

Electronic effect

Electronic effects: inductive and mesomeric effects :

Introduction : The effect which appears due to electronic distribution is called electronic effect.

Classification : We note 2 types of electronic effects :

- ✚ The inductive effects : which are related to the polarization of a σ bond.
- ✚ The mesomeric effects : which are due to the delocalization of π electrons and n electrons.

Both effects can exist together in the same molecule. In the case of a coexistence of 2 inductive and mesomeric effects of opposite signs, it is always the mesomeric effect that prevails.

Many of its effects are related to the electronegativity of atoms, it is good to recall the evolution of the electronegativity (Pauling scale) of the most common atoms :

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

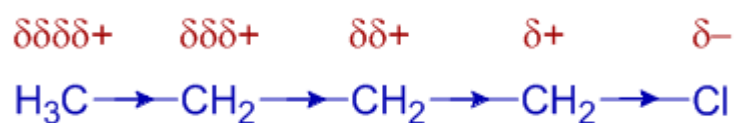
H								
2.1								
Li		B	C	N	O	F		
1.0		2.0	2.5	3.0	3.5	4		
Na	Mg	Al	Si	P	S	Cl		
0.9	1.3	1.6	1.9	2.1	2.5	3.2		
K						Br		
0.8						3.0		
						I		
						2.5		

Salient features of inductive effect

- * It arises due to electronegativity difference between two atoms forming a sigma bond.
- * It is transmitted through the **sigma bonds**. No pi bonds are involved.
- * The magnitude of inductive effect decreases while moving away from the groups causing it.
- * It is a **permanent** effect. It may create permanent dipole in the molecule.
- * In general, the inductive effect is relatively weak and is overshadowed by other electronic effects like [resonance](#) effect, [hyperconjugation](#) etc.
- * It influences the chemical and physical properties of compounds.

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Example :

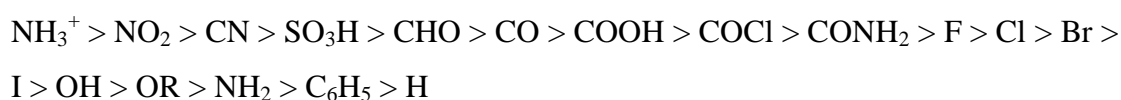


The inductive effect is divided into two types based on the electron withdrawing or electron releasing nature of atom/group inducing it. The strength of inductive effect is measured by comparing with that of hydrogen.

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1. Negative inductive effect (-I):

The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:

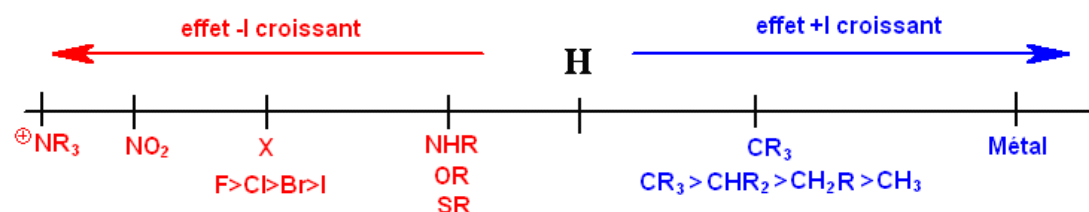


2) Positive inductive effect (+I):

It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.



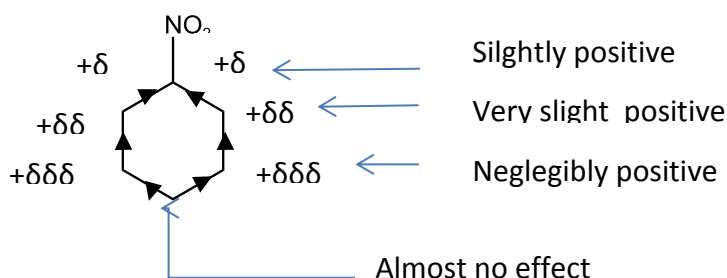
Classement des effets inductifs



Electronic effect

Examples :

- Since $-\text{NO}_2$ is $-I$ group it pulls or withdraws electron from cyclohexane ring making it electron deficient

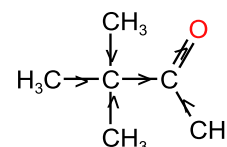
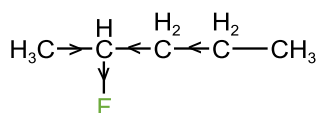
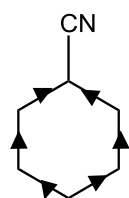
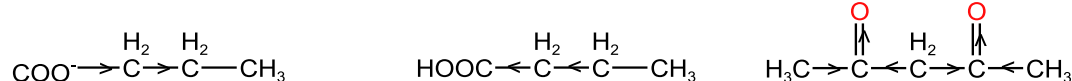


- Let us consider effect of COOH & $-\text{COO}^-$ in carbon chain



Due to e^- donating nature of carbon chain has become partially negative but $-\text{COOH}$ is $-I$ group therefore carbon chain has become partially positive.

- Direction of electron displacements



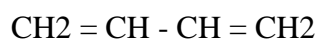
-I Effect	+ I Effect
<ul style="list-style-type: none"> • If the first atom of the group is more electronegative than sp^3 hybridised C • e.g. O, N, S, halogens, $=\text{C}$ (sp^2C), C (sp C), -C of CCl_3 • All positively charged groups • e.g. $-\text{NH}_3^+$, $-\text{CH}_2^+$ 	<ul style="list-style-type: none"> • If the first atom of the group is lesser electronegative than sp^3 hybridised C • e.g. H, Mg, 3°, 2° and 1° alkyl groups (Except $-\text{CCl}_3$) • All negatively charged groups Eg : $-\text{O}^-$, $-\text{NH}^-$, $-\text{CH}_2^-$

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II. Mesomeric effect: Resonating Structures & Conjugation :

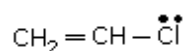
In a normal π bond, the π electrons are localised between the constituent atoms. However, if double and single bonds are present alternately in a molecule, it is called **conjugation**

e.g. : in 1,3-butadiene, the double bonds are conjugated



Similarly, if the double, single and a lone pair are present, alternatively, it is also called conjugation

e.g. vinyl chloride.

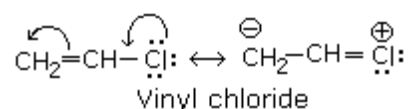


The presence of conjugation alters the properties of the compound and there is a difference in the actual and expected properties.

To explain the anomalous properties of such conjugated compounds, Robinson and Ingold gave the concept of **mesomerism**, which was subsequently modified and developed by Pauling as the theory of **resonance** which you already know.

The **theory of resonance** states that when a molecule can be represented by two or more classical structural (or electronic) formula, all of which can explain some but not all the properties, then the molecule has neither of these structures (called contributing or canonical or limiting structures) but is a hybrid of all these contributing structures.

Example :

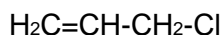


Note that the electrons are not necessarily present where one would expect them, but are rather delocalised over the entire molecule which gives it extra stability expressed in terms of **delocalisation energy** or **resonance energy**. **Also**, normally, we find chlorine withdrawing electrons towards itself by -I effect but here we find that the same chlorine has got a positive charge and is involved in a double bond. Does this mean that chlorine has lost its -I effect? No, this is not true as -I effect is a permanent effect. In fact, in addition to the -I effect, it now also has **an electron donating mesomeric or resonance effect (called +M or +R effect)**.

Since the two effects are operating in opposite directions, one of them will overwhelm the other. Remember there was no such possibility if halogen's lone pair was not

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conjugated. For example in the following case, the Cl is not conjugated to the double bond and hence in the following molecule, Cl is exerting its only -I effect.

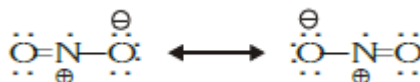


Types of Conjugation:

1. Conjugation between C=C and C=C ($\text{H}_2\text{C}=\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}=\text{CH}_2 \longleftrightarrow \text{H}_2\overset{\oplus}{\text{C}}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\overset{\ominus}{\text{C}}\text{H}_2$)
2. Conjugation between +ve charge and C=C ($\text{H}_2\text{C}=\overset{\text{H}}{\text{C}}-\overset{\oplus}{\text{CH}_2} \longleftrightarrow \text{H}_2\overset{\oplus}{\text{C}}-\overset{\text{H}}{\text{C}}=\text{CH}_2$)
3. Conjugation between lone pair and C=C ($\overset{\cdot\cdot}{\text{Cl}}-\overset{\text{H}}{\text{C}}=\text{CH}_2 \longleftrightarrow \overset{\ominus}{\text{Cl}}=\overset{\text{H}}{\text{C}}-\overset{\ominus}{\text{CH}_2}$)
4. Conjugation between odd electron and C=C ($\text{H}_2\overset{\cdot}{\text{C}}-\overset{\text{H}}{\text{C}}=\text{CH}_2 \longleftrightarrow \text{H}_2\overset{\text{H}}{\text{C}}=\overset{\cdot}{\text{C}}-\text{CH}_3$)
5. Conjugation between negative charge and C=C ($\text{H}_2\overset{\ominus}{\text{C}}-\overset{\text{H}}{\text{C}}=\text{CH}_2 \longleftrightarrow \text{H}_2\overset{\text{H}}{\text{C}}=\overset{\ominus}{\text{C}}-\text{CH}_2$)

Characteristics of Resonance

- i. In the resonance effect, only electrons are delocalised, not atoms.
- ii. The number of lone pair electrons or the number of unpaired in all resonating structures must be equal.



- iii. All the resonating structures must possess the same energy.
- iv. This is a permanent effect.
- v. All the resonating or canonical structures must conform to Lewis structures.

The mesomeric effect can be subdivided into two types:

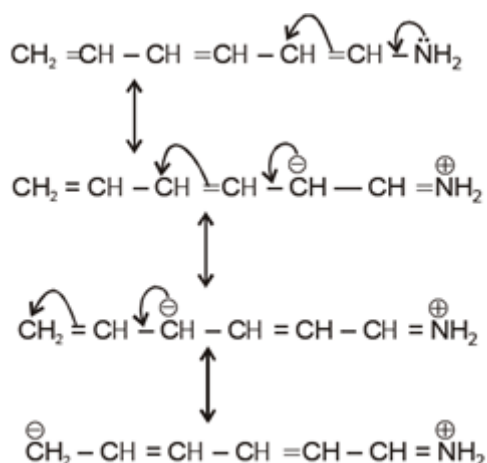
- +M effect
- -M effect

+M effect (Positive mesomeric effect)

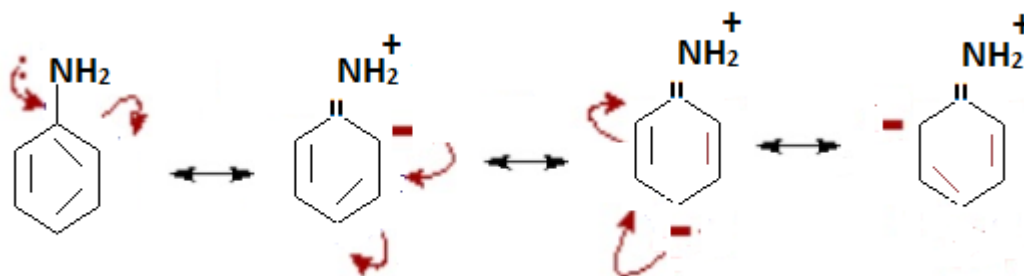
When the electrons or the π electrons are transferred from a particular group towards a conjugate system, thus increasing the electron density of the conjugated system, such a phenomenon is known as the (+M) effect or positive mesomeric effect.

Example 1 :

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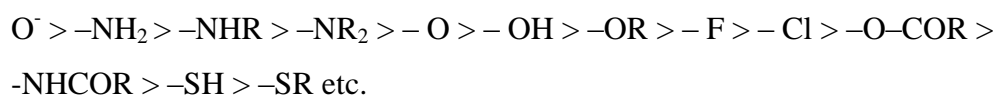


Example 2:



- For the +M effect, the group should have either a lone pair of electrons or should have a negative charge.
- The +M effect gives a negative charge to the conjugate system, or it can be said that the electron density increases in the conjugate system due to this. These conjugate systems show more reactivity towards electrophiles and less reactivity towards a nucleophile.

Group showing +M effect

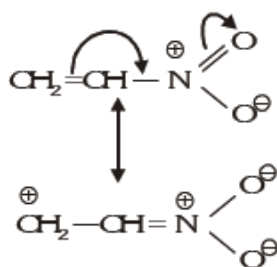


-M Effect (Negative Mesomeric Effect)

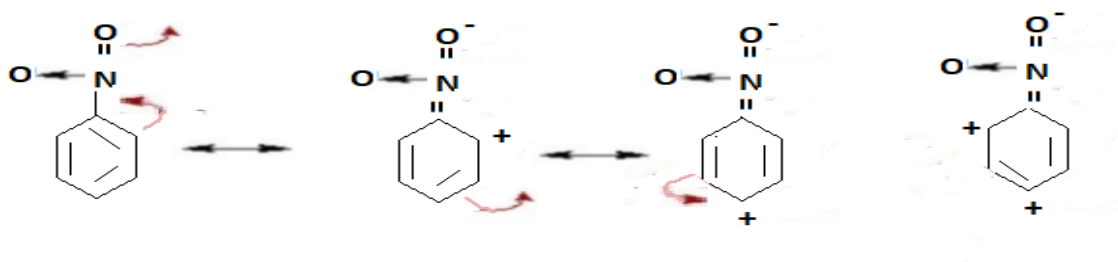
When the π bond electrons are transferred from the conjugate system to a particular group, the electron density of the conjugate system is decreased, then this phenomenon is known as the negative mesomeric (-M) effect.

Example 1:

Electronic effect



Example 2:



- For the $-M$ effect, the group should have either a positive charge or should have a vacant orbital.
- The $-M$ effect makes the compound more reactive towards a nucleophile as it decreases the electron density in the conjugate system, and at the same time, it is less reactive towards electrophile due to the same reasons.

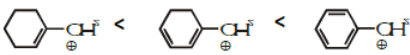
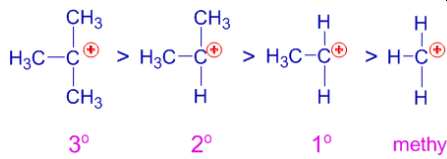
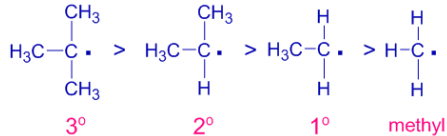

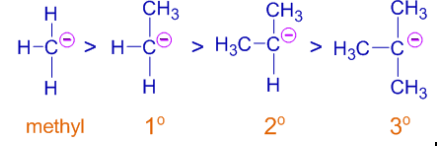
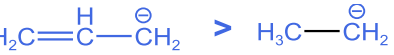
The group which shows the $-M$ effect includes

$-\text{NO}_2 > -\text{CN} > -\text{COX} > -\text{SO}_3\text{H} > -\text{CHO} > -\text{CONH}_2 > -\text{COR} > -\text{COOH} > -\text{COOR} > \text{COO}^-$ etc.

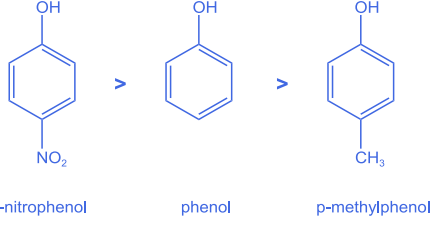
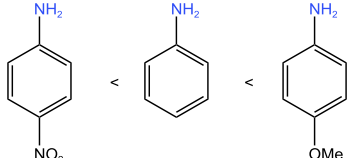
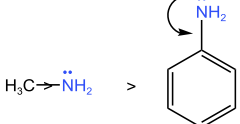
+ M/+R Effect	-M/+R Effect
<ul style="list-style-type: none"> •1. If the first atom of the group either has a lone pair or negative charge. •e.g. $-\text{NH}_2$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{NHCOCH}_3$ etc. 	<ul style="list-style-type: none"> •1. If the first atom of the group has positive charge and after withdrawing a pair of electrons, it is not violating its octet. e.g. $-\text{PH}_3^+$ and NOT $-\text{NH}_3^+$ (octet of N will be violated if it withdraws electrons) •2. If the first atom of a neutral group has neither a lone pair nor any charge, and is joined to more electronegative atom(s) than itself by double/triple bond. •e.g. $-\text{CHO}$, $-\text{CN}$, $-\text{SO}_3\text{H}$, etc.

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Applications of electronic effect :

Applications	Inductive effect	Mesomeric effect
Carbocation Stability :	The stability of carbocations increase when +I groups adjacent to positively charged carbon. Whereas, the -I groups destabilize the carbocations as they increase the positive charge by withdrawing electron density.	Carbocation's stability is enhanced by resonance. All the aromatic compounds are always more stable as compared to non-aromatic compounds due to the effect of resonance.   Resonance increases, and stability increases.
	Compare stability order of: $\text{CH}_2=\text{CH}-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_2=\text{CH}-\text{CH}-\overset{\oplus}{\text{C}}\text{H}_2$ mesomeric effect +I effect - I effect	
Stability of free radicals:	In the same way the stability of free radicals increases with +I 	Resonance increases the stability of free radicals. 
Stability of carbanions:	the +I groups decrease the stability of carbanions while the -I groups increases their stability. 	Carbanion's stability is increased by resonance. 
Acidic	A protonic acid is always in equilibrium with its conjugate base that is formed by loss of a proton. Any factor that stabilizes the	

Electronic effect

<p>strength:</p>	<p>negatively charged conjugate base favors greater ionization of acid. i.e increases the acidic strength.</p> $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}\text{OH} \rightleftharpoons \text{R}-\overset{\text{O}}{\parallel}{\text{C}}\ominus$	
	<p>Acidic strength is directly proportional to the -I effect. Acidic strength is indirectly proportional to the +I effect. $\text{CH}_3\text{COOH} < \text{CH}_2\text{FCOOH} < \text{CHF}_2\text{COOH} < \text{CF}_3\text{COOH}$</p>	<p>Acidic strength is directly proportional to the -M effect. Acidic strength is indirectly proportional to the +M effect.</p>  <p style="text-align: center;">p-nitrophenol phenol p-methylphenol</p>
	<p>-M effect. Increases the acidity > -I effect</p>	
<p>Basic strength of amines:</p>	<ul style="list-style-type: none"> Basic strength is directly proportional to the +I effect. Basic strength is indirectly proportional to the -I effect. <p>$\text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{CH}_2\text{FNH}_2$</p>	<ul style="list-style-type: none"> Basic strength is directly proportional to the +M effect. Basic strength is indirectly proportional to the -M effect.  <p style="text-align: center;">p-nitroaniline aniline p-methoxyaniline</p>
	<p>+I effect increases the basicity > +M effect</p>  <p style="text-align: center;">$\text{H}_3\text{C}-\ddot{\text{N}}\text{H}_2 > \text{C}_6\text{H}_5\text{NH}_2$</p>	