## Hydrogen Bond

To understand the concept of hydrogen bond let us consider a molecule, say, AH in which H atom is linked with a strongly electronegative but very small atom A (A may be N, O or F) by a normal covalent bond. The electron pair being shared between H and the strongly electronegative atom A will evidently lie far away from H and thus partial positive and negative charges will be developed on H and A atoms respectively. Consequently AH molecule will behave as a dipole which is represented as;
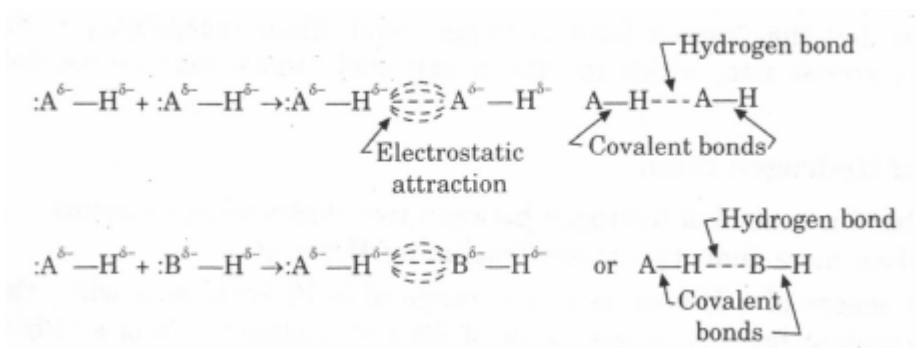
Evidently the dipole has A as its negative end and H as its positive end. Since the electronegative atom, A attracts the electron pair constituting the covalent bond between A and H almost completely towards itself, the atom A takes almost full possession of the electron pair, i.e. the atom A will have a lone pair of electrons. This leaves H atom with a large partial positive charge and AH molecule, therefore, becomes highly polar and hydrogen end of it becomes nearly bare hydrogen nucleus or proton (H^+), i.e. H-atom is reduced to a proton which is almost devoid of electrons.

Now if another molecule like AH (same molecule) or BH (different molecule) (A and B are strongly electronegative atoms) which also forms a dipole $A^{\delta-}$ -- $H^{\delta+}$ or $B^{\delta-}$ -- $H^{\delta+}$ respectively is brought near $A^{\delta-}$ -- $H^{\delta+}$ dipole, these two dipoles will be attracted towards each other by electrostatic force of attraction which is represented by a dotted or dashed line and is called hydrogen bond or hydrogen bonding.

Thus we see that in H-bond H-atom forms a bridge between two electronegative atoms and for this reason H-bond is also called a H-bridge. Thus H-bond can be defined as;

The attractive electrostatic force between a hydrogen atom which is already covalently attached with a strongly electronegative atom of a molecule and another electronegative atom of some other molecule (same molecule or different molecule) is known as hydrogen bond.

OR

Under appropriate conditions a hydrogen atom may be linked to two similar or different electronegative atoms. It is bonded to one of the two atoms by a covalent bond while to the other atom it is attached by a special type of bond which is much weaker than the covalent bond and is called hydrogen bond.
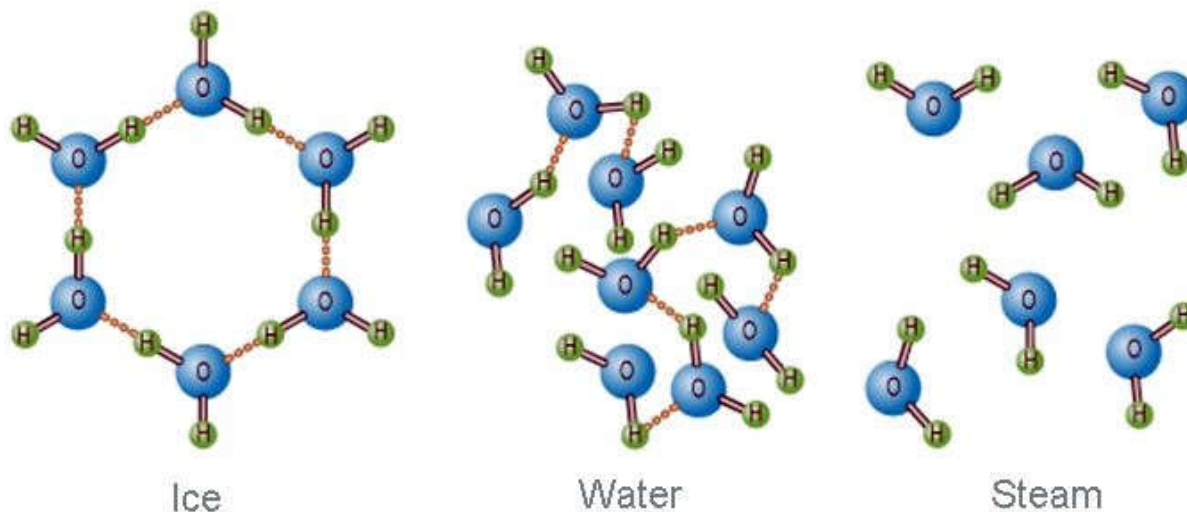
Nature of Hydrogen Bond

It is difficult to ascertain the exact nature of hydrogen bond. We know that the covalency of H-atom is limited to one, i.e., H- atom can be linked to only one atom, say A. This is because of the fact that Is atomic orbital of H-atom becomes completely filled after it has formed a covalent bond, A-H. Thus H-atom already covalently bonded to atom A in A-H bond cannot form a second covalent bond with another atom, say B. This shows that A-H-B in which H-atom shows bivalency is unlikely, because, if it is likely at all, it would require the use of 2sor 2p -orbitals of H-atom which are of much higher energy and consequently are useless for bonding. Further if A-H-B is supposed to be correct, we should expect H-atom to be equidistant from A and B atoms, if the elecnegativities of A and B are the same. However, it has been found by experiments that H-atom in hydrogen bond is close to that atom with which it forms a covalent bond. This shows that hydrogen bond is electrostatic in nature, i.e. hydrogen bond is merely an electrostatic force rather than a chemical bond.

A question may now arise as to why H-atom alone is capable of forming hydrogen bond. The reason, probably, is that H-atom has small size with only one electron in its only one energy shell. When this electron is taken away, the proton (H^+) left behind can easily manage to stap in between two electronegative atoms bringing them closer together by creating an electrostatic field, though weak. That is why the proton is in a state of oscillation between the-electronegative atoms.

Atoms of sulphur, phosphorus, chlorine, bromine and iodine are also highly electronegative, but they cannot form. hydrogen bond. Their

incapability is due to their larger atomic size, which results in extremely weak electrostatic field about them.

| Ice | Water | Steam |

Properties of Hydrogen Bond

(i) A H-bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms (excluding H-atom).

(ii) Bond energy of a H-bond is in the range of 3-10 kcal/ mole while that of a normal covalent bond is in the range of 50-100 kcal/mole. Thus a H-bond i.e. H….B bond) is much weaker and longer than a covalent bond, A-H and hence it can be readily ruptured. The difference in energy between A-H and H ...B bonds indicates that these have different bond lengths which, in turn, show that H-atom in A--H ...B is never midway between the two atoms, A and B ; it is rather always nearer to atom A which is covalently bonded to H-atom. H bond has more energy (3-10 kcal/mole) than van der Waals forces (1 kcal/mole).

With the increase of electronegativity of the atom to which H-atom is covalently linked; the strength of H-bond also increases. Thus the strength of H-bonds in N -- H ... N, O -- H ... O and F-- H ... F is in the following order:

Order of strength : N - H ...N < O - H ...O < F - H ...F

Order of electronegativity values : N (= 3.0) < 0 (=: 3.5) < F (= 4.0)

The numbers given in brackets indicate the electronegativity values of the elements concerned.

The strength of H-bond also depends on the size of the atom to which H-atom is linked. For example the larger Cl and S atoms whose electronegativities are almost the same.as that of N form H-bond to a lesser degree.

(iii) The formation of a H-bond does not involve any sharing of electron pairs. It is, therefore, quite different from a covalent bond.

(iv) Only O, N and F which have high electro negativity and small atomic size, are capable of forming H-bonds.

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

(vi) Like a covalent bond, H-bond has a preferred bonding direction. This is attributed to the fact that H-bonding occurs through p orbitals which contain the lone pair of electrons on A atom. This implies that all the three atoms in A -- H ... A will be in a straight line.

Types of Hydrogen Bond

Hydrogen bond is two types;

1. Inter-molecular hydrogen bond (Association)

This type of H-bond occurs between two or more molecules of the same or different compound. Thus NH_3, H_2O and HF molecules are associated by inter-molecular H-bond.

2. Intra-molecular hydrogen bond (Chelation)

This type of H-bond is formed between a H-atom and an electronegative atom present in the same molecule (intra means within). In intramolecular H-bonding, the Hsatom is bonded to two atoms of the same molecule. This type of H-bonding may lead to the linking of two groups to form a ring structure and such an effect is one kind of chelation. The occurrence of this type of H-bond does not disturb the normal bond angles. Examples of molecules showing intra-molecular hydrogen bonding are provided by o-nitropenol, o-hydroxy benzaldehyde, o-chlorophenol, o-hydroxy benzonic acid (salicylic acid), o-nitro benzoic acid, maleic acid etc.

o-nitro phenol   o-hydroxy   o-hydroxy benzoic
                      benzaldehyde   acid (salicylic acid)
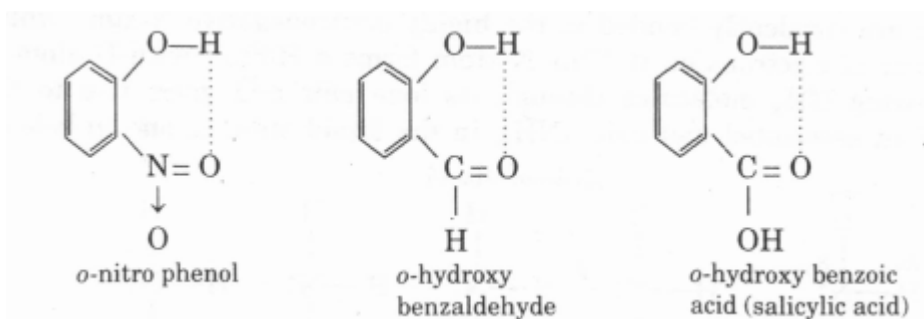
Thus we see that intra-molecular H-bonding in these molecules leads to the , formation of a six-membered ring (chelation). The occurrence of H-bond of this type is not possible in m-nitrophenol and p-nitrophenol because of the size of the ring that would result. It is because of the non-existence of H-bond in m- and p isomers that o-nitrophenol has different properties from those of other isomers.

For example :

(i) Melting point of o-nitrophenol is 2140 while those of its m- and p-isomers are 2900 and 2790 respectively.

(ii) o-nitrophenol is volatile in steam and less soluble in water than the other two isomers. p-nitrophenol shows inter-molecular H-bonding, resulting in the association of two molecules as shown below.
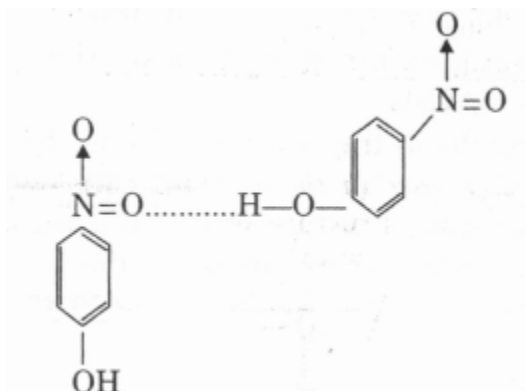
**Physical Properties (*Consequences of Hydrogen Bond*)**

Some of the unusual properties of the compounds containing .H-bond can be explained on the basis of the concept of H-bonding. For example:

A. Association of molecules.

Because of the fact that N,O and F atoms are of small size and high electronegativity, their hydrides *viz.* NH_3, H_2O and HF associate by H-bonds and form the bigger. aggregates (polymerised molecules) of various sizes. The formation' of aggregates (bigger units) is called association or polymerization. The bigger aggregates are polymerized molecules. Within the associated unit, the molecules are bonded together by H-bonding. The associated unit can be broken to smaller unit or to single molecules on heating, i.e. by suppling enough energy which overcomes H-bonding present in the associated unit. Now let us discuss the association in NH_3, H_2O and HF molecules.

a).Association of liq. NH₃ molecules.

In NH_3 molecules there are three H-atoms which are covalently bonded to the highly electronegative N-atom which has a lone pair of electrons on it. This N-atom forms a H-bond with H-atom of the neighboring NH_3 molecules through its lone pair and gives rise to the formation of an associated molecule, $(NH)_x$ in the liquid state as shown below :
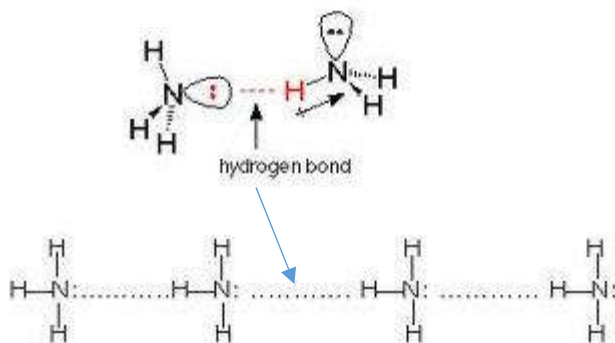

Fig 1. Association of ammonia molecules $(NH_3)_x$

(2) Association of H₂O molecules (*Solid state of water/ice*).

Here each O-atom of each $iH20$ 'molecule is linked with two H-atoms of its own molecule by covalent bonds and with two H- atoms of the neighboring H_2O molecule by H-bonds. Two H-bonds are formed between the two lone pairs of electrons present on O-atom and two H-atoms of the neighboring H_2O molecules as shown in Fig. 2, This type of bonding between O-atom and four H-atoms gives a tetrahedral structure to ice. In this structure

two H-atoms are linked covalently and lie close to O-atom at a distance of 1.0A° whereas the other two H-atoms (of other H_2O molecule) are linked by H-bonding and are at a distance of 1.76A° from O-atom. Since the H-bonds joining adjacent H_2O molecules are weaker and longer than normal covalent bonds in water molecules, the structure of ice so obtained is cage-like rigid structure. Unlike other crystalline structures, H_2O molecules in the tetrahedral structure of ice are not packed very closely together and hence' there is vacant space in the structure. Thus, ice has cage-like open structure. This cage-like open structure of ice can well explain the following properties of water :
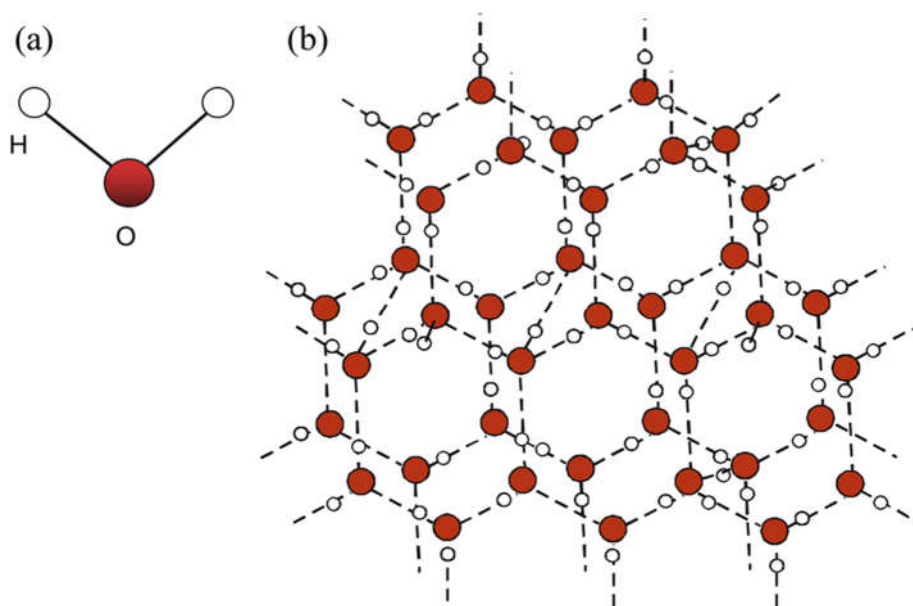

Fig 2. Structure of Ice

(a) Liquid water has higher density than solid ice. We have seen that the cage-like open structure of ice has vacant space in it. The presence of vacant space gives a large volume to a given mass of ice. When "ice is allowed to melt to come in the liquid-state, some of the H-bonds in the cage-like structure of ice are broken to some extent and water molecules come closer to each other. This results in a decrease of volume and hence density is increased. Thus we see that liquid water (which is at O°C) has higher density than solid ice while most of the other liquids have lower density than the solids. That liquid water has higher density than solid ice implies that ice is lighter than water.

(b) Ice floats on liquid water. Since ice has lower density than liquid water, ice is lighter than water and hence floats on liquid water.

(c) Density of water is maximum at 4°C. As the temperature of liquid. Water (O°C) is increased above O°C, density of water also increases. The increase in density continues only upto 4°C. Above 4°C, kinetic energy of H20 molecules increases and hence H_2O molecules move away from each other, i.e. the volume of water molecules is increased. The increase in volume decreases the density of water. Therefore, above 4°C, the density of water starts decreasing again. Thus we see that the density of water is maximum at 4°C.

(ii) Liquid state of water. Here each 0 atom of each H_2O molecule is covalently linked with two H-atoms of its own molecule and with another H-atom of the adjacent H_2O molecule by H-bonding. The formation of H-bond occurs through one of the two lone pairs of electrons present on O-atom in H_2O molecule. The association of different H_2O molecules by H-bonding gives an associated unit or cluster, $(H_2O)_x$ which consists of a large number of H_2O molecules as shown below :
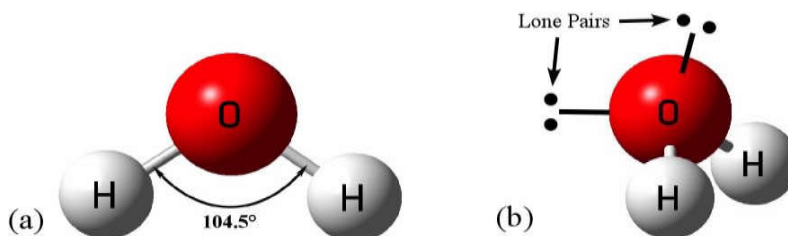
However the most stable cluster is the double molecule, $(H_2O)_2$ which consists of two H-bonds as shown below :
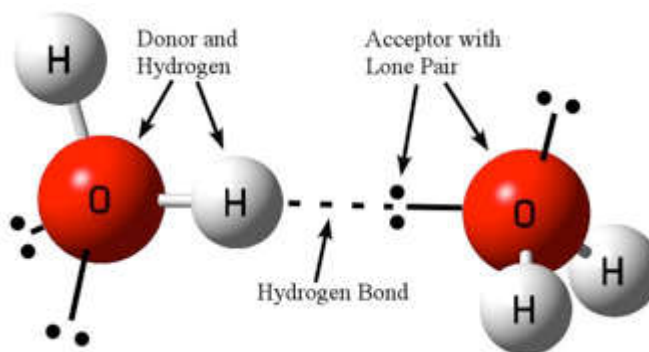
The formation of polymerised molecule, $(H_2O)x$ by H-bonding can well explain the fact that water exists as a liquid under the ordinary conditions

while the hydrides of other elements of the same group (VI A group) namely H_2S, H_2Se and H_2Te exist as gases under the same conditions. This is explained as follows;

Due to the fact that the electronegativity of O-atom is higher than that of S, Se and Te atoms, there is considerable H-bonding in liquid H_2O molecules while the same is absent in H_2S, H_2Se and H_2Te molecules. Thus H_2O molecules can associate to form a polymerised molecule. $(H_2O)x$ while H_2S, H_2Se and H_2Te cannot do so. It is. due to the formation of polymerised molecule, $(H_2O)x$ that water exists as a liquid under the ordinary conditions while H_2S, H_2Se and H_2Te exist as gases under the same conditions.

(3) Association of HF molecules

(i) HF crystals contain infinitely long zigzag chains of HF molecules which are associated to $(HF)x$ unit by H-bonding. F atom is covalently bonded to the H-atom of its own molecule while the same "atom is bonded to the H-atom of the neighboring HF molecule by a H-bond. F-atom forms Ii-bond with H-atom of the other HF molecule by its lone pair present in p-orbitals. H-F and H...F bond lengths are 1.0A and 1.55A respectively.
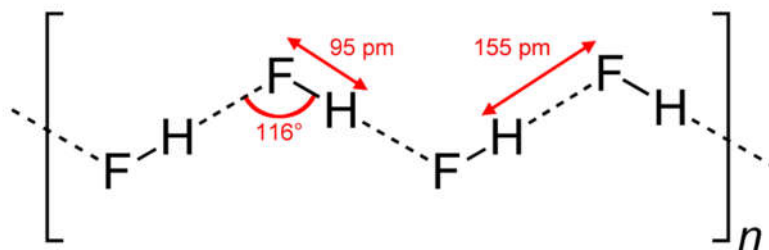
On heating the length of the chains shortens progressively till the unit, $(HF)x$ becomes fairly small and -x assumes any. value upto six.

(ii) Gaseous HF molecule contains molecular species, $(HF)_2$' $(HF)_3$ and so on upto $(HF)_6$ as well as some single HF molecules.

(iii) In aqueous solution HF ionizes to give HF_2^- ion (F^-...H -- F) rather than F^- ion.

b).Higher Boiling Points of NH$_3$, H$_2$O and HF Hydrides

Let us consider the boiling points of the binary hydrides of the elements of groups VA, VI A and VII A as given below in Table 1.

It may be seen from the table that on proceeding from SbH₃ to PH₃ (Group VA),from H₂Te to H₂S (Group VIA) and from HI to Hel (Group VIIA), the boiling points of the hydrides decrease with the decrease of their molecular weights while those of NH₃, H₂O and HF show a sudden increase, although they have the minimum molecular weights in their respective groups. The abnormal high boiling points of NH₃, H₂O and HF are due to the fact that these molecules are capable of forming the associated molecules, (NH₃)x, (H₂O)x and (HF)x by H-bonding between them, while other molecules exist as single molecules as they are incapable of forming associated molecules (clusters) by H-bonding. In order to break H-bonds existing in the associated molecules and thus to separate molecules of the clusters as they enter the gaseous state or the liquid state, relatively more energy is required and hence NH₃, H₂O and HF molecules have abnormally higher boiling points compared to other hydrides of the elements of the same group which do not form any H-bonds.

Table 1. Boiling points of binary hydrides of the element of groups VA,VIA and VIIA

Group VA			Group VIA			Group VIIA		
Hydride	Mol. wt.	B. pt. (°C)	Hydride	Mol. wt.	B. pt. (°C)	Hydride	Mol. wt.	B. pt. (°C)
SbH₃	125	−17	H₂Te	130	−1.8	HI	128	−35.5
AsH₃	78	−55	H₂Se	81	−42.0	HBr	81	−67.1
PH₃	34	−85	H₂S	34	−59.6	HCl	365	−85.0
NH₃	17	−33	H₂O	18	100	HF	20	19.4

c. High Solubilities of Covalent compounds

Hydrogen bonding also accounts for the abnormally high solubilities of some covalent compounds containing N, and F such as NH₃ and CH₃OH in certain hydrogen containing solvents noteably water. For example NH₃ and CH₃OH are highly soluble in H₂O because their molecules can associate with H₂O (solvent) molecules through H-bonds as shown below;
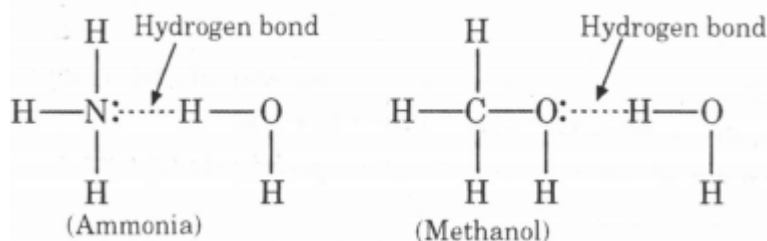
In addition, compounds containing oxygen such as sulphates freely dissolve in water through H-bond formation.

D. High viscosity, high heat of vaporization and high dielectric constant

Glycerol (CH_2OH-$CHOH$-CH_2OH) is far, more viscous than ethyl alcohol (C_2H_5OH) because of the fact that glycerol with three OH groups in its molecule can form many more H-bonds per molecule. This results in greater attraction among the molecules of glycerol and hence its resistance to flow is increased. Thus glycerol is more viscous. The molecules which are capable of forming associated molecules through H-bonding have naturally high heat of vaporization and high dielectric constant.

Significance of Hydrogen Bonding

Apart from providing explanation for a number of abnormal properties of certain compounds containing H-bonding, it is also useful in explaining physiological and geological processes occurring around us. *For example,*

1. Physical state of water

Without H-bonding, H_2O would have existed as a gas like H_2S. In that case no life would have been possible without liquid H_2O.

2. Structure of compounds

H-bonding is directional and on this account it helps in studying and establishing the structure of many compounds like ice, solid hydrogen fluoride, hydrates, solid acids, acid salts etc. For example H-bonding accounts for the tetrahedral structure of ice, zig-zag arrangement of HF molecules in solid hydrogen fluoride and sheet structure of boric acid (Fig.3) which is obtained by joining molecules of boric acid (H_3BO_3) by H-bonding, resulting in the formation of infinite parallel sheet.

3. Explanation of polymerization

H-bonding gives a satisfactory explanation for the mechanism of polymerization and hence of the formation of bigger aggregates of organic as well as inorganic molecules,

4. Applications in biological investigations

H-bonding also exists in molecules of living systems proteins like various tissues, organs, blood, skin and bones in animals. Fibrous like those found in hair, silk and muscles consist of long chains of a large number (sometimes 1000 or so) of amino acids as shown below. Here R = methyl isopropyl or butyl group.
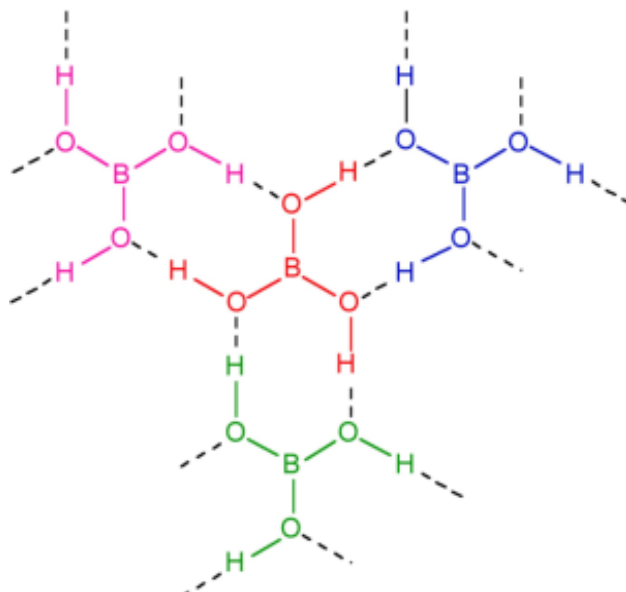

Fig 3. Hydrogen bonding in Boric acid and water

The long chains of amino acids are coiled about one another into a spiral celled helix. Such a helix may be either right-handed (called α-helix) or left handed (celled β-helix) as in the case screws.
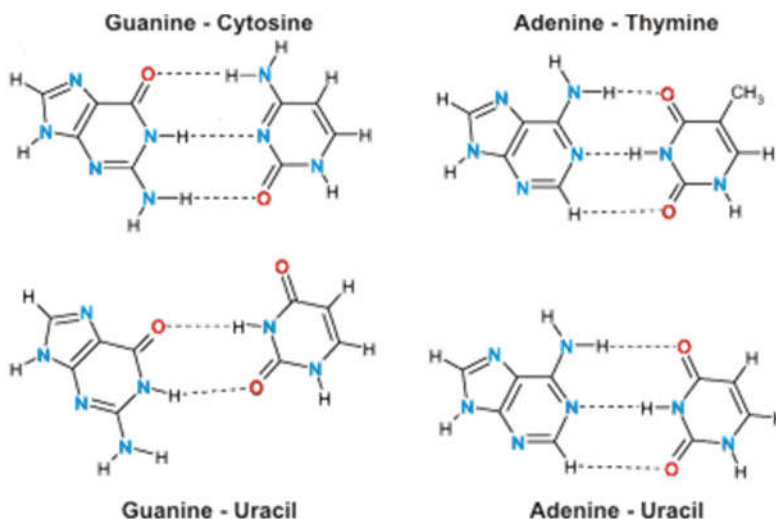
Fig 4a. Hydrogen bonding in Nucleic acid bases

It has been found that a-helix constitutes the more stable arrangement. N-H and C=O groups which are vertically adjacent to one another in the helix are linked together by H-bonds. The H-bonds link one spiral to the other (Fig. 4a & b). X-ray studies have shown that on an average there are 2.7 amino acid units for each turn of the helix (coil).
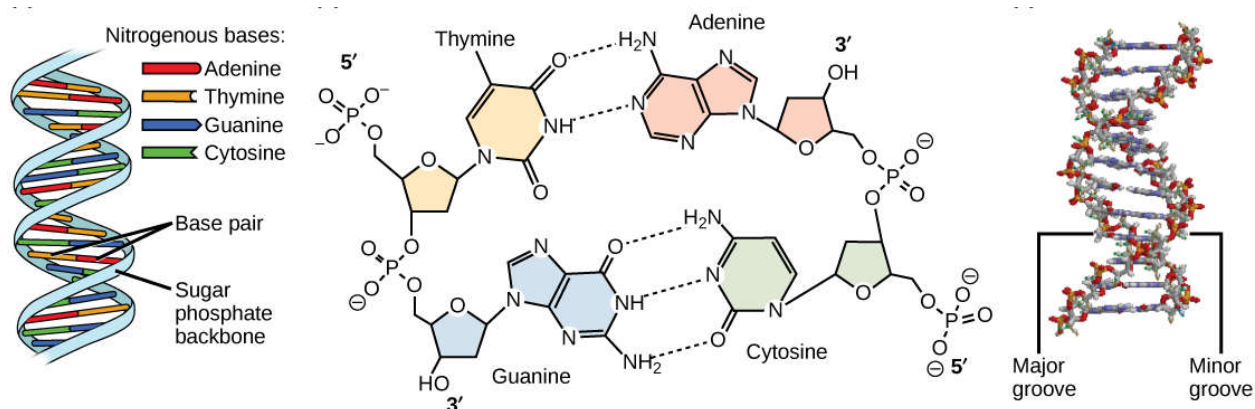
Fig 4b. Hydrogen bonding in DNA helical structure

Similarly deoxyribonucleic acid (DNA)has two spiral chains which are coiled about each other on a common axis to form a double helix, 18-20 A in diameter. They are 'linked' together by H- bonding between their sub-units.

5. Applications in geology

Many geological products such as organic compounds contained in petroleum, coal products and complex hydrates of minerals are formed and established by means of H-bonding.

6. In paints and dyes

The adhesive action (i.e. stickness) of glue, honey, dyes and paints is also due to the presence of R-bonding in them.

7. In clothing

R-bond is of vital importance for our clothing. For example the rigidity and tensile strength of cotton, silk or synthetic fibres is due to the H-bonding in them.

8. Food materials

Molecules of most of our food materials like sugars, carbohydrates etc. also consist of H-bonding. For example a-atom of one – OR group of one

molecule of sugar and carbohydrate is bonded with -OR group of another molecule through H-bonding.

9. Wood fibres

H-bonding also plays a significant role in making wood fibres more rigid so that they may be used to meet the requirements of housing, furnitures etc.