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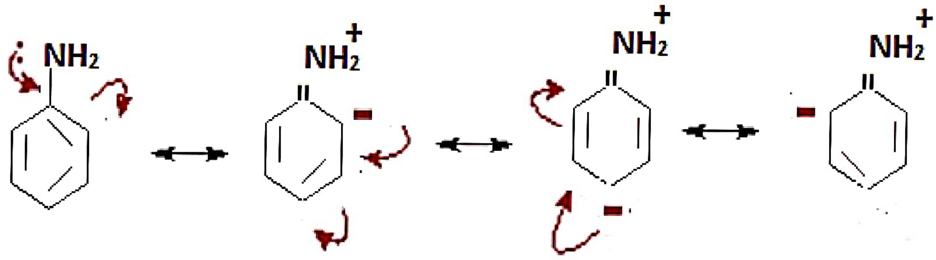
Mesomeric effect: Mesomeric effect is defined as polarity developed in the molecule by the interaction of two π bonds or between a π bond and a lone pair of electrons present on an adjacent atom. It is represented by M or R. There are two types of mesomeric effect.

1. Positive mesomeric effect: When the substituent is an electron releasing group i.e. a lone pair of electrons is donated, the group donating the electrons has a positive mesomeric effect (+**M effect**).

- If the first atom of the group either has a lone pair or negative charge. e.g. – NH2 , -OH, -OCH_3 , -$NHCOCH_3$, -OCOR etc.

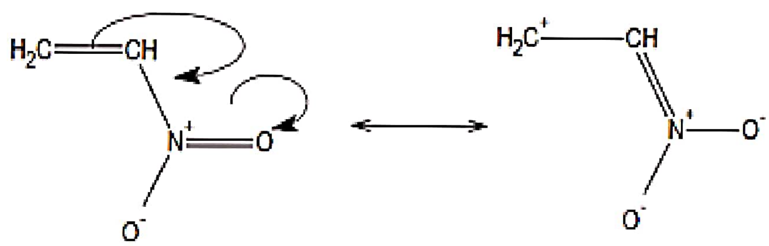


+M Effect order

$–O^- > –NH_2 > –NHR > –OR > –NHCOR > –OCOR > –Ph > –F > –Cl > –Br > –I$

2. Negative mesomeric effect: : when the substituent is an electron-withdrawing group i.e. a π –system accepts electrons, the π –system has a negative mesomeric effect (**–M effect**).

- If the first atom of the group has positive charge and after withdrawing a pair of electrons, it is not violating it's octet. e.g. -PH_3^+
- If the first atom of a neutral group has neither a lone pair nor any charge, and is joined to more electronegative atom(s) than itself by double/triple bond. e.g. -CHO, -CN, -SO_3H, etc.



-M Effect order

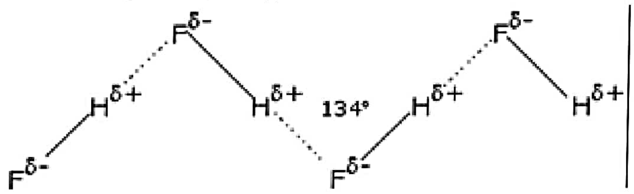
$–NO_2 > –CN >$ --S(=O)2–OH $> –CHO > –C{=}O > –COOCOR > –COOR > –COOH > –CONH_2 > –COO^-$

Hydrogen bonding: In a molecule, when a hydrogen atom is linked to a highly electronegative atom, it attracts the shared pair of electrons more and so this end of the molecules becomes slightly negative while the other end becomes slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called the hydrogen bond. The H-bond is mostly strong in comparison to normal dipole-dipole and dispersion forces. However, they are weak compared to the covalent or ionic bonds.

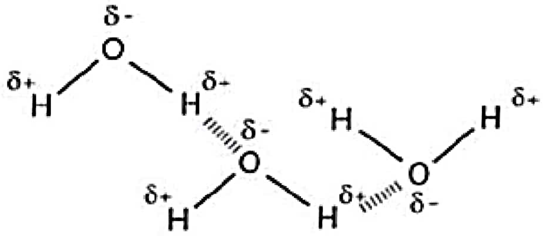
- In hydrogen bonding, a hydrogen atom links the two electronegative atom simultaneously, one by a covalent bond and the other by a hydrogen bond.
- The conditions for hydrogen bonding are:
  1. The molecule must contain a highly electronegative atom linked to the hydrogen atom. The higher the electronegativity more is the polarization of the molecule.
  2. The size of the electronegative atom should be small. The smaller the size, the greater is the electrostatic attraction.

Examples:

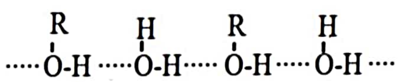
Hydrogen Bonding in Hydrogen fluoride: Fluorine having the highest value of electronegativity forms the strongest hydrogen bond.



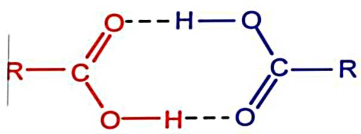
Hydrogen Bonding in Water: A water molecule contains a highly electronegative oxygen atom linked to the hydrogen atom. Oxygen atom attracts the shared pair of electrons more and this end of the molecule becomes negative whereas the hydrogen atoms become positive.



Hydrogen Bonding in Alcohols and Carboxylic acid: Alcohol is a type of an organic molecule which contains an -OH group. Normally, if any molecule which contains the hydrogen atom is connected to either oxygen or nitrogen directly, then hydrogen bonding is easily formed.



Hydrogen Bonding in Alcohols

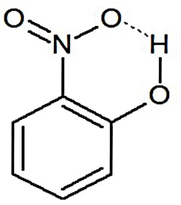


Hydrogen Bonding in Carboxylic acid

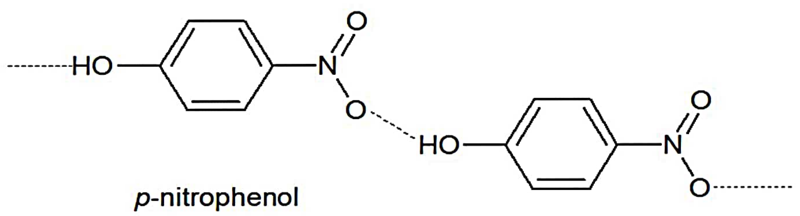
Types of Hydrogen Bonding: There are two types of H bonds, and it is classified as the following: (1)Intermolecular Hydrogen Bonding and (2) Intramolecular Hydrogen Bonding

(1) Intermolecular Hydrogen Bonding: When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding. For example: hydrogen bonding in water, alcohol, ammonia etc.

(2) Intramolecular Hydrogen Bonding: The hydrogen bonding which takes place within a molecule itself is called intramolecular hydrogen bonding. It takes place in compounds containing two groups such that one group contains hydrogen atom linked to an electronegative atom and the other group contains a highly electronegative atom linked to a lesser electronegative atom of the other group. The bond is formed between the hydrogen atoms of one group with the more electronegative atom of the other group. For example:



o-nitrophenol
(intramolecular hydrogen bonding)



p-nitrophenol
(intermolecular hydrogen bonding)

Properties of Hydrogen Bonding

- Solubility: Because of the hydrogen bonding, lower alcohols are soluble in water.
- Boiling point and Volatility: The compounds having hydrogen bonding between different molecules have a higher boiling point, so they are less volatile.
- Viscosity and surface tension: The substances which contain hydrogen bonding exists as an associated molecule. So their flow becomes comparatively difficult. So, they have higher viscosity and high surface tension.
- The lower density of ice than water: In ice, each water molecule is linked tetrahedraly to four water molecules by hydrogen bonding which results in a cage-like structure of water molecules. The molecules are not as closely packed as they are in a liquid state. When ice melts, this case like structure collapses and the molecules come closer to each other. Thus for the same mass of water, the volume decreases and density increases. Therefore, ice has a lower density than water at 273 K.

Assignment:

Q1: Which of the following molecule does not form H-bond?

(a) H_2O (b) CH_4 (c) HF (d) CH_3COOH

Q2: Which of the following compounds has the highest boiling point?

(a) CH_4 (b) CH_3CH_3 (c) CH_3CH_2OH (d) CH_3OCH_3

Q3: The boiling point of p-nitrophenol is higher than that of o-nitrophenol because:

(a) NO_2 group at a para position behaves in a different way from that at o-position.
(b) intramolecular hydrogen exists in p-nitrophenol.
(c) intermolecular hydrogen bonding in p-nitrophenol.
(d) p-nitrophenol has a higher molecular weight than o-nitrophenol.