CHAPTER

13

Inductive Effect

ELECTRON DISPLACEMENT EFFECTS IN COVALENT BONDS

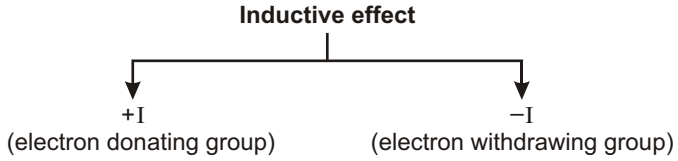
- Electron shifting in a covalent bond is known as electron displacement effects.
- Electron displacement effects are of mainly 3-types :
  (i) Inductive effect
  (ii) Resonance
  (iii) Hyperconjugation

INDUCTIVE EFFECT

Inductive effect is the polarization of shared pair (covalently bonded pair) of electrons towards more electronegative atoms. Let us consider a molecule.

- A permanent effect
- The electrons never leave their original atomic orbital.
- Operates through s bonds
- Polarisation of electrons is always in single direction.
- Its magnitude (*i.e.,* electron withdrawing or donating power) decreases with increase in distance.
- There occurs partial movement of shared pair of electrons.
- This is a very weak effect.
- This effect is additive in nature, *i.e.* two electronegative atoms exert greater induction effect than one atom of greater electronegativity from the same position.

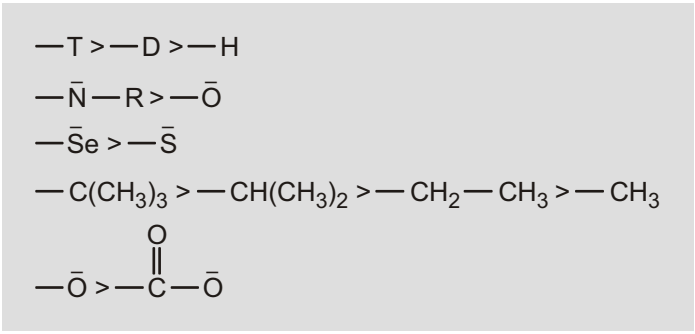
Inductive effect showing groups can be divided into 2 types.



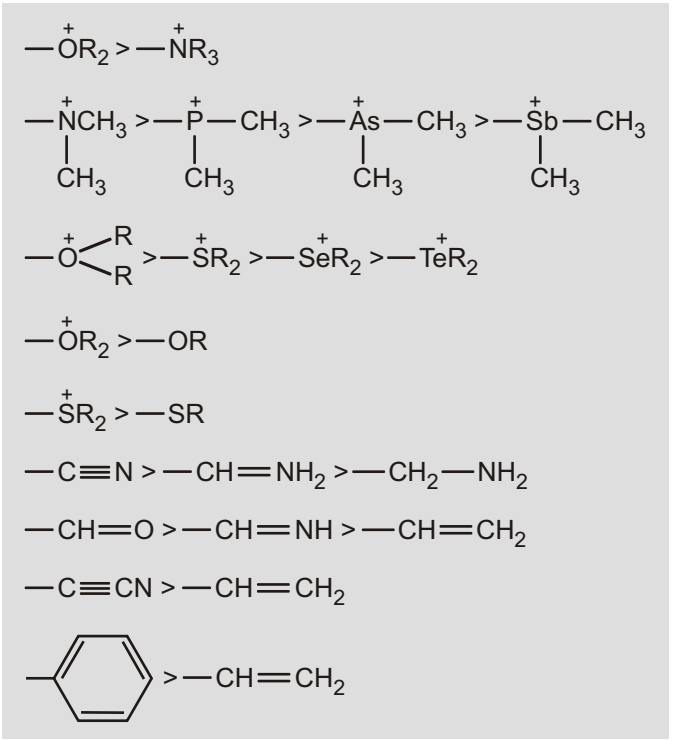
INDUCTIVE EFFECTS

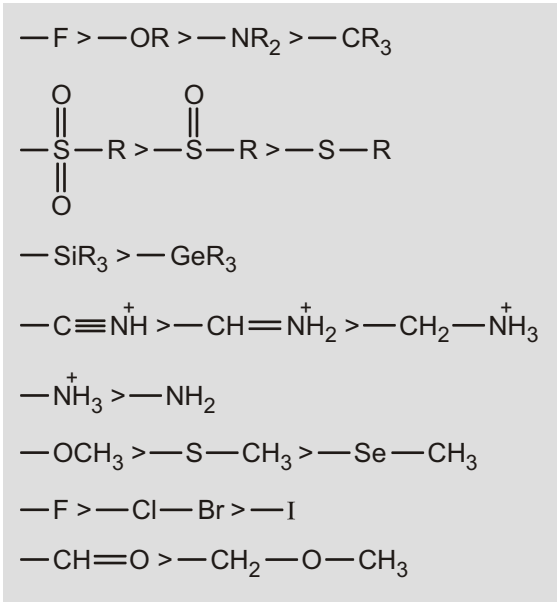
Inductive Effect (I Effect of Groups)

Electron donating groups show positive inductive effect (+I). For example,



Electron withdrawing groups show negative inductive effect (–I). For example,





APPLICATION OF INDUCTIVE EFFECT

Carbocations, carbanions and carbon radicals :

Carbocations, which include carbenium and carbonium ions, contain a positive charge on carbon. Carbenium ions have three bonds to the positively charged carbon (*e.g.* Me_3C^+).

☞ Carbenium ions ($R_3C^{\oplus}$) are generally planar and contain an empty *p* orbital. They are stabilised by electron-donating groups (R is I and/or +M), which delocalise the positive charge; +M groups are generally more effective than I groups.

(a) Stability of Alkyl Carbocation :

Stability of alkyl carbocation I effect

If the I effect will increase then magnitude of positive charge on carbon will decrease so it will stabilised carbocation.

Stability increases →

$$\overset{\oplus}{C}H_3 < CH_3-\overset{\oplus}{C}H_2 < CH_3-\overset{\oplus}{C}H-CH_3 > CH_3-\overset{\oplus}{C}H_3 < \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{}}}}\!\!-\overset{\oplus}{C}$$

(b) Stability of Alkyl Carbanion :

Stability of alkyl carbanion I effect

For examples :

$$\overset{\ominus}{C}H_3 > CH_3-\overset{\ominus}{C}H_2 > CH_3-\overset{\ominus}{C}H-CH_3 > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{}}}}\!\!-\overset{\ominus}{C}-CH_3$$

(c) Stability of Alkyl and Vinyl Carbocation :

$CH_3-\overset{\oplus}{C}H_2$ (sp^2-hybrid carbon; sp^2-hybridised carbon is less EN) — more stable

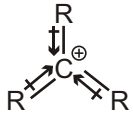
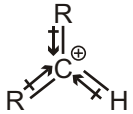
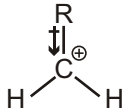
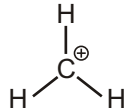
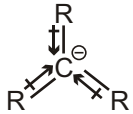
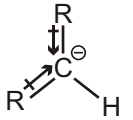
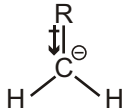
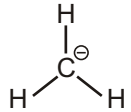
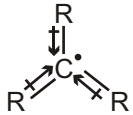
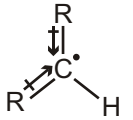
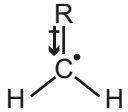
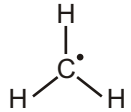
$> CH_2=\overset{\oplus}{C}H$ (sp-hybrid carbon; sp-hybrid carbon is more electronegative) — less stable

(d) Stability of Alkyl, Vinyl and Acetylenic Carbanions :

$CH_3-\overset{\ominus}{C}H_2$ (sp^3-hybrid carbon) (Least stable) > $CH_2=\overset{\ominus}{C}H$ (sp^2-hybrid carbon) (more stable) > $CH\equiv\overset{\ominus}{C}$ (sp-hybrid carbon) (most stable)

ORDER OF STABILITY

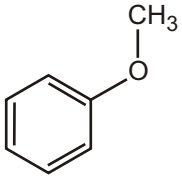
The order of stability of carbocations, carbanions and carbon radicals bearing electron donating (I) alkyl groups, R, is as follows. (Free radicals will be formed by homolytic fission)

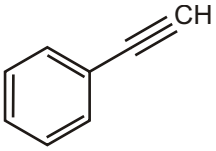
	Tertiary three +I groups		**Secondary** two +I groups		**Primary** one +I groups		**Methyl** no +I groups
Cation Stability		>		>		>	
Anion Stability		<		<		<	
Radical Stability		>		>		>	

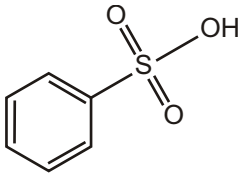
Carbanions can be stabilised by electron-withdrawing groups (I, –M groups), whereas carbocations can be stabilised by electron-donating groups (I, +M groups).

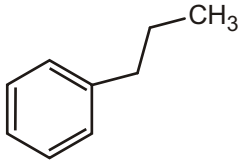
Solved Example

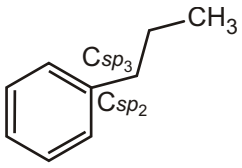
- Which of the side chain attached to benzene ring have I effect

(i) 

(ii) 

(iii) 

(iv) 

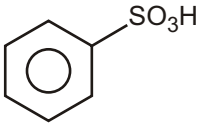
Sol. 

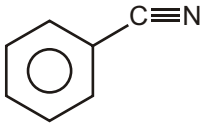
I effect Due to E.N. difference.

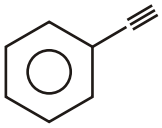
E.N. order : c_{sp} c_{sp_2} c_{sp_3} due to % s-character.

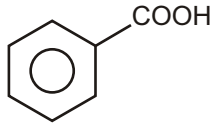
Solved Example

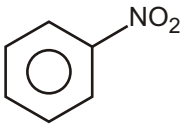
- '*X*' = Number of compound having I group directly attached to benzene.

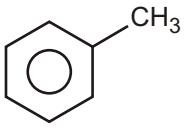


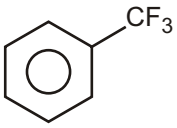


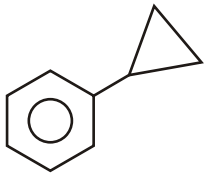


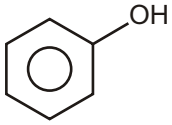


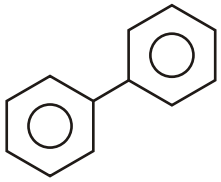




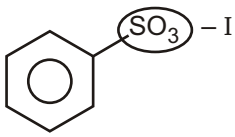


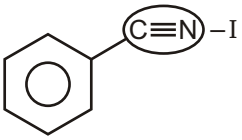


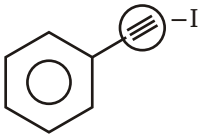


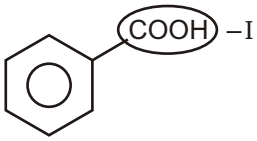


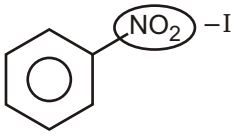
Find the value of '*X*' ?

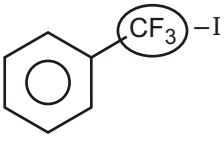
Sol. 

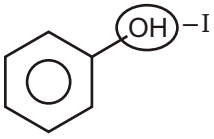










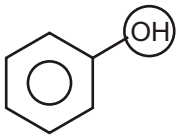


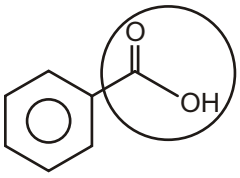
So x 7

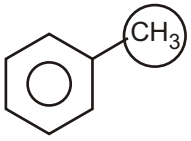
EXERCISE

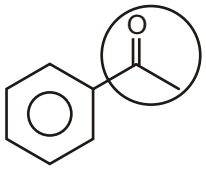
WORK SHEET

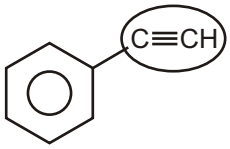
1. Identify I or I effect which is present by circled group ?

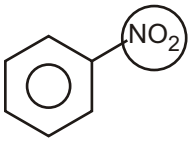
(a) 

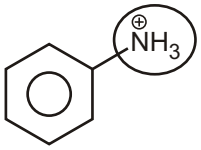
(b) 

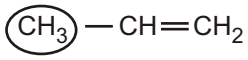
(c) 

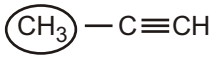
(d) 

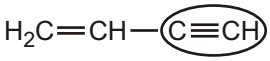
(e) 

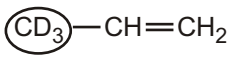
(f) 

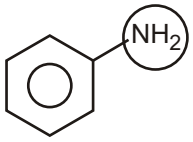
(g) 

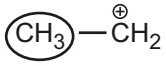
(h) 

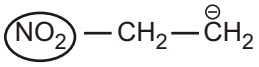
(i) 

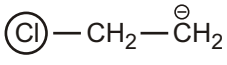
(j) 

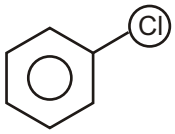
(k) 

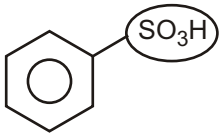
(l) 

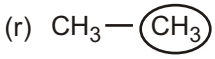
(m) 

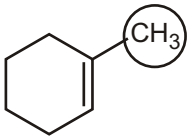
(n) 

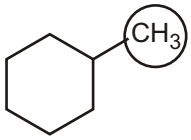
(o) 

(p) 

(q) 

(r) 

(s) 

(t) 

Answers

Work Sheet

1. (a) I	(b I	(c) I	(d) I
(e) –I	(f) –I	(g) I	(h) I
(i) I	(j) I	(k) I	(l) I
(m) I	(n) I	(o) I	(p) I
(q) I	(r) None	(s) I	(t) None

(Note : Inductive effect does not operate in alkanes)

❑❑❑