School of Basic and Applied Sciences

Course Code : BSCC2001

Course Name: Organic Chemistry I

# Electronic displacements

## Part-1

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Program Name: B.Sc. (H) Chemistry

# Learning outcome

After studying this lecture, you shall be able to:

- Explain different types of electronic displacements in covalent bonds: inductive effects, resonance, hyperconjugation, and electromeric effects
- Discuss how these effects influence molecular stability and chemical reactivity.

## Introduction to Electronic Displacements in Covalent Bonds

- An electronic displacement occurs when electrons move toward one side or part of a molecule. Electronic displacements are often responsible for the chemical reactivity of some molecules and the relative inertness of others.

There are four different types of electronic displacements to consider:

- Inductive effect
- Mesomeric effect
- Hyperconjugation
- Electromeric effect

## ❖ INDUCTIVE EFFECT

- **“The shifting of shared pair of electrons in a covalent bond towards more electronegative atom is called Inductive effect.”**
- It is a permanent effect which is present in all dipolar molecules.

**Or**

**“It is the permanent partial displacement of bonded electron pair along a saturated chain due to the presence of electron withdrawing or electron releasing group present at the end of the chain.”**

- It involves the displacement of **sigma (σ) electrons**.
- This displacement is effective only up to $C_4$ carbon atom in a carbon chain.
- Inductive effect is represented by the symbol → the arrow pointing towards the more electronegative substituent. With an electron releasing substituent X, the inductive effect will be represented as follows–

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

With an electron donating substituent Y, the inductive effect will be reversed and may be represented as –

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

# Types Of Inductive Effect

It is of two types

**+I Effect**

When displacement of electrons takes place away from the group.

Some common groups which cause **-I effect groups (electron attracting)** are given below–

$NO_2 > F > COOH > Cl > Br > I > OH > C_6H_5$

**−I Effect**

When displacement of electrons takes place towards the group.

Some common groups which cause **+I effect groups (electron releasing)** are given below–

$(CH_3)_3C– > (CH_3)_2CH– > CH_3CH_2– > CH_3–$

# APPLICATIONS OF INDUCTIVE EFFECT

## (i) DIPOLE MOMENT

Greater the inductive effect more will be the dipole moment in the molecule since inductive effect leads to a dipolar character in the molecule. For example Dipole moment of

$$CH_3{-}F > CH_3{-}Cl > CH_3{-}Br > CH_3{-}I$$

Since –I effect of F > Cl > Br > I

## (ii) REACTIVITY OF ALKYL HALIDES

Due to the presence of C–X polar bond in alkyl halides, They are more reactive than the corresponding alkanes. Reactivity increase with increase of (+I) effect, we know (+I) effect of–

$$R_3C > R_2CH > RCH_2$$

## (iii) STRENGTH OF CARBOXYLIC ACIDES

The strength of acid depends upon the tendency of an acid to release proton. If an atom or group help in release proton, increase strength of acid. i.e. Groups having −I Effect strengthen the acidity.

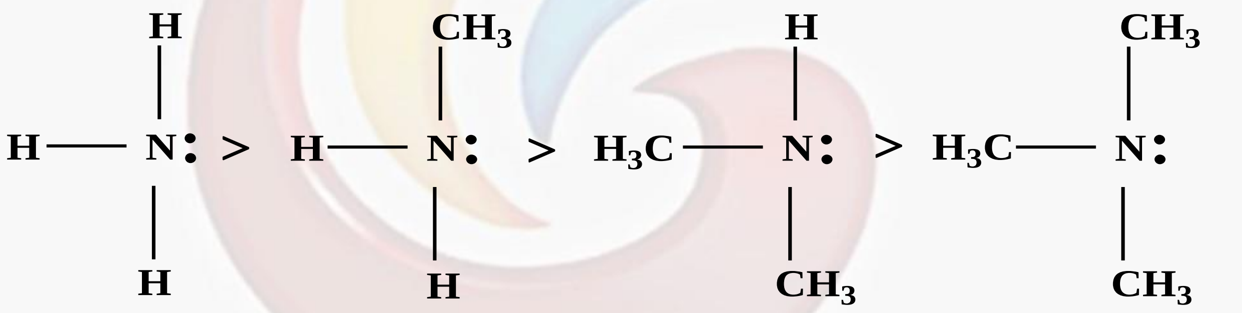
$$\textbf{+I group} \ \alpha \ \frac{\textbf{1}}{\textbf{Acid Strength}}$$

$$\textbf{–I group} \ \alpha \ \textbf{Acid Strength}$$

For example, acidic strength order is

$F–CH_2COOH > Cl–CH_2COOH > Br–CH_2COOH > I–CH_2COOH > H–CH_2COOH$
and $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

## (iv) BASIC STRENGTH OF AMINES



$$NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$$

**Ammonia** **Primary Amine** **Secondary Amine** **Tertiary Amine**

But due to steric hindrance effect the correct order is as follows–

**Secondary Amine** > **Primary Amine** > **Ammonia** > **Tertiary Amine**

## ❖ MESOMERIC EFFECT

- This effect involves **permanent displacement** of electrons in the organic molecules.
- This effect is transmitted through the **π-electrons** of multiple bonds in the carbon chain of the molecule.
- **It operates only in those systems which have an extended chain with conjugate π-bonds.**

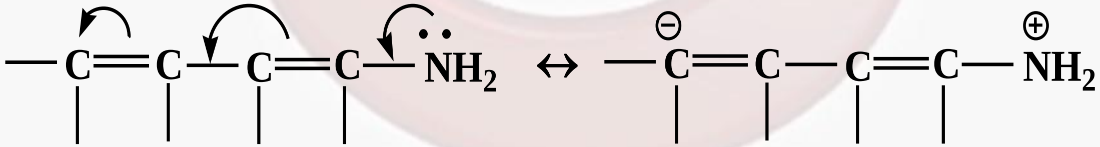
When an electron donating or withdrawing group is conjugated with a conjugated system, the electron displacement is transmitted through π electrons in the chain.

# TYPES OF MESOMERIC EFFECT

Mesomeric effect is of two types–

## (A) +M EFFECT

It involves the transfer of electron pairs **away from the atom or group** attached. Such groups have lone pair of electrons and furnish the electron pair of conjugation with an attached unsaturated system, for example. –OH, –OR, –SH, –SR, $–NH_2$, $–NR_2$ etc. groups have +M effect. The presence of $–NH_2$ group at the end of a conjugate π -bond system brings about following displacement of electrons.



## (B) –M EFFECT

It involves the transfer of electron pair **towards the atom or group** attached. Group such as >C=O, $–NO_2$, –CN, $–SO_3H$ etc. have –M effect due to the presence of highly electro negative atom like O or N. for example,

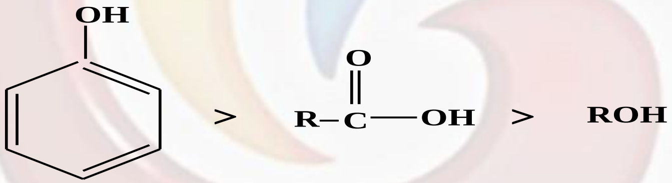
# APPLICATIONS OF MESOMERIC EFFECT

## (i) DIPOLE MOMENT

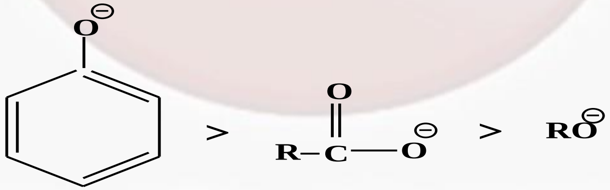
Dipole moment of $CH_3\text{-}CH_2\text{-}Cl > CH_2\text{=}CH\text{-}Cl$ due to resonance in vinyl chloride.

## (ii) STRENGTH OF ACIDS

Acidic strength of



because the stability of corresponding conjugate bases is in the order-



**Phenoxide ion** **Carboxylate ion** **Alkoxide ion**

This is due to the more resonance stabilization of phenoxide ion.

## (iii) STRENGTH OF BASES

Base strength of $RNH_2 > NH_3 > C_6H_5\text{-}NH_2$ . It is due to (+I) effect of R in $R \rightarrow NH_2$. Thus lone pair is more easily available. But in $C_6H_5\text{-}NH_2$ phenyl group has (—M effect). Hence the lone pair present at the nitrogen delocalized in the ring by resonance, so it is not free for protonation leading to decrease of strength of aniline.

## References

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# Thank You