Paper II- Organic Chemistry

Chapter-I
Structure and Bonding

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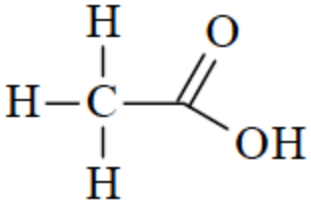
Induction or the inductive effect of an atom or a group is a function of that group's following parameter:

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

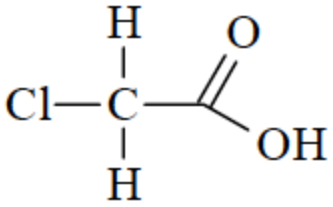
Electronegativity: Electronegative atoms like nitrogen, halogens, oxygen, etc. may have a negative inductive effect (-I), depending upod their bonding order.

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 readicals.

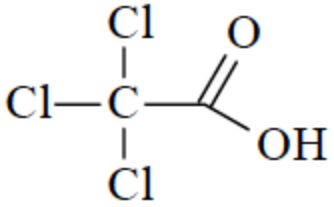
-I groups have a stabilizing (enhancing) effect on the ionization of acids. For example, out of acetic acid, chloroacetic acid and trichloroacetic acid as shown below, tricholoroacetic acid is strongest acid. This is due to the fact that greater are the number of Cl atoms, greater is the –I effect and 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, $-NH_2$ is a –I effect group; -NH- is a +I effect group and $–NH_3+$ 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 it's 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)

More acidic

(I)

Less acidic

(II)