# Chapter 2
# Electronic effects

## Introduction :

There are 2 types of electronic effects, inductive effects which are linked to the polarization of a σ bond, and mesomeric effects, which are due to the delocalization of π electrons. The two effects can exist together in the same molecule. In the case of a coexistence of 2 inductive and mesomeric effects, it is always the mesomeric effect which prevails.

## 2.1. Inductive effects:

### 2.1.1. Definition:

The polarization of the bond induces a displacement of electrons along the σ bond: this is the inductive effect. In other words, the inductive effect is the transmission of the polarity of a σ bond by groups of atoms.

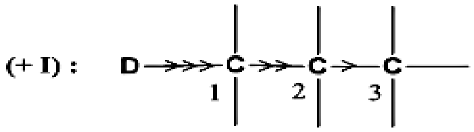
There are two types of inductive effects:

- Donor inductive effect (+I)
- Attractor inductive effect (-I)

### 2.1.2. Types of inductive effects:

#### 2.1.2.1. Inductive Donor Effect (+I):

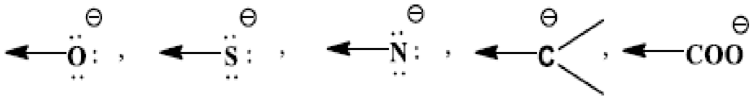
Donor inductive effects (noted +I), i.e. donor atoms or groups (less electronegative than carbon) which exert an effect (+I).



**Metals:** **←Na, ←Mg, ←Hg, ←Zn,….**

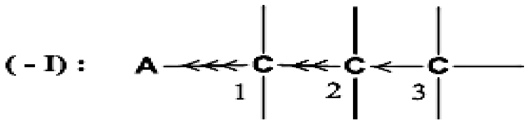
**Alkyl groups:** **$\leftarrow CH_3 < \leftarrow C_2H_5 < \leftarrow CH(CH_3)_2 < \leftarrow C(CH_3)_3$**

**Negatively charged ions:**

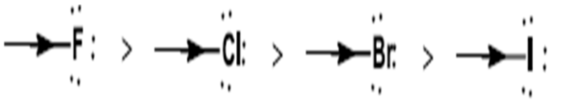


#### 2.1.2.2. The Inductive Attractor Effect (-I):

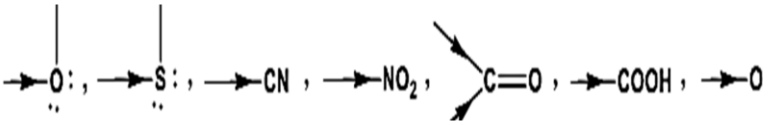
Attractive inductive effects (noted -I), i.e. attractive atoms or groups (more electronegative than carbon) which exert an effect (-I).



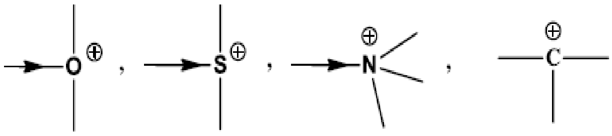
**Halogens:**



## Neutral groups:

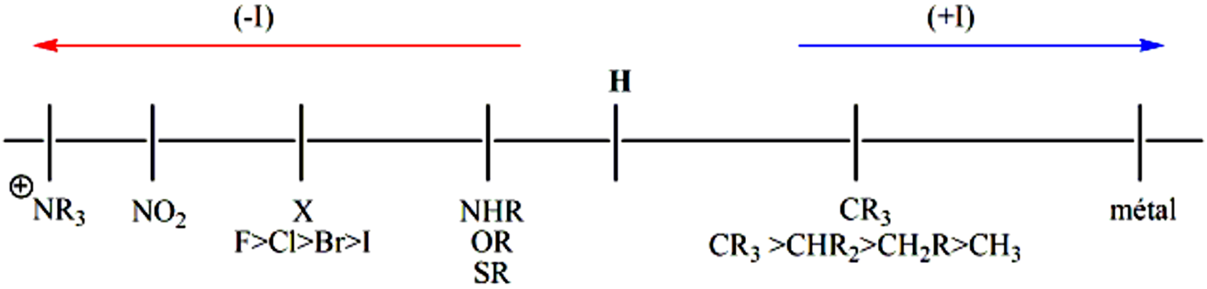


## Positively charged ion.



**Note:** the attractor effect of A or donor effect of D decreases rapidly with distance (practically zero beyond 3 to 4 bonds).

## Ranking of inductive effects :

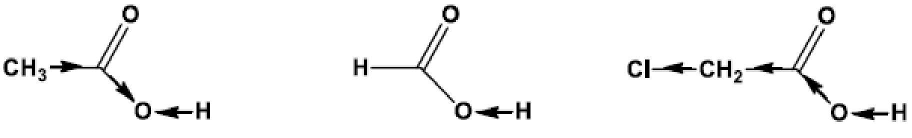


## 2.1.3. Influence of the inductive effect on the acidity of carboxylic acids:

The presence of a donor group (Effect +I) will tend to decrease the acidity of the compound by increasing the electron density on the oxygen of the O-H group. The polarization of the O-H bond will decrease, the breaking of this bond will be less favored, and the acidity will decrease.

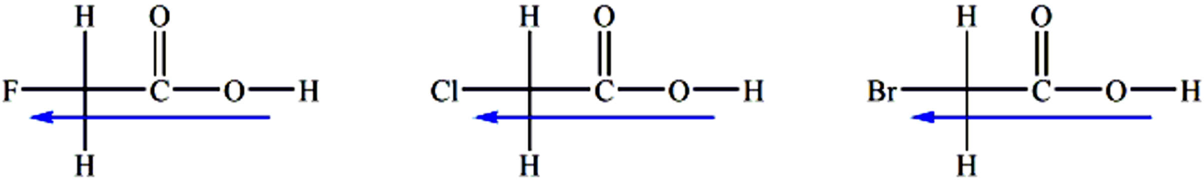
Conversely, the presence of an attracting group (Effect -I) will increase the acidity because the electron-hungry oxygen (very electronegative) will attract the doublet of the O-H bond all the more strongly. The polarization of the O-H bond will increase, this bond will therefore be all the easier to break, and the compound will therefore be more acidic.

**Example:**



PKa = 4,7 PKa = 3,8 PKa = 2,8

## 2.1.3.1. Electronegativity of the element:

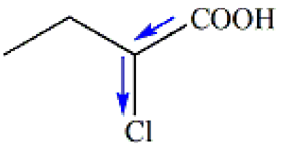


**pKa = 2,6** **pKa = 2,8** **pKa = 2,9**

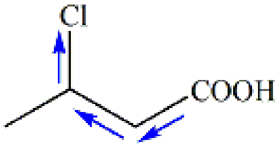
Electronegativity: F > Cl > Br > I, which further increases the acidity of the molecule from F to Br.

### 2.1.3.2. Distance:

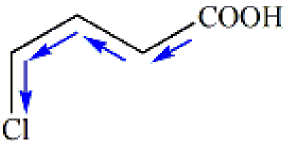
The inductive effect decreases with distance.



**pKa = 2,86**



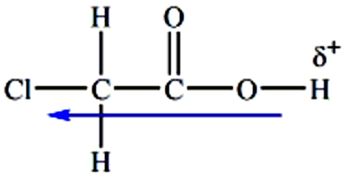
**pKa = 4,05**



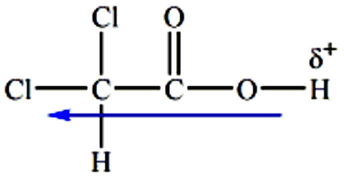
**pKa = 4,52**

### 2.1.3.3. Number of groups:

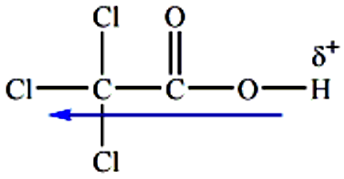
The acidic character of a given molecule increases considerably with the number of groups exhibiting an attractive inductive effect.



**pKa = 2,82**



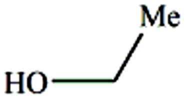
**pKa = 1,30**



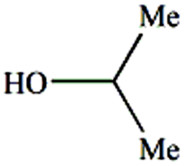
**pKa = 0,70**

For the inductive effect donor groups, the acidic character decreases.

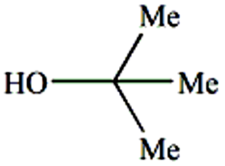
**pKa = 15,5**



**16,0**



**17,1**



**19,2**

An increase in the acidity of the chemical species implies a decrease in the pKa value.

### 2.1.4. Influence of the inductive effect on basicity:

The donor inductive effects (+I) increase the basicity while the attractor inductive effects (-I) decrease the basicity.

In the case of amines, alkyl groups with electron-donating effects (+I) strengthen the partial negative charge on the nitrogen more than hydrogens do and make the amine more basic (enhancement of the non-bonding electron pair on the nitrogen).

For groups with an inductive attractor effect (-I), the basicity of the corresponding amine decreases by weakening the negative partial charge of the nitrogen.

**Increase in basicity**

## 2.2. Conjugation-Resonance-Mesomerism:

### 2.2.1. Conjugation:

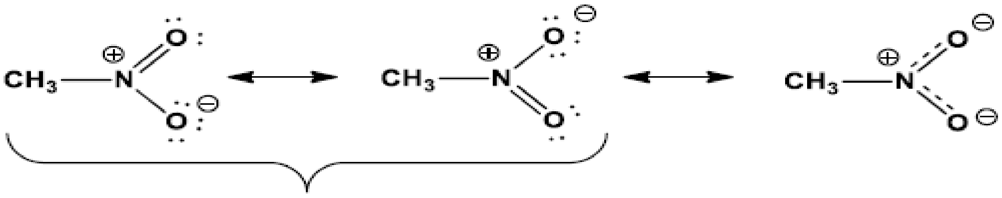
It is the alternation between double bonds and single bonds.

### 2.2.2. Mesomerism and Resonance:

#### 2.2.2.1. Definition:

The different mesomeric effects due to the delocalization of p and n electrons, favored by the relative electronegativity of the bonded atoms. The higher the number of mesomeric formulas for a molecule, the greater the stability.

**Mesomerism** describes the delocalization of π electrons, free electron pairs n and charges in conjugated molecules.

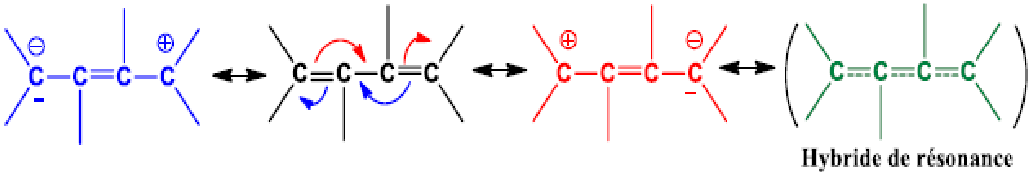


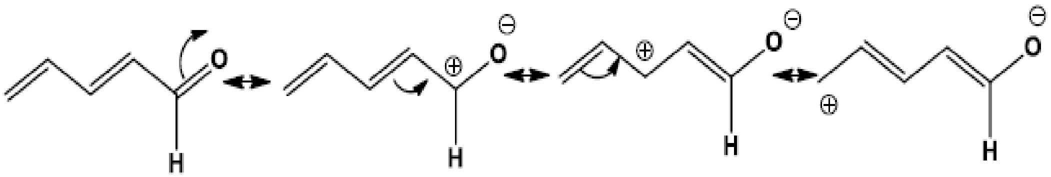
The two Lewis representations are equivalent and are called resonance structures or mesomeric forms.

Resonance hybrid
Real form

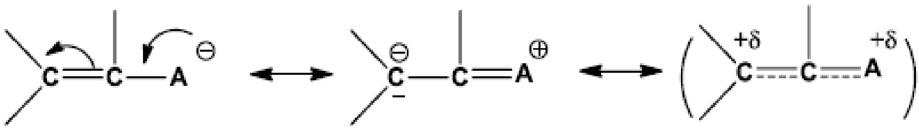
#### 2.2.2.2. Mesomerism of unsaturated systems:

**Conjugation of π electrons:**

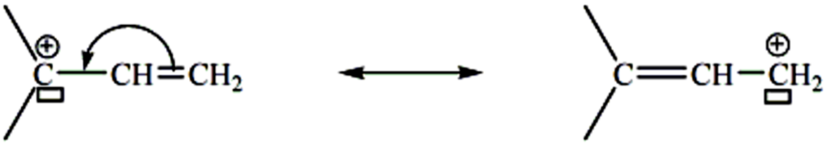




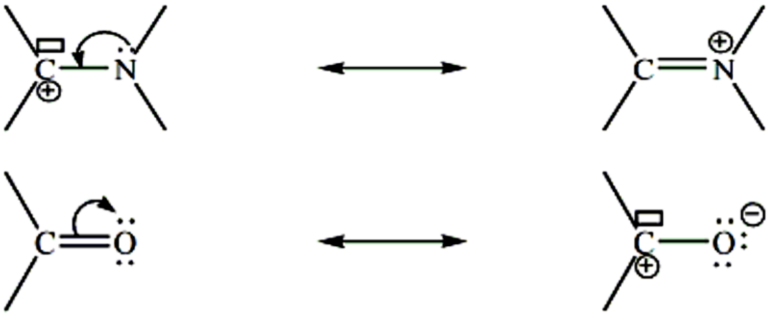
**n electrons and π electrons:**



**π electrons and vacant orbital:**



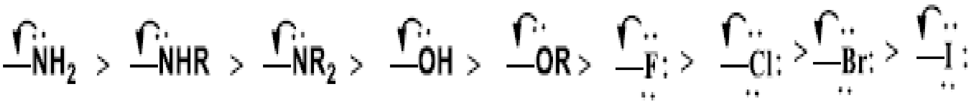
**n electrons and vacant orbital:**



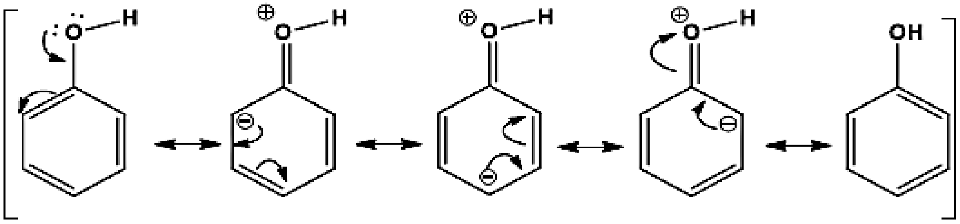
### 2.2.2.3. Types of mesomeric effect:

We will define two types of mesomeric effect.

**A. The donor mesomeric effect:** noted: (+M) for electron donor groups:

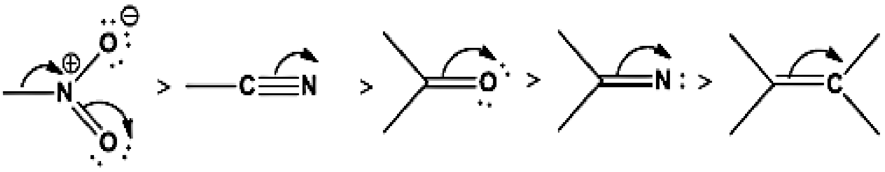


**Example:** phenol

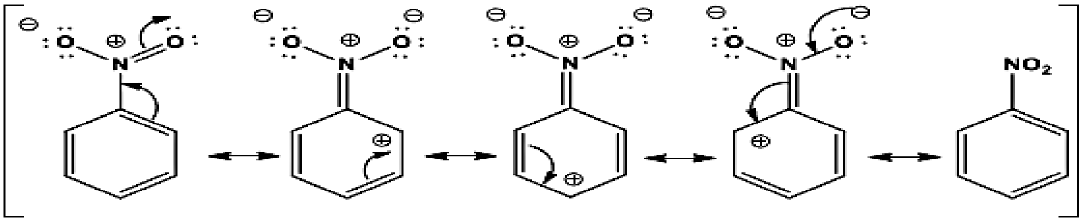


The above limiting forms explain the electrophilic substitutions produced at ortho and para positions.

**B. The attractive mesomeric effect:** noted: (-M) for electron-attracting groups:

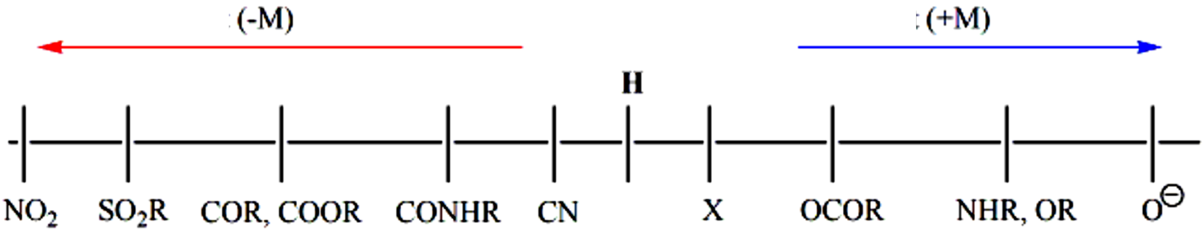


**Example:** Nitrobenzene



Meta sites are more nucleophilic, more apt to receive electrophilic substitutions

**Ranking of mesomeric effects :**



### 2.2.2.4. Mesomeric effect and acidity:

Some groups can have a significant influence on the pKa of organic compounds. In the case of phenol, it can be observed that:

The more the O-H bond is rich in electrons, the more difficult it will be to break it, therefore the higher the pKa will be.

On the other hand, the poorer this bond is in electrons, the easier it will be to break it, therefore the pka will be low.

Thus, if we place an electron-withdrawing group on the phenyl, the O-H bond will become poorer in electrons, therefore easier to break and the pKa value will decrease (stronger acidity).

Whereas an electron-donating group on the phenyl will increase the pKa value (therefore reduce the acidity of the phenol).

**Example:**

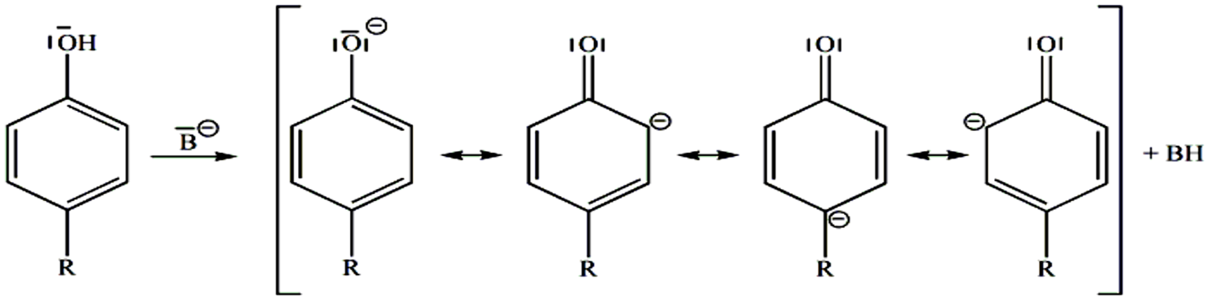
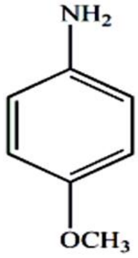


Tableau 2.1: Relationship between pKa and mesomeric and inductive effect groups.

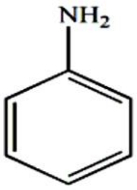
| **R** | **$NH_2$** | **OMe** | **$CH_3$** | **H** | **$COCH_3$** | **CN** | **$NO_2$** | **$^+NH(CH_3)_3$** |
|---|---|---|---|---|---|---|---|---|
| pka | 11,2 | 10,86 | 10,25 | 9,89 | 8,79 | 8,56 | 8,24 | 8,08 |
| Effect | +M | +M | +I | | -M | -M | -M | -I |

### 2.2.2.5. Mesomeric effect and basicity:

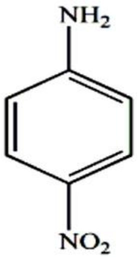
Amines are Lewis bases, their basicity is due to the non-bonding (free) electron pair of the nitrogen atom. An electron-donating group (by +M effect) increases this basicity, while an electron-withdrawing group (-M effect) decreases it.



**pKa = 5,36**



**pKa = 4,61**



**pKa = 1,01**

**Note:** A base will be weaker to the extent that its electron pair is engaged in delocalization. a base will be all the weaker as its pair is engaged in delocalization

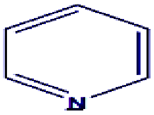
### 2.3. Aromaticity:

Hückel's rule: a molecule is aromatic if it is:

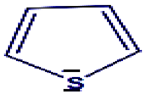
- cyclic.
- planar
- fully conjugated.
- it has (4n+2) delocalizable $\pi$ electrons (n integer 0, 1, 2, 3…).

Planar cyclic molecules have (4n+2) $\pi$ electrons. These molecules have great stability due to the delocalization of $\pi$ electrons. These molecules are therefore not very reactive. Aromaticity is a concept applicable to other cyclic molecules that do not necessarily have a benzene ring:

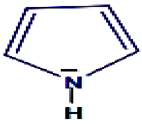
**Example:**



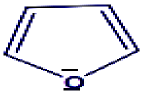
**Pyridine n= 1**



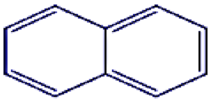
**Thiophene n= 1**



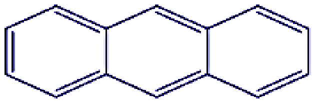
**Pyrrole n= 1**



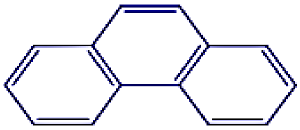
**Furan n= 1**



**Naphtalene n= 2**



**Anthracene n= 3**



**Phenanthrene n= 3**