B. Sc. Part III.
Organic chemistry.
Paper VII
Group A (continued.....)

1. General Principles :

Hydrogen bonding : When-ever a molecule contains a hydrogen atom linked to a highly electronegative atom (F, O, N), this atom attracts the shared pair of electrons more and so this end of the molecule becomes slightly negative while the ~~the~~ other end becomes ~~highly~~ +ve. The -ve end of one molecule attracts the +ve end of the other and as a result of this electrostatic attraction, a weak bond is formed between them. This bond is called hydrogen bond. It is represented by dotted lines.

$$\overset{\delta^+}{H}-\overset{\delta^-}{X}\cdots\overset{\delta^+}{H}-\overset{\delta^-}{X}\cdots\overset{\delta^+}{H}-\overset{\delta^-}{X}$$

Conditions for hydrogen bonding :

In the formation of hydrogen bond, the following conditions must be fulfilled :

(i) The molecule must contain a highly electronegative atom linked to H-atom.
(ii) The size of the electronegative atom should be small.

Only F, O, N atoms can form hydrogen bonds, as these atoms are small in size and have high electronegativities. Chlorine having the same electronegativity as that of Nitrogen usually does not form hydrogen bond due to its large size.

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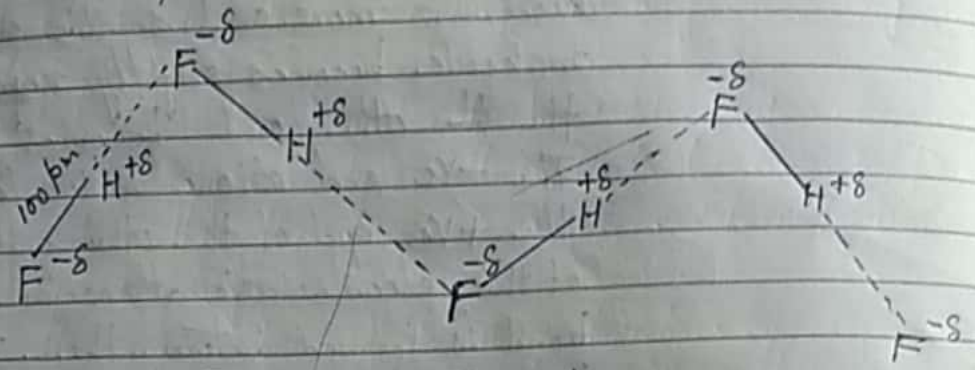
Types of hydrogen bonding : There are two types of hydrogen bonding :

Intermolecular hydrogen bonding :

When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding.

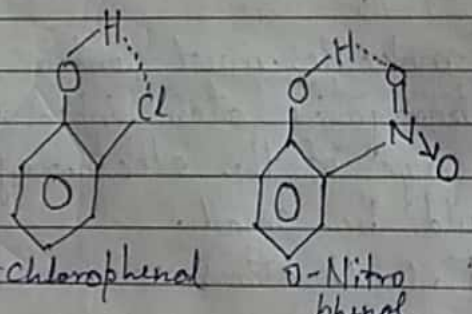
For Example ;



In case of HF, H_2O, NH_3, ROH etc; the hydrogen bonding causes association of several molecules but in carboxylic acids, it is limited to two molecules.

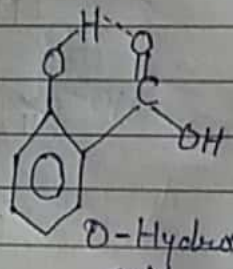
Intramolecular hydrogen bonding :

The hydrogen bonding which takes place entirely within a molecule itself is called intramolecular hydrogen bonding.

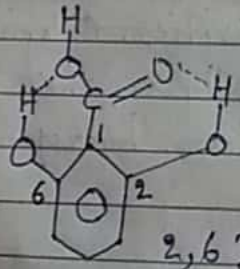


O-Chlorophenol

O-Nitro phenol



O-Hydroxybenzoic acid.
(Salicylic acid)



2,6 Dihydroxybenzoic acid.

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Conditions for intramolecular hydrogen bonding.

The following conditions must be satisfied for intermolecular hydrogen bonding:

(i) The molecule should be contain two groups such that one group contains H-atom linked to a highly electronegative atom and the other group should also contain a highly electronegative atom linked to a lesser electronegative atom.

(ii)

(ii) The molecules should be planar.

(iii) The hydrogen bonding should lead to the formation of either a five or a six-membered ring including the H-atom.

Effect of intermolecular hydrogen-bonding on melting point and boiling points.

In general, intermolecular hydrogen bonding leads to association of molecules. As a result, such molecules have high melting and boiling point.

Some important examples are give below:

(a) Water.

Water is a liquid at room temp. while all other hydrides like H_2S, H_2Se, H_2Te of group 16 are gases. This may be explained as follows:

Melting and boiling points of the hydrides of Gr. 16.

Physical constant	H_2O	H_2S	H_2Se	H_2Te
Molecular Mass	18	34	81	130
Melting point	273K	190K	209K	219K
Boiling point.	373K	213.4K	231K	271.2K

In H_2O, the H-atoms are linked to the highly electronegative oxygen atom and hence undergoes intermolecular H-bonding.

Sulphur and other elements of this group

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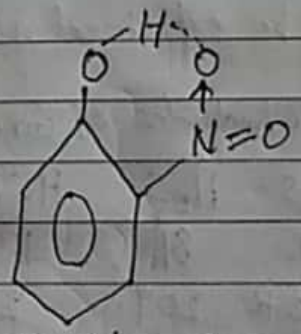
are not only less electronegative than oxygen but are also bigger in size than oxygen. As a result H_2S, H_2Se and H_2Te do not form H-bonds and hence exist as discrete molecules.

(b) Hydrogen fluoride (HF). In a similar way amongst the hydrides of Gr. 17, HF has the lowest molecular mass but still in a liquid and has the highest boiling point.

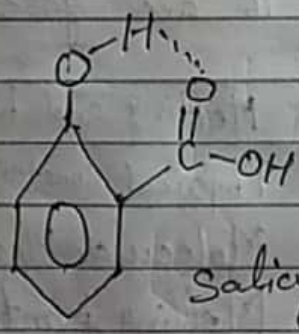
Effect of intramolecular hydrogen bonding on melting and boiling points.

Compound which involve intramolecular hydrogen bonding usually melt or boil at a lower temperature than those which involve intermolecular hydrogen bonding.

The reason being that intramolecular hydrogen bonding takes place between two ortho substituted groups and thus prevents association of the molecules. As such these compounds exist as discrete molecules and to melt or boil them only a small amount of energy is required. Intramolecular hydrogen bonding is not possible in case of m- and p- isomers because of the large size of the ring which would be formed. m- and p- isomers melt and boil at higher temp. than o- isomers.



o-Nitrophenol
(Intramolecular H-bonding)



Salicylic acid.

Intramolecular H-bonding

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