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## Pharmaceutical Organic Chemistry-I. (PC 111)

# Lecture 2

# Theories of electron displacement inside organic molecules.

## The Inductive & Mesomeric effects

## I & M Effects

**-The electron displacement through covalent bonds determines the polarity of the molecule which in turn affect the physical properties (*solubility and volatility*) and chemical properties of the organic compound.**

**-Electron displacement of the covalent bonds inside organic molecules is described in terms of two effects: *The Inductive and Mesomeric effects***

# The Inductive Effects [ I –Effect]

**Definition:** ***The polarization of the electron density of a σ (sigma)-bond caused by the electronegativity of a nearby atom***

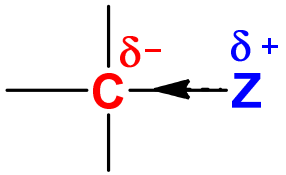
**Or** ***Induction of charge due to less or more electronegative element .***

**Or** ***The electrons are attracted towards the most electronegative atom. The direction of polarization is shown by placing an arrowhead midway along the line of σ bond.***

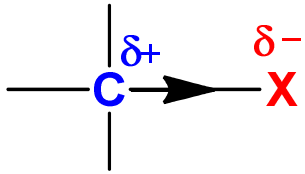
**+ I Groups**
which attract electrons less strongly than Hydrogen.
e.g. **Electron Donating Groups**
Ex: **Alkyl Groups**

**Hydrogen**
**+I effect** ← → **–I effect**
**Zero Effect**

**- I Groups**
which attract electrons more strongly than Hydrogen.e.g.
**Electron Attracting Groups**
Ex: **-$NO_2$, -COOH**




**Z has a +I effect**




**X has a –I effect**

**Z = R ( Alkyl or aryl grous), metals ( e.g Li or Mg)**

**X = Br , Cl , $NO_2$ , OH, OR, SH, SR, $NH_2$, NHR, $NR_2$, CN, COOH, CHO, COR.**

**when the atom (Z) is less electronegative than carbon, electrons are attracted to carbon atom**

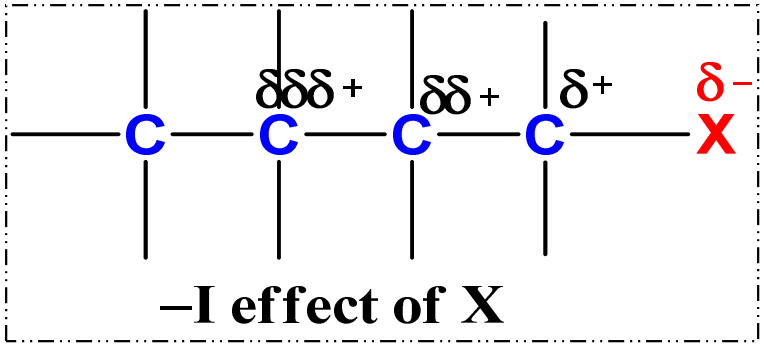
## Characters of Inductive Effect:-

***a.*** *Electron displacement is supplied* ***from atom to atom along a chain without the transference*** *of any electron from one atom to another .*

***b.*** *Changes in polarity produced by such a displacement are all in* ***the same direction.***

***c.*** *The effect becomes* ***progressively less*** *as it proceeds away from the atom or group producing it. It occurs till* ***four carbon atom*** *and* ***maximum at first carbon*** *atom due to closeness impact*

***d.*** *It is a* ***polarization effect, not a polarizability effect****, and the dipoles it produces are present in molecules which are in their normal state.*



# The Mesomeric Effects [ M–Effect]

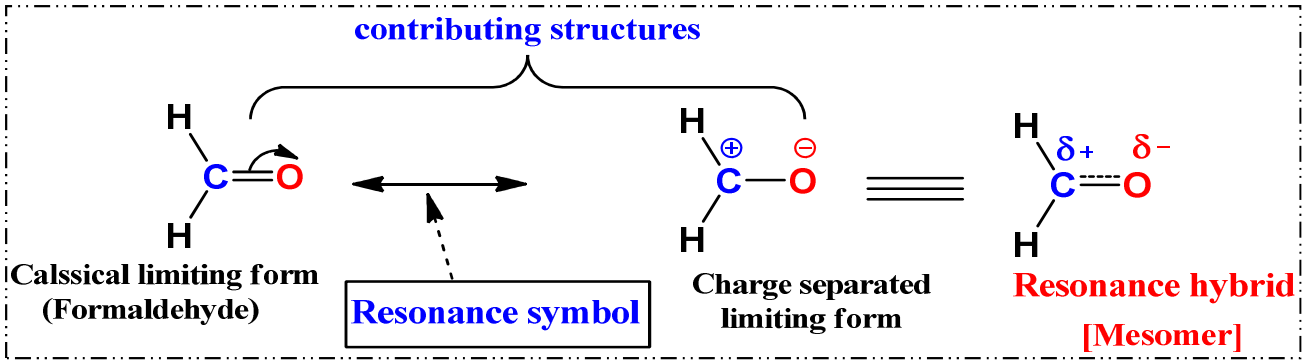
# [ Mesomerism ] = [ Resonance ]

***Definition*: The re-distribution of electrons which takes place in *unsaturated* and *especially in conjugated systems via their π-orbitals*.**

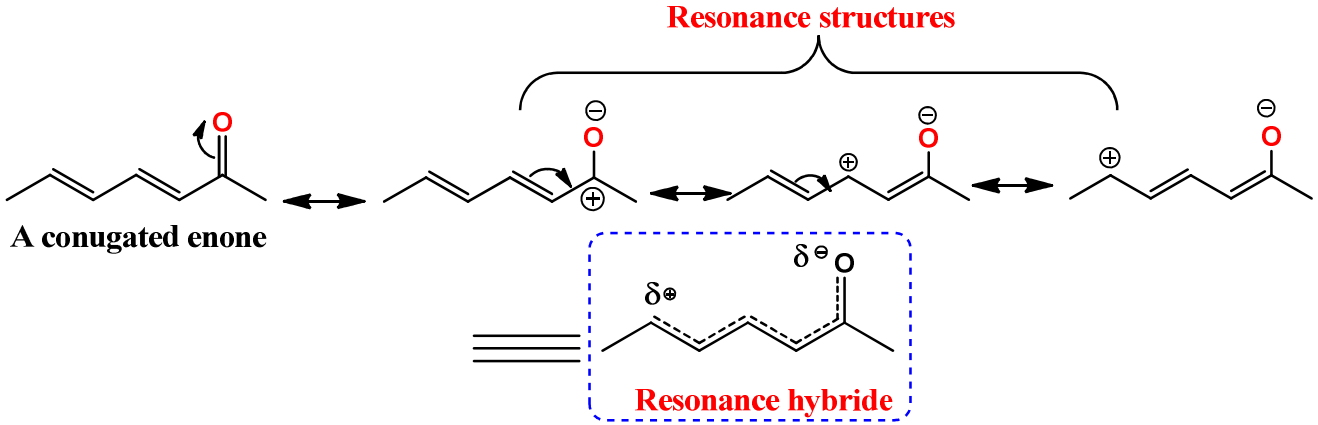
Or *The displacement of electrons at any number of **p** atomic orbitals*

- The direction of ***mesomeric*** displacement is shown by a ***curved (curly) arrow***

-The interrelation of ***limiting forms*** is depicted by a resonance symbol, ***double headed arrow***

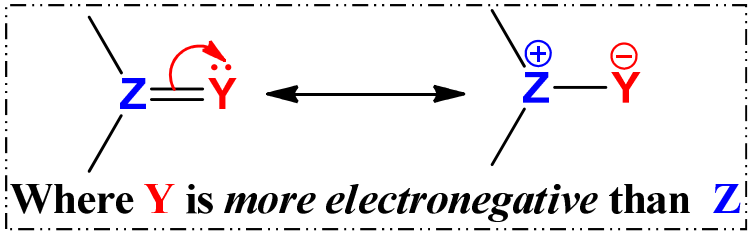



-None of the ***resonance structures (resonance contributors)*** will be a **correct representation** for the molecule. The actual molecule is a **hybrid of these hypothetical resonance structures**.

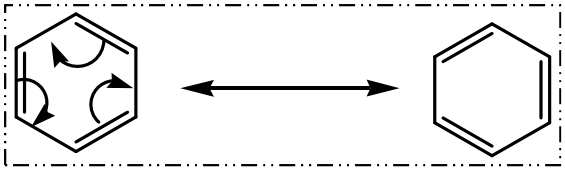


# There are 5 patterns in which displacement of electrons can take place by Resonance.

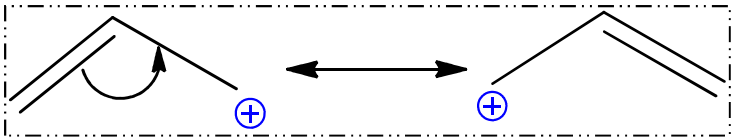
**1.** A **π**-bond between two atoms where one of these atoms is ***more electronegative***



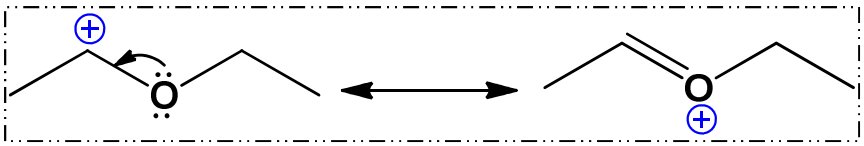

**2.** **π**-Bonds going all the way around a ring.

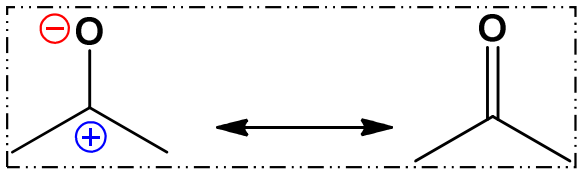


**3.** A **π** bond next to a ***positive charge*** .

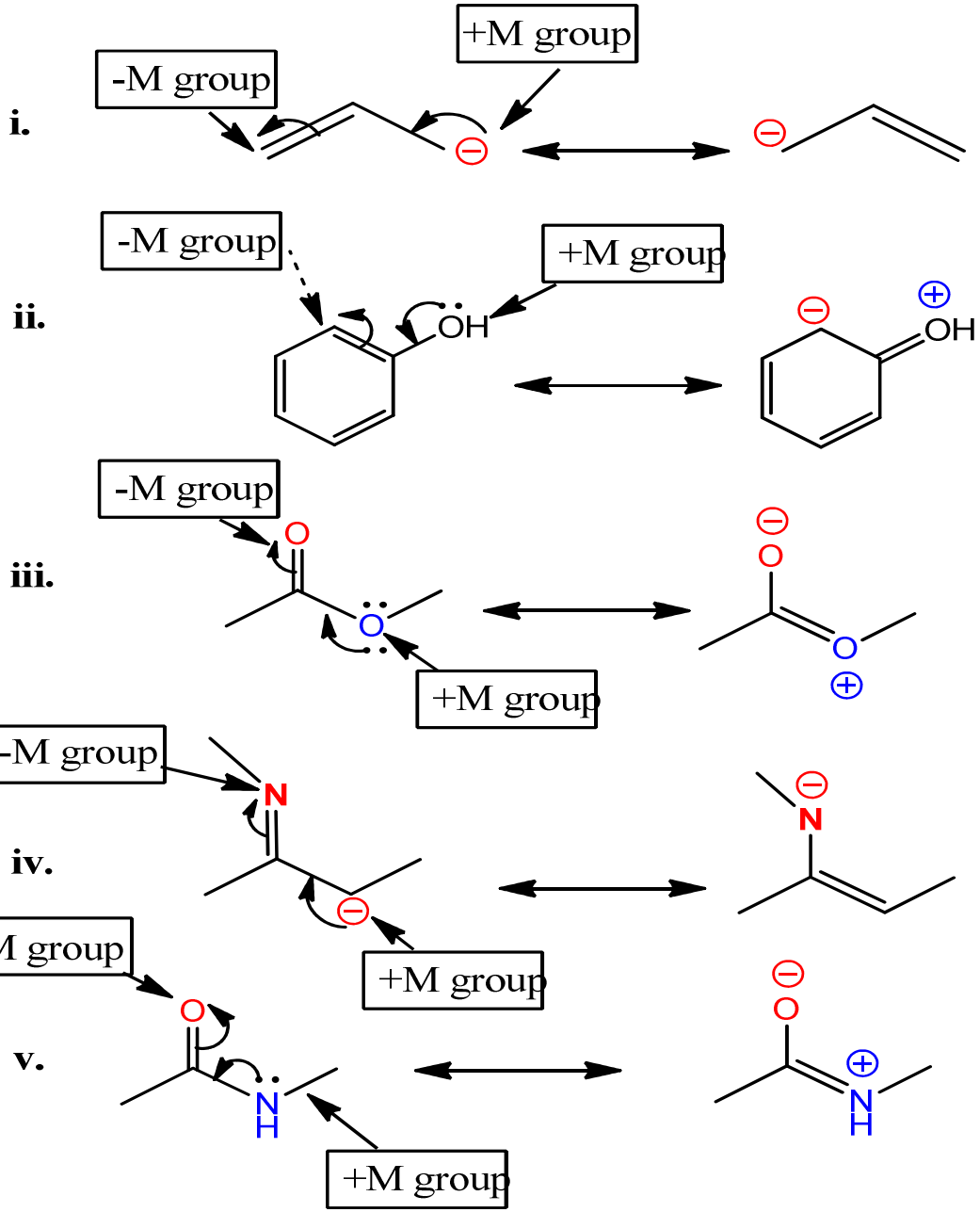


**4.** A ***lone pair or negative charge*** next to a ***positive charge***



**5.** A ***lone pair or a negative charge*** next to a **π-bond** (the lone pair or the negative is separated from the double bond by exactly one single bond)



# *+M* and *–M*

- When a **π** system donates electrons**,** the **π** system has a ***positive mesomeric effect (+M).***

-When a ***lone pair of electron*** is donated, the group donating the electrons has a **positive mesomeric effect (*+M*).**

-When a **π**-system accepts electron, the π-system has a ***negative mesomeric effect (-M***).
-**In neutral compounds**, there will always be a ***+M*** and ***–M*** groups: one group donates (***+M***) the electrons and the other accepts the electrons (***-M***).

## *Characters of Mesomeric Effects*

**a. Mesomeric** , *like* ***inductive effects*** are ***permanent polarizations*** *in the ground state of the molecule* .

**b.** As a rule, ***the more resonance structure of an anion, cation or neutral π-system can have, the more stable it is, because*** *Delocalization of electrons* through resonance is the most powerful factor that affects the stability of charged molecules.

**c.** Mesomers of charged molecules in which ***electron density is localized on an electronegative atom are important contributors*** (***more stable, less energetic***).

**The essential difference between the inductive and mesomeric effect is that :-**

***1-*** *The former occurs essentially in* ***saturated*** *compounds while the latter in* ***unsaturated*** *and especially* ***conjugated*** *compounds .*

***2-*** *The former involves the* ***electrons in σ-bonds*** *, the latter those in* ***π- bonds****.*

***3- Inductive effects*** *are* ***transmitted over only short distance in saturated chain*** *whereas* ***mesomeric effect*** *may be* ***transmitted from one end to the other of large molecules provided that conjugation*** *is present though which they can proceed .*

*The inductive and mesomeric effect influence can proceed*

# Inductive versus Mesomeric effects.

•Mesomeric effects are generally stronger than inductive effects.

•A ***+M*** group stabilizes an ***anion*** more effectively than a ***+I*** group.

•Mesomeric effects is ***more effective over much longer distances*** than inductive effects.

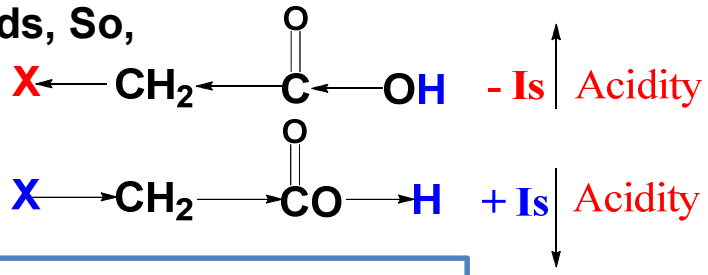
**The Inductive and Mesomeric effect influence:-**

**1- The strength of acids and bases.**
**2- Reactivity of alkyl halides.**
**3- Equilibria and rate of reaction.**
**4- Substitution in aromatic species.**
**5- Reactivity of Carbonyl Compounds.**

# Acidic strength of Carboxylic acid.

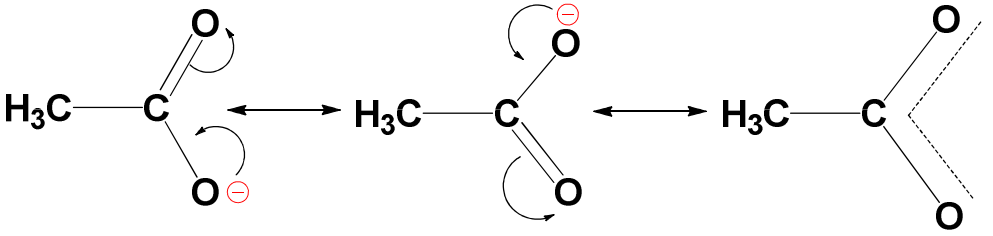
**Compound which easily donates H+ to others are good acids, So,**

- **- I effect and – M increase acidic nature.**
- **$sp > sp^2 > sp^3$ in acidity**

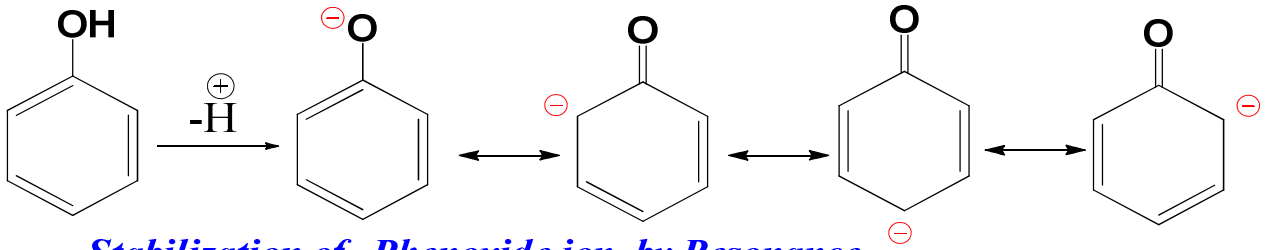



**$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > HCOOH > CH_3COOH$**

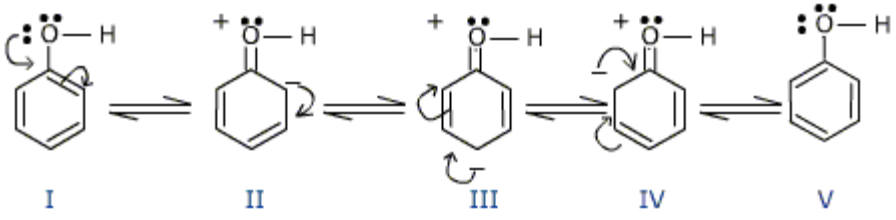
**$CH{\equiv}C\text{-}CH_2\text{-}COOH > CH_2{=}CH\text{-}CH_2\text{-}COOH > CH_2CH_2CH_2COOH$**




***Stabilization of the Conjugate Base of acetic acid by Resonance***

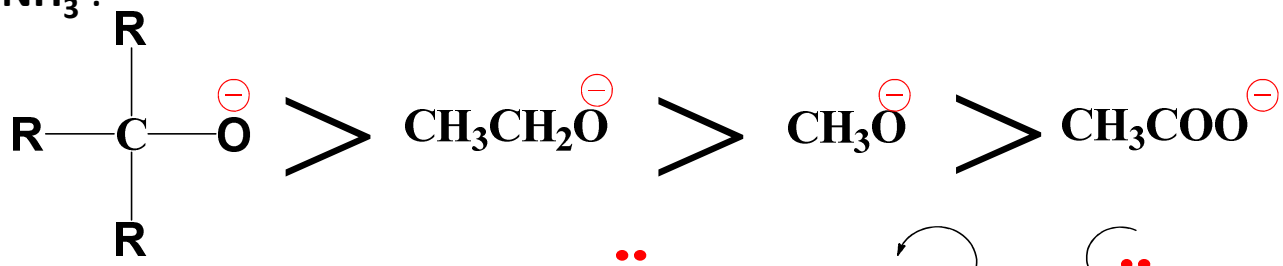



***Stabilization of Phenoxide ion by Resonance***

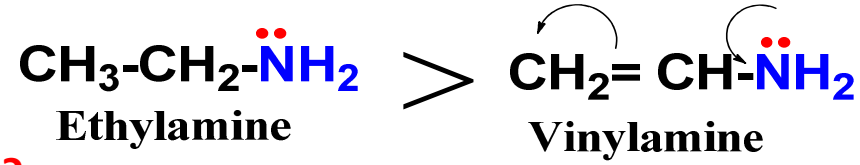


# Bases & Basic strength of amines

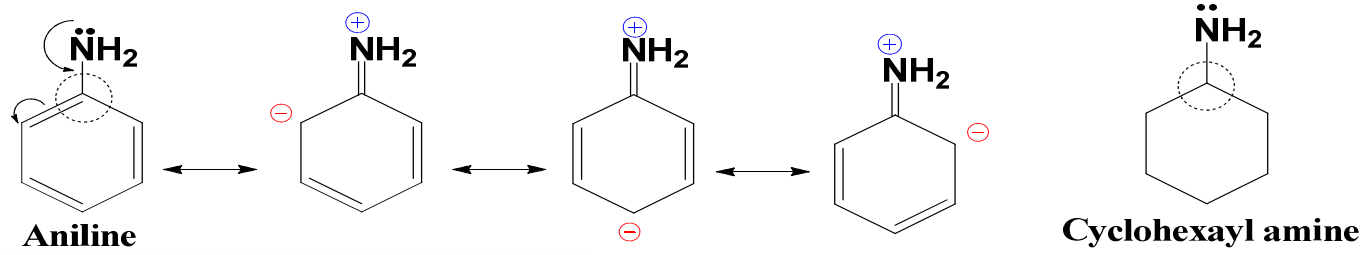
-The **bases** include **anions *e.g.*** $^-NH_2$, $^-OEt$ , $^-OH$ and **neutral molecules** containing at least *one unshared pair of electrons* ***e.g.*** $:NH_3$ .




**Which is more basic Ethylamine or Vinylamine ?**



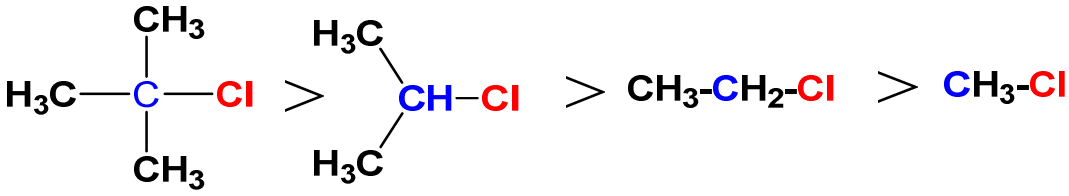

**Which is more basic Aniline or Cyclohexyl amine ?**




**Which one is more basic in Pyridene and Piperedine ?**

**Which one is more basic in Aniline and Benzylamine?**

# Reactivity of Alkyl Halides:




Why Chlorobenzene is less reactive than Benzyl chloride ?

# * Questions:

## 1. Compare between:-

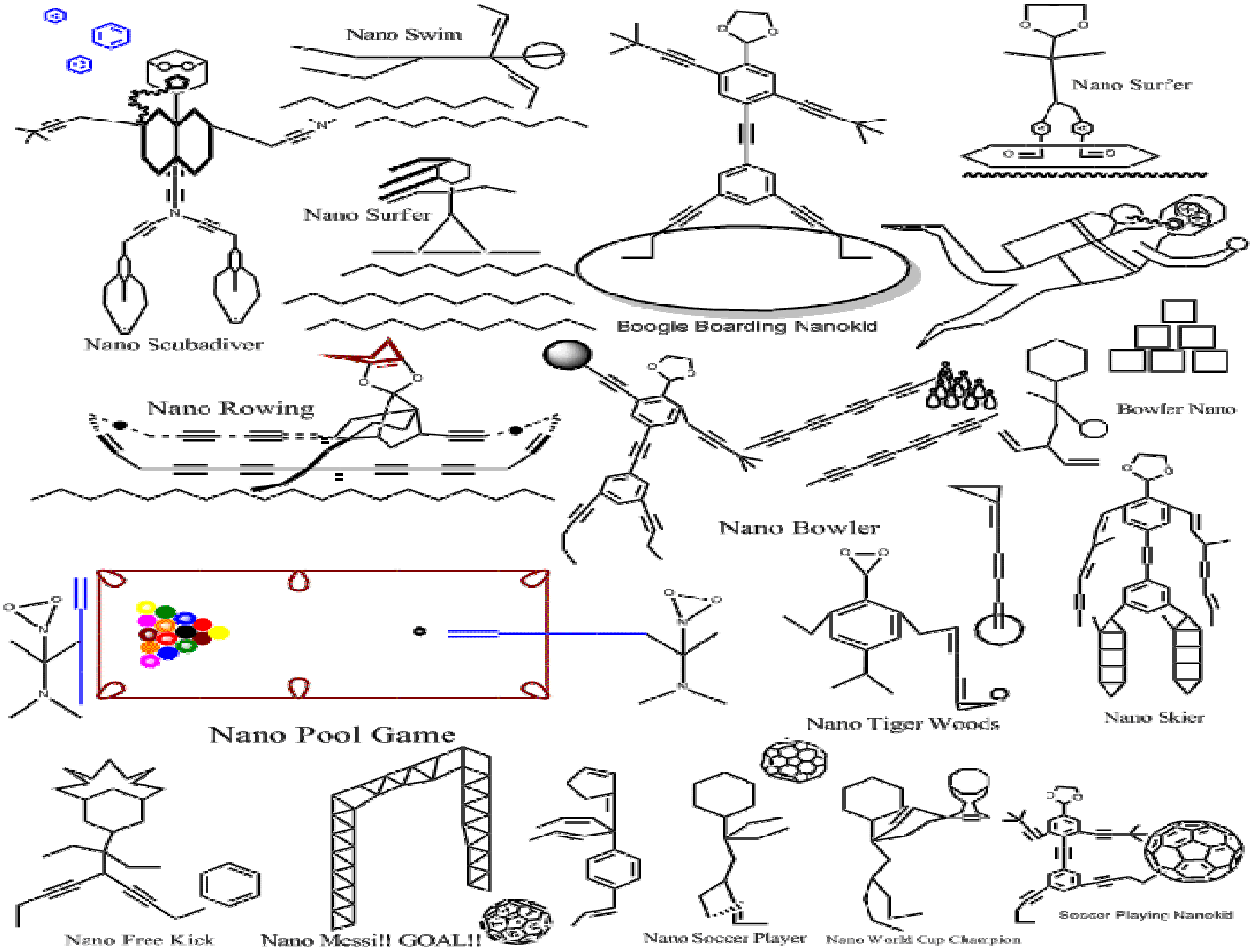
a. $C_2H_5OC_2H_5$ , $CH_3COOH$ , $C_2H_5OH$ [ B.P. & Water miscibility ]

b. $CH_3CHO$ & $C_2H_5OH$ [ B.P. & Water miscibility ]

c. $CH_3NH_2$, $(CH_3)_2NH$ & $(CH_3)_3N$ [ B.P. & Water miscibility ]

**2. $C_2H_5OH$ has B.P. and Water Miscibility higher than $CH_3$-O-$CH_3$. Explain ?**

**3. Benzoic acid is example for aromatic carboxylic acid, is more acidic than Acetic acid ?**


Nano Swim
Nano Surfer
Nano Surfer
Nano Scubadiver
Boogie Boarding Nanokid
Nano Rowing
Bowler Nano
Nano Bowler
Nano Pool Game
Nano Tiger Woods
Nano Skier
Nano Free Kick
Nano Messi!! GOAL!!
Nano Soccer Player
Nano World Cup Champion
Soccer Playing Nanokid