


Subject	Chemistry
Paper No and Title	Paper 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)
Module No and Title	Module 1: Revisit to Electronic Effects: Inductive and Mesomeric Effects
Module Tag	CHE_P1_M1

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CHEMISTRY
PAPER 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)
MODULE 1: Revisit to Electronic Effects: Inductive and Mesomeric Effects

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CHEMISTRY

PAPER 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)

MODULE 1: Revisit to Electronic Effects: Inductive and Mesomeric Effects

1. Learning Outcomes

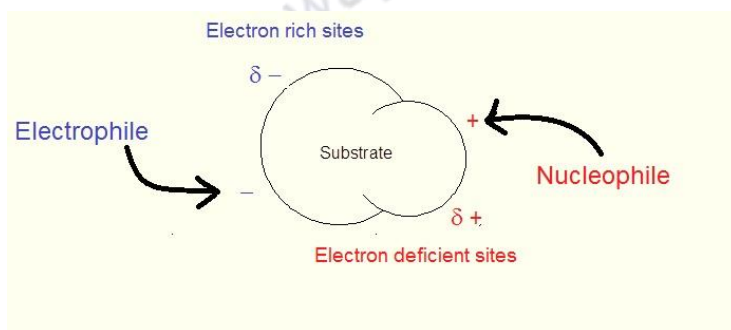
After studying this module you shall be able to:

- Understand inductive effects
- Classify a group into +I or –I group
- Understand mesomeric or resonance effect
- Classify a group into +M or –M group.
- Apply these effects on organic substrates to locate electron deficient and electron rich sites.

2. Introduction

You are already familiar with various electronic effects. But to understand the properties of organic molecules, like acidity, basicity, stability of various species, and to understand the organic reactions and their mechanism, it is very important that we revisit the electronic effects operating especially with a detailed study of conjugated chemical bonding.

During most of the organic reactions, reagents either undergo heterolysis to give rise to electrophiles and/ or nucleophiles; or they undergo homolysis to give rise to free radicals. Electrophiles being electron deficient search for electron rich site in the organic substrate to attack and form the bond. But, if there are more than one electron rich sites in the organic substrate, the electrophile obviously would prefer to attack on the most electron rich site. On the other hand, nucleophiles being electron rich, search for electron deficient sites in the organic substrate.



How these electron deficient and electron rich sites are created (or occur) in the substrate and how can we predict them by looking at the structure of the substrate so that we may predict the attack

and hence the course of the reaction? This can be done by understanding and analyzing the electronic effects operating or present in the substrate.

Electronic effects are the effects originating or present in the organic molecules due to which the reactivity at one part of a molecule is affected by electron attraction or repulsion originating in another part of a molecule.

Let us know about different types of electronic effects.

3. Types of Electronic Effects

There are four types of electronic effects mainly, viz. inductive effect, mesomeric (or resonance) effect, electromeric effect and hyperconjugative effect. Of these, electromeric effect is temporary while rest are permanent and are exhibited as the dipole moment of the molecule.

If we consider hydrocarbons, they are non-polar. But the compound having functional groups i.e. having hetero atom (i.e. atoms other than carbon) or groups are polar. While studying all these effects, we shall consider how the presence of a hetero atom/group introduces polarity in the organic molecules. It is in the context of this group which is known to exert different types of effects on the remaining part of the molecule.

3.1 Inductive effect

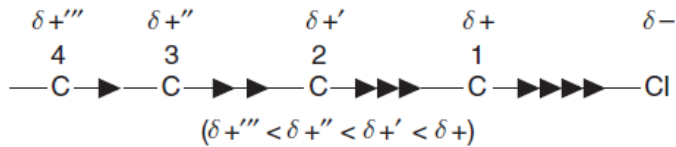
Ideally, a covalent bond between two atoms must share the pair of electrons equally. If the electronegativities of the two atoms are different, this sharing of electrons is not equal and the more electronegative atom gets a fractional negative charge due to the greater attraction of the shared pair of electrons towards itself and the other atom gets a fractional positive charge. Fractional or partial negative charge is represented by δ^- (pronounced as delta minus) and Fractional or partial positive charge is represented by δ^+ (pronounced as delta plus), δ signifying the very less magnitude of charge.

For example, C - X (X = halogen) bond is polar with C having a δ^+ charge and the halogen having a δ^- charge. The magnitude or value of these fractional charges increases with an increase in the electronegativity of the halogen i.e. for halogens, it is in the order $F > Cl > Br > I$.

Let us consider a carbon chain, with the end carbon joined to a more electronegative atom say Cl, then Cl will attract electrons (σ electrons between C and Cl) more towards itself. Hence, the carbon atom will become slightly electron deficient and get a fractional positive charge (δ^+) due to a difference of electronegativity.

This polarization is not restricted till here, but it induces polarity further and hence the name as inductive effect.

Let us consider the case of chlorobutane to understand this.



Here, C_1 acquires slight positive charge (δ^+) due to the electronegativity of Cl which in turn acquires slight negative charge (δ^-). C_1 thus becomes electron deficient and it exerts a pull on the electrons forming covalent bond between C_1 and C_2 but less strongly. As a result, C_2 acquires a lesser positive charge ($\delta\delta^+$) as that on C_1 . C_3 similarly acquires even lesser positive charge ($\delta\delta\delta^+$) and so on. Thus a polarity is slowly *induced* throughout the carbon chain.

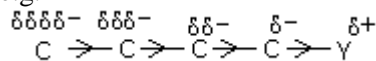
However, the effect is very very less beyond carbon 3 or 4. In other words, the effect diminishes as one moves further in the carbon chain relative to the position of the group. *The phenomenon of transmission of charge arising due to electronegativity difference in a covalent bond (i.e. dipole) through a chain of carbon atoms linked by sigma bonds is called **inductive effect**.*

Such an effect is therefore propagated in the entire chain of carbon atoms, which were otherwise non-polar (in the absence of group Cl).

So the atom/group responsible for the induction in polarity is Cl. Remember that group Cl attracting electrons towards itself is normal due to the difference of electronegativity but induction of polarity in an otherwise non-polar bond due to the attachment of a more electronegative atom in the chain is known as **inductive effect**. *The atoms/groups like Cl which are more electronegative than carbon gain a slight negative charge on them and withdraw the electrons of the carbon chain towards themselves are known to exert **-I Effect** (pronounced as “minus I effect”)*

Similarly, if a more electropositive group (say Y) is attached to an otherwise non-polar carbon chain, the group Y gets a fractional positive charge and the carbon linked to it gets a fractional negative charge. This slightly electron rich carbon then acquires induced electropositive character and shares its excess electron density with the next carbon, which also acquires a fractional negative charge and so on.

e.g.



Induced electropositive character

*The atoms/groups which are more electropositive than carbon gain a slight positive charge on them and push the electrons of the carbon chain away from themselves are known to exert **+I Effect** (pronounced as “plus I effect”)*

There are very few atoms or groups forming compounds with carbon which are more electropositive than carbon e.g. H and Mg. However, the most important group exhibiting +I effect is the alkyl group, which due to a difference in electronegativities of hydrogen and carbon, makes the carbon slightly electron rich.

Inductive effect has the following characteristics:

1. It is a permanent effect.
2. It operates through sigma bonds. (Note that all the single, double and triple bonds have a sigma bond in them.)
3. Its magnitude goes on decreasing with increase in distance from the atom/group responsible for the same. Inductive effect is almost negligible after the third or fourth atom.

4. **-I effect** of some groups is in the order



+I effect of some of the groups is in the following order:



Inductive effect is not a hypothetical phenomenon but is actually operative in the molecules. This has been demonstrated by the fact that it is commonly used to explain the properties like origin of dipole moment, increase or decrease in bond lengths, strength of acids or bases, etc.

In order to classify most of the neutral groups into +I or -I just look at the following parameters required (given in following table) for the nature of first atom. If it is a charged group, then every positively charged group shall exert -I effect because it shall be electron attracting/withdrawing and similarly every negatively charged group shall exert +I effect because it shall be electron repelling.

Nature of Group	- I Effect	+ I Effect
<ul style="list-style-type: none"> Neutral groups 	<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, Hal, =C (sp^2 C), \equivC (sp C), -C of CCl_3 	<ul style="list-style-type: none"> If the first atom of the group is equal to or lesser electronegative than sp^3 hybridised C e.g. H, Mg, 3°, 2° and 1° alkyl groups (Except $-CCl_3$)
<ul style="list-style-type: none"> Charged groups 	<ul style="list-style-type: none"> All positively charged groups e.g. $-NH_3^+$, $-CH_2^+$ 	<ul style="list-style-type: none"> All negatively charged groups $-O^-$, $-NH^-$, $-CH_2^-$

How to compare the extent of $-I$ or $+I$ in the comparable groups (having same first atom)?

$-I$ Effect: Here, due to the electronegativity of the first atom, the electrons are withdrawn or pulled towards itself. The further attached atoms or groups shall enhance the $-I$ if they also pull by $-I$ effect, but will decrease the $-I$ effect if they are electron donating by $+I$ effect

For example, the order of $-I$ effect between the following groups is
 $-N(CH_3)_2 < -NH-CH_3 < -NH_2 < -NH-COCH_3$

$+I$ Effect: Here, due to the electropositivity of the first atom, the electrons are pushed away from itself. The further attached atoms or groups shall enhance the $+I$ if they also push by $+I$ effect, but will decrease the $+I$ effect if they are electron withdrawing by $-I$ effect

For example, the order of $+I$ effect between the following groups is
 $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3$

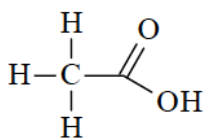
Induction or the inductive effect of an atom or a group is a function of that group's following parameter:

- Electronegativity
- Bonding order and charge
- Position within a structure

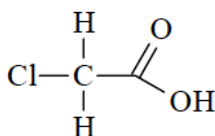
Electronegativity: Electronegative atoms like nitrogen, halogens, oxygen, etc. may have a negative inductive effect (-I), depending upon their bonding order.

Due to the -I effect, these electronegative atoms withdraw electron density through the single bond and can assist in the stabilization of negative charge that may form in reactions like carbanions, oxygen anions etc. On the contrary, they shall destabilise the positively charged species like carbocations and electron deficient species like free radicals.

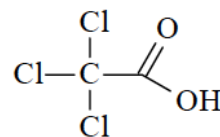
-I groups have a stabilizing (enhancing) effect on the ionization of acids. For example, out of acetic acid, chloroacetic acid and trichloroacetic acid as shown below, trichloroacetic acid is strongest acid. This is due to the fact that greater are the number of Cl atoms, greater is the -I effect and hence greater ionisation as well as stability of conjugate anion.



Acetic acid
pKa = 4.76



Chloroacetic acid
pKa = 2.87



Trichloroacetic acid
pKa = 0.64

Atoms or functional groups that are electron donating (hydrocarbons, anions) have a positive inductive effect (+I). These groups can help stabilize positive charges in reactions such as protonation of bases. On the contrary they shall destabilise the anions.

- Bonding order and charge: It is important to consider both the electronegativity and bonding order when analyzing the inductive potential of an atom.

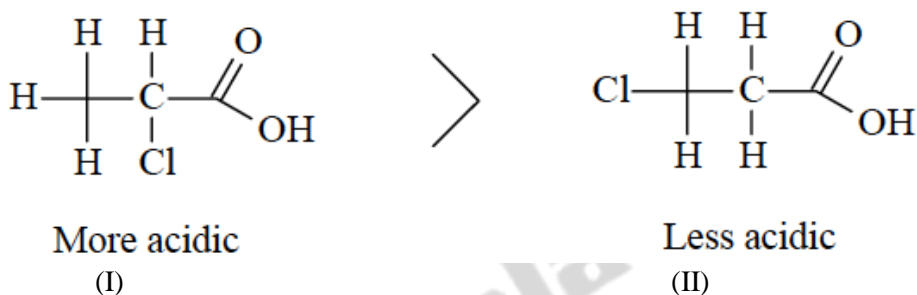
As a rule, negatively charged group shall be electron repelling and hence +I. On the other hand positively charged group shall be electron attracting and hence -I.

For example, oxygen in a hydroxyl group (OH) is electron withdrawing by -I effect because the oxygen atom is relatively electronegative and is uncharged in that bonding arrangement. On the other hand, oxygen in an "alkoxide ion" (O⁻) is electron donating by +I effect because in this bonding order (a single bond to oxygen) it has an "excess" of electron density.

Similarly, -NH₂ is a -I effect group; -NH⁻ is a +I effect group and -NH₃⁺ is a -I effect group.

- Bonding position: The strength of the inductive effect diminishes as we move farther away from the group. The I effect produced by a particular atom or functional group is dependent on its position within a structure.

For example, out of the following acids, (I) is more acidic than (II). This is because the Cl atom is closer to the -COOH group in (I) than it is in (II)



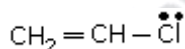
3.2 Mesomeric or Resonance Effect

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



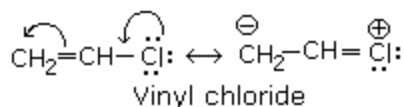
Similarly, if the double, single and a lone pair are present, alternatively, it is also called conjugation e.g. vinyl chloride.



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.



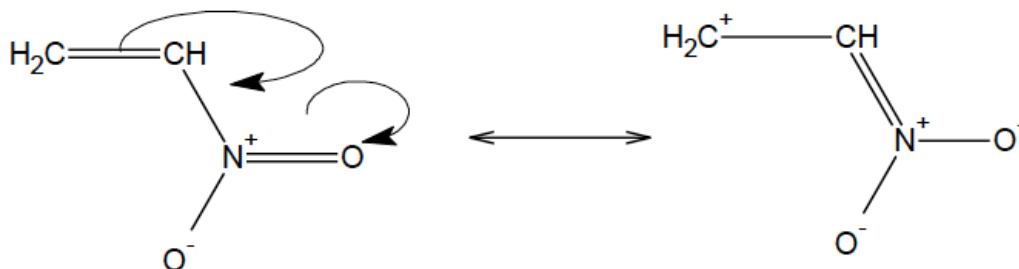
Note that the π electrons are not necessarily present where one would expect them, but are rather delocalised over the entire molecule which gives it extra stability expressed in terms of **delocalisation energy** or **resonance energy**. Also, normally, we find chlorine withdrawing electrons towards 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 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.



The atoms/groups like Cl in which lone pair (or electrons of negative charge) is in conjugation with double or triple bond are electron donating and gain a formal positive charge in the resonating structure in the process and are known to exert +M/+R Effect.

Consider the case of $-\text{NO}_2$ joined to a conjugated system, where the nitro withdraws the conjugated electrons and gives rise to polarization as shown below



The atoms/groups like $-\text{NO}_2$ which are in conjugation with double or triple bond and are electron withdrawing and gain a formal negative charge in the resonating structure in the process and are known to exert -M/-R Effect.

The resonance effect also alters the electron density distribution in the molecule significantly and its direction may be different from the normal inductive effect. In case the two effects are

operating in opposite directions, the relative strengths of the two effects will determine which will dominate. Mesomeric/resonance effect introduces total delocalization of charges while inductive effect introduces partial polarization, hence, **in general M > I**. But there are exceptions to it like when halogens are attached to a conjugated system like benzene, $-I > +R$ (negative inductive effect is greater than resonance effect).

In order to classify most of the groups into +M/+R or -M/-R just look at the following parameters required (given in following table) for the nature of first atom.

+ 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.

How to compare the extent of -M or +M in the comparable groups (having same first atom)?

-M Effect: Here, due to the vacant p orbital on the first atom, the conjugated π electrons are withdrawn towards it. The further attached atoms or groups shall enhance the -M if they also pull by -I or -M effect, but will decrease the -M effect if they are electron donating by +I or +M effect

For example, the order of -M effect between the following groups is

-CHO > -COC₂H₅

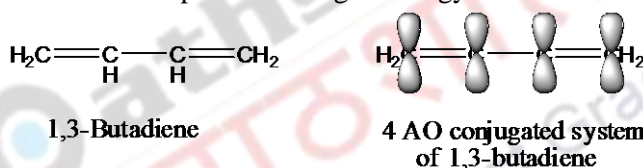
+M Effect: Here, due to the lone pair or –charge in the p orbital of the first atom, the electrons are donated to the conjugated system away from itself. The further attached atoms or groups shall enhance the +M if they push by +I or +M effect, but will decrease the +M effect if they are electron withdrawing by –I or –M effect.

For example, the order of +M effect between the following groups is
 -N(CH₃)₂ > -NH-CH₃ > -NH₂ > -NH-COCH₃

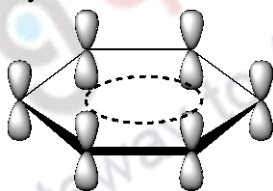
Delocalization may involve:

(i) **Overlap of p orbitals involved in the formation of π bonds (π-π overlap).**

Delocalization of π electrons through π-π overlap occurs in conjugated systems (alternate single and double bonds) i.e. systems where π bonds are separated through a sigma bond only, for example, in 1,3-butadiene, each carbon is sp² hybridized and thus each carbon has a p orbital. These four p orbitals overlap each other to form π bonds. The π bonds are not localized between two carbons, C-1 and C-2, but are delocalized or distributed equally over all four carbons. It is this delocalization that helps in lowering of energy and stabilizes the system.

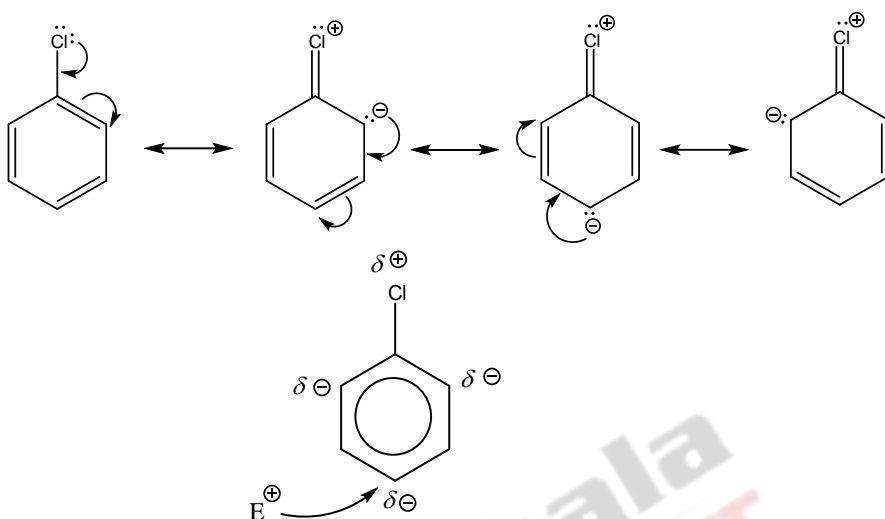


Similarly, in benzene the π electrons are delocalized over all the six carbon atoms.



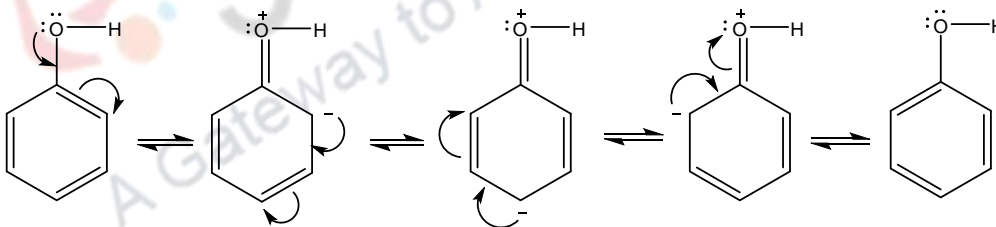
(ii) **Overlap of p orbital of an atom (vacant or filled) with p orbitals involved in π bond formation (p-π overlap)**

Delocalization of π electrons through p-π overlap occurs in a system where p orbital of an atom (vacant or filled) is separated from a π bond through one σ bond only. In other words, the p orbital may contain a lone pair of electron or a single electron or may be vacant, for example, in case of chlorobenzene or vinyl chloride, the lone pair of electrons is present in p orbital of chlorine. Although chlorine is highly electronegative (-I effect), the lone pair present in p orbital of chlorine is in conjugation with the π bond. As a result, it participates in delocalization by giving its lone pair towards the π bonded systems of vinyl or benzene ring and stabilizes the system. The chlorine behaves as an electron donor when it is in conjugation with the π bond.



Halogens are deactivating inductively,
but activate the ring through resonance

In general, halogens are *o*, *p* directing because the electron donating resonance effect is more dominant than the withdrawal through inductive effect of these electronegative elements. The mesomeric effect or resonance effect is a property of substituent or functional group in a chemical compound and is symbolized by the letter **M**. It is a kind of electron redistribution in unsaturated compounds conjugated with electron releasing or electron withdrawing groups or atoms. When the donation of electrons is by a lone pair, or a π system or by the groups or atoms during delocalization, positive mesomeric effect is shown +M (+R effect). Such +M groups contain lone pair of electrons or π bonds for example, -Cl, -Br, -OH, -OR, -SH, -NR, -N₂, aromatics, alkenes, etc.



Positive mesomeric effect in phenol

Acidity of phenol is due to +M effect of -OH group. Mesomeric transfer of the lone pair on the oxygen atom of phenol to the π system of the benzene ring results in several resonance structures with a positive charge on the oxygen atom. This aids the H atom of OH group to leave as proton.

5. Summary

- The atoms/groups which are more electronegative than carbon gain a slight negative charge on them and withdraw the electrons of the carbon chain towards themselves are known to exert **-I Effect** (pronounced as “minus I effect”)
- The atoms/groups which are more electropositive than carbon gain a slight positive charge on them and push the electrons of the carbon chain away from themselves are known to exert **+I Effect** (pronounced as “plus I effect”)
- The atoms/groups in which lone pair(or electrons of negative charge) is in conjugation with double or triple bond are electron donating and gain a formal positive charge in the resonating structure in the process and are known to exert **+M/+R Effect**.
- The atoms/groups which are in conjugation with double or triple bond and are electron withdrawing and gain a formal negative charge in the resonating structure in the process and are known to exert **-M/-R Effect**.