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Chapter4: Electronic effects

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IV.3. Inductive effect: definition,
- Classification of inductive effects,
- Influence of the inductive effect on the acidity of a chemical compound,
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IV.4. Mesomere effect: definition, conjugated systems and electron delocalization.
- Classification of mesomere effects,
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IV.1/ Definition

Electronic effects are the effect which appears due to electronic distribution. There are two major types: inductive effect and mesomere effect.

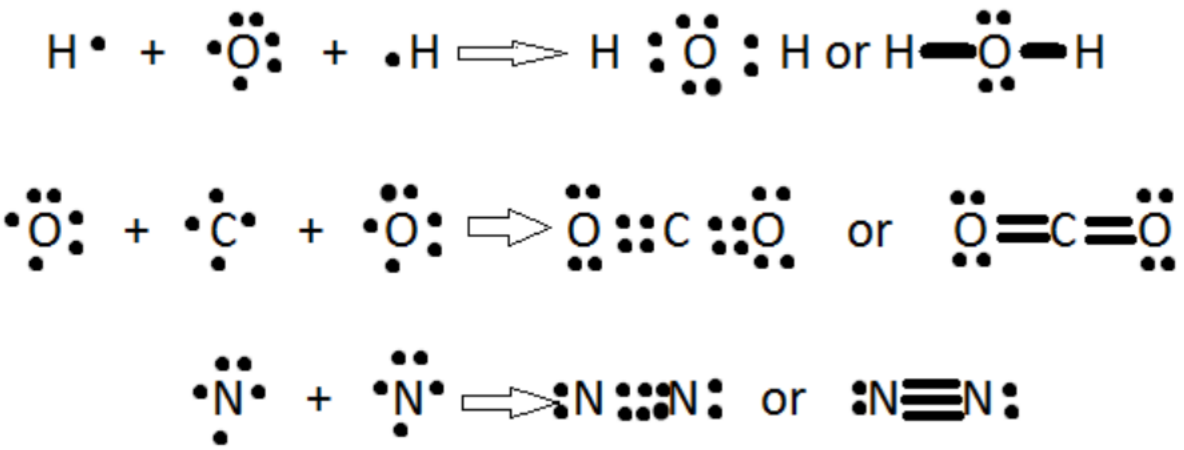
IV.2/ Chemical bonds:

A chemical bond is a force of attraction between atoms or ions. Bonds form when atoms share or transfer valence electrons (Valence electrons are the electrons in the outer energy level of an atom that may be involved in chemical interactions. Valence electrons are the basis of all chemical bonds).

IV.2.1. Pure covalent bond:

Covalent bonding is the process of sharing a pair of electrons where each atom provides one electron. The bonds are typically between a nonmetal and a nonmetal.

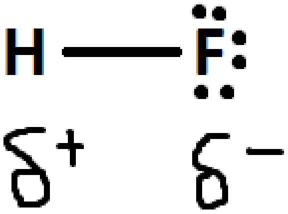
In the case of two identical atoms that are bonded to each other (also known as a nonpolar bond), they both emit the same force of pull on the electrons, thus there is equal attraction between the two atoms (i.e. oxygen gas, or O_2, have an equal distribution of electron affinity. This makes covalent bonds harder to break.



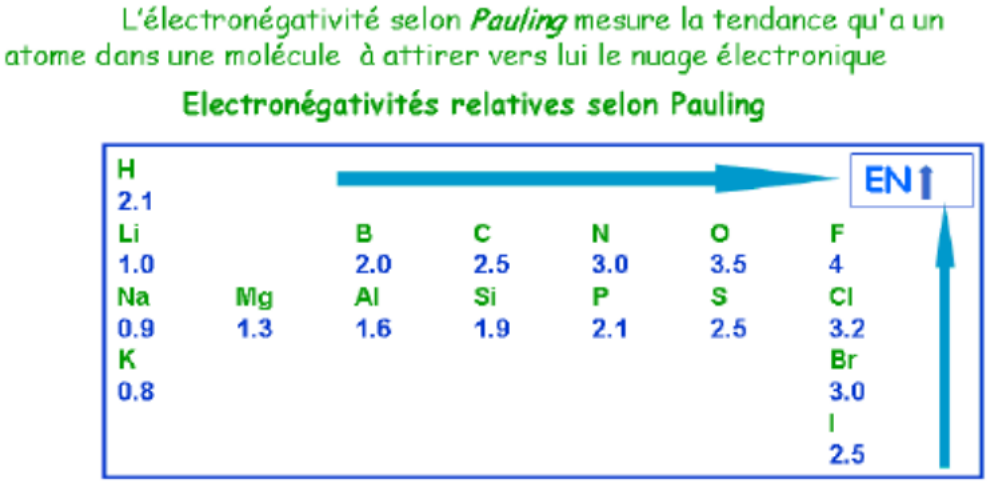
All these diagrams show the formation of covalent bonds as electrons from elements are shared to form single, double, and triple bonds

IV.2.2. Polarized covalent bond:

Polar covalent bonding is the process of unequal sharing of electrons. It is considered the middle ground between ionic bonding and covalent bonding. It happens due to the differing electronegativity values of the two atoms. Because of this, the more electronegative atom will attract and have a stronger pulling force on the electrons. Thus, the electrons will spend more time around this atom.



The symbols above indicate that on the flourine side it is slightly negitive and the hydrogen side is slightly positive.



L'électronégativité selon *Pauling* mesure la tendance qu'a un atome dans une molécule à attirer vers lui le nuage électronique

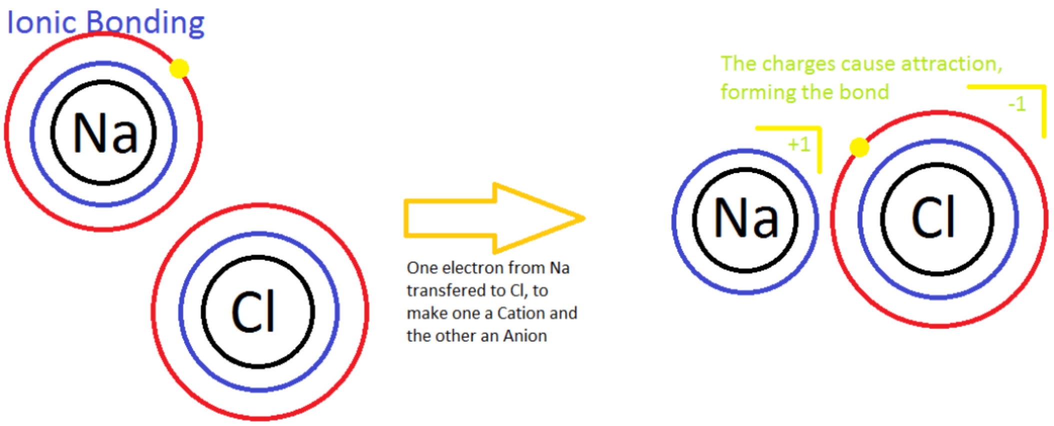
Electronégativités relatives selon Pauling

H 2.1						
Li 1.0		B 2.0	C 2.5	N 3.0	O 3.5	F 4
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.1	S 2.5	Cl 3.2
K 0.8						Br 3.0
						I 2.5

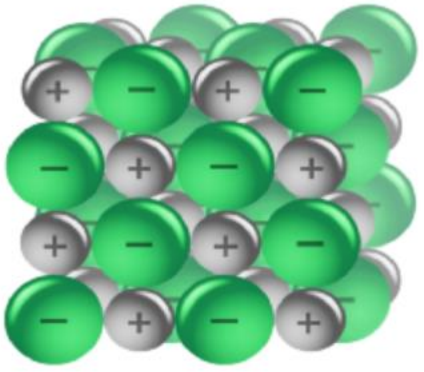
IV.2.3. Ionic covalent bond:

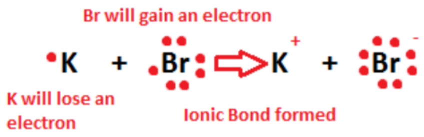
Ionic bonding is the process of not sharing electrons between two atoms. It occurs between a nonmetal and a metal. Ionic bonding is also known as the process in which electrons are "transferred" to one another because the two atoms have different levels of electron affinity.

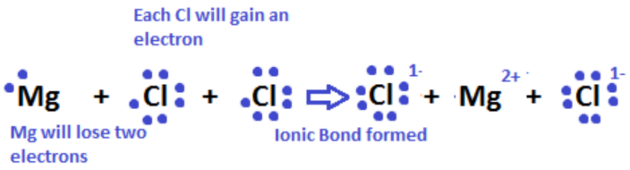
E.g. In the picture below, a sodium (Na) ion and a chlorine (Cl) ion are being combined through ionic bonding. Na^+ has less electronegativity due to a large atomic radius and essentially does not want the electron it has. This will easily allow the more electronegative chlorine atom to gain the electron to complete its 3rd energy level. Throughout this process, the transfer of the electron releases energy to the atmosphere.



Another example of ionic bonding is the crystal lattice structure shown below. The ions are arranged in such a way that shows unifomity and stablity; a physical characteristic in crystals and solids.







IV.3. Inductive effect:

IV.3.1. Definition:

- The inductive effect is the shifting (or pulling) of electrons through single sigma (σ) bonds in a molecule, caused by the electronegativity difference between atoms.
- When one atom is more electronegative than its neighboring atom, it pulls the bonding electrons slightly towards itself, creating a partial charge. This effect can spread along a chain of atoms — though it weakens with distance.

Generally speaking,

$$C^{\delta+}–X^{\delta-}$$

- The atom X above acquires a slightly negative charge ($^{\delta-}$), and the carbon atom a slightly positive charge ($^{\delta+}$), which means the bond is polarized:

$$C^{\delta\delta\delta\delta^+} \longrightarrow C^{\delta\delta\delta^+} \longrightarrow C^{\delta\delta^+} \longrightarrow C^{\delta^+} \longrightarrow X^{\delta^-}$$

$$C^{\delta\delta\delta\delta^-} \longleftarrow C^{\delta\delta\delta^-} \longleftarrow C^{\delta\delta^-} \longleftarrow C^{\delta^-} \longleftarrow Y^{\delta^+}$$

- If the electronegative atom X is connected to a chain of carbon atoms, then the positive charge is relayed to the other carbon atoms.
- C1, with its positive δ charge, exerts a pull on the electrons of C2, but the pull is weaker than it is between X on C1.
- The effect rapidly dies out and is usually not significant after the 2nd carbon atom, or at most the 3rd.
- The inductive effect is permanent, but relatively weak, and can be easily overshadowed by other electronic effects.
- There are two categories of inductive effects: the **electron-withdrawing** (-I effect) and the **electron-releasing** (+I effect called also the ***electron-donating effect***). In the image above, X is electron-withdrawing and Y is electron-donating.
- These relative inductive effects are measured with reference to hydrogen:

$NO_2 > COOH > F > Cl > Br > I > OR > OH > C_6H_5$(Benzene)$> H > Me_3C- > Me_2CH- > MeCH_2- > CH_3-$.

e.g. Consider the **chloroethane molecule (CH_3 CH_2 Cl)**:

- Chlorine is more electronegative than carbon.
- It pulls electrons through the C–C and C–H bonds, making the carbon chain slightly positive.

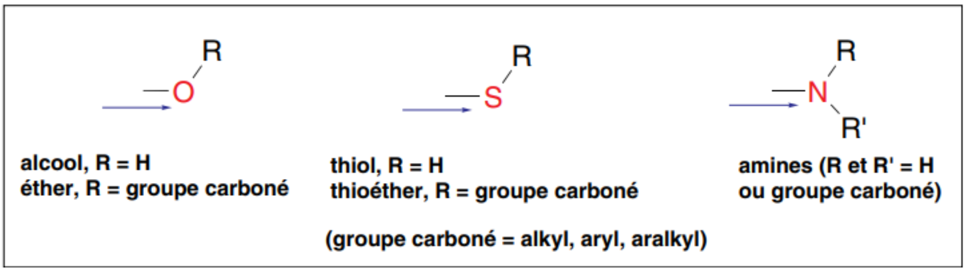
e.g. Consider the chlorobutane chain: **$Cl{-}CH_2{-}CH_2{-}CH_2{-}CH_3$**

- The chlorine (Cl) is very electronegative and pulls electrons toward itself.
- The carbon directly bonded to Cl (1st carbon) feels a strong **–I effect**.
- The next carbon (2nd carbon) feels a weaker effect.
- The 3rd carbon feels an even weaker effect.
- By the time you reach the 4th carbon, the effect is **practically gone**.

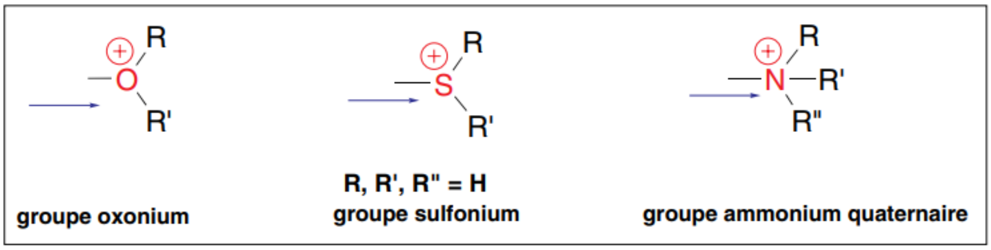
IV.3.2. Classification of inductive effects

IV.3.2.1. -I effect (Electron-Withdrawing Inductive Effect)

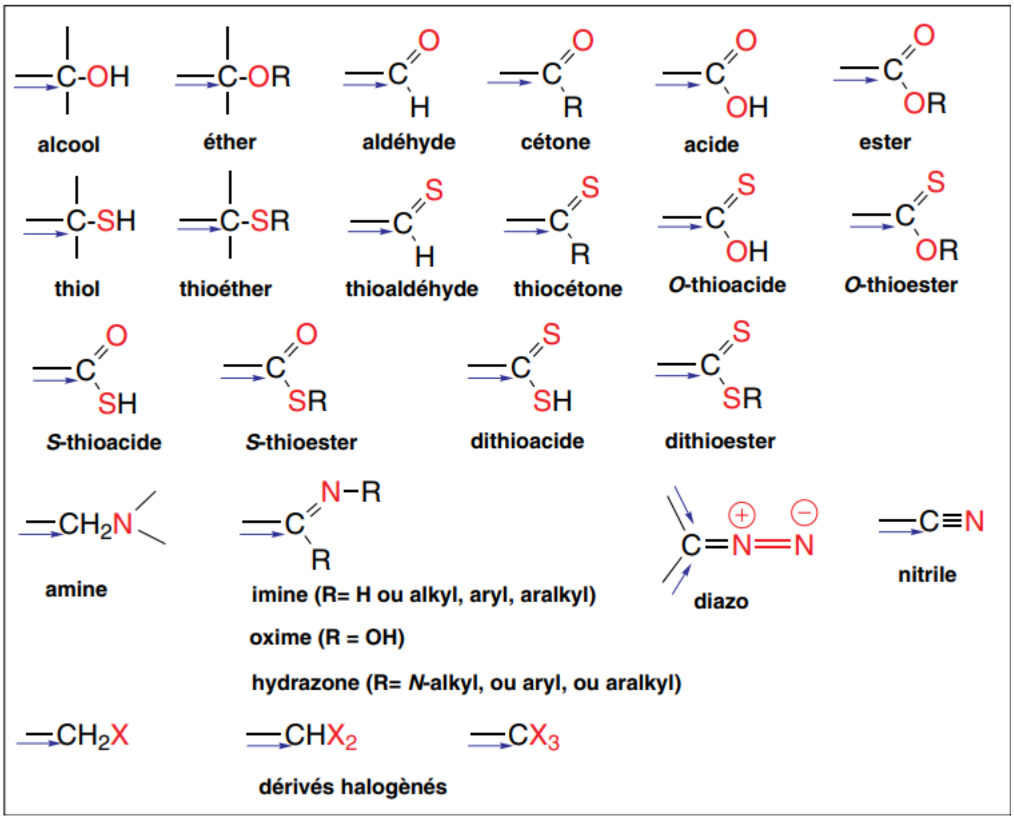
- ✓ The **-I** effect is seen around a more electronegative atom or group, and electron density is higher there than elsewhere in the molecule.
- ✓ Electron-withdrawing groups include halogen, nitro (-NO_2), cyano (-CN), carboxy (-COOH), ester (-COOR) and aryloxy (-OAr).
- ✓ Halogens, -F, -Cl, -Br, -I,
- ✓ Neutral groups formed from a bi- or trivalent heteroatom such as oxygen, sulfur or nitrogen



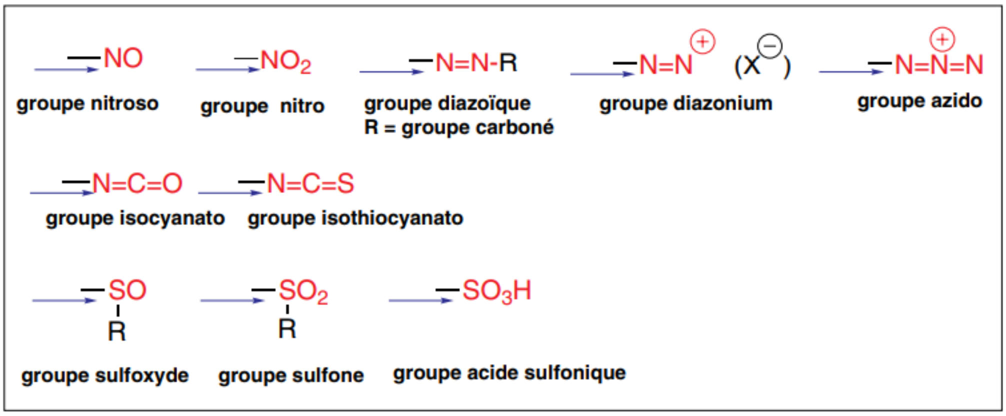
- ✓ positively charged groups formed from a bi- or trivalent heteroatom (very strong inductive effect –I). Their effect is particularly powerful.



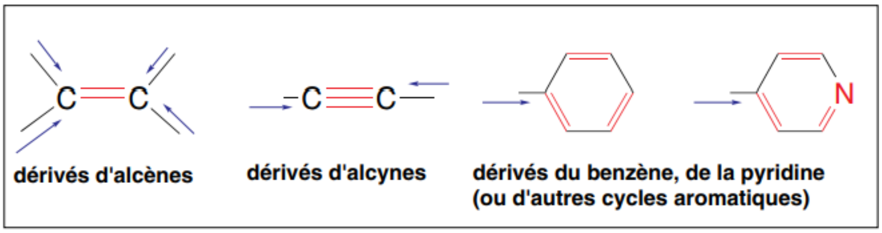
- ✓ Groups consisting of a carbon bonded to one or more electronegative heteroatoms



- ✓ Groups, charged or not, made up of several electronegative hetero atoms, (strong inductive effect)

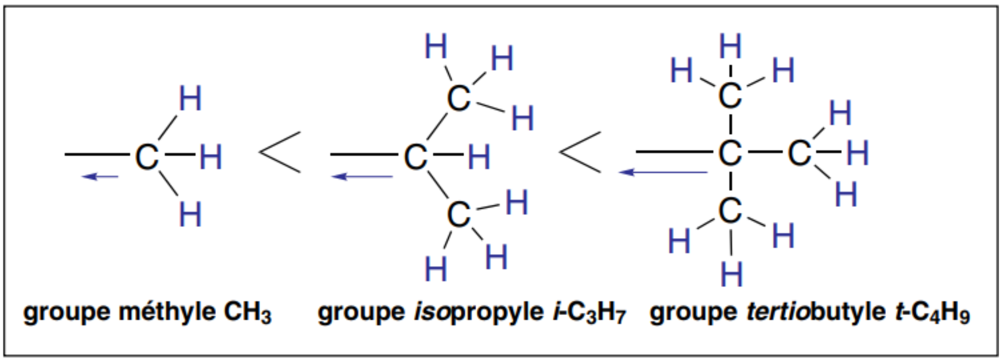


- ✓ Groups derived from alkenes, alkynes, or benzene (and their polycyclic derivatives or any other aromatic ring



IV.3.2.2. +I effect (Electron-Donating Inductive Effect)

- ✓ The **+I** effect is observed among the less electronegative atoms of the molecule by electron-releasing (or electron-donating) groups.
- ✓ The alkyl groups are usually considered electron-releasing (or electron-donating) groups.



IV.3.3. Influence of the inductive effect on the acidity or basicity of chemical compounds:

Acid: is a substance that can **donate a hydrogen ion (H^+)** to another substance.

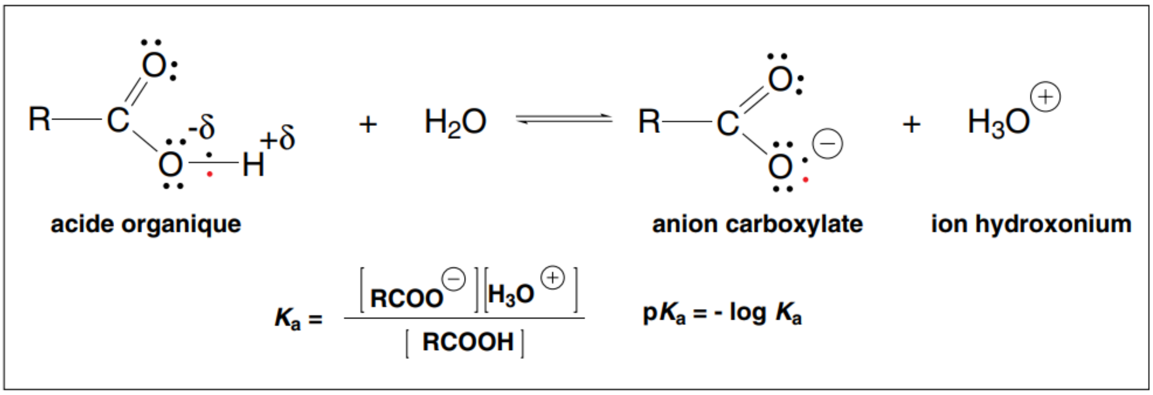
Base: is a substance that can **accept a hydrogen ion (H^+)** from another substance.

The inductive effect is the way electron density is shifted through a chain of atoms in a molecule, caused by the electronegativity of nearby atoms. This effect can either increase or decrease the acidity of a compound.

The influence of **–I** or **+I** groups can be easily demonstrated by studying the ''pKa'' values of acids substituted with such a group. The pKa value defines the strength of the acid.

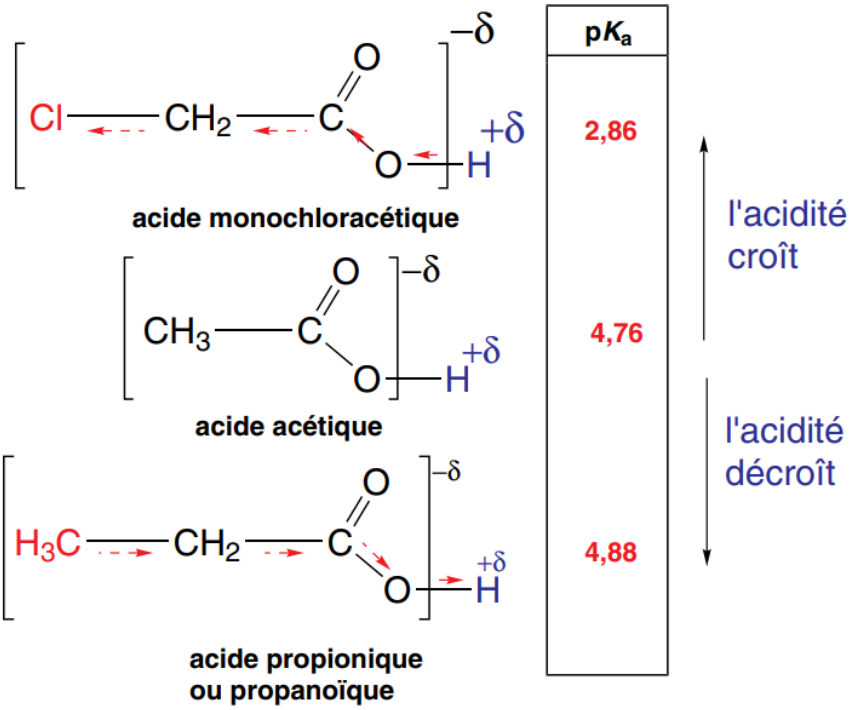
The lower the pKa, the stronger the acid, which corresponds to a high polarization of the OH bond with facilitated release in aqueous media of a hydroxonium ion, H_3O^+, alongside the carboxylate anion, RCOO-, for an organic acid, RCOOH.

As a generalisation, it may be said that the electron-withdrawing groups (EWG) increase the acidity of a compound, and the electron-donating group decrease the acidity of a compound.



$$K_a = \frac{[RCOO^{\ominus}][H_3O^{\oplus}]}{[RCOOH]} \qquad pK_a = -\log K_a$$

Such as: $\mathbf{K_A}$ is the acidity constant, and $\mathbf{pK_A}$ is



IV.4. Mesomer effect:

IV.4.1. Definition:

- The mesomeric effect (also called the resonance effect) is how electrons move through a molecule by delocalization, especially through π (pi) bonds or lone pairs n electron (les doublet libres). This phenomenon is called also resonance.
- mesomerism (meaning "between several forms")
- This phenomenon is symbolized by the double arrow ↔ that separates the different boundary structures.
- In chemistry, the mesomeric effect, also known as the resonance effect, is a feature of substituents or functional groups in a molecule.
- The effect is symbolized by the letter ‘M’ and is used to describe the electron-withdrawing or releasing properties of substituents depending on the relevant resonance structure.
- The mesomeric effect is negative when a substituent is an electron-withdrawing group, and the effect is positive when a substituent is an electron-releasing group.

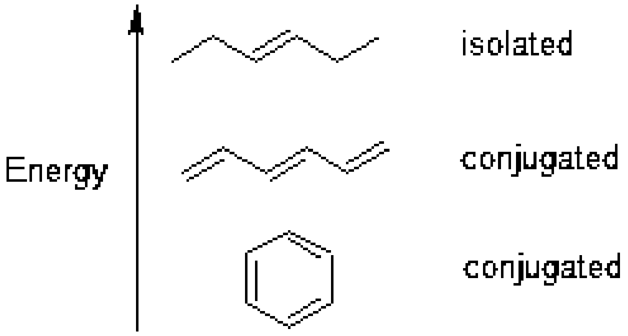
IV.4.2. Conjugated systems and electron delocalization:

Alternating **σ** single and double bonds create a conjugated **π** pi bond system across multiple atoms that lowers the energy and stabilizes the molecule or ion.

When we look at carbon-carbon double bonds (C=C), we need to look and see if they are isolated or conjugated.

We have 5 types of alterations:

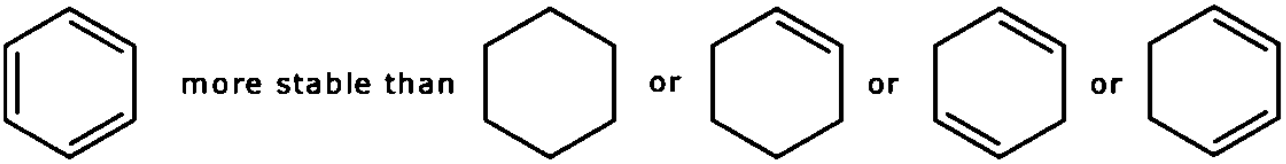
π σ π, π σ n, π σ +, π σ -, π σ .

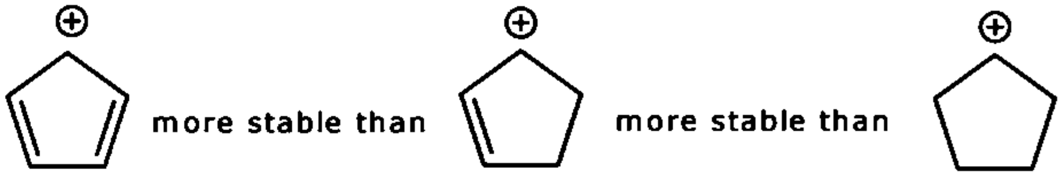


- The presence of alternating *pi* π and sigma σ bonds in a molecule such as benzene is known as a **conjugated system**, or **conjugated *pi* bonds**.
- Conjugated systems can extend across the entire molecule, as in benzene, or they can comprise only part of a molecule.
- A conjugated system always starts and ends with a *pi* bond (i.e. an *sp*^{2} or an *sp*-hybridized atom), or sometimes with a charge.
- The atoms that form part of a conjugated system in the examples below are shown in blue, and the ones that do not are shown in red. Most of the times it is *sp*^{3} hybridized atoms that break a conjugated system.

- Since conjugation brings up electron delocalization, it follows that the more extensive the conjugated system, the more stable the molecule (i.e. the lower its potential energy). If there are positive or negative charges, they also spread out as a result of resonance.
- The corollary is that the more resonance forms one can write for a given system, the more stable it is. That is, the greater its resonance energy.

E.g. Examine the following examples and write as many resonance structures as you can for each to further explore these points:



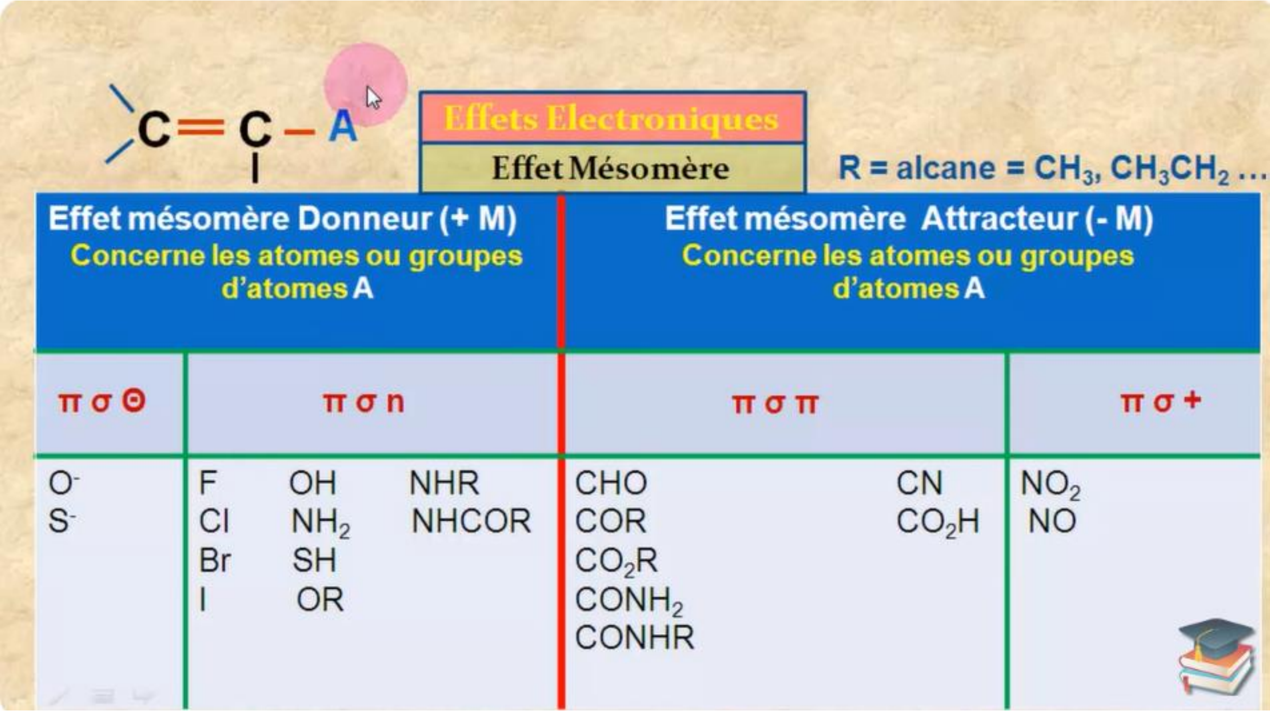


IV.4.2. +M Mesomeric Effect:

In a positive mesomeric effect, the electron density of the molecule or conjugated system increases when an electron moves away from a specific group and towards the rest of the molecules. This is demonstrated by electron-releasing substituents. OH, SH, -OR, -OCOR, NH_2, $-NR_2$, –NHCOR, Ph, $–CH_3$, –F, –Cl, –Br, –I are some of the +M substituents.

IV.4.3. -M Mesomeric Effect

In a negative mesomeric effect, the electron density of the molecule or conjugated system falls when electrons are transported from the rest of the molecules to a specific group. This is demonstrated by electron-withdrawing substituents. NO_2, –CN, $–SO_3H$, –COOH, –COOR, –CONH2, –COO, –CHO, –COR are some of the -M substituents.



Effets Electroniques
Effet Mésomère
R = alcane = CH_3, CH_3CH_2 …

Effet mésomère Donneur (+ M) Concerne les atomes ou groupes d'atomes A		Effet mésomère Attracteur (- M) Concerne les atomes ou groupes d'atomes A	
π σ ⊖	π σ n	π σ π	π σ +
O^- S^-	F Cl Br I OH NH_2 SH OR NHR NHCOR	CHO COR CO_2R $CONH_2$ CONHR CN CO_2H	NO_2 NO

IV.4.4. Influence of the mesomeric effect on the acidity or basicity of chemical compounds:

➢ The mesomeric effect plays a crucial role in determining the acidity of compounds by influencing the stability of their conjugate bases. Electron-withdrawing groups enhance acidity by stabilizing the conjugate base, while electron-donating groups reduce acidity by destabilizing it. This effect can significantly influence the acidity of a compound. Here's how it works:

➢ Acidity is the tendency of a compound to donate a proton (H^+). The more stable the conjugate base (the species that remains after the proton is lost), the stronger the acid.

- **Electron Donation (Positive Mesomeric Effect, +M)**: Groups that donate electron density through resonance (like -OH, $-OCH_3$) can stabilize the negative charge on the conjugate base. This increased stability makes the compound a weaker acid because the base is less likely to accept a proton.
- **Electron Withdrawal (Negative Mesomeric Effect, -M)**: Groups that withdraw electron density (like $-NO_2$, -CN) can destabilize the negative charge on the conjugate base. This destabilization makes the compound a stronger acid, as the conjugate base is more likely to exist in a stable form when the acid donates a proton.

Impact on Acidity

- **Acids with Electron-Withdrawing Groups**: When a compound has electron-withdrawing groups, the stability of the conjugate base increases. For example, in carboxylic acids, the presence of a -NO_2 group increases acidity because it stabilizes the negative charge on the carboxylate ion through resonance.
- **Acids with Electron-Donating Groups**: Conversely, if an acid has electron-donating groups, it results in a less stable conjugate base. For instance, a phenol with an alkyl group (which has a +M effect) will be less acidic than phenol itself because the alkyl group destabilizes the negative charge.