Chapter 4 :

Electronic effects

(Inductive and Mesomeric effects)

Chapter 4: Electronic effects
(inductive and mesomeric effects)

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The different types of chemical bond :

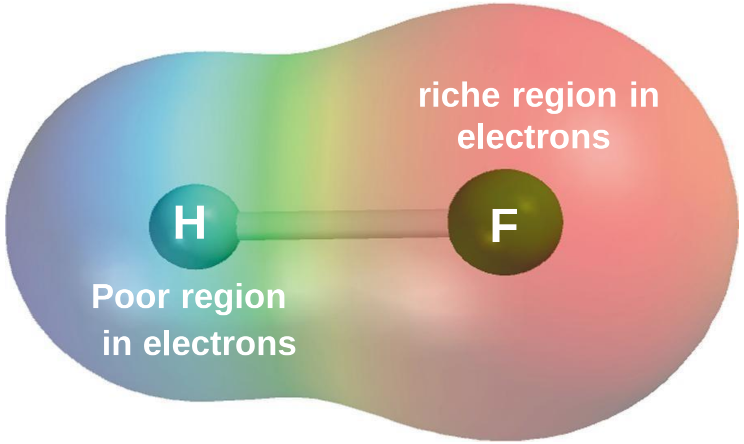
We can have 3 types of chemical bond identifiable according to the difference in electronegativity between the atoms.

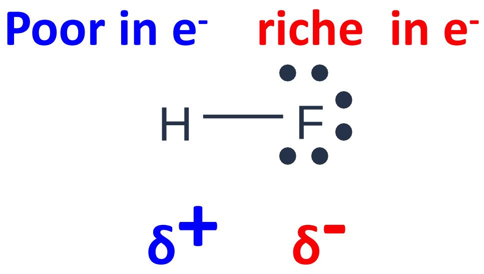
Covalent bond :

A covalent bond is a chemical bond in which two or more electrons are shared by two atoms. The covalent bond normally occurs between a non-metal and a non-metal and the electron is only shared between the elements (there is no transfer from one element to another) [2].

Polarized covalent bond :

A polar covalent bond is a covalent bond between 2 atoms of different electronegativities (a higher density of electrons around one of the two atoms) [2].

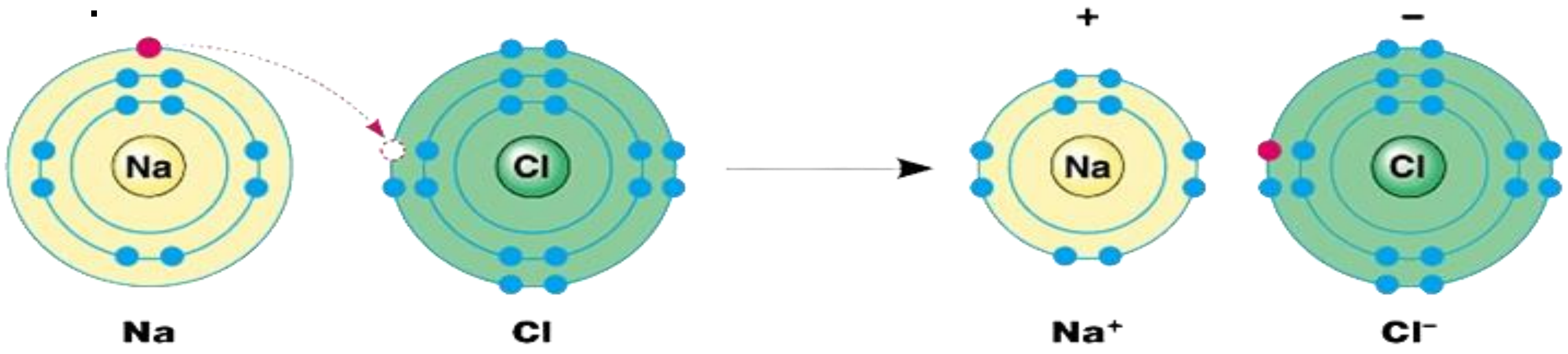




The electrons in the bond belong more to the more electronegative atom and therefore partial charges (δ) are present.

Ionic bond :

Ionic bonding is the electrostatic force that holds ions together in an ionic compound [2].



Le Cl being more electronegative than Na, attracts Na's valence electron in order to make the peripheral octet. The Na atom loses an electron and thus becomes the Na^{+} ion in order to also achieve the peripheral octet. The Cl atom gains an electron and becomes the Cl^{-} ion.

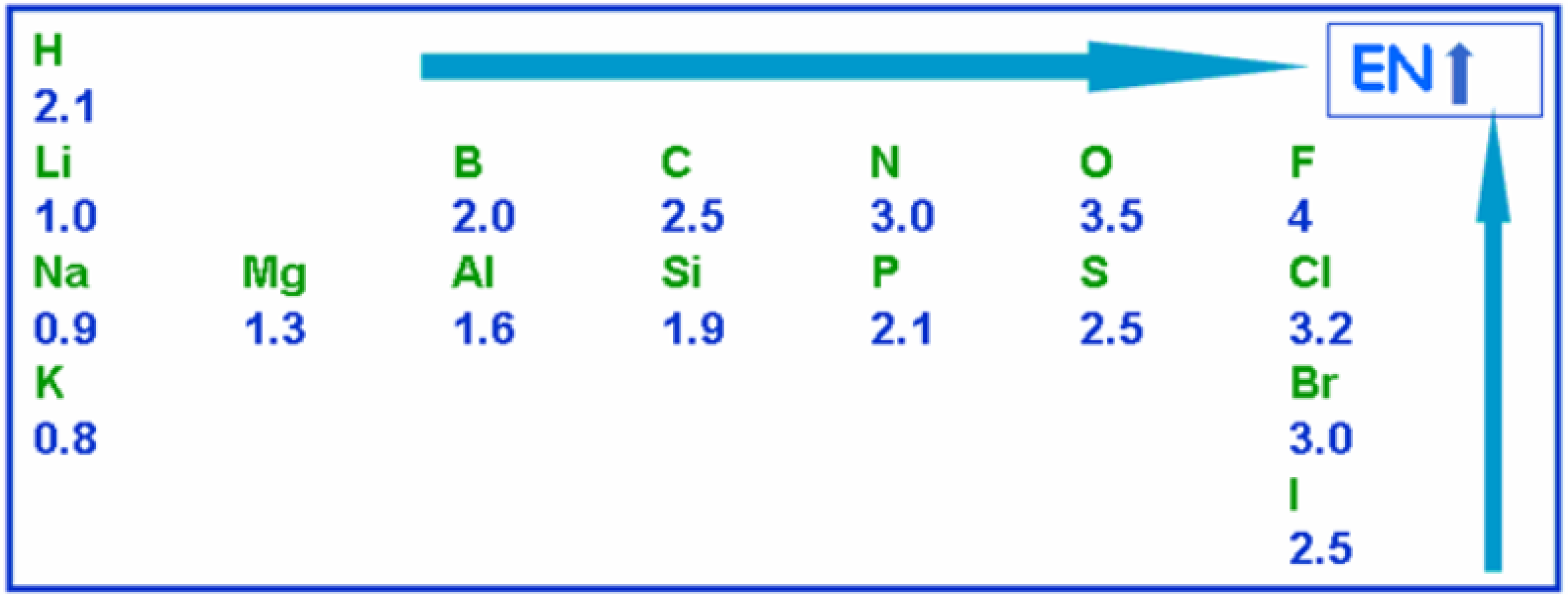
The formed Na^{+} and Cl^{-} ions thus formed, being of opposite signs, attract each other by electrostatic attraction and form an ionic bond [1].

Ionic bond

Polarized covalent bond

Pure covalent bond

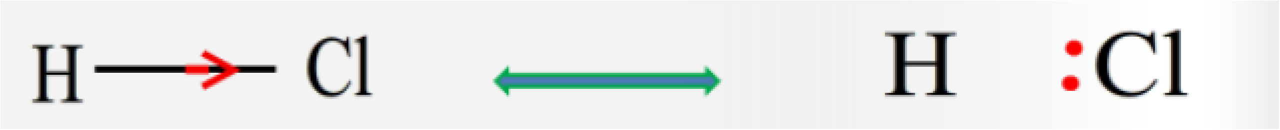
According to Pauling, the electronegativity measures the ability of an atom in a molecule to attract the electron cloud towards itself.



Electronegativity increases from left to right over the same period, and from down to up over the same column.

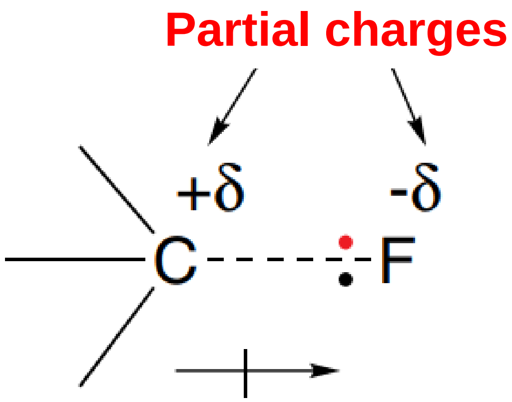
If the two atoms are different (X-Y), it is the more **electronegative** atom that attracts the electron doublet. The electron cloud is no longer symmetrical: it moves towards the more electronegative atom , for example the chlorine and the hydrogen atoms :

$$\chi(Cl) > \chi(H)$$



The most electronegative atom polarize the electron cloud. The bond is then polarized, creating **partial charges** on the atoms: δ+ on the least electronegative atom and δ- on the most electronegative atom.

Example 2 :



Bond electrons much close to the fluorine then the carbon

Electronegativity scale :

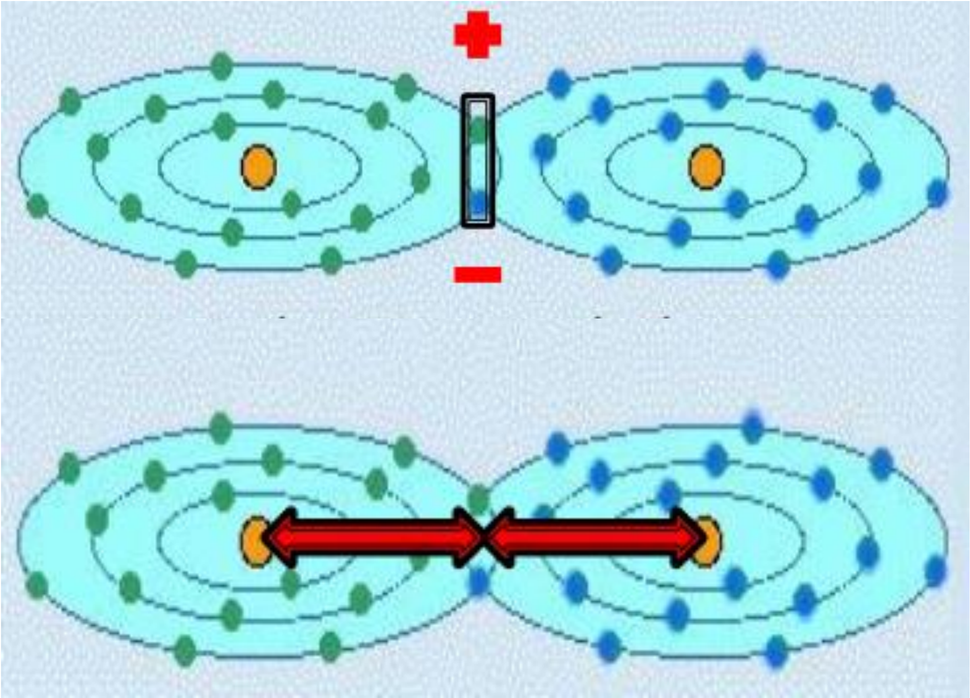
F > O > Cl > N > Br > I > S > C > P = H > B > Si > Al > Mg > Li > Na > K

The electronegativity of carbon varies according to its state of hybridization :

Electronegativity of ‘sp’ carbon > ‘sp2’ carbon > ‘sp3’ carbon.

Polarity and polarization of bonds :

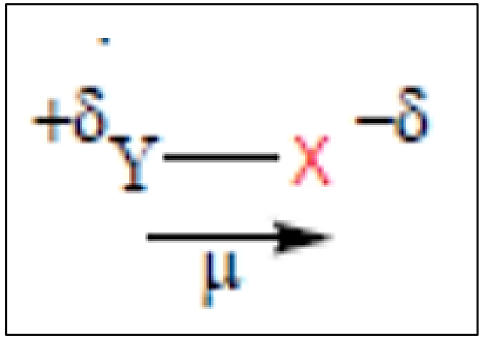
When a covalent bond links two identical atoms (X-X), the electron doublet is shared between the two atoms. The electron cloud is distributed equally between the two atoms. There is therefore no polarity (μ = 0).



Example : Cl_2 molecule

Dipole moment :

The polarization of a bond gives rise to an electric dipole characterized by a dipole moment. The larger the difference in electronegativity between the atoms (or groups of atoms), the larger the dipole moment of the bond.

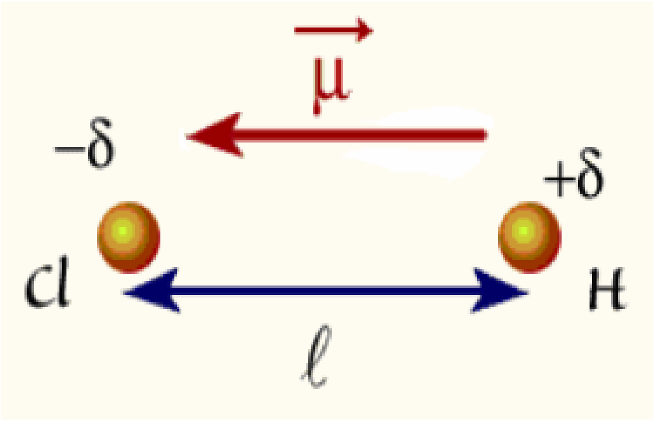


μ: dipole moment, a function of the charge δ and l the distance between the center of the positive charges and that of the negative charges,

$$\mu = \delta . l \text{ (debye)}$$

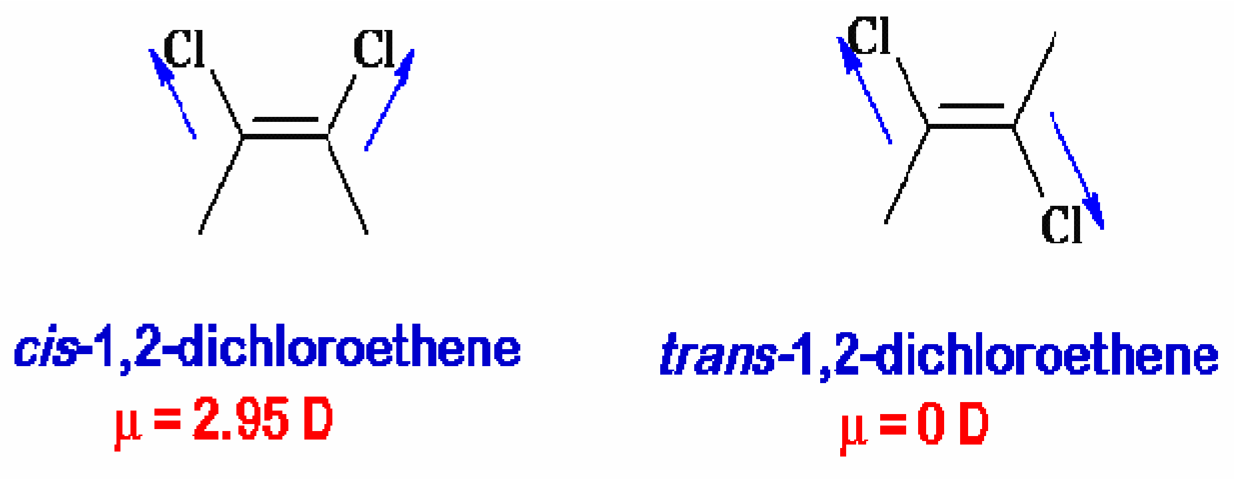
In this formula, μ is in Debye, ℓ is in (Angstrom A), δ is unitless.

Some values can be given:
C-H (0,4 D)
C-F (1,41 D)
C-Cl (1,46 D)
C-N (0,22D),
C-O (0,74D)



(other unite can be used : Coulomb x metre C.m, where 1 Debye = 0,33 × 10^{-29} C.m)

A molecule can have polarized bonds and be apolar (μ=0 debye).



Electronic effects

There are 2 types of electronic effects :

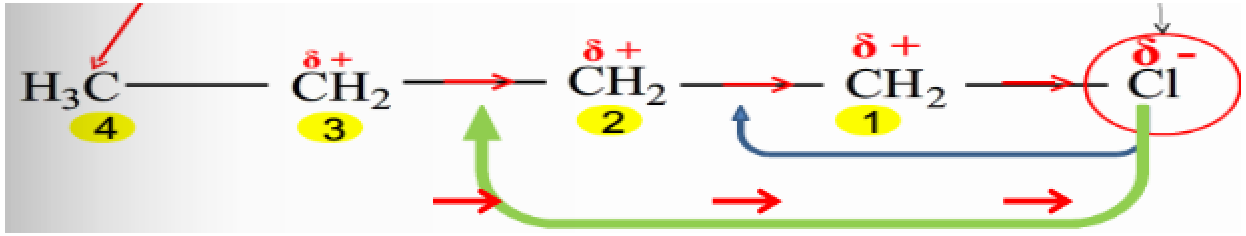
- The **inductive effects,** which are linked to the **polarization** of a **σ bond**.
- The **mesomeric effects**, which are due to the **delocalization** of **π electrons** and **n electrons**.

In the case of the coexistence of 2 inductive and mesomeric effects of opposite signs, it is always the mesomeric effect that will take priority.

2 - Inductive effect :

2-1- Definition :

This effect involves the electronegativity of the atoms. It is the polarization of the electron cloud of a σ bond, caused by a neighboring atom or group of atoms.

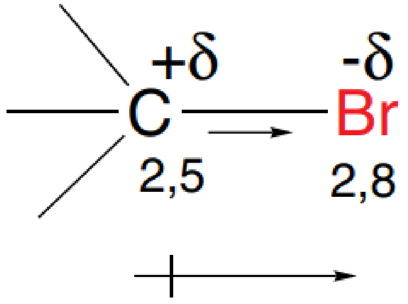


The asymmetry in the distribution of electrons can be transmitted from close to close, but becomes less pronounced as we move away from the disturbing center.

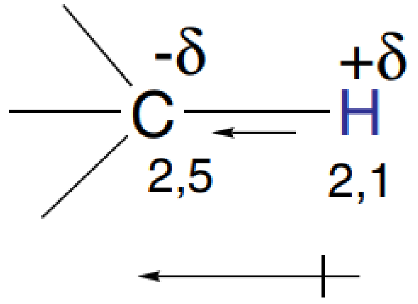
2-2- Classification of inductive effects :

Inductive effects can be classified according to the atoms or groups of atoms that cause this phenomenon of polarization at a distance into two categories:

- Inductive donor effect (+I)
- Inductive attractive effect (-I)



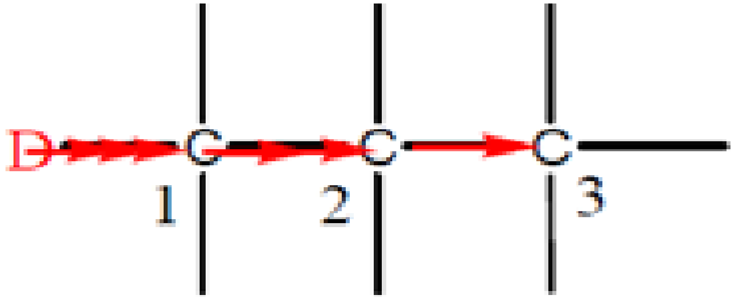
Inductive attractive effect (-I)
from bromine on carbon

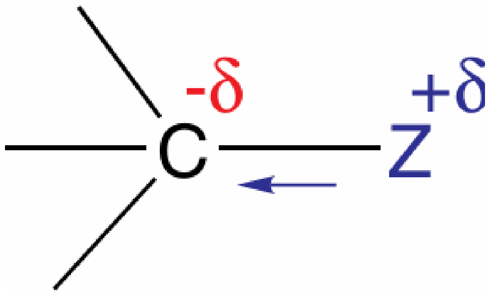


Inductive donor effect (+I)
from hydrogen on carbon

Donor inductive effect (+I) :

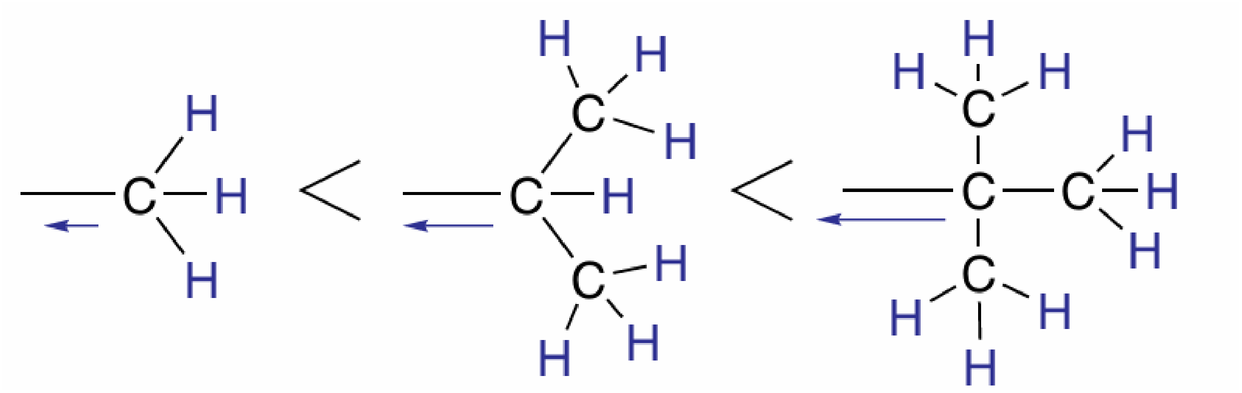
There are fewer groups with an electron-donating inductive effect +I than those with an electron-attractive inductive effect - I.



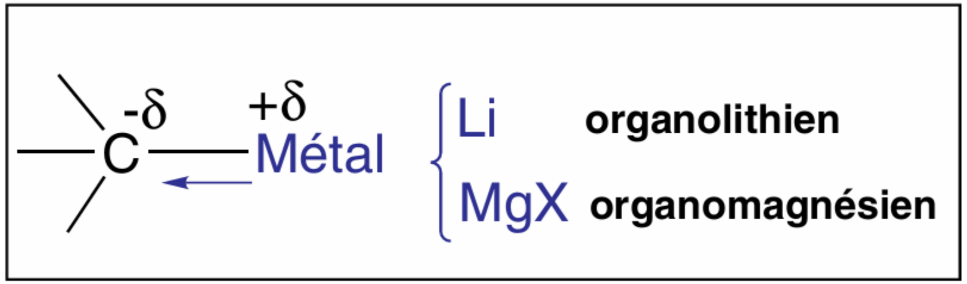


Examples : metals (Na, Mg, …), alkyl groups (CH_3, C_2H_5, $(CH_3)_3C$…)

The more C-H bonds an alkyl group has on a limited number of carbon atoms, the greater its electro-inductive effect. For example, the tertiary butyl group (t-Bu) has the strongest effect compared with isopropyl (i-Pr) and methyl (Me).

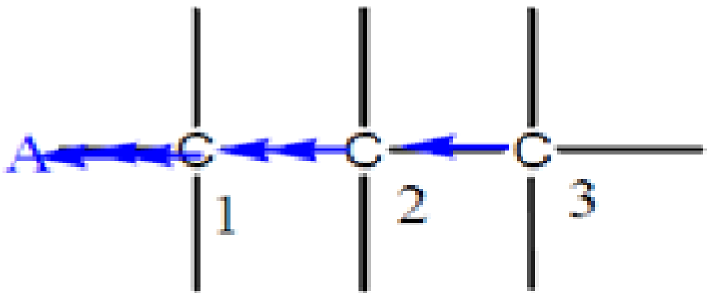


To this can be added the covalent bonds formed between carbon and certain metals such as lithium, magnesium, cobalt and copper.



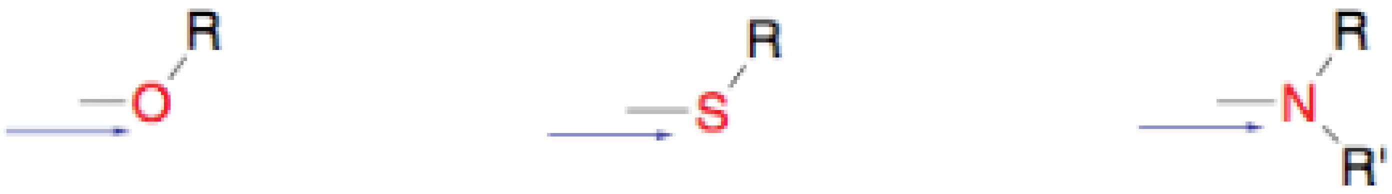
Attractive inductive effect (-I) :

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

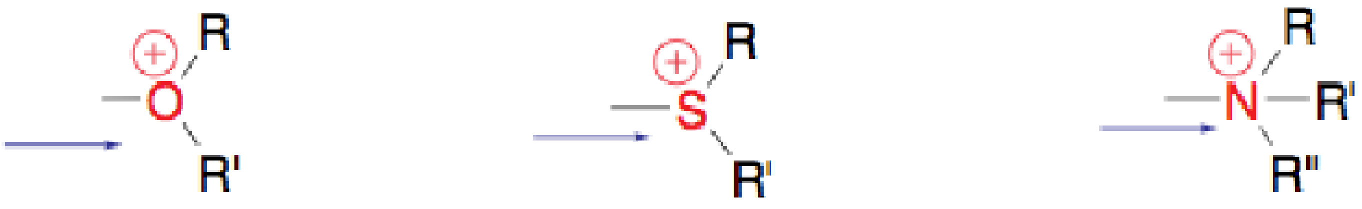


Examples: Halogen as F - , Cl- , Br- , OH- , NH_2 - , CN- , NO_2 -

Neutral groups: a bi or trivalent heteroatom such as oxygen, sulphur or nitrogen.

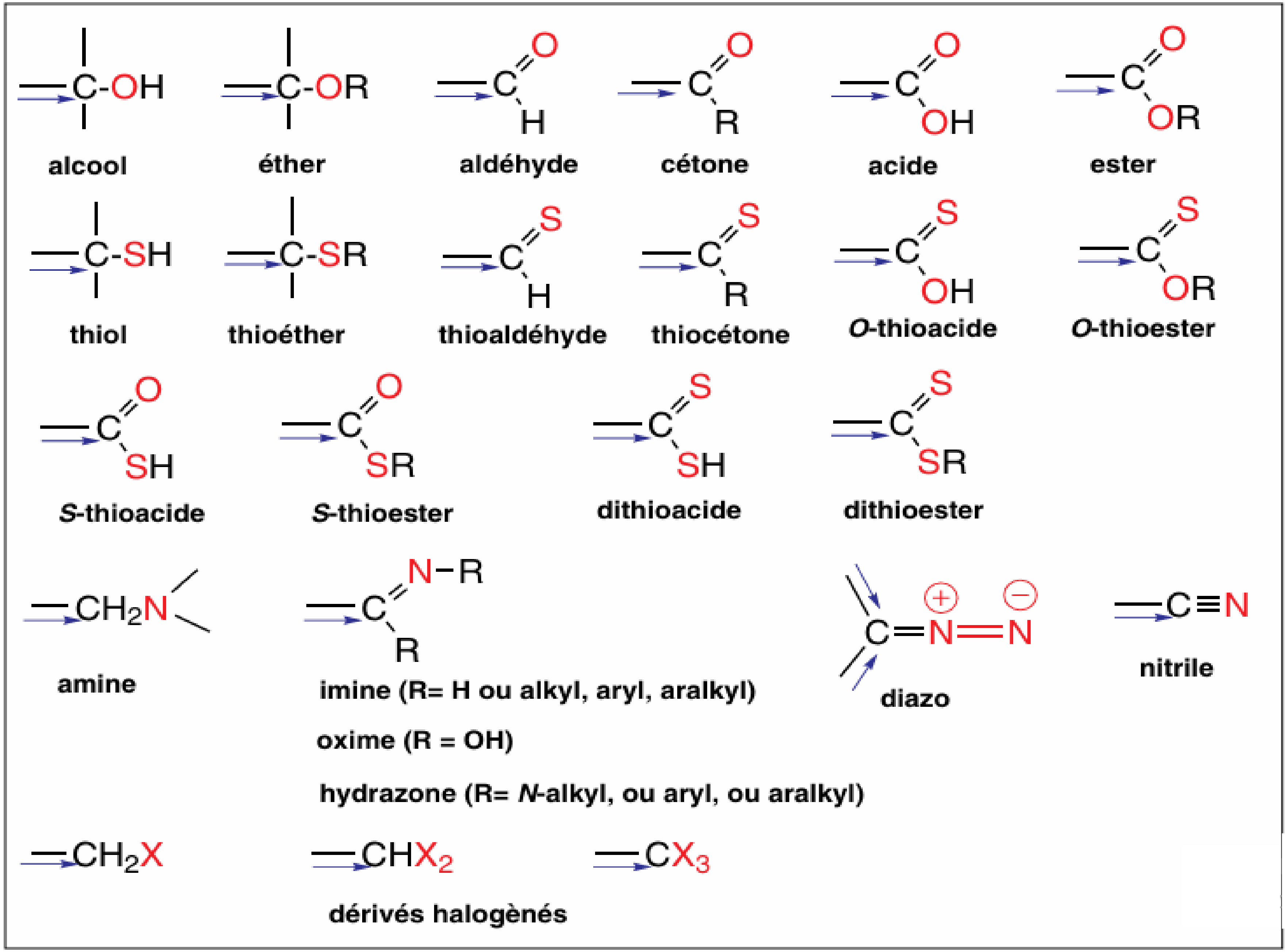


Positively charged groups: a bi or trivalent heteroatom (very strong inductive effect -I). Their effect is particularly powerful.

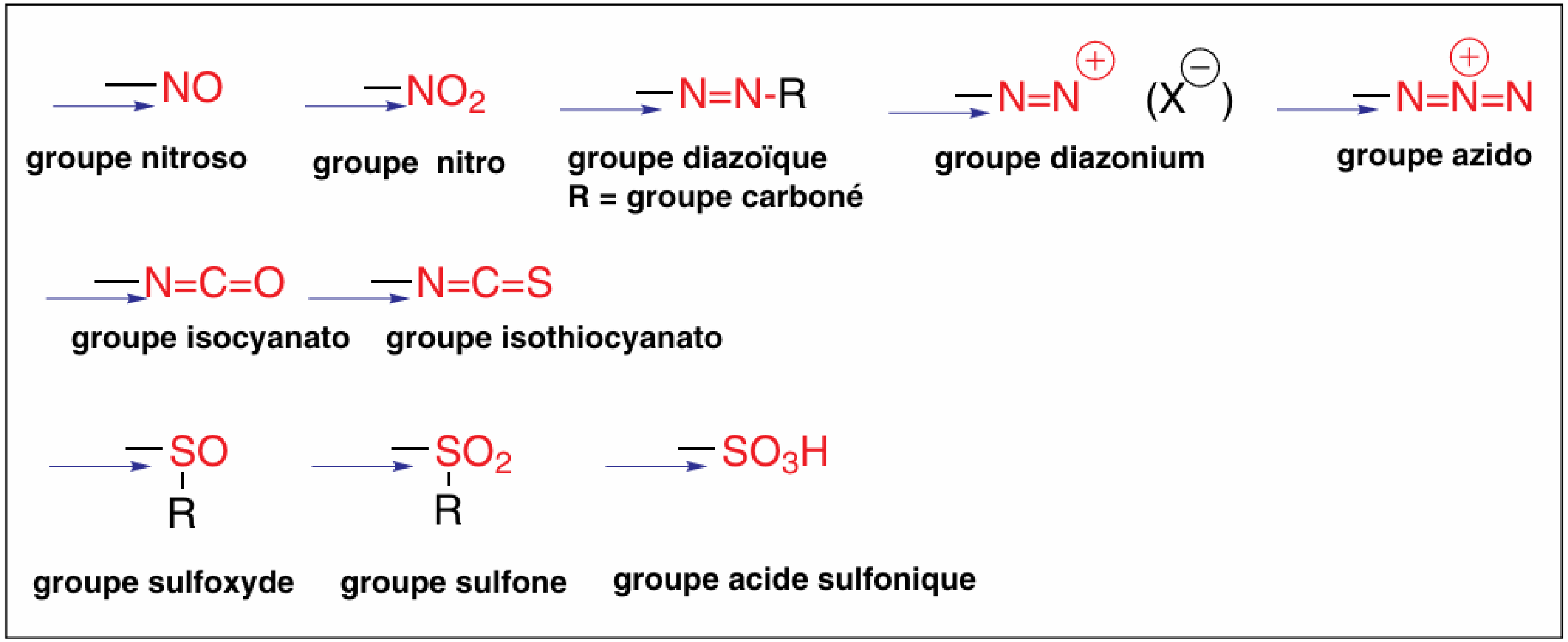


Attractive inductive effect (-I) :

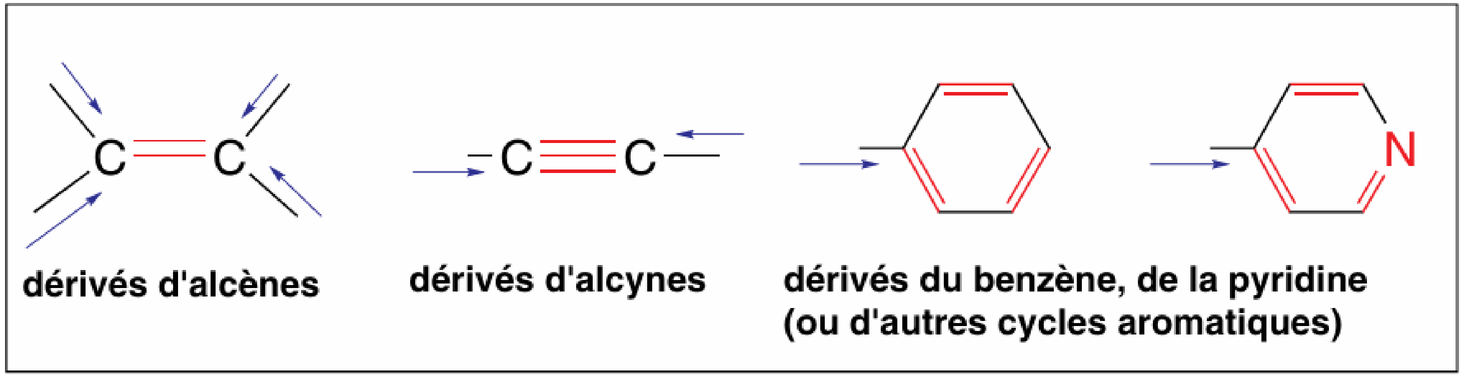
Carbon linked to one or more electronegative heteroatoms.



Groups, charged or not, made up of several electronegative heteroatoms (strong inductive effect).

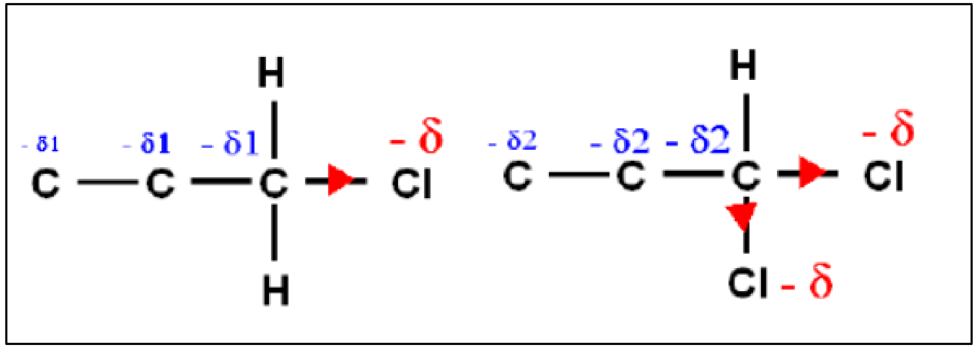


Groups derived from alkenes, alkynes or benzene (and their polycyclic derivatives or any other aromatic ring).



Additivity of the inductive effect :

To a first approximation, inductive effects can be considered additive. The intensity of the inductive effect will be greater the greater the number of atoms that cause it.[4]

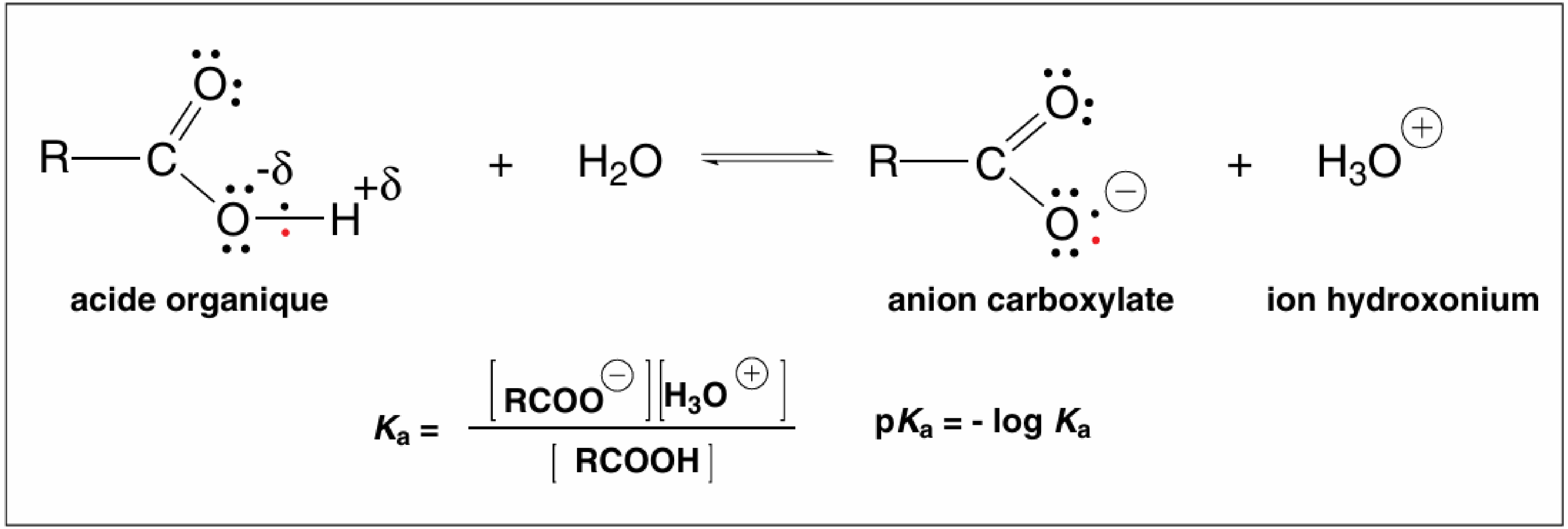


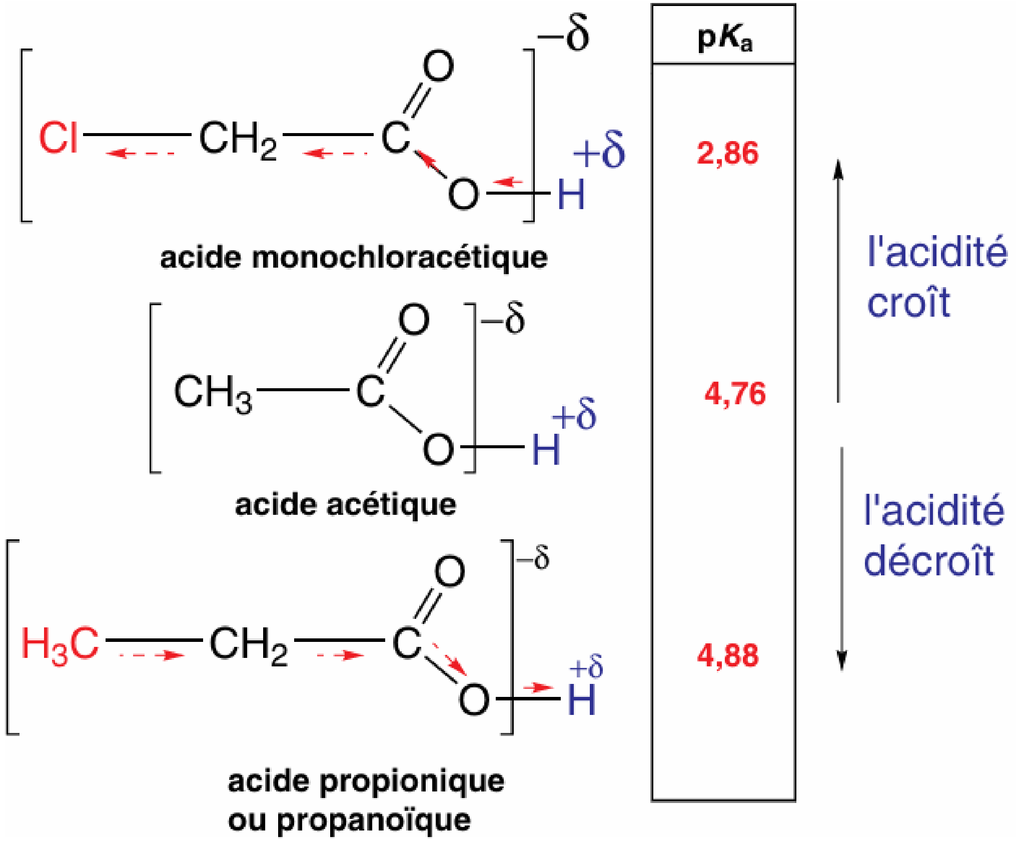
Note :

The inductive effect exerted by an -I or +I group on a chain made up solely of σ bonds, as in linear alkanes, is transmitted by gradually decreasing to generally cancel out at a distance of three carbons. [4]

2-3- Influence of the inductive effect on the acidity of a chemical compound :

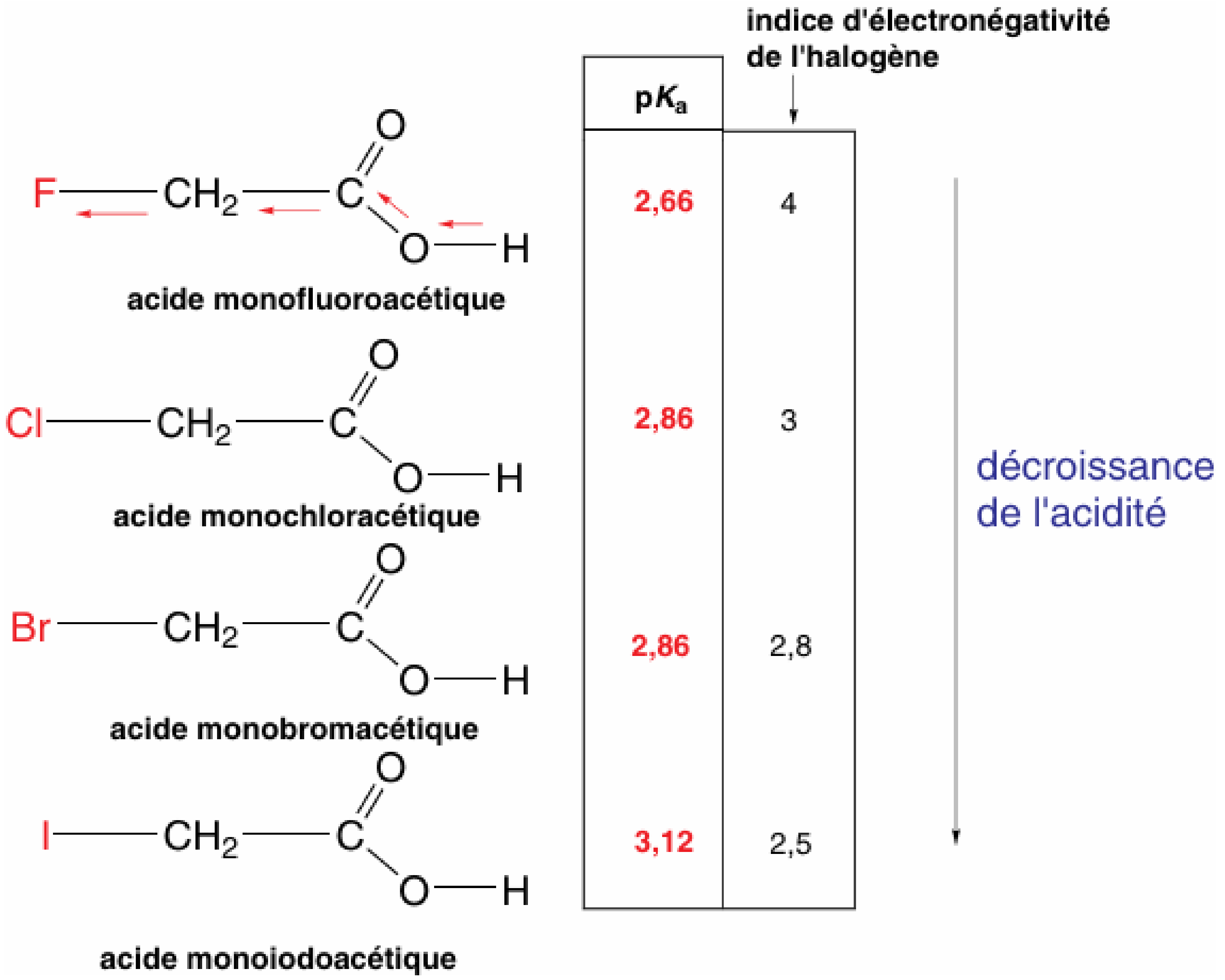
The influence of -I or +I groups can be easily demonstrated by studying the pKa of acids substituted with a group of this nature.




Cl
CH2
C
O
O
H
−δ
+δ
acide monochloracétique
CH3
C
O
O
H
−δ
+δ
acide acétique
H3C
CH2
C
O
O
H
−δ
+δ
acide propionique
ou propanoïque
pKa
2,86
4,76
4,88
l'acidité
croît
l'acidité
décroît

Among the four monohalogen acids derived from acetic acid, and according to their pKa,

the following ranking of inducing effects can be observed - I : F > Cl = Br > I, en rapport avec les indices d'électronégativités de ces atomes

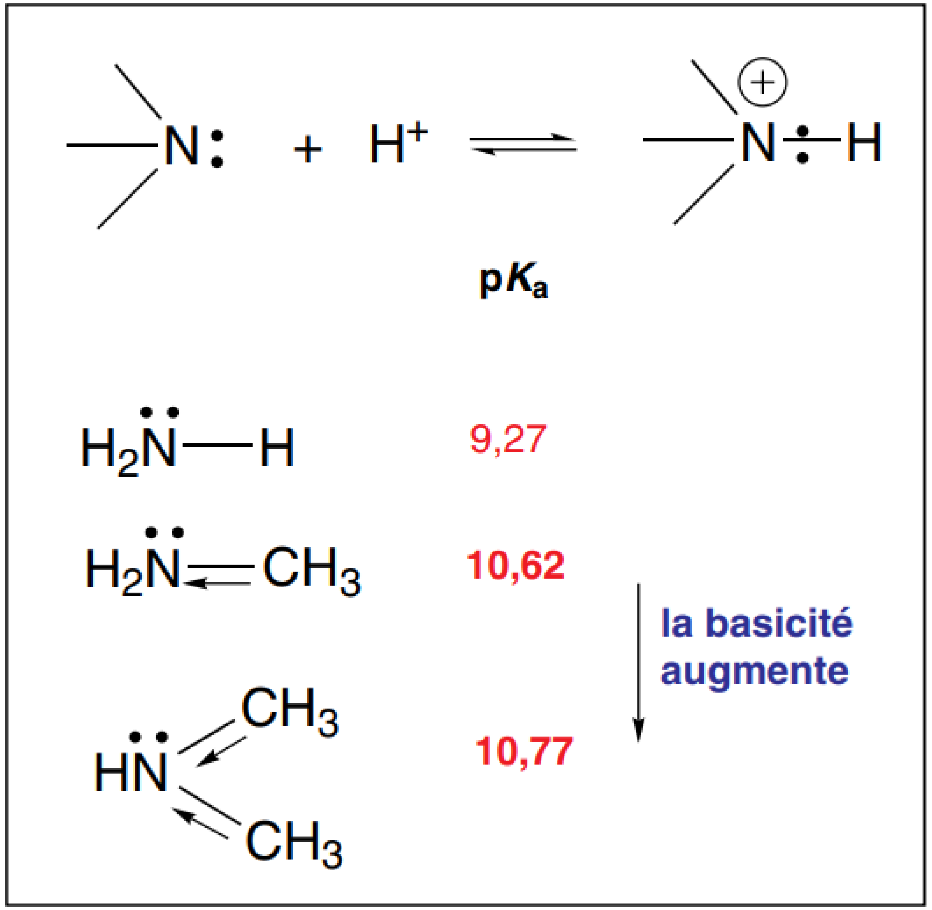


2-4- Influence of the inductive effect on the basicity of a chemical compound :

Conversely, +I electron-donating groups increase the basicity of a basic compound such as an amine.

Example:

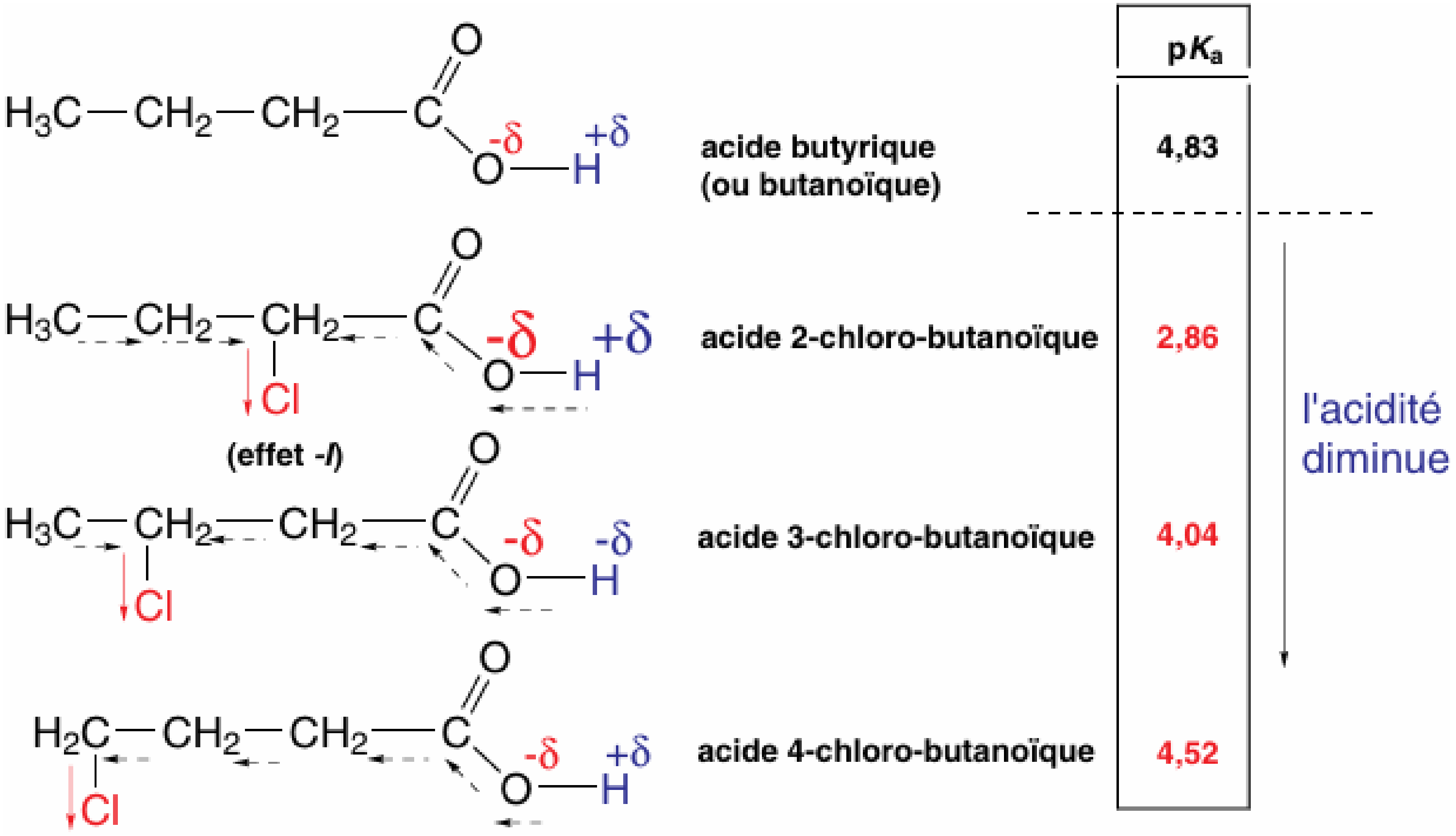
Ammonia NH_3 has a pKa of 9.27 and methylamine CH_3-NH_2 has a pKa of 10.62, making it more basic.



2-5- Transmission of the inductive effect through a carbon chain

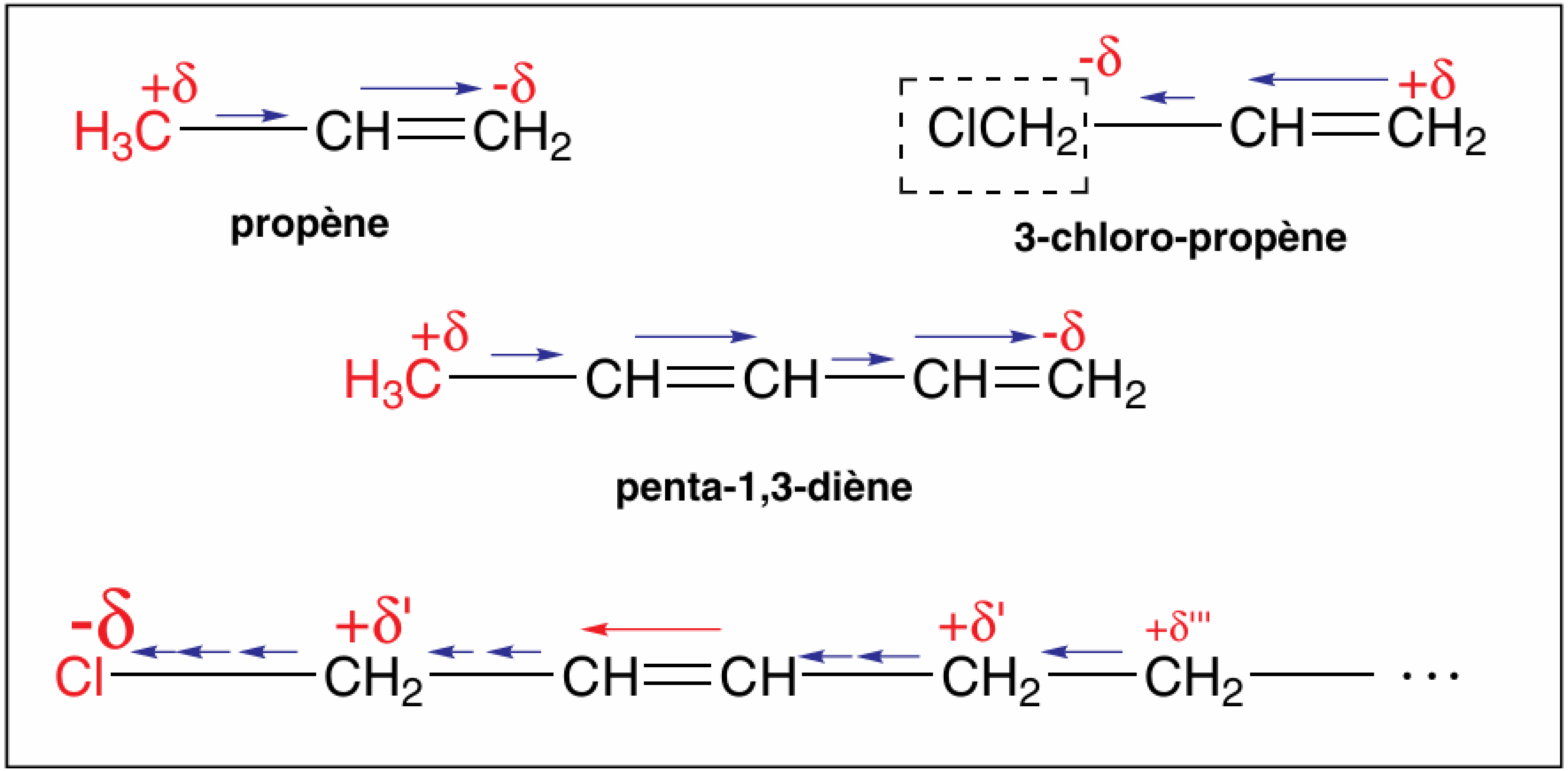
Through the bonds σ

The inductive effect exerted by an -I or +I group on a chain made up solely of σ bonds, as in linear alkanes, is transmitted by gradually decreasing to generally cancel out at a distance of three carbons.



Through the bonds π

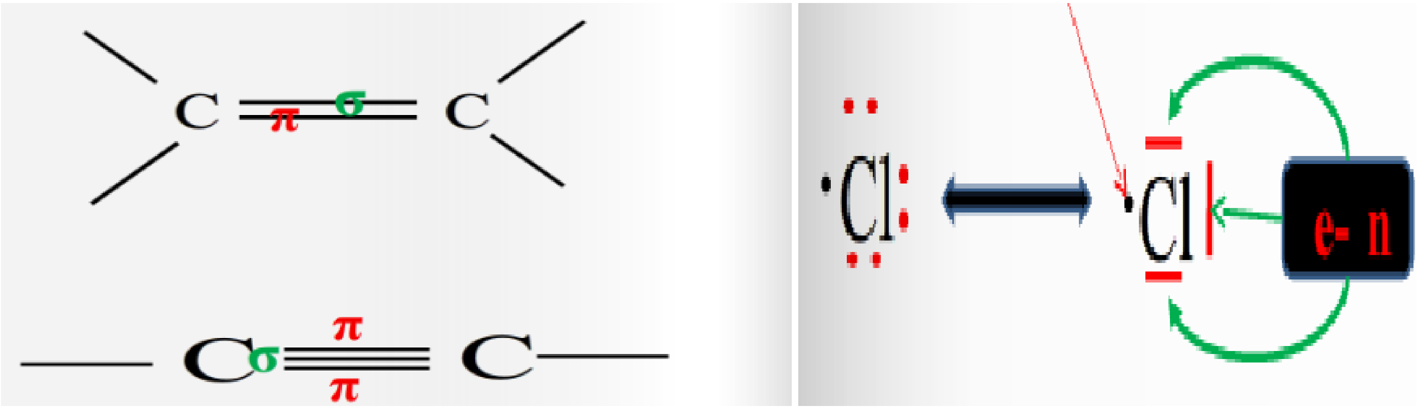
The electrons that make up π bonds are 'more mobile' than the electrons in σ bonds. The consequence of this property is that the effect exerted by an inductive group linked to one carbon of a double bond is almost completely transmitted to the other carbon of the double bond.



3 – Mesomeric effect :

3-1- Definition:

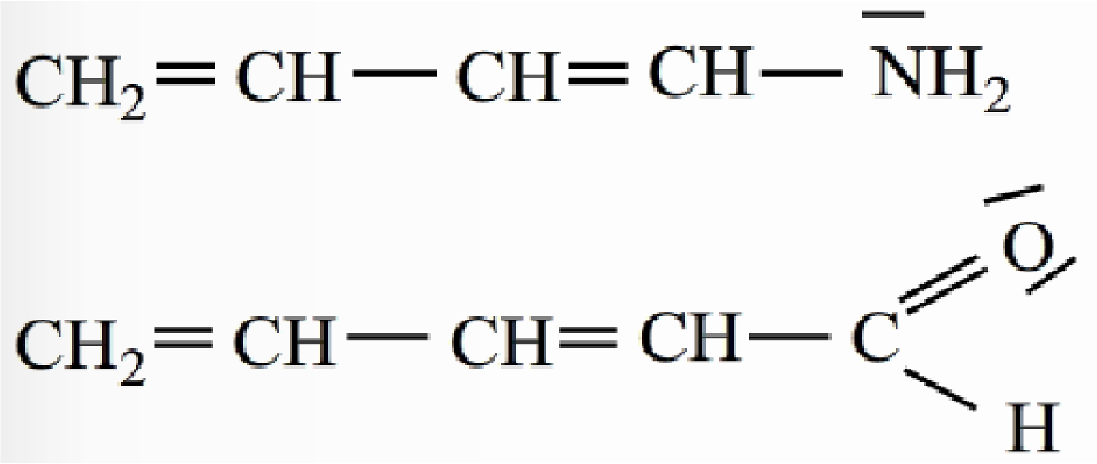
Mesomeric effects are due to the delocalization of **π** or **n** electrons, favored by the electronegativity of the atoms that form the molecule.



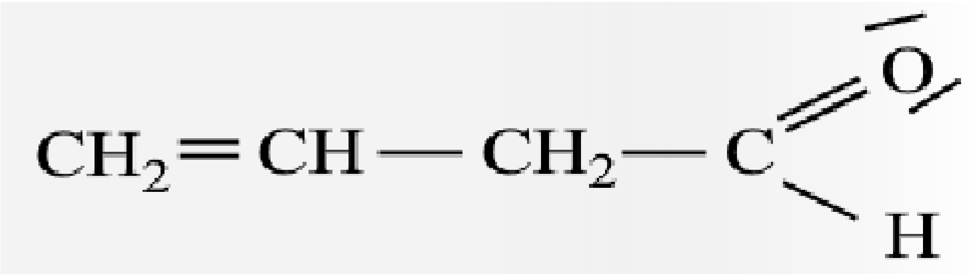
The molecule presents a mesomeric effect if this molecule has a conjugated system

Conjugated system :

When 2 doublets (**π** electrons or free **n** pair) are separated by a single sigma **σ** bond.



Non-Conjugated system :



The pi electrons are separated by two sigma σ bonds

$$CH_2=C=C=CH_2$$

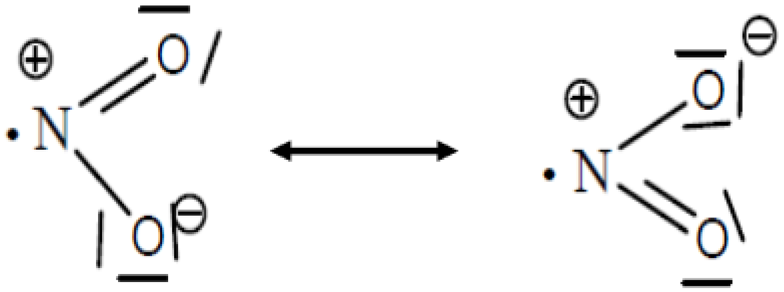
Accumulation of π electrons

Resonance forms :

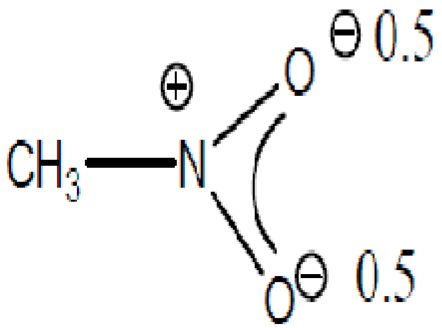
The 2 Lewis representations are equivalent and are called resonance structures or mesomeric forms.

The real molecule is called a **resonance hybrid**, it is a combination, its real structure is an average of all these limit forms.

The mesomeric forms are imaginary, but the resonance hybrid is real.



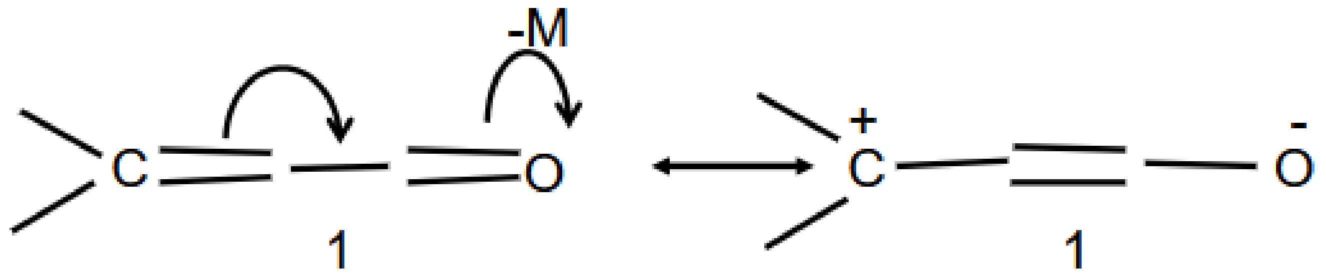
Resonance hybrid



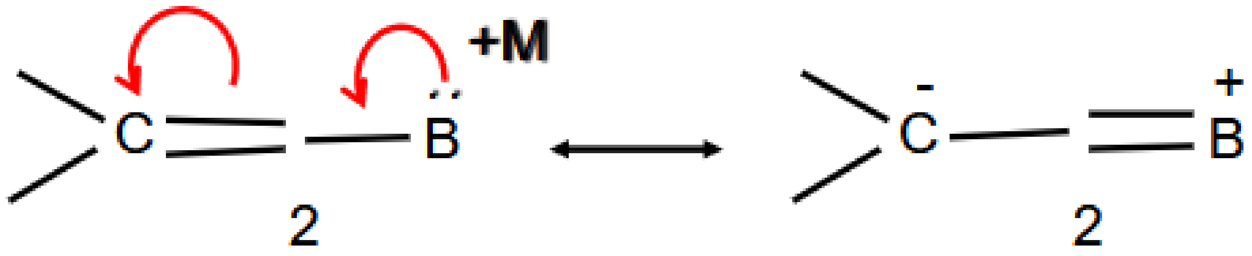
Conditions for mesomerism :

Resonance is only possible in a conjugated structure comprising, always, 2 double bonds separated by a single bond and only.

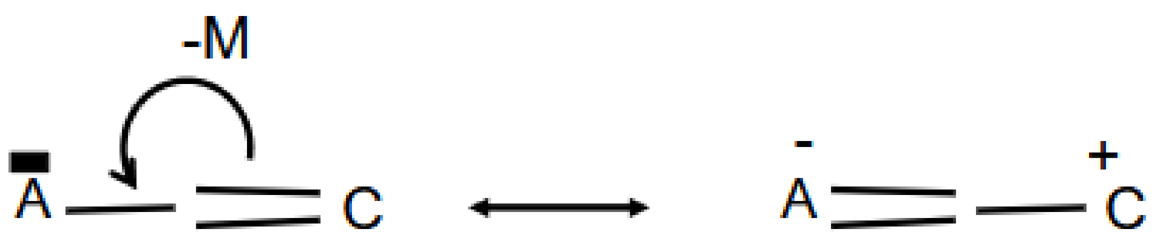
- 2 double bonds (conjugation between 2 electrons π)



- 1 double bond and a free pair



- 1 empty orbital and a pair π



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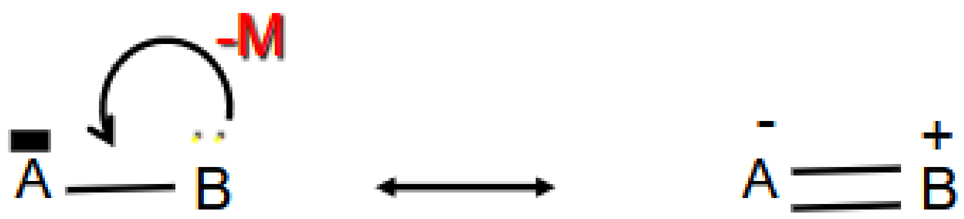
- 1 empty orbital and one free pair



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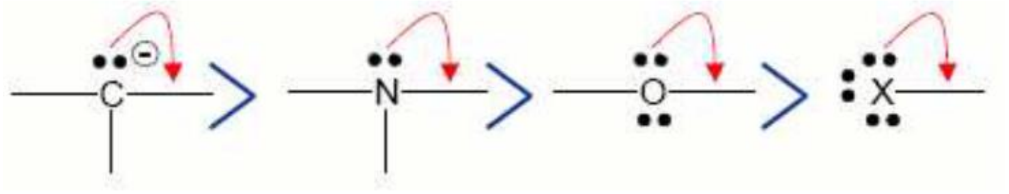
There are two mesomeric effects

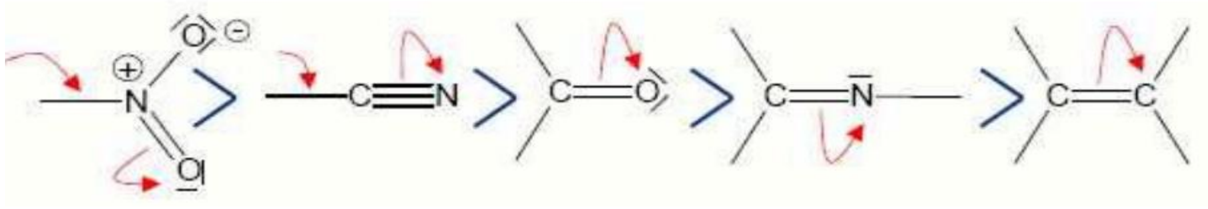
Mesomeric donating effect (+M)

1 atom or 1 group of atoms that activates C=C by creating a negative charge on doubly bonded C.



Mesomeric withdrawing (giving) effect (−M)

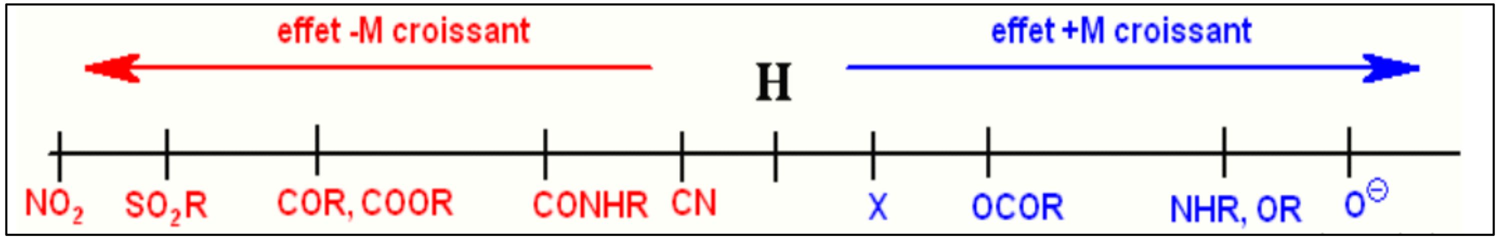
1 atom or group of atoms that deactivates C=C by creating a positive charge on the 1st double-bonded C.



3-2- Classification of substituents with a mesomeric effect :

The mesomeric effect is transmitted by conjugation. This effect is more powerful than the inductive effect and can be propagated more easily over the molecular skeleton by conjugation. It can be an attractor or a donor depending on the nature of the atom or group. Donor groups (note +M) are OH, NH_2 and Attractor groups (note -M) are C=O, C=N.

Donneur (+M)			Attracteur (-M)		
O^-	S^-	NR_2	NO_2	CHO	CN
NHR	NH_2	NHCOR	COR	CO_2H	SO_2R
OR	OH	OCOR	CO_2R	SO_2OR	$CONH_2$
SR	SH	Br	NO	CONHR	Ar
I	Cl	F	$CONR_2$		
R	Ar				

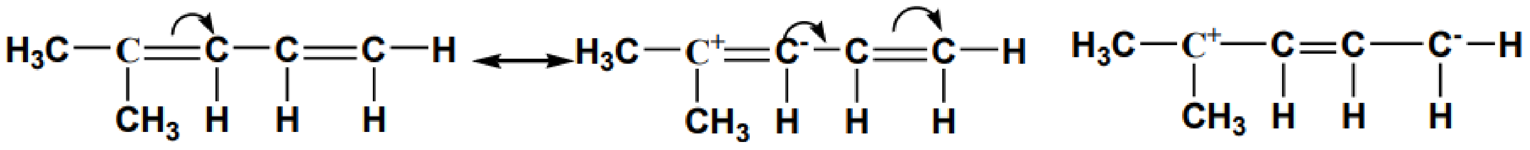


3-3- Conjugated systems and electron delocalization :

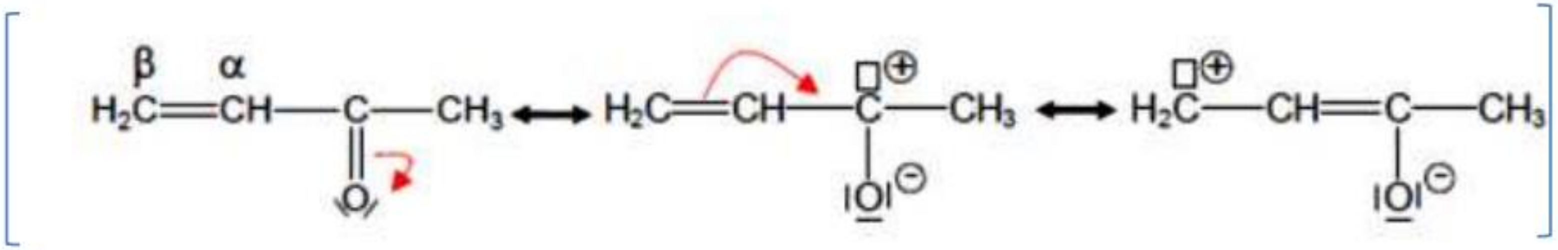
Electronic movements are induced by a phenomenon known as conjugation or resonance, leading to stabilization of the molecule.

3-3-1- Positive charge, single bond, multiple bond (π-σ-π) 1st case :

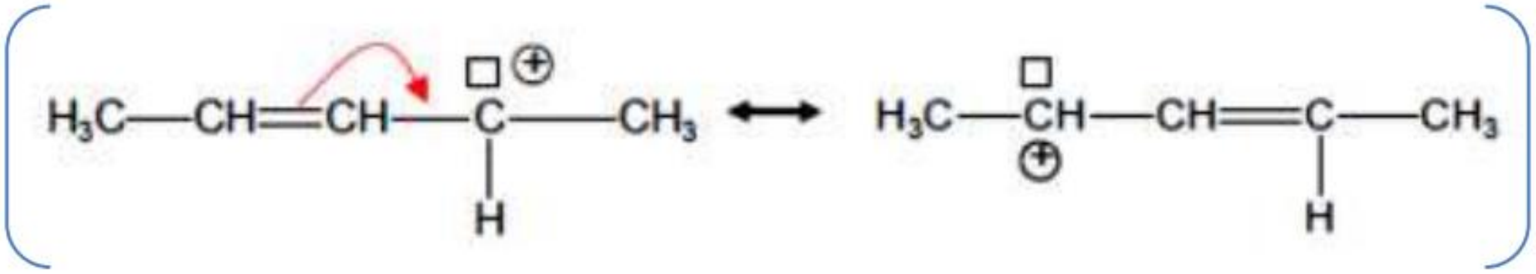
A- Conjugation of π electrons with a non-polar covalent bond :



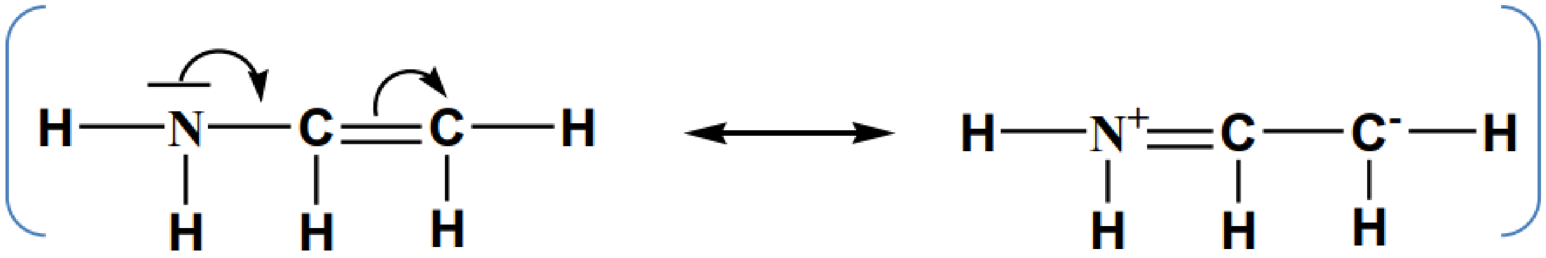
B- Conjugation of π electrons with a polar covalent bond :



3-3-2- Positive charge, single bond, multiple bond (+ -σ-π) 2nd case :

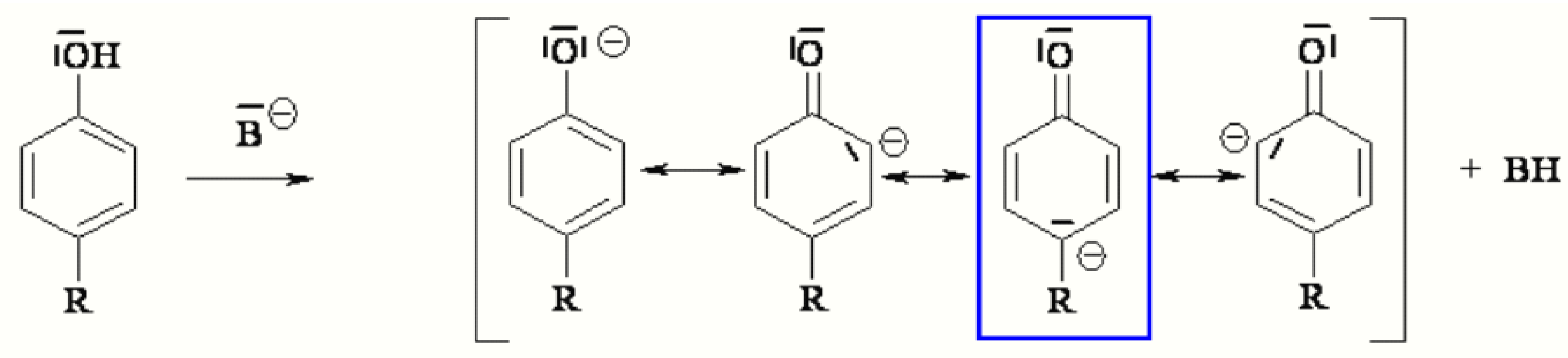


3-3-3- Free electron pair, single bond, multiple bond (n-σ-π) 3rd case :



3-4- Mesomeric effect and acidity :

Some groups can have a very large influence on the pKa of organic compounds. In the case of phenol, we can see that :



- The more electrons the O-H bond has, the more difficult it will be to break, and therefore the higher the pKa.
- The more electron-poor the bond, the easier it will be to break, so the pKa will be low.

An electron-donating group on the phenyl will increase the pKa value (and therefore decrease the acidity of the phenol).

If an electron-withdrawing group is placed on the phenyl, the O-H bond will be electron-depleted, making it easier to break, and the pKa value will fall (higher acidity).

R-	NH_2	OMe	CH_3	H	$COCH_3$	CN	NO_2	$NH(CH_3)_3$
pKa	11,28	10,86	10,25	9,89	8,79	8,56	8,24	8,08
	+M	+M	+I		-M	-M	-M	-I

3-5- Mesomeric effect and basicity:

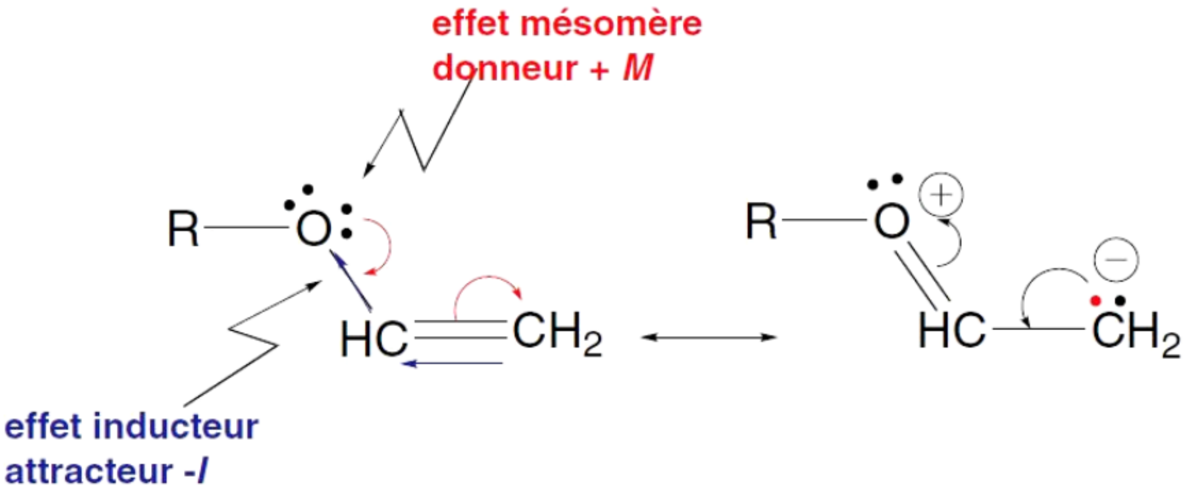
Donating effects increase basicity, whereas attractor effects decrease basicity.

Competition between inductive effect and mesomeric effect :

Groups with an electron-donating mesomeric effect +M also exert an electron-attracting inductive effect -I . the mesomeric effect +M takes precedence over the inductive effect -I.

Example: oxygen in an alkoxy group, R-O- of a vinyl ether, >C=C(OR)-, vinyl halides, >C=C(X)-, or vinyl amines (or enamines), >C=C(NH_2)-.

On the other hand, groups with an electron-withdrawing effect - M also have an effect - I. The two effects are superimposed, but the mesomeric effect is more powerful than the inductive effect. It is the mesomeric effect that dictates the orientation of reactions with electrophilic or nucleophilic reagents.



Chapter 5