C3T

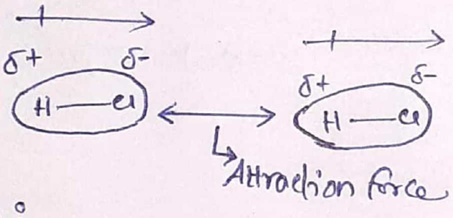
Intermolecular Forces (Vander Waal's forces):

Intermolecular forces are the forces of attraction existing among the molecules of a substance (Solid, liquid or gaseous). The magnitude of these forces is maximum in the Solids and decreases on passing from Solid to liquid and from liquid to gas. These forces are purely electrostatic and thus physical in nature.

Types and Origin of Intermolecular forces —

(a) Dipole - dipole Attractions (or Keesom forces):

These force exist between polar molecule like HF, H_2O etc. Such molecules have a partial possitive charge at one end and a partial negative charge at the other end. They are called dipoles. The possitive end of one dipole attracts the negative end of the other.



Characteristics:

(i) It is more stronger than London force having energy 5 - 25 kJ $mole^{-1}$.

(ii) The attraction force is depend on polarity of the bond (molecule) which is depend on electronegativity difference. Greater polarity greater will be attraction force.

(iii) If 'r' is distance between two dipole, the attraction force is directly proportional to $\frac{1}{r^6}$.

(b) Dipole - induced dipole attraction:

It is the attraction force between a molecule having parmanent dipole and a non-polar molecule.

Ex- H_2O…… I_2, Kr …… $(phenol)_2$ etc.

when a non-polar molecule reaches to a polar molecule, non-polar molecule induces some dipole by the influence of electron cloud of polar molecule. By the induction of polar molecule, non-polar molecule gain some temporarily dipole character. For this reason there arrise attraction force between two molecule. This attraction force is known as dipole-induced dipole attraction.

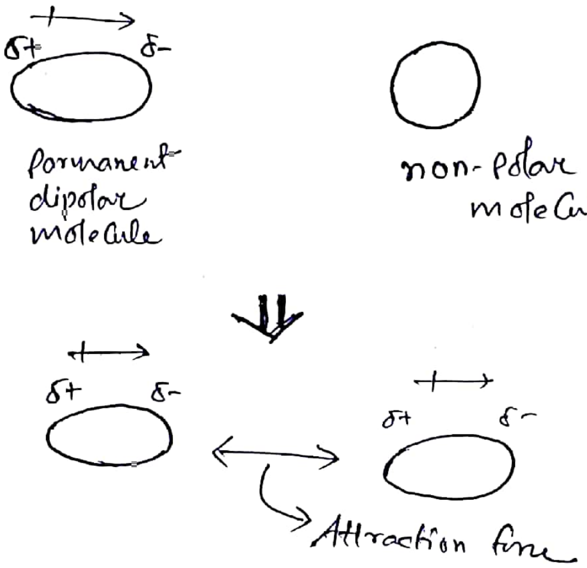


Fig — dipole - induced dipole attraction.

Characteristics

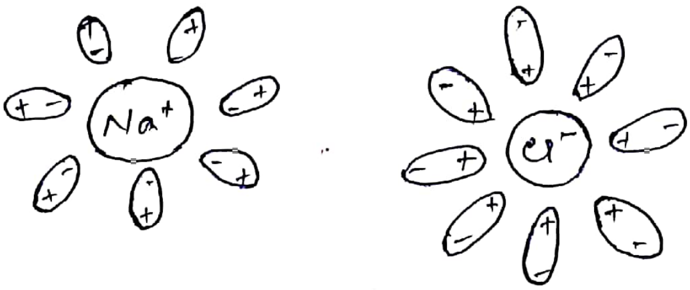
① attraction force $\propto \frac{1}{r^6}$

(ii) force energy $\simeq$ 2−10 KJ mol^{-1}

(iii) Its depend on polarity of polar molecule & polarisibility of non-polar molecule

(c) <u>Ion - dipole attraction</u> :

It is an attraction force between an ion and a polar molecule. when a ionic compound is dissolve in polar solvent, then cation / anions of ionic compound are sorrounded by the opposite end of the solvent polar molecule. Ex- when NaCl is dissolve in water, then this type of interaction are observed. $NaCl \rightleftharpoons Na^+ + Cl^-$



Ion-dipole interaction.

(d) Instantaneous induced dipole - instantaneous induced dipole: attraction force :

All types of molecule (polar or non-polar) and molecule Consist this type of attraction. All gaseous non-polar molecule like H_2, O_2, N_2, CH_4 or noble gas He, Ne, Ar have this type of interaction by which gases can converted easily to liquid. This type of force is also known as **London force**.

All molecule or atom consist (+)ve & (-)ve charge accordiningly. But if in an atom have an fractuation of electron cloud from nucleous, then induced dipole in appear. when this instantaneous dipoles comes to another molecule or atom the another molecule/atom can be induceds ands an electrostatic force of attraction arrise. This is London force.

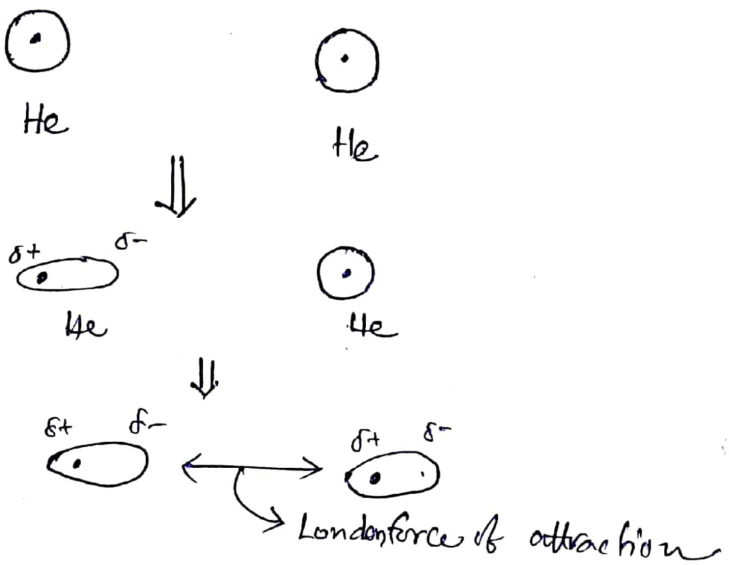


Fig: Intantaneous induced dipole - instantaneous induced dipole attraction.

Characteristics:

(i) This attraction force is also directly proportional to $\frac{1}{r^6}$.

(ii) Force energy 0.05 - 40 KJ mol^{-1}

(iii) It also depends on polarity of molecule & poralisibility of atoms.

Factors affecting the strength of London's force :

(i) Atomic and molecular size :

Atoms and molecules with large size have large surface area. Their electron clouds thus become diffused and distored. As a result, these force become stronger, e.g; Argon gas has higher BP (87.3 K) than Ne gas (27 K) which suggests the presence of stronger attractive forces in argon.

(ii) Molecular weight :

As the molecular wt. of a substance or atomic wt for inert gas increases, its molecular size increases. Also its surface area increases. Hence these forces become stronger.

N:B:
Q. Boilling point of Octane (C_8H_{18}) is more than hexane (C_6H_{14}) — Explain.

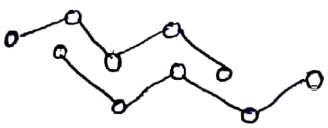
Ans: Hints; molecular wt. of octane is greater than hexane.

(iii) Molecular shape :

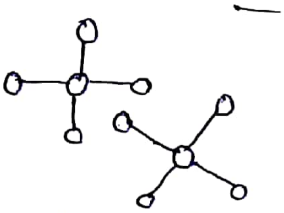
Certain molecules have such a shape which provides maximum chances of attraction between them. These molecules have high boiling point. These molecules have low boiling points have ~~mi~~ a shape where have lesser chances of attraction between them.

N:B: Q. n-pentane have less boiling point than neo-pantane. — Explain.

Ans: Hints:



n-pentane (B:P = 309 K)
Close interaction is possible



neo-pantane (B.P = 282 K)
less interaction is possible.

(iv) Temperature :

At low tempr. the K.E. of atoms (inert gas) or molecules decreases. Thus, the magnitude of London's forces increases.

(v) pressure : At high pressure, the atoms (inert gas) or molecules come close. The interaction between them increases. Thus the magnitude of London's forces increases.

(vi) Number of electrons in atoms (inert gases) and molecules :

Atoms or molecules having large size have large number of electrons. Large number of electrons result in a greater diffusion of electron clouds and greater polarization. As a result, there is stronger inter-atomic or inter-molecular interactions. This causes higher boiling points of atoms or molecules with large number of electrons.

General characteristics of Van der waal's forces :

(i) These forces are much weaker than ionic and covalent bonds. Their strength is minimum among gases, more in liquids and maximum in solid state.

(ii) The magnitude of vander waal's forces is indicated by the melting and boiling points of substances. Higher the melting and boiling points, stronger are these forces between them.

(iii) These forces are not affected by the presence of other atoms or molecules.

Q. F_2 & Cl_2 are gas, Br_2 liquid and I_2 is solids — Explain.

Hydrogen Bonding

Defination : A hydrogen bond is formed between an H-atom attached to an electronegative atom, and an electronegative atom that possesses a lone pair of electron.

In $X-H\cdots Y$, H-bonding is formed between H & Y. where atom Y may or may not be same as X. It is not necessary for the electronegative atom X to be highly electronegative for there to be a meaningful H-bonded interaction. Thus, in addition to hydrogen bonds of the type $F-H\cdots F$, $O-H\cdots F$, $O-H\cdots O$, $N-H\cdots O$, $O-H\cdots N$ and $N-H\cdots N$, it is now well recognised that weaker H-bonds, in particular $C-H\cdots O$ interactions. play an important role in the solid state structure of small molecules and biological system.

A modern defination of a hydrogen bond which does not rely directly on the concept of electronegativity has been proposed by Steiner.

An $X-H\cdots Y$ interaction is called a hydrogen bond if it constitutes a local bond and if X—H acts as a proton doner to Y.

A ~~bo~~ broad definition has recently been proposed by the IUPAC :

A hydrogen bond is an attractive interaction between the hydrogen from a group X—H and an atom or a group of atoms Y, in the same or different molecule(s), where there is evidence of bond formation.

The strength of the H-bond depends on the electronegativity of the atoms, classifies hydrogen bonds as very strong $[F\cdots H\cdots F]^-$ or $(O{-}H\cdots OC)$ and weak $(EH\cdots O)$ depending on the bonds energy

Molecule	Bond Dissociation energy (KJ mole^{-1})
H-F	567
H—Cl	431
H—Br	366
H—I	298

Hydrogen bonding may be symmetrical or unsymmetrical. In unsymmetrical H-bonding, the H-atom is not midway between ~~to~~ two nuclei, even when the heavier linked atoms are identical. for example, the $[Cl\,HCl]^-$ ion is linear but the H-atom is not midway between the Cl-atoms. By contrast, in the bifluoride ion, $[FHF]^-$, the H-atom lies midway between the F-atoms, the ~~bd~~ F–F bond distance (226 pm) is significantly less than twice the van der Waals radius of the F atom (2 × 135 pm). This is shown in fig: 10.9.

The structures of hydrogen bonded complexes have been observed in the gas phase by microwave spectroscopy. The lone pair orientation of electron rich compounds implied HF orientation fig- 10.11. For example, HF is oriented along the threefold axis of NH_3, collinear with HCN and, out of the H_2O plane in its complex with H_2O, and off the HF axis in the HF dimers.

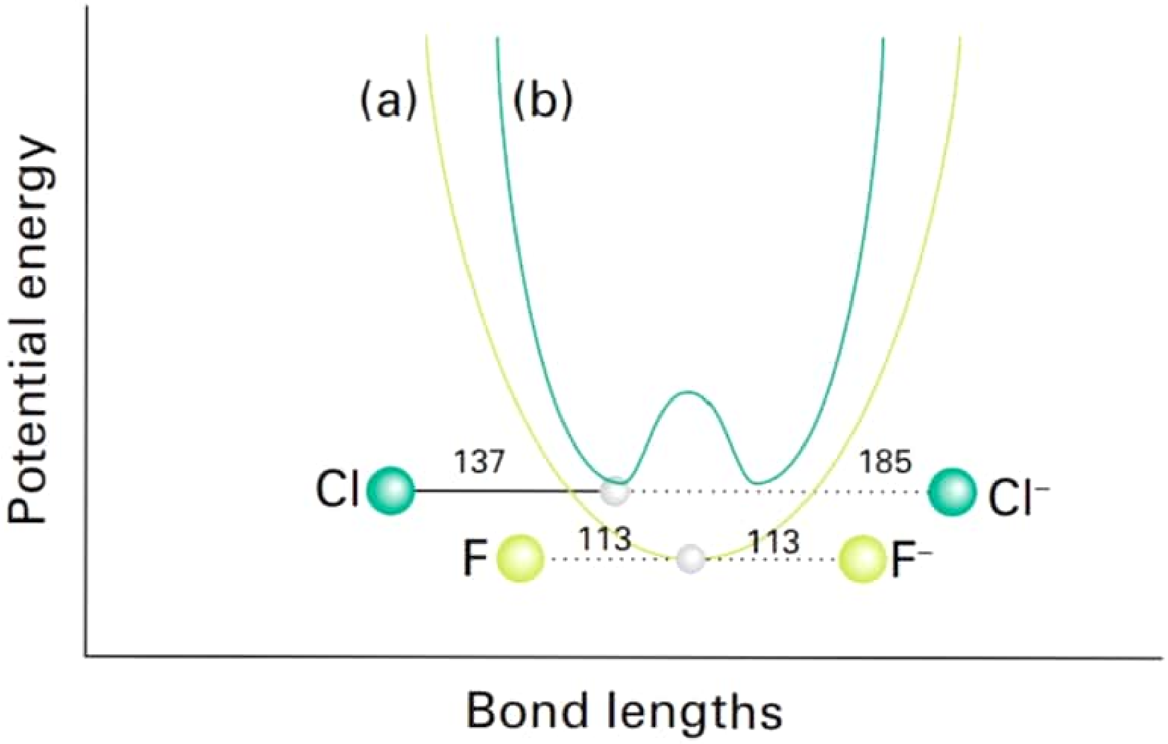


Figure 10.9 The variation of the potential energy with the position of the proton between two atoms in a hydrogen bond. (a) The single minimum potential characteristic of a strong hydrogen bond. (b) The double minimum potential characteristic of a weak hydrogen bond.

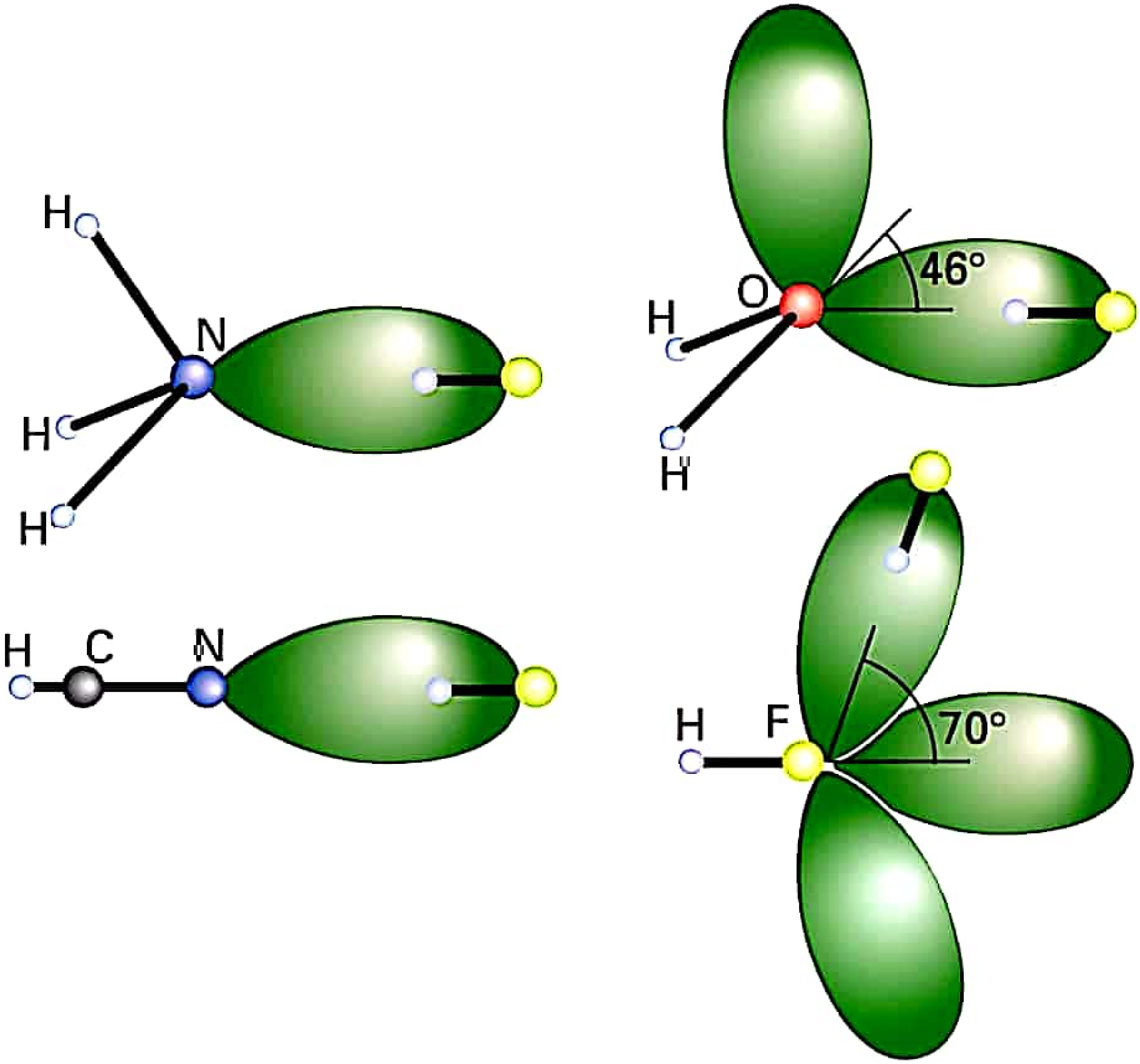


Figure 10.11 The orientation of lone pairs as indicated by VSEPR theory compared with the orientation of HF in the gas-phase hydrogen-bonded complex. The HF molecule is oriented along the threefold axis of NH_3, collinear with HCN, out of the H_2O plane in its complex with H_2O, and off the HF axis in the HF dimer.

It is now well recognized that the term hydrogen bonding covers a wide range of interaction with a corresponding variation in strength of interaction. Table 10.4 lists representative examples.

~~Some application of H-bonding~~ -

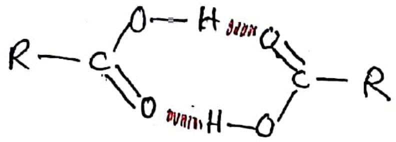
~~(i)~~ Classification :

H-bonding is generally two types -

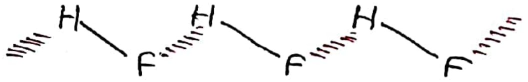
(i) Intermolecular H-bonding :

When H-bonding occurs between two molecule, i,e; Hydrogen atom and nearest electronegative atom are ~~two~~ ~~differ~~ have to be two different molecule (same type/different atom). This is known as Intermolecular H-bonding. As example -

(a) Carboxylic acid can form dimer in its vapour phase.



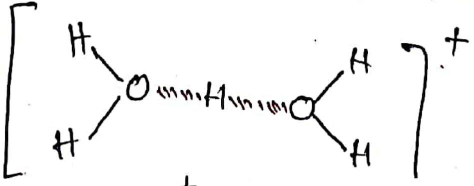
(b) H-F is liquid due to intermolecular H-bonding.



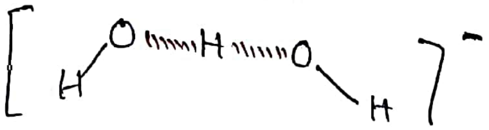
(c) In some hydrogen bonded interactions, the H-atom is symmetrically positioned, e.g; $[HF_2]^-$.

$$[F-H\cdots F^-]$$

(d) Common examples involves interactions between an acid and its conjugate base where there is no distinction between the donor (X) and acceptor (Y) atom.



$H_3O^+ + H_2O$



$H_2O + [OH]^-$

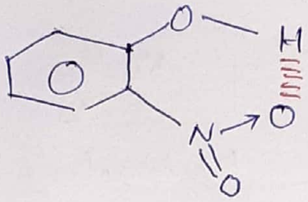
Table 10.4 Typical values for the bond dissociation enthalpy of different types of hydrogen bonds. Values are calculated for gas-phase species.†

Category of hydrogen bond	Hydrogen bond (····)	Dissociation enthalpy / kJ mol^{-1}
Symmetrical	F····H····F in $[HF_2]^-$ (see eq. 10.26)	163
Symmetrical	O····H····O in $[H_5O_2]^+$ (see structure **10.2**)	138
Symmetrical	N····H····N in $[N_2H_7]^+$ (see structure **10.4**)	100
Symmetrical	O····H····O in $[H_3O_2]^-$ (see structure **10.3**)	96
Asymmetrical	N–H····O in $[NH_4]^+$····OH_2	80
Asymmetrical	O–H····Cl in OH_2····Cl^-	56
Asymmetrical	O–H····O in OH_2····OH_2	20
Asymmetrical	S–H····S in SH_2····SH_2	5
Asymmetrical	C–H····O in HC≡CH····OH_2	9
Asymmetrical	C–H····O in CH_4····OH_2	1 to 3

(ii) Intramolecular H-bonding :

Intermolecular H-bonding exists between H-atom and highly electronegative atom within same molecule.

For-example- o-nitrophenol.

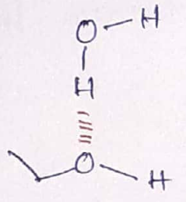


Q. Boiling point of o-nitrophenol is less than p-nitrophenol- why?

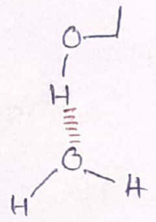
Q. HF is liquid but HCl is gas - why?

Q. Suggest why $EtNH_2$ and EtOH are miscible.

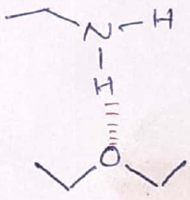
Ans:



or

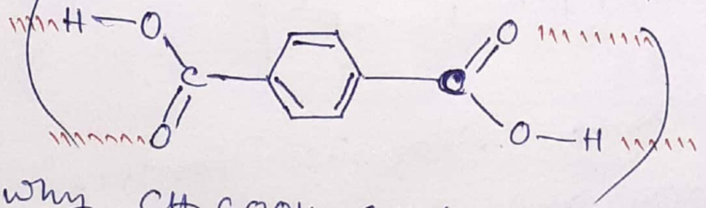


and.



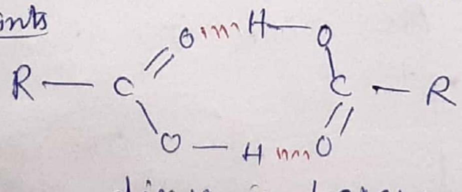
Q. Suggest how the solid state str. of benzene-1,4-dicarboxylic acid is affected by H-bonding.

Ans: Intermolecular H-bonding between difunctional carboxylic acids can results in the formation of chains.



Q. Suggest why CH_3COOH exists mainly as dimers in hexane but as monomers in water.

Ans: Hints



dimer in hexane

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

dissociation in polar H_2O medium.