

## Revision Notes

### Class 11 Chemistry

#### Chapter 12 - General Organic Chemistry

#### 1. General Organic Chemistry

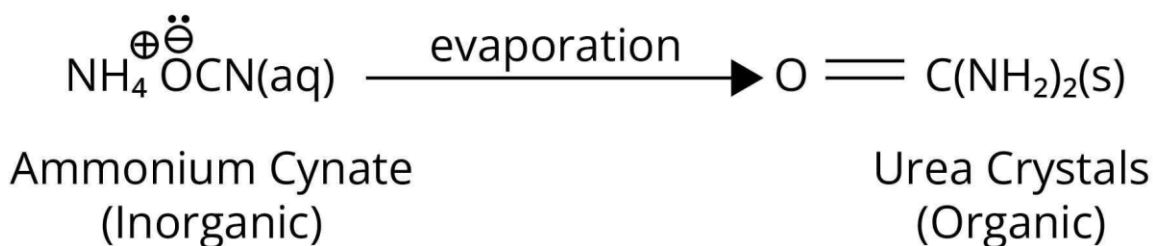
##### 1.1 Introduction

Berzelius coined the term "Organic Chemistry" in 1807 to describe the study of compounds derived from natural sources. This was based on the vitalism theory, which stated that all living systems possessed a 'vital force' that non-living systems lacked. Organic compounds were thought to be fundamentally different from inorganic compounds because they were derived from living natural sources.



Philosophically, the vital force could be thought of as the mysterious force that God instilled in living systems.

Friedrich Wohler became Berzelius' student in 1823. Wohler made a discovery in 1828 that changed the definition of organic chemistry. Wohler carried out the following experiment.



Wohler was able to successfully synthesize an organic compound from an inorganic compound. Many others followed suit, synthesizing organic compounds from inorganic compounds. As a result, the theory of vitalism and the definition of organic chemistry became meaningless.

The presence of carbon, however, was shared by all of the compounds synthesized above. Catenation is a unique property of carbon. Carbon can form long chains and rings with other carbon atoms (self-catenation), as well as with atoms of many other elements in the periodic table (cross-catenation). As a result, carbon can form a wide range of compounds.

The vital force is probably explained by the fact that most of the life-giving and life-sustaining functions are performed by carbon compounds, for example, human tissues and skin are formed by proteins, respiration is possible because of haemoglobin, information in our genes is carried out in the form of DNA/RNA, and so on.

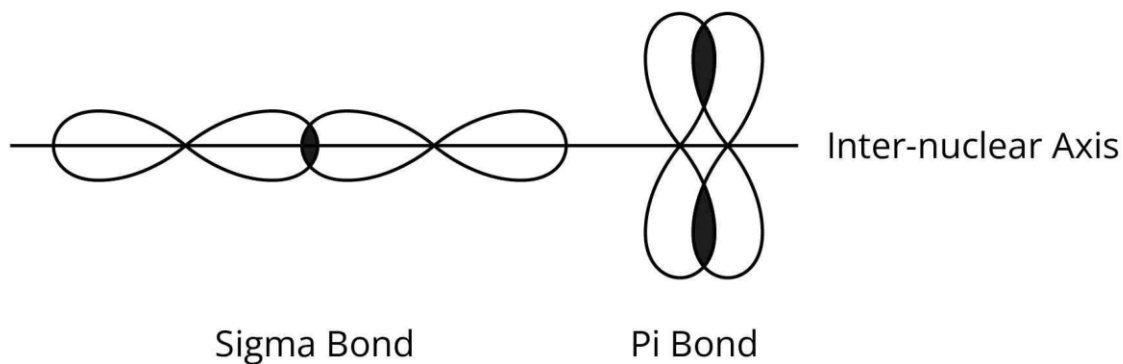
The detailed study of the fundamental concepts and factors that govern the progression and outcome of reactions is known as general organic chemistry.

**Note:**

Before transforming into products, bonds are typically formed and broken in a series of discrete steps. The mechanism of the reaction is a detailed sequential description of all the steps.

**1.2 Sigma and Pi bond**

Property	Sigma Bond	Pi Bond
Overlap	Axial/Head-on	Parallel/Lateral/Side-ways
Electron Cloud	Along the inter - nuclear axis	Perpendicular to the inter - nuclear axis
Bond - Strength	Stronger	Weaker



### 1.3 Structural Formulas

Organic chemists use a variety of formulas to represent organic compounds.

#### 1.3.1 Complete Formulas

Lewis structures are used to represent all bond pairs of electrons as a dash (–) in complete formulas. A lone pair of electrons is represented by a pair of dots.

#### 1.3.2 Condensed Formulas

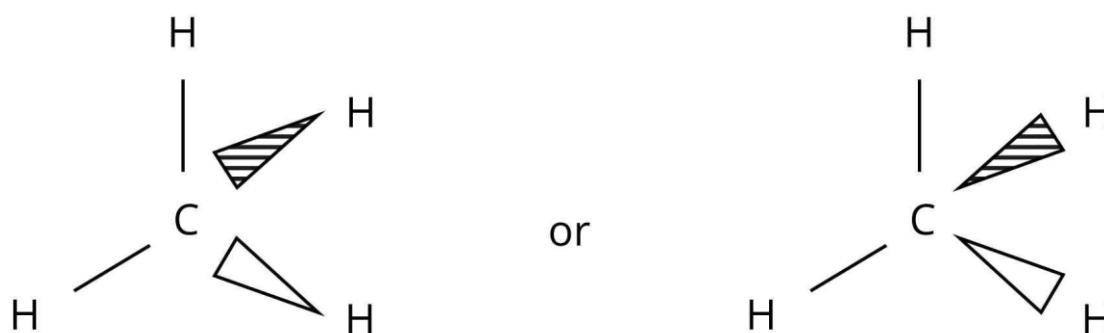
Condensed formulas do not include all of the individual bonds. Each central atom is depicted, along with the atoms that are bonded to it.

#### 1.3.3 Line-Angle Formulas

These are also referred to as skeletal structures or stick figures. Line-angle formulas are frequently used for cyclic compounds and, on rare occasions, non-cyclic compounds. Lines represent bonds, and carbon atoms are assumed to be present where two lines intersect or where a line begins or ends. In most cases, hydrogens are implied in these drawings.

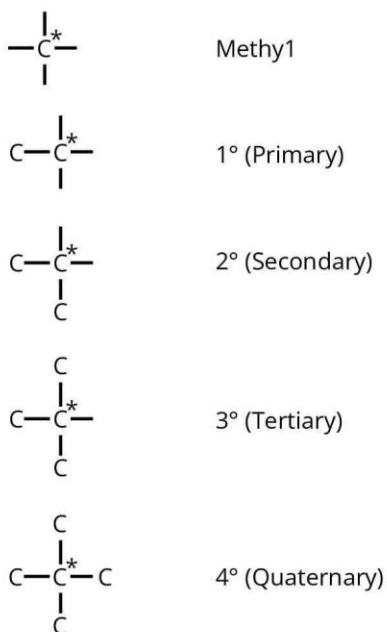
### 1.3.4 Tetrahedral representation

This is the three-dimensional (3-D) representation of molecules in general. Bonds projecting behind the plane (away from the observer) or out of the plane (towards the observer) are denoted by a dashed Wedge or a solid Wedge, respectively. Bonds in the plane of paper are represented by a normal line (—).



## 2. Degrees of Carbon

It is defined as the number of carbons attached to the carbon under study.



## 2.1 Hybridization

Hybridisation is a process in which two or more atomic orbitals of comparable energy in the valence-shell of an atom (central atom of a molecule or ion) mix together and give rise to the formation of new degenerate orbitals known as hybrid orbitals.

## 2.2 Applications of Hybridization

Hybridisation	% Character
$sp^3$	25
$sp^2$	33.3

sp	50.0
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### 2.2.1 Size of Hybrid Orbitals

The size of the hybrid orbital decreases as the percentage of s-character increases. As a result, the size of the hybrid orbital is:  $sp^3 > sp^2 > sp$ .

### 2.2.2 Electronegativity of Hybrid Orbitals

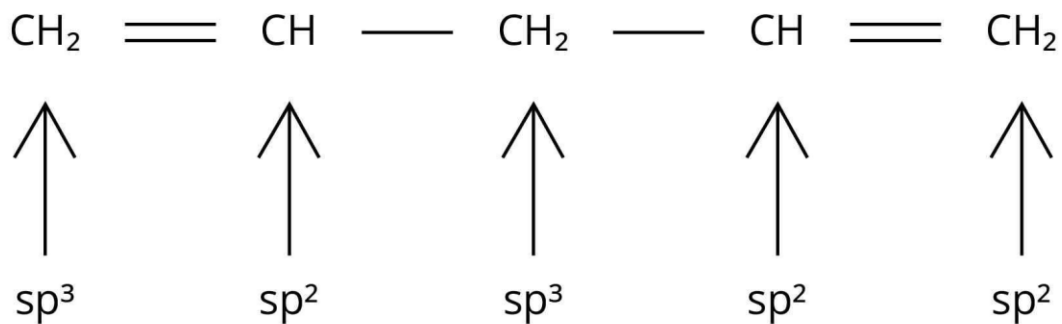
As the percentage of s-character increases, so does the electronegativity of the hybrid orbital. As a result, the EN of the Hybrid Orbital is  $sp > sp^2 > sp^3$

## 2.3 Dienes

Dienes are organic compounds that have two double bonds in them. Dienes are classified into three types: Isolated, Conjugated and Cumulated

### 2.3.1 Isolated Diene

In this case, double bonds are separated by at least one  $sp^3$  carbon.

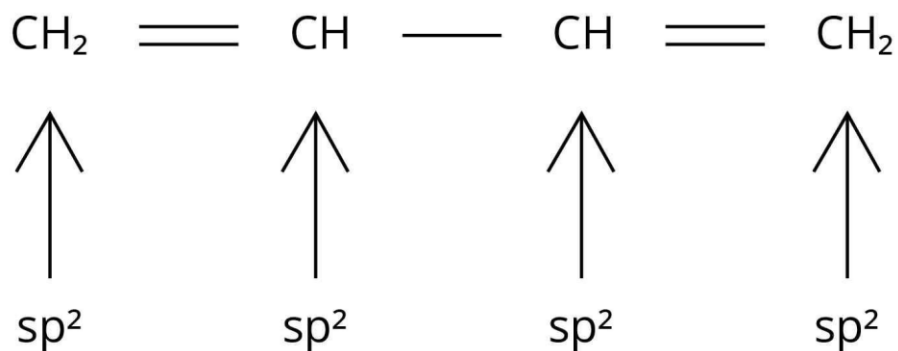


Molecule	$\sigma$	$\pi$	L.P	Hybridization	Shape
$\text{CH}_4$	4	0	0	Tetrahedral	Tetrahedral
$\text{NH}_3$	3	0	1	Tetrahedral	Trigonal Pyramidal
$\text{H}_2\text{O}$	2	0	2	Tetrahedral	V-shape or bent
$\text{CH}_2 = \text{CH}_2$	3	1	0	Trigonal Planar	Trigonal Planar
$\text{CH} \equiv \text{CH}$	2	2	0	Linear	Linear



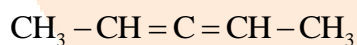
### 2.3.2 Conjugated Diene

A single bond separates two double bonds (or 4  $sp^2$  carbons in a row).



### 2.3.3 Cumulated Diene

Both sets of double bonds are located on the same carbon atom.



### 2.3.4 Stability Diene

The relative stabilities of dienes are arranged in the following order:

Isolated > Conjugated > Cumulated

## 2.4 Commonly occurring forms of carbon

Carbon's most common forms are

- (a) Diamond,
- (b) Graphite
- (c) Carbides.
- (d) Fullerenes
- (e) Charcoal

**Note:**

Each C in a diamond is  $sp^3$ . The solid is tetrahedral.

Each C in graphite is  $sp^2$ . Solid layers with weak van der Waal forces between them.

**3. Breaking of Bonds:**

The bond that is important for the study of reactions in organic chemistry is the covalent bond. As a result, we investigate how a covalent bond can be broken.

- (a) Homolytic Fission
- (b) Fission by Heterolysis

**3.1 Homolytic Fission or Homolytic Cleavage**

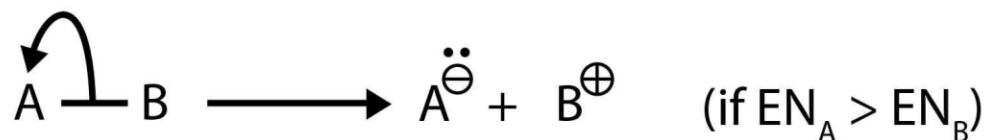
Each atom separates with one electron in this type of bond breaking, resulting in the formation of highly reactive species known as radicals (or free radicals).



Two half-headed or fishhook arrows represent bond breaking. One electron's movement is depicted by a half-headed arrow. Radicals are odd electron species that are neutral.

### 3.1 Heterolytic Fission or Homolytic Cleavage

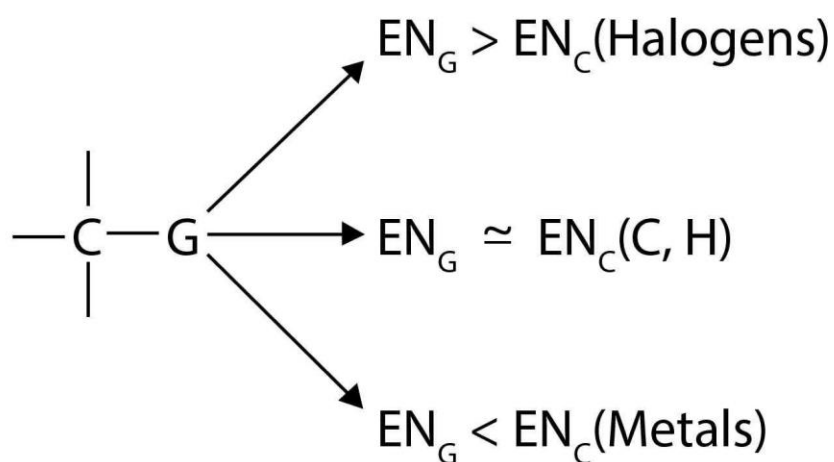
The shared pair of electrons are transferred to the more electronegative part in this type of covalent bond breaking. As a result of this fission, a cation and an anion are formed (ion-pair).



A full-headed arrow represents the bond breaking. A full-headed arrow depicts the movement of two electrons. In organic chemistry, electron movement is always represented by curved arrows, either half-headed or full-headed.

#### 4. Inductive Effect:

When two unlike atoms form a covalent bond, the electron- pair that forms the sigma bond is never shared equally between the two atoms, but is shifted slightly towards the more electronegative species.



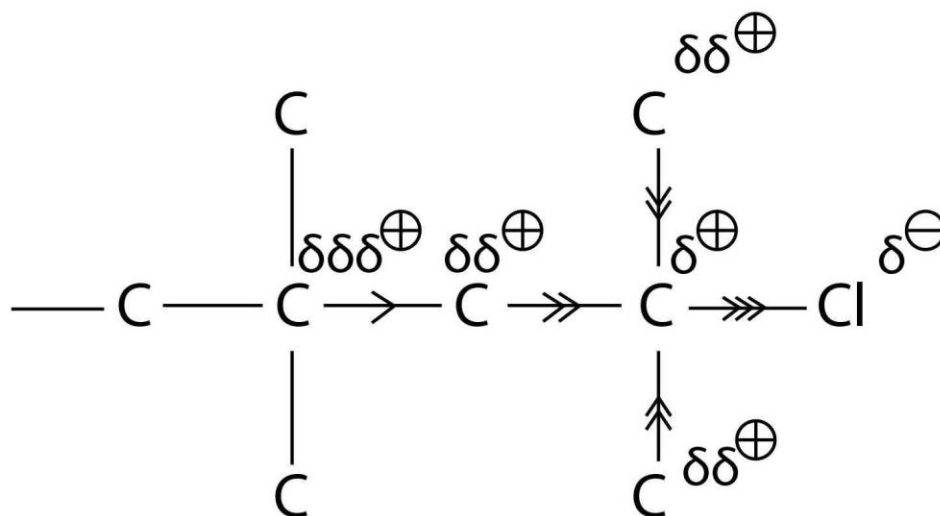
As illustrated, there are three types of groups/atoms that can be attached to carbon. Although C is more electronegative than H, the difference in electronegativity is small, and the bond is generally considered non-polar.

#### 4.1 Nature of Inductive Effect:

The inductive effect is a permanent effect that is directly proportional to the dipole moment. It is a minor effect because electrons are only shifted via sigma bonds.

#### 4.2 Effect of Branched carbon chain

An example of the operation of the inductive effect has been marked, which is self-explanatory.



### 4.3 Electron Donating and Electron withdrawing Groups

The inductive effect can be caused by a single atom or by a group of atoms. The relative inductive effects are measured in relation to hydrogen. Electron-donating groups (EDG) or electron-releasing groups (ERG) are those that donate electrons to the carbon chain and are said to exert a +I effect. Electron-withdrawing groups (EWG) are those that withdraw electrons from the carbon chain and are said to exert the -I effect.

#### Important:

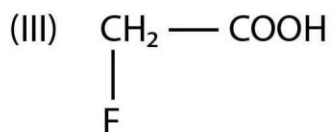
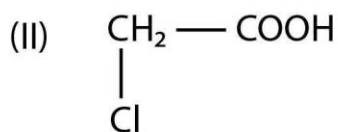
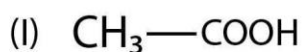
1. I.E. of alkyl groups :  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3 -$
2. In general, the number of carbons in an alkyl group increases the +I effect.
3. To solve the problem, we assume that the electronegativity of  $sp$  hybridized carbon is greater than that of  $sp^3$  hybridized nitrogen.

## 4.4 Applications of Inductive Effect

### 4.4.1 Effect on Acidic/Basic Strength

EWG raises acidic strength while decreasing basic strength. ERG reduces acidic strength while increasing basic strength.

**Example:** Compare the acidic strength:



**Solution:** An alkyl group will only donate if no other EWG is present. As a result, electron withdrawing groups such as  $-\text{CH}_2\text{Cl}$  and  $-\text{CH}_2\text{F}$  form.

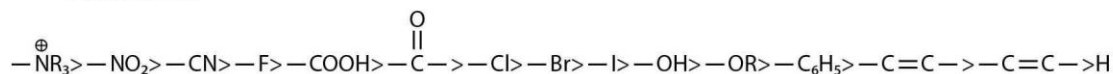
Order of Acidic Strength  $\text{III} > \text{II} > \text{I}$

### 4.4.2 Effect of Distance

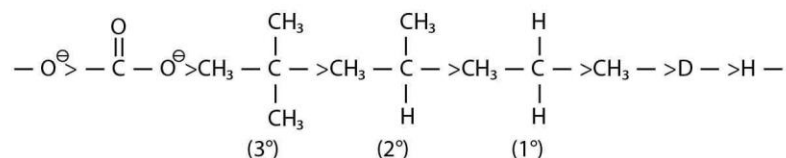
The inductive effect decreases as the ERG/EWG moves away.

Series of +I and -I groups in order of their strength

-I Series (EWG)



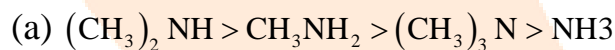
+I Series (EWG)



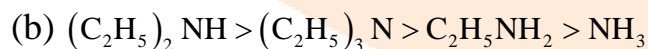
### 4.4.3 Basicity of Amines

The order in gaseous or liquid phase is:  $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$

To ascertain the basic strength of amines in aqueous solution. We must consider the inductive effect, the solvation effect, and the steric hinderance. The order of basic strength is thus experimental in the aqueous state because we cannot prioritize the stability provided by any single factor. For the aqueous phase, two results are critical:



i.e.  $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$  (R = CH<sub>3</sub>)



i.e.  $2^\circ > 3^\circ > 1^\circ > \text{NH}_3$  (R = C<sub>2</sub>H<sub>5</sub>)

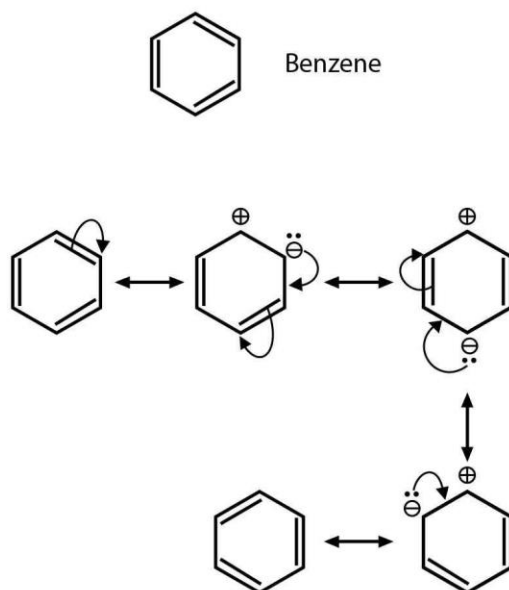
## 5. RESONANCE



Simple Lewis structures are commonly used to represent molecules, but some molecules cannot be represented by a single Lewis structure. As a result, the concept of resonance was discovered. The delocalization of electrons (generally pi electrons) is referred to as resonance.

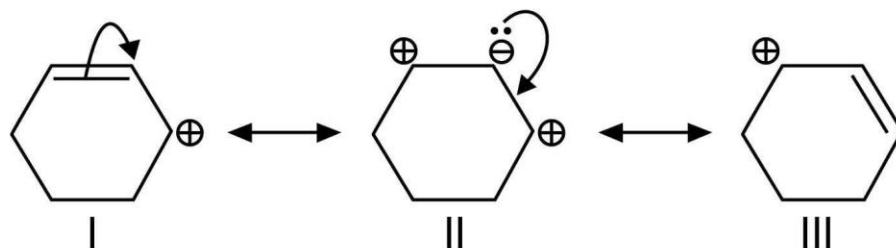
## 5.1 Conjugated Systems

### 5.1.1 Pi alternate Pi



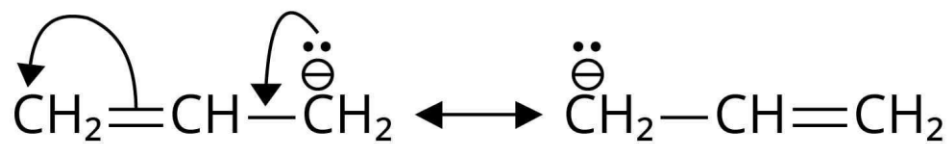
### 5.1.2 Pi alternate Positive Charge

#### Example - 4



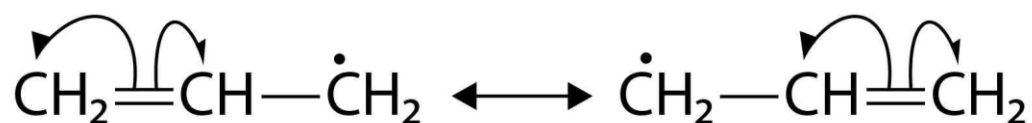
### 5.1.3 Pi alternate Negative Charge

#### Example - 5



### 5.1.4 Pi alternate Odd Electron

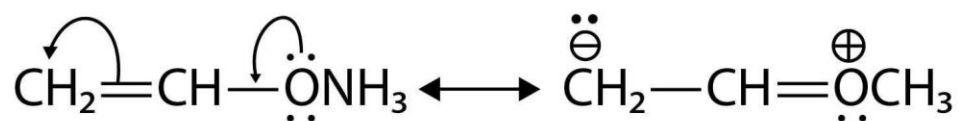
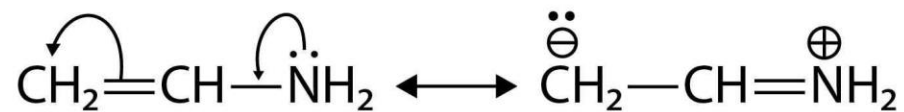
#### Example - 6



### 5.1.5 Pi alternate Lone Pair

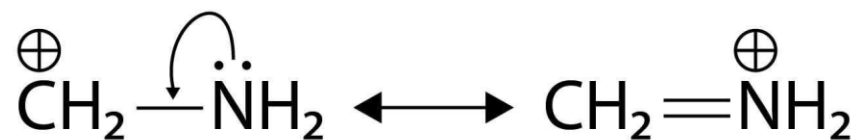
Since lone pair and negative charge are treated similarly, this case is similar to 'pi alternate negative charge'.

#### Example - 7



### 5.1.6 Lone Pair and Positive Charge on Adjacent Atoms

#### Example - 8



## 5.2 Rules for Validity of Lewis Structures

Rule 1: All Lewis structures must adhere to the Lewis octet rule.

Rule-2: Atoms in all resonating structures must be in the same position. Only the electrons are in motion.

Rule-3: All resonating structures must have the same number of paired and unpaired electrons, that is, the sum of bond pairs and lone pairs must be constant.

Rule-4: All of the atoms in a molecule that participate in resonance must be coplanar. This is required for effective p orbital overlap and electron delocalization, as in buta-1,3-diene.

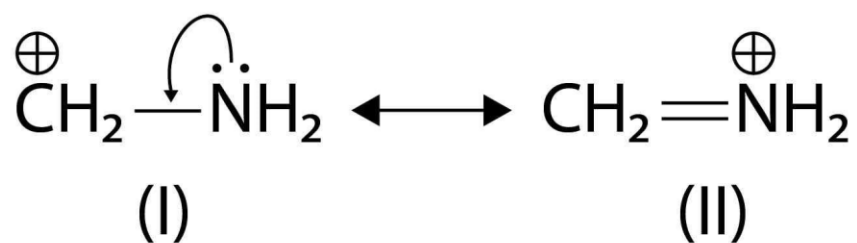
## 5.3 Criteria for Major/Minor Contributors

The following criteria, in the following order, can be used to compare resonance forms:

1. Use as many octets as you can (a neutral molecule is always more stable in which its octet is complete).
2. Attempt to form as many bonds as possible.
3. The presence of a negative charge on a more electronegative atom is stable.
4. The separation of charges
  - (a) Similar charges - Keep them as far away from each other as possible to reduce repulsion and instability.
  - (b) Opposite charges should be kept as close together as possible to maximize attraction and stability.

Example - 9

Which of the following structures is more stable?



Solution: II is more stable as all the octets are complete.

## 6. MESOMERIC EFFECT

The permanent polarization caused by a group conjugated with a pi bond or a set of alternate bonds is transmitted through the system's electrons, resulting in a different electron distribution in the unsaturated chain. Mesomeric Effect or Resonance Effect refers to the redistribution of electrons in unsaturated compounds conjugated with electron-releasing or electron-drawing groups (or atoms). The dipole moment indicates that this effect is permanent.

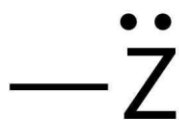
### 6.1 Electron-Releasing and Electron-Withdrawing Groups

The M or R effect refers to groups that release or withdraw electrons via resonance.

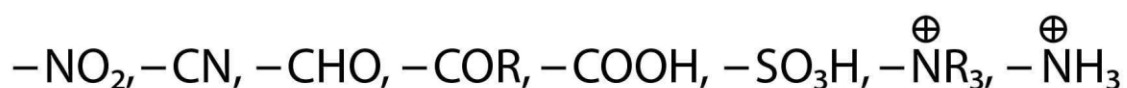
### 6.1.1 Electron-Releasing Groups (+R or +M effect)



The atom connected with the conjugated system has a lone pair to donate, which is shared by all of the groups listed. As a result, a generic representation can be represented.



### 6.1.2 Electron-Withdrawing Groups (-R or -M effect)



All of the groups listed have one thing in common: the atom connected with the conjugated system has a bond with another more electronegative atom that either withdraws electrons or directly has a positive charge on them. As a result, a generic representation can be represented - Y=Z ( $\text{EN}_Z > \text{EN}_Y$ )

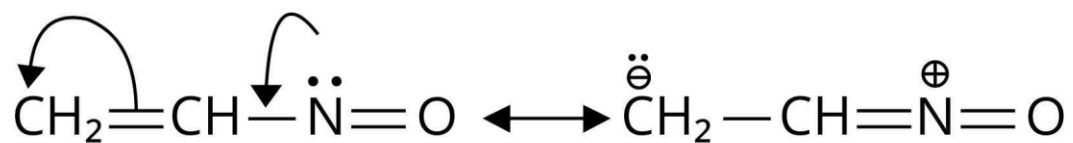
### 6.1.3 Dual Behaviour

As shown, some groups are both electron-releasing and electron-drawing.

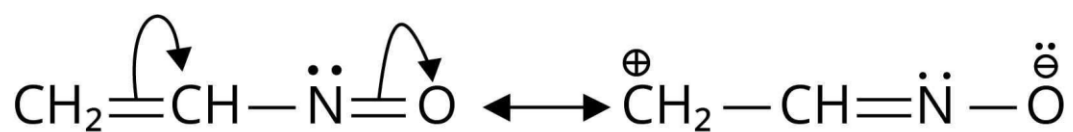
#### Example - 12

As electron releasing group





As electron withdrawing group



Which behaviour dominates and which is used in a particular context will be discussed later in Electrophilic Aromatic Substitution later.

Resonance Effect does NOT depend upon distance unlike inductive effect.

## 6.2 Applications of Mesomeric Effect

### 6.2.1 Effect on Acidic Strength of Carboxylic Acids and Phenols

The resonating structure of carboxylic acid results in a charge-separated structure that is less stable than the charge-delocalized carboxylate ion. As a result, carboxylic acid easily loses proton (H) to form a carboxylate ion.

Similarly, in phenol, resonance causes charge separation, which increases the rate of ionization and results in the formation of phenoxide ion, which is stabilized by charge delocalization.

### 6.2.2 Effect on Reactivity of Carboxylic Acid Derivatives

A typical nucleophilic reaction is represented as: The stronger is the bond between C and Z, the more difficult it is for a nucleophile to break a bond and therefore, lower reactivity. Reactivity order of carboxylic acid derivatives towards nucleophilic acyl substitution is: Acyl Chloride > Acid Anhydride > Ester > Amide

### 6.2.3 Effect of ERG/EWG on Acidic/Basic Strength

EWG increases the acidic strength and decreases the basic strength. ERG decreases the acidic strength and increases the acidic strength.