2.15 Hydrogen Bonding

"The electrostatic attraction between a hydrogen atom covalently bonded to a small, highly electronegative atom and a lone pair of electrons on highly electronegative atom in another molecule, is called ***hydrogen bonding".*** Hydrogen bond is represented by a dotted or dashed line. It is much weaker than a covalent or ionic bond but it is much stronger than the van der Waals attractive forces, i.e., the forces between the molecules of nonpolar compounds. It should be noted that:

(i) A hydrogen atom can participate in hydrogen bonding if it is bonded to O, N or F which have highly electronegativity and small atomic size.

(ii) Hydrogen bond is longer and much weaker than a normal covalent bond. The energies (strengths) of the hydrogen bonds are in the range 8 – 42 kJ/mol, while the O – H covalent bond dissociation energy in water is 464 kJ/mol.

(iii) Hydrogen bonding results in long chains or clusters of a large number of associated molecules like many tiny magnets.

(iv) Like a covalent bond, hydrogen bond has a preferred bonding direction. This is attributed to the fact that hydrogen bonding occurs through p orbital which contain the lone pair of electrons on O, N or F atom.

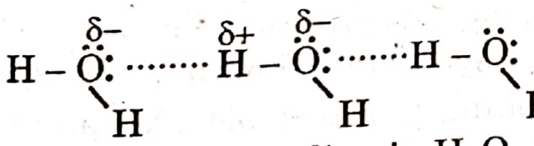
Conditions for Formation of Hydrogen Bonding

(i) H atom is covalently bonded to O, N or F, i.e., the molecule must contain a polar bond.

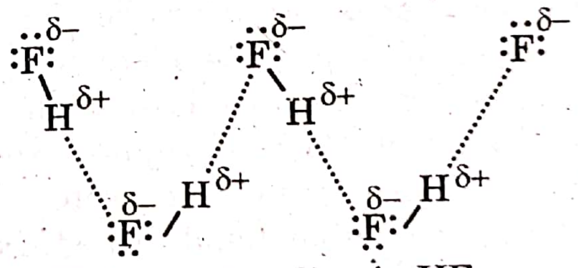
$$^{\delta-}O - ^{\delta+}H \quad \text{or} \quad ^{\delta-}N — ^{\delta+}H \quad \text{or} \quad ^{\delta-}F - ^{\delta+}H$$

(ii) The electronegative atom O, N or F in the polar bonds must have unshared electron pair.

When hydrogen atom is covalently bonded to highly electronegative atom such as N, O or F, it carries partial positive charge and interacts with the lone pair of highly electronegative atom of another molecule near by. In general whenever polar molecules come near to one another, the positive end (δ^+) of one molecule interacts with the negative end (δ^-) of another because of electrostatic attraction between them and thus these molecules will associate together to form large clusters of molecules. In water and HF these interactions can be represented as:



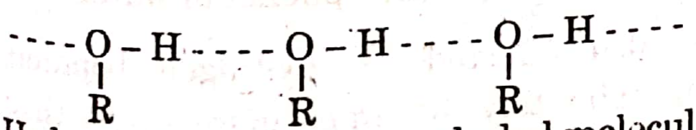
Hydrogen bonding in H_2O



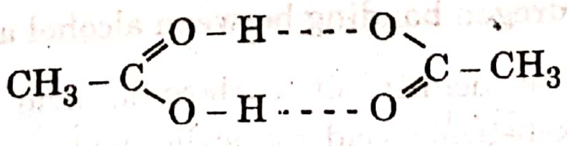
Hydrogen bonding in HF

Types of hydrogen bond. There are two types of hydrogen bonds.

(i) Intermolecular H - bonding (Association). This type of hydrogen bonding is between two or more similar or different molecules. As a result of this type of bonding two or more molecules are associated together. Ammonia, water, hydrogen fluoride, alcohols, carboxylic acids etc are the examples containing intermolecular H- bonds.

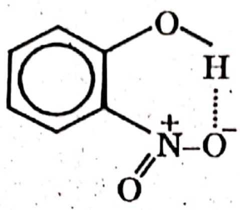


Hydrogen bonds between alcohol molecules.

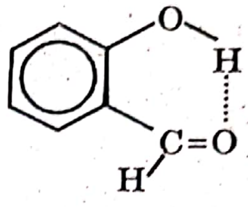


Acetic acid dimer

Intramolecular H - bonding (Chelation). In some cases a hydrogen bonding can occur within a single molecule. This types of H - bonding is between two functional groups of the same molecule and thus leads to the formation of a ring structure. This type of hydrogen bonding is therefore, a kind of chelation. *o*-hydroxybenzaldehyde (i.e., salicylaldehyde), *o-nitrophenol*, *o-chlorophenol* are the examples containing intramolecular hydrogen bonding.



o - nitrophenol



Salicylaldehyde

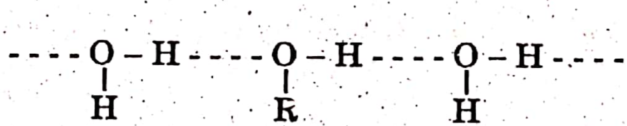
Effects of Hydrogen bonding on various properties of organic compounds

Hydrogen bonding has a significant effect on the physical properties (boiling points, solubility) of organic compounds. It is understandable that substances having nearly the same molecular masses have the same boiling point. The boiling points of alkanes and ethers of comparable molecular masses are not far apart, but the boiling points of alcohols having the same molecular masses are considerably higher.

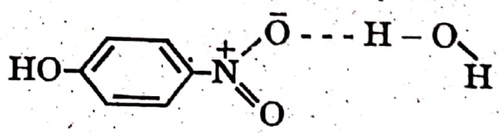
$CH_3CH_2CH_3$	CH_3OCH_3	CH_3-CH_2-OH
propane (b.p; –45°C)	Dimethyl ether; b.p. –25°C	Ethanol; b.p. 78°C

This can be explained on the basis of hydrogen bonding. Ethanol forms hydrogen bonds and extra energy is required to break the hydrogen bonds holding the molecules together before it can be volatilized. Propane and dimethyl ether do not form hydrogen bonds and, therefore, have low boiling points.

If hydrogen bonding is possible between solute and solvent, this greatly increases solubtility of a substance. For example, substances like methanol and ethanol are highly soluble in water due to hydrogen bonding between their molecules. On the other hand, if hydrogen bonding is intramolecular and forms a chelate ring as in *o*-nitrophenol, then the hydrogen bonding between the solute and solvent is restricted and reduces solubility in H_2O. Thus solubility of *o*–nitrophenol in water is lower as compared to its *p*-isomer (*p*-nitrophenol) which is free to form hydrogen bonding with water.

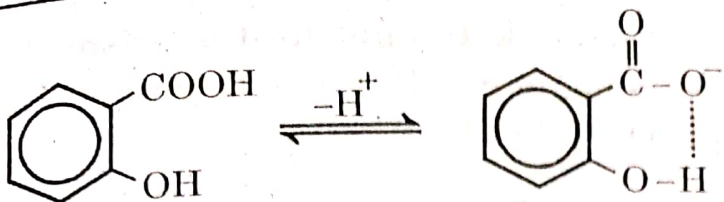


Hydrogen bonding between alcohol and H_2O

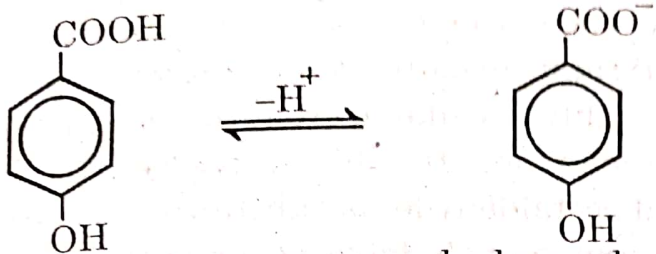


***p* - nitrophenol in water**

The acidity of carboxylic acid is also effected by hydrogen bonding. *o*-hydroxybenzoic acid (salicylic acid) is approximately 40 times more acidic than *p*-hydroxybenzoic acid, because the anion produced after ionization of salicylic acid is stabilized through intramolecular hydrogen bonding, by chelation, whereas the anion of *p*-hydroxybenzoic acid has no intramolecular hydrogen bonding since the hydroxy group is far away from the carboxylate ion.



molecular hydrogen bonding



no hydrogen bonding

Intramolecular hydrogen bonding is also responsible for the large amount of enol present in certain tautomeric equilbria. The larger enol content (76.4%) in the equilibrium mixture of acetylacetone may be described to intramolecular hydrogen bonding.