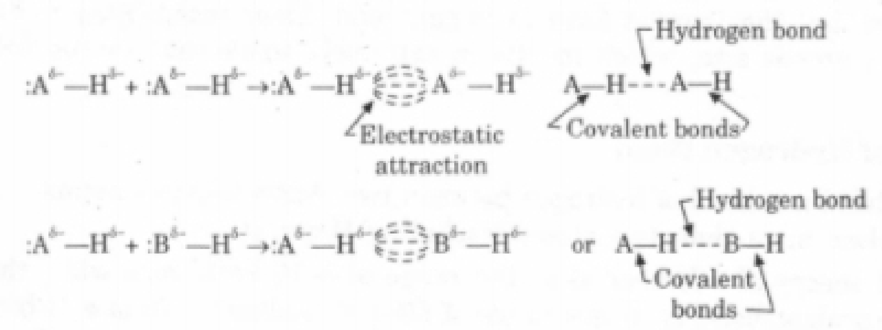
Hydrogen Bond

In order 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+ 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

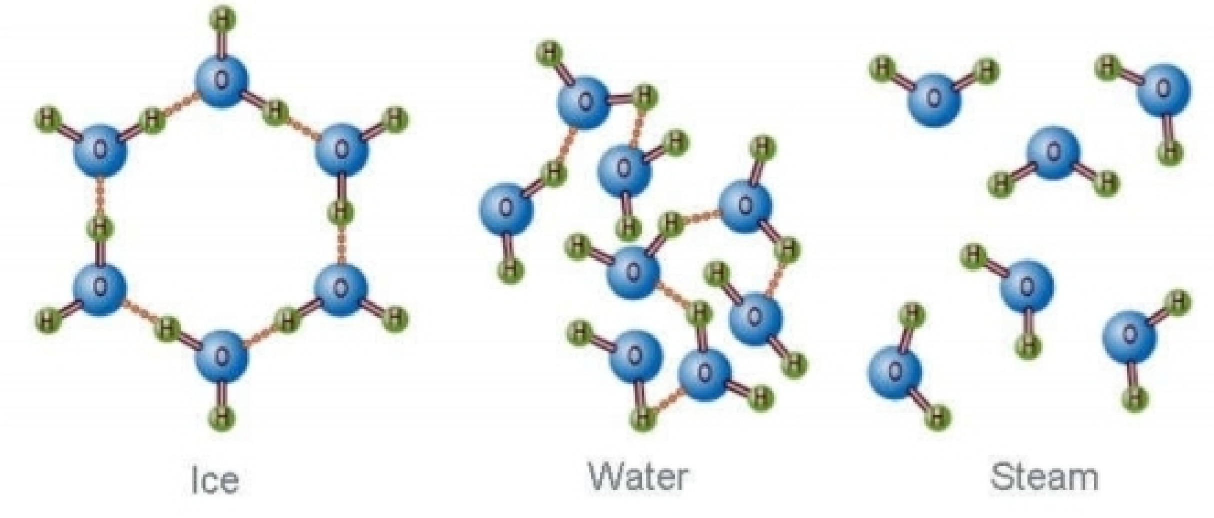
Under appropriate conditions a hydrogen atom may be linked to two similar or different electronegative atoms. It is bonded to one of the two atoms by a covalent bond while to the other atom it is attached by a special type of ond which is much weaker than the covalent bond and is called hydrogen bond.

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.



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)

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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.

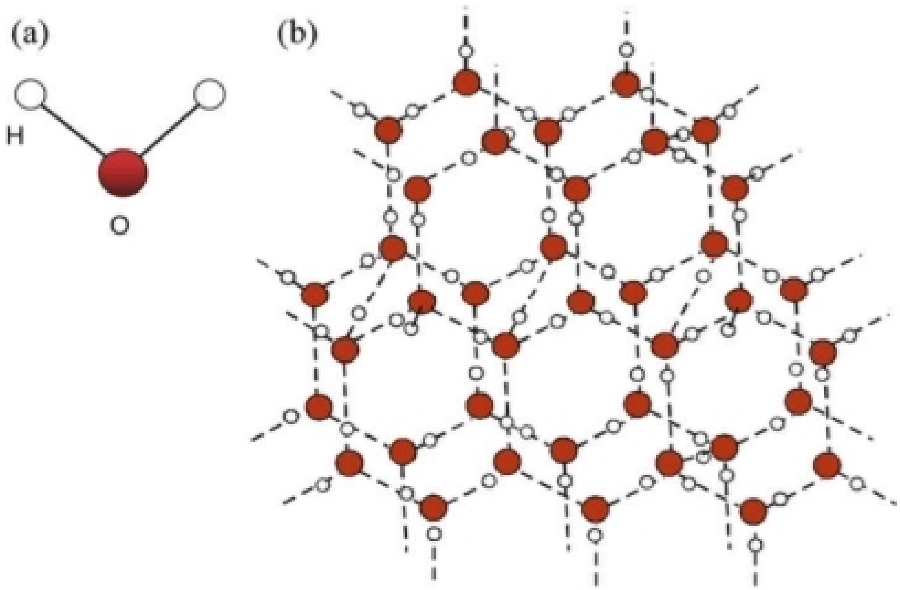


Fig 2. Structure of Ice

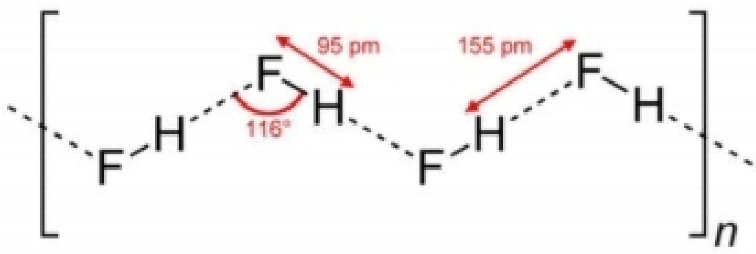
(a) Liquid water has higher density than solid ice. We have seen that the cage-like open structure of ice has vacant space in it. The presence of vacant space gives a large volume to a given mass of ice. When "ice is allowed to melt to come in the liquid-state, some of the H-bonds in the cage-like structure 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

(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 li-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.

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.

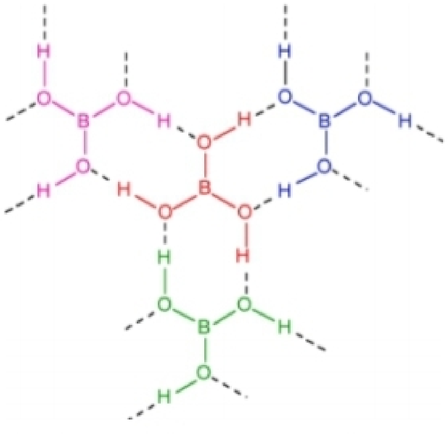
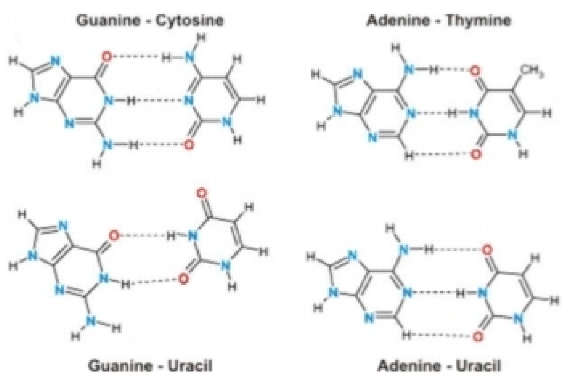


Fig 3. Hydrogen bonding in Boric acid and water

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.



& b). X-ray studies have shown that on an average there are 2.7 amino acid units for each turn of the helix (coil).

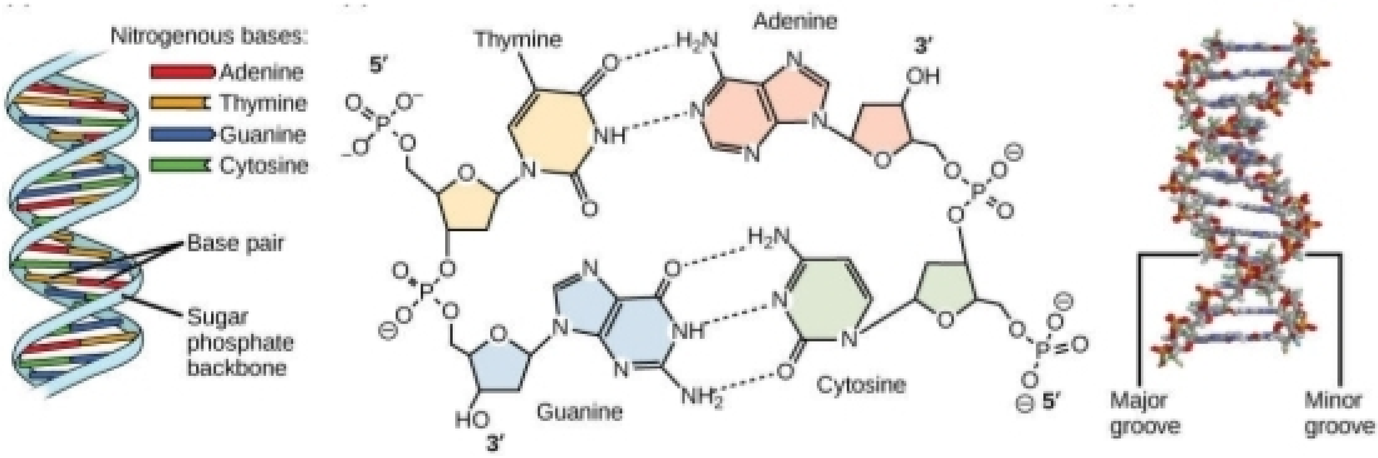


Fig 4b. Hydrogen bonding in DNA helical structure

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.