µ rom the center of positive charges to the center of negative charges:



The greater the difference in electronegativity between the atoms, the larger the dipole moment of the bond.



H-X	H-F	H-Cl	H-B	H-I H-F
$\lvert\vec{\mu}\rvert$	1,98	1,03	0,78	0,38

➢ *Polarization*

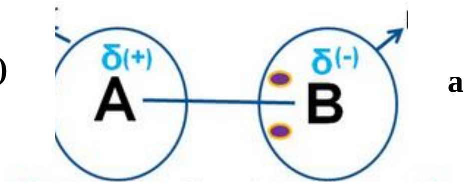
Polarization is the ability of an atom to attract the electrons of a covalent bond towards itself. This electronic displacement results in the appearance of partial charges on the two atoms, with the polarized bond exhibiting a permanent polarization characterized by its dipole moment μ (D). Polarity increases with electronegativity:

$$\mathrm{C{-}F} > \mathrm{C{-}Cl} > \mathrm{C{-}Br} > \mathrm{C{-}I}$$

I. *Inductive effect*

The inductive effect refers to the transmission of the polarity of a **σ** (***sigma***) bond through groups of atoms.

Electron-donor (+I)



Electron-attractor (-I)

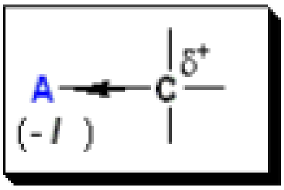
B is more electronegative than A

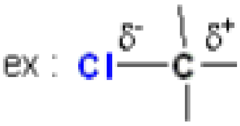
B has an attractor inductive effect (or electron-withdrawing inductive effect, denoted as **–I**).

A has a donor inductive effect (or electron-donating inductive effect, denoted as **+I**).

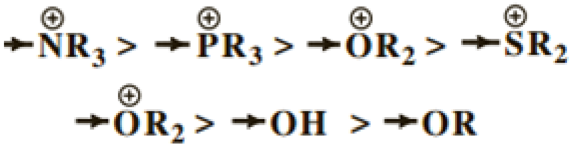
1. *Electron-attractor inductive effect (-I)*

If the electronegativity of atom **A** is greater than that of carbon atom C, it is said that **A** exerts an ***attractor inductive effect*** on carbon C. This is denoted as (**-I**).





Attractor substituents (-I)

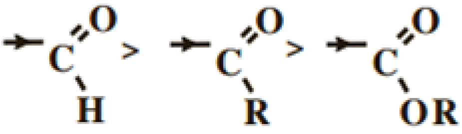


$\rightarrow \overset{\oplus}{N}R_3 > \rightarrow \overset{\oplus}{P}R_3 > \rightarrow \overset{\oplus}{O}R_2 > \rightarrow \overset{\oplus}{S}R_2$

$\rightarrow \overset{\oplus}{O}R_2 > \rightarrow OH > \rightarrow OR$

$\rightarrow F > \rightarrow OR > \rightarrow NR_2$

$\rightarrow F > \rightarrow Cl > \rightarrow Br > \rightarrow I$



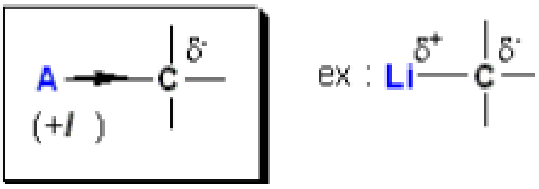
$\rightarrow OR > \rightarrow SR$

$\rightarrow C\equiv C-R > \rightarrow RC=CR_2$

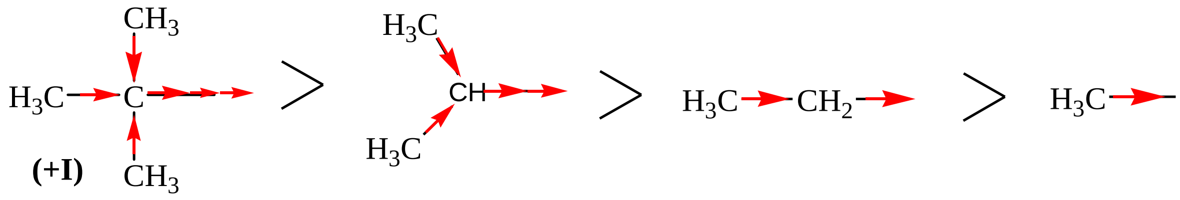
$\rightarrow NO_2 > \rightarrow CN$

1. Inductive electron donor effect (+I)

If the electronegativity of carbon (C) is greater than that of **A**, atom **A** is said to exert an **inductive donor effect** on C. This is denoted as (**+I**).



This effect (**+I**) is exerted by atoms that are less electronegative than carbon, such as metals (Li, Mg, Na, K, etc.) and alkyl radicals (-R):

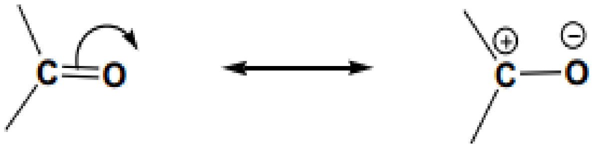


II. Mesomeric effect (Resonance effects)

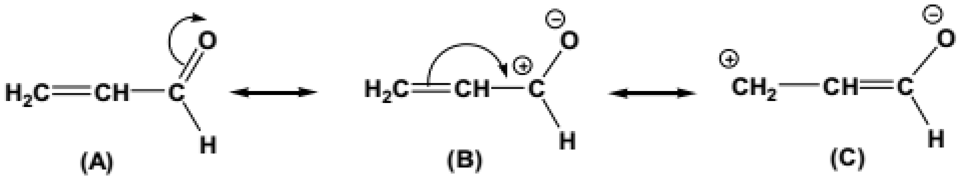
The ***resonance effects*** are due to the delocalization of **π** (pi) and **n electrons**, which is favored by the relative **electronegativity** of the bonded atoms. There are two types of ***resonance effects***: ***Electron donor effects*** (**+M**) and ***electro-attractor effects*** (**-M**).

1. Attractor mesomeric effect (-M)

a. Carbonyl Group (delocalization of π electrons)



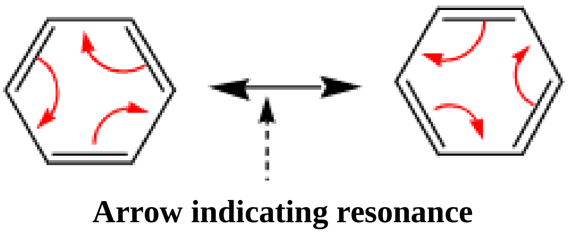
Example:



(A), (B), and (C) are resonance structures (or limiting forms).

Case of Benzene :

Benzene can be represented by two formulas. It is said that there is resonance or mesomerism between these two formulas. Each formula is referred to as a ***limiting form*** or ***mesomeric form***.



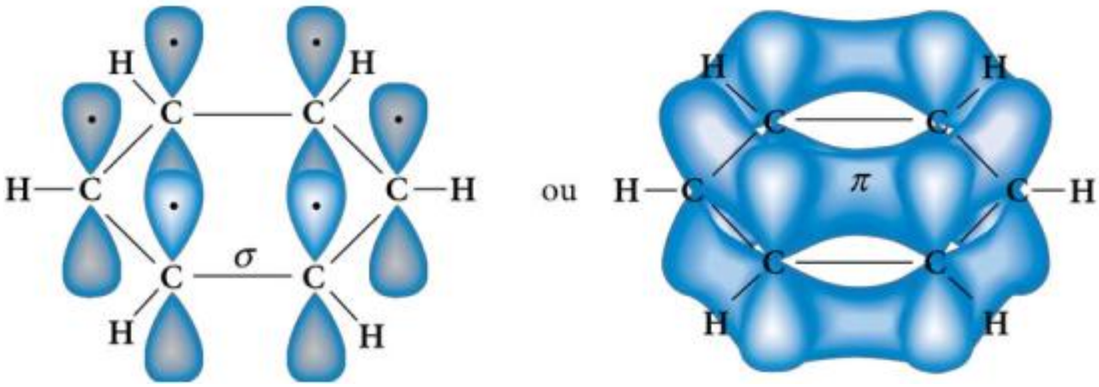
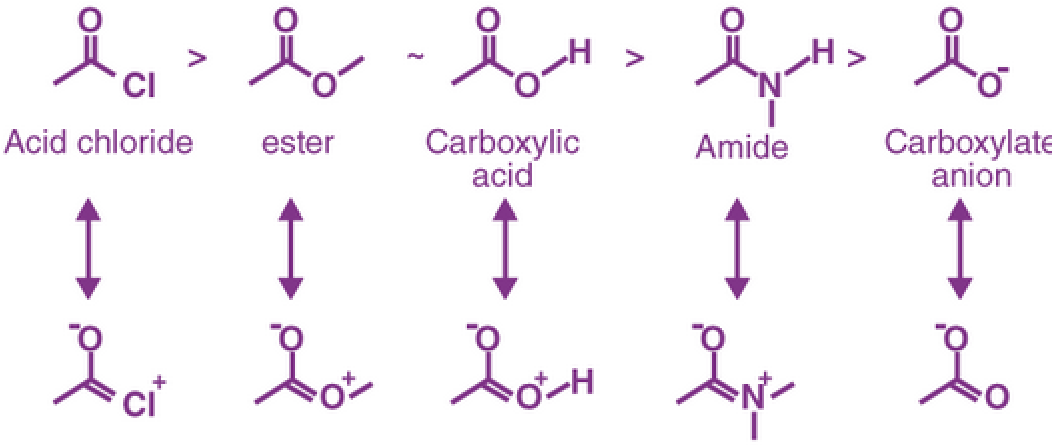
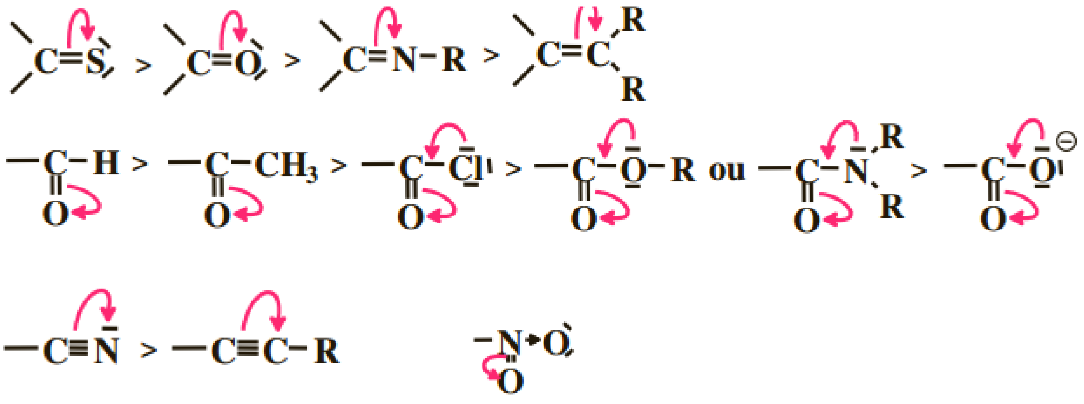


Figure.1 Representation of the Delocalization of π Electrons in the Structure of Benzene.

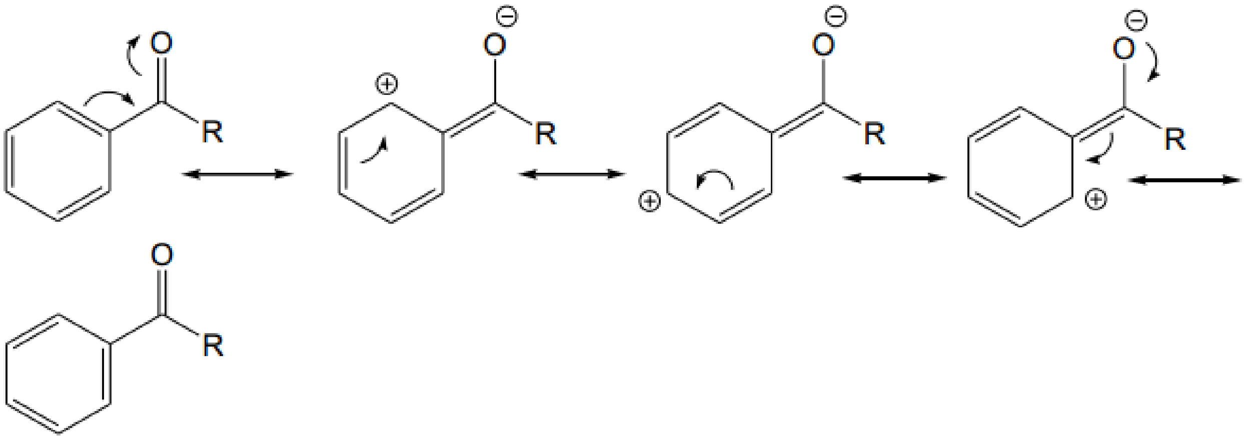
Case of Functional groups:



Attractor substituents (-M)



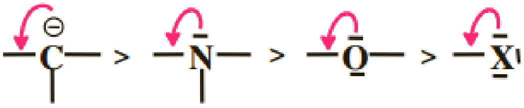
Example:

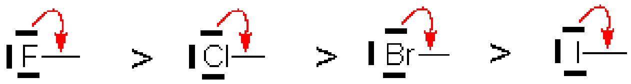


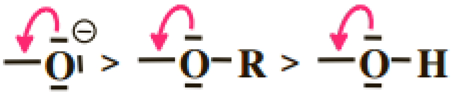
2. Donor mesomeric Effect (+M)

The donor groups by the **+M** effect include **Sp³** hybridized heteroatoms, halogens (Cl, Br, I, F), and negatively charged atoms.

Donor substituents (+M)

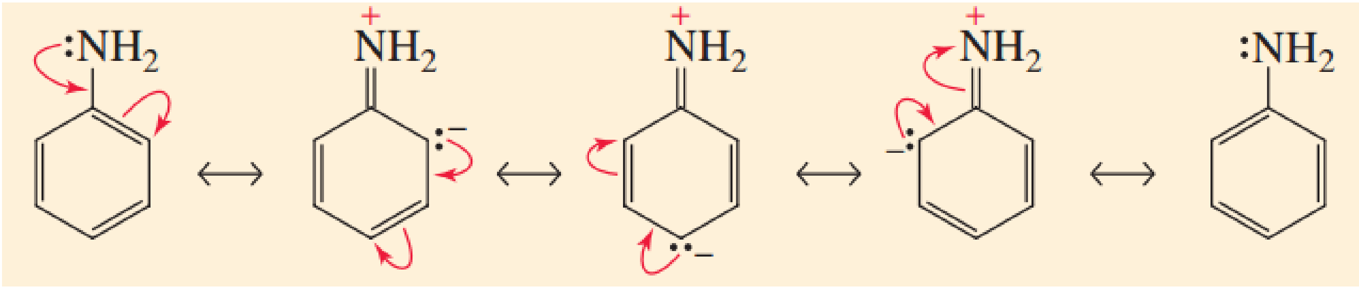






Delocalization of non-bonding electrons (denoted as n)

Example:



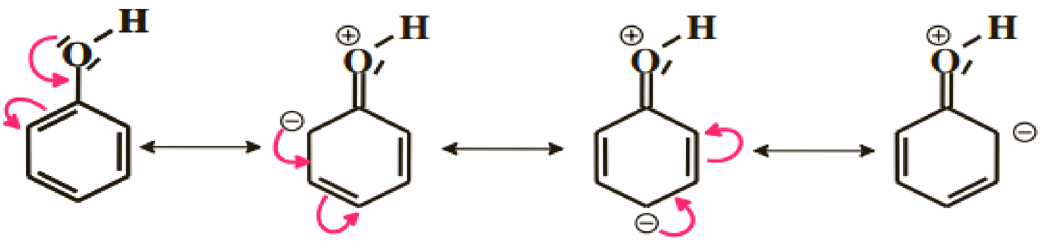
III. Consequences of Electronic Effects:

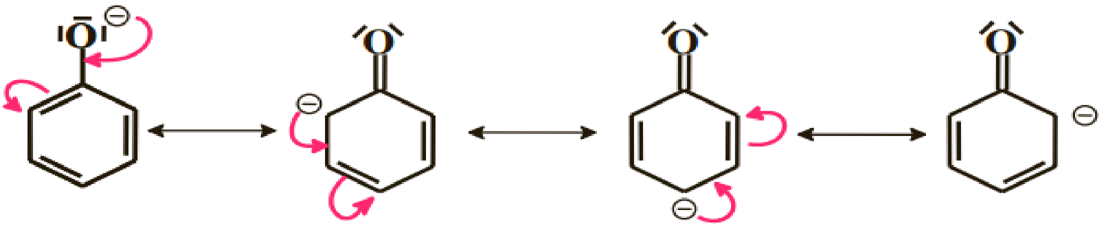
1. On the Stability of Aromatics

Delocalization of π or free n electrons.

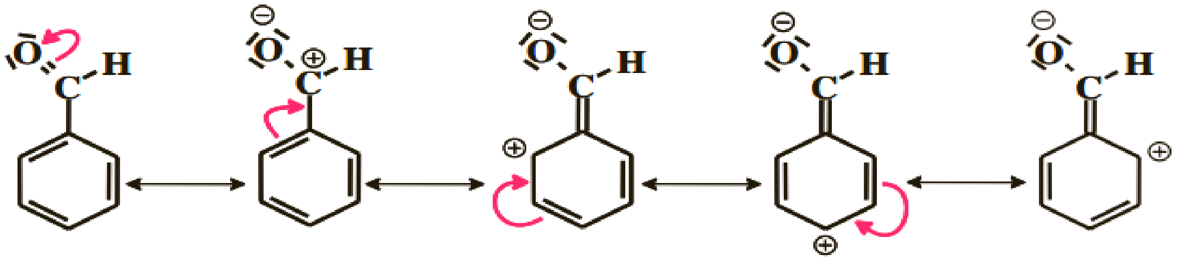
Example:

- *Phénol*





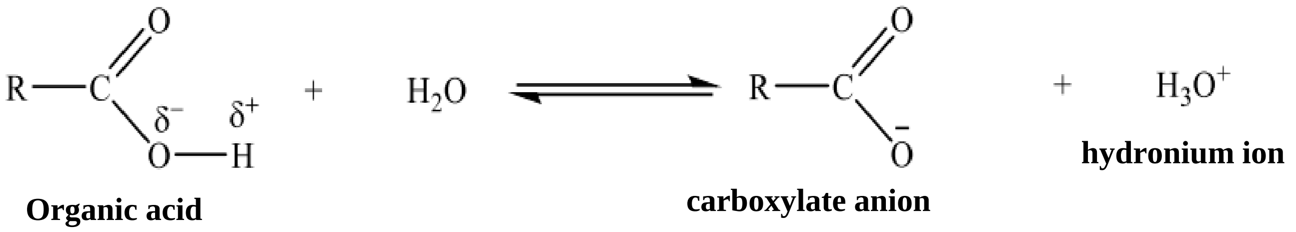
- *Benzaldéhyde*



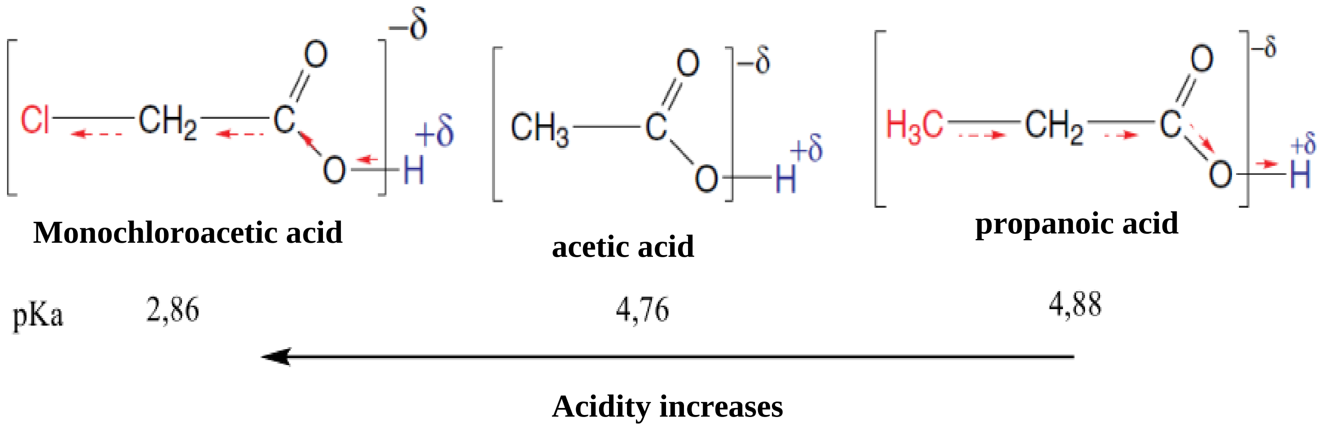
2. On the Acidity or Basicity of Organic Molecules:

Acidity of Carboxylic Acides

The ***pKa*** value defines the strength of an acid; the lower the pKa, the stronger the acid. This corresponds to a higher polarization of the OH bond.



$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} \qquad pKa = -\log K_a$$



When comparing the ***pKa*** values of the three acids, it is observed that chlorine, an element with a ***-I*** effect, increases acidity by enhancing the polarization of the O-H bond in the acidic function. In contrast, the methyl group, which has a ***+I*** effect, decreases acidity.

Basicity of amines

The increase in the basicity of amines is related to the presence of electron-donor alkyl groups (***+I***).

Ammonia (**NH_3**) has a ***pKa*** of **9.27**, while methylamine (CH_3-NH_2) has a ***pKa*** of **10.62**, indicating that methylamine is more basic than ammonia. The methyl group, being an electron-donor group (***+I***), enhances the basicity of amines.

Example: