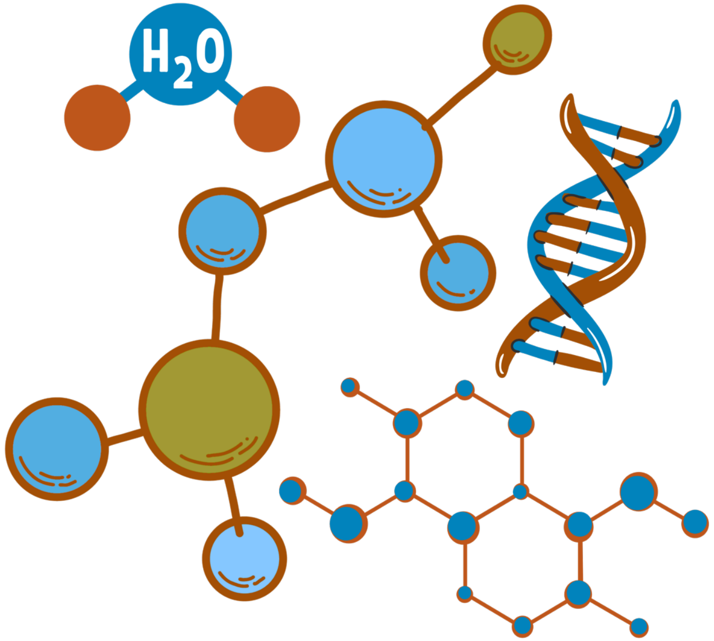
Introduction to Organic Chemistry
CHEM 109

جامعة الملك سعود
King Saud University
COLLEGE OF SCIENCES
CHEMISTRY DEPARTMENT

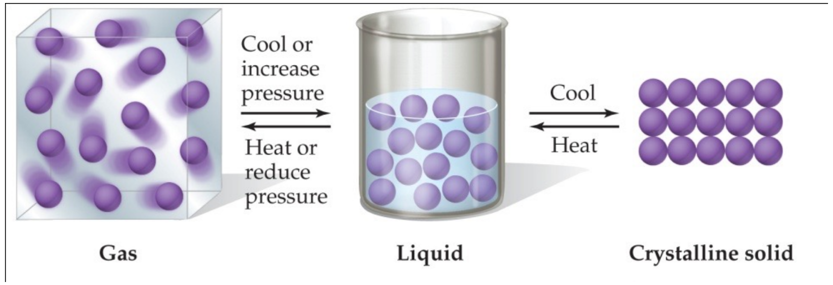
Chapter 4: *Physical Properties and Intermolecular Forces*



Chapter 4: Physical Properties and Intermolecular Forces

4.1 The States of Matter

- **The fundamental difference between states of matter (gas, liquid, solid) is the distance between particles.**
- **Physical properties of compounds; such as melting point (m.p.), boiling point (b.p.) and solubility, etc.**



- **Factors affecting the physical properties are:**

1. Molecular weight:

Increasing the molecular weight will increase b.p. and m.p.,

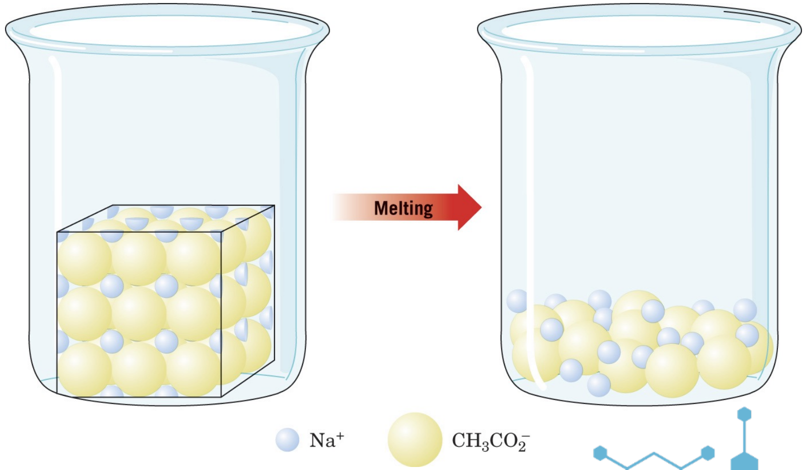
Example; **ethane (CH_3CH_3) boils at -88.3 °C higher than methane (CH_4) which boils at -162 °C.**

2. Intramolecular forces.

These forces work within the molecule which include ionic bonds (ion-ion forces) and covalent bonds.

The ionic bond holds atoms very strongly than covalent bond.

- Ion-Ion Forces are between positively and negatively charged ions.
- Boiling points are high that organic ions often decompose before they boil.
- *Example;* **Sodium acetate**



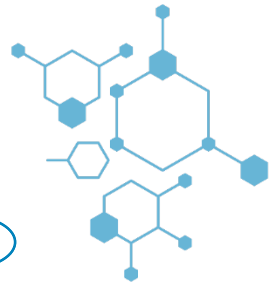
3. Intermolecular forces.

- **The strength of intermolecular forces (forces between molecules) determines the physical properties (i.e. m.p., b.p. and solubility) of a compound.**
- More energy must be expended to overcome very strong forces between molecules.

- **The physical properties of some representative compounds are shown**

Compound	**Structure**	**mp (°C)**	**bp (°C) (1 atm)**[a]
Methane	CH_4	– 182.6	– 162
Ethane	CH_3CH_3	– 183	– 88.2
Ethene	$CH_2"CH_2$	– 169	– 102
Ethyne	$HC\#CH$	– 82	– 84 subl
Chloromethane	CH_3Cl	– 97	– 23.7
Chloroethane	CH_3CH_2Cl	– 138.7	13.1
Ethyl alcohol	CH_3CH_2OH	– 115	78.5
Acetaldehyde	CH_3CHO	– 121	20
Acetic acid	CH_3CO_2H	16.6	118
Sodium acetate	CH_3CO_2Na	324	dec
Ethylamine	$CH_3CH_2NH_2$	– 80	17
Diethyl ether	$(CH_3CH_2)_2O$	– 116	34.6
Ethyl acetate	$CH_3CO_2CH_2CH_3$	– 84	77

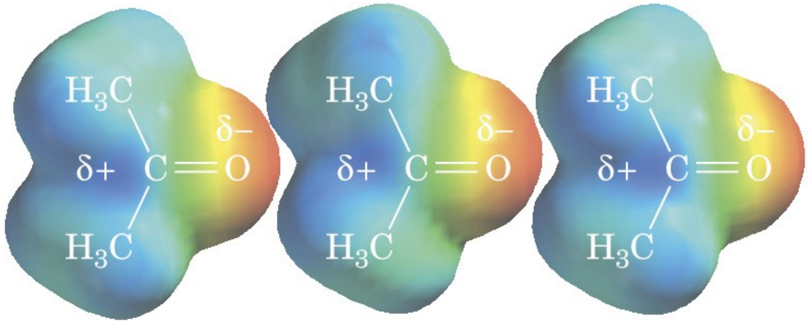
[a] In this table dec = decomposes and subl = sublimes.

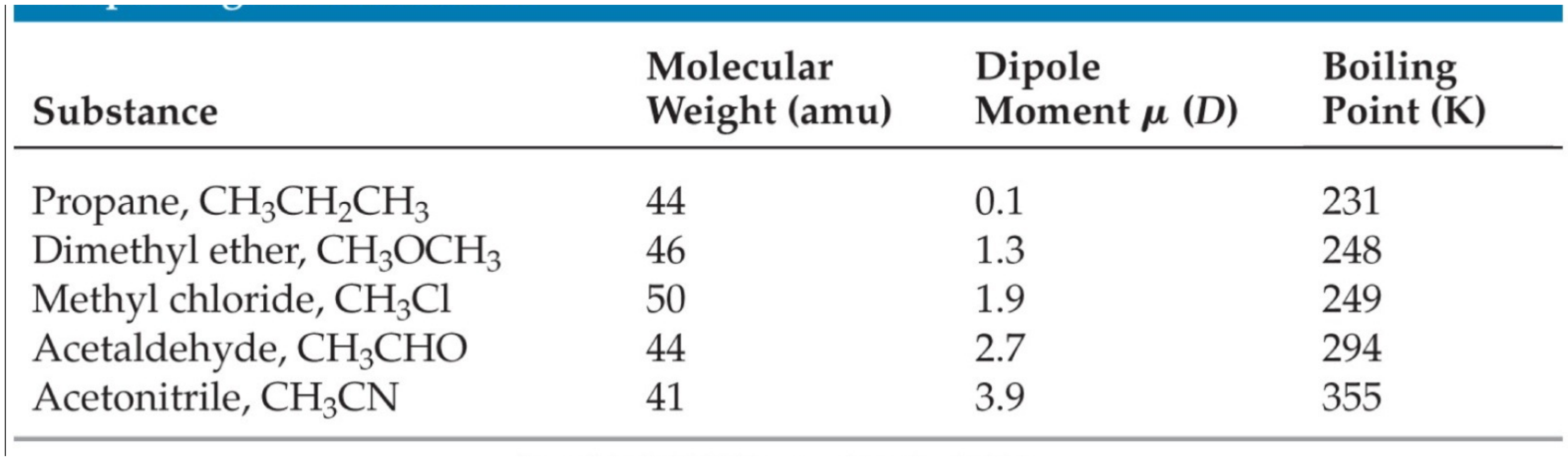


Chapter 4: Physical Properties and Intermolecular Forces

- *4.2 The Intermolecular Forces*
- *Three types of intermolecular forces controlling the physical properties.*

1. Dipole-Dipole Forces:
    - **Dipole-dipole forces are between molecules with permanent dipoles.**
    - **There is an interaction between δ+ and δ- areas in each molecule; these are much weaker than ion-ion forces.**
    - **Molecules align to maximize attraction of δ+ and δ- parts of molecules,**
    - *Example;* **acetone.**
    - **The more polar the molecule, the higher is its boiling point.**



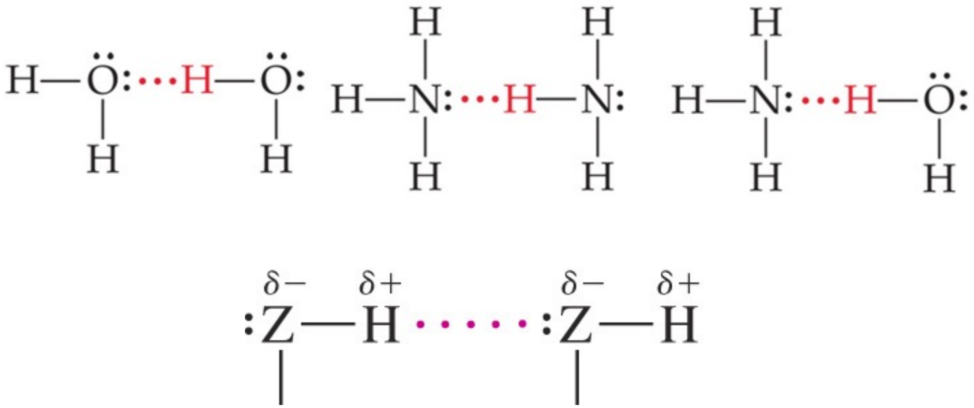


Substance	Molecular Weight (amu)	Dipole Moment μ (D)	Boiling Point (K)
Propane, $CH_3CH_2CH_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

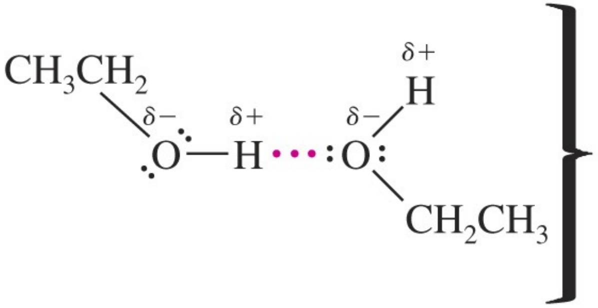
2. Hydrogen Bonds

- **Hydrogen bonds result from very strong dipole-dipole forces.**
- **There is an interaction between hydrogens bonded to strongly electronegative atoms (O, N or F) and nonbonding electron pairs on other strongly electronegative atoms (O, N or F).**
- *Example;* **Ethanol (CH_3CH_2OH) has a boiling point of +78.5 °C; its isomer methyl ether (CH_3OCH_3) has a boiling point of -24.9 °C (a gas).**

  Ethanol molecules are held together by hydrogen bonds whereas methyl ether molecules are held together only by weaker dipole-dipole interactions.

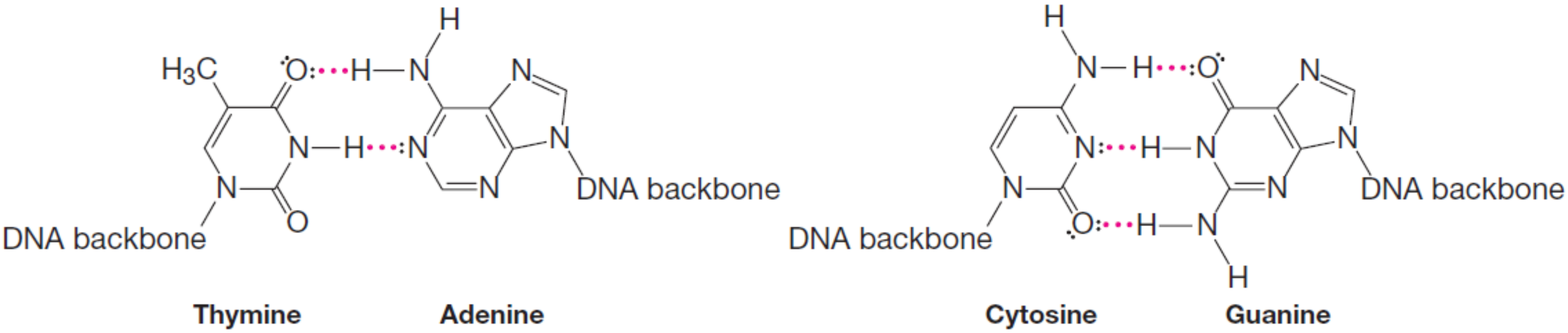


Red colored bond is hydrogen bond, Z = N,O,F

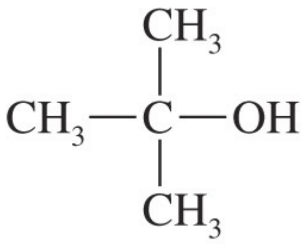


The dotted bond is a hydrogen bond. Strong hydrogen bonding is limited to molecules having a hydrogen atom attached to an O, N, or F atom.

- *Example;* **Hydrogen bonds hold the base pairs of double-stranded DNA together.**
  Thymine hydrogen bonds with adenine and Cytosine hydrogen bonds with guanine.



- **Molecules that are symmetrical generally have abnormally high melting points.**
- *Example; tert*-**Butyl alcohol has a much higher melting point than the other isomeric alcohols shown here:**

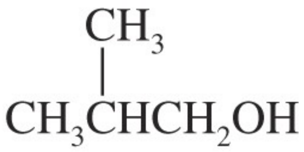


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$$

***tert*-Butyl alcohol**
(mp 25°C)

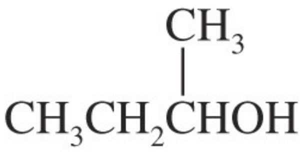
$CH_3CH_2CH_2CH_2OH$

Butyl alcohol
(mp −90°C)



$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH$$

Isobutyl alcohol
(mp −108°C)

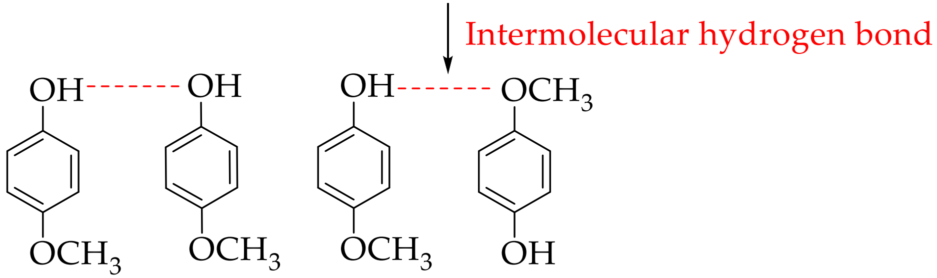


$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HOH$$

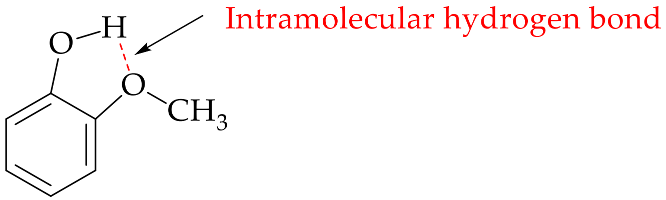
***sec*-Butyl alcohol**
(mp −114°C)

Intermolecular and Intramolecular hydrogen bonds

- **Intermolecular hydrogen bonds occur between separate molecules in a substance. For example, there are exist an intermolecular hydrogen bond in *p*-methoxyphenol. This is the normal situation for the hydrogen bonding.**
- **Intramolecular hydrogen bonds: This kind of hydrogen bonds occur within one single molecule. This occurs when two groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor and a hydrogen acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, *o*-methoxyphenol can form intramolecular hydrogen bond in contrast to its *p*-isomer.**



In *p*-Methoxyphenol the only possible hydrogen bonds occur only between molecules (intermolecular hydrogen bonds)



In *o*-Methoxyphenol the hydrogen bonds occur within molecule (intramolecular hydrogen bonds)

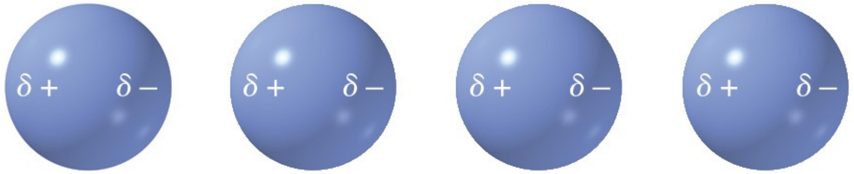
- **The intramolecular hydrogen bond results in lowering the melting, boiling points and solubility as shown in the table.**

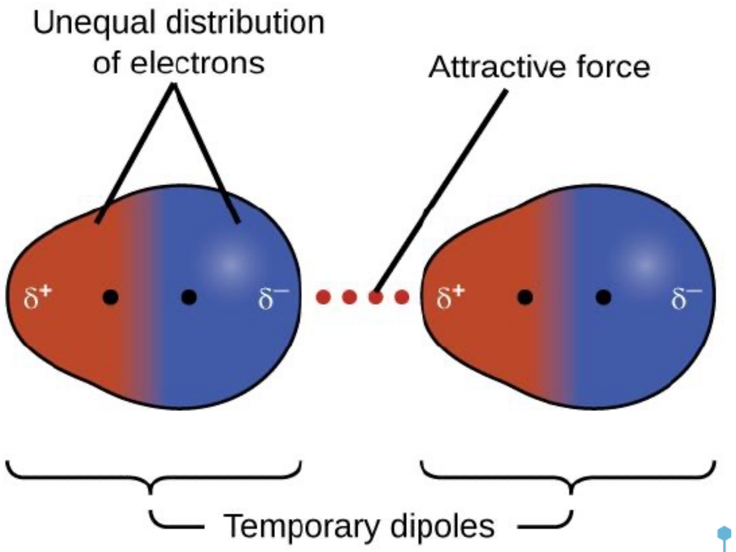
compound	Boiling point °C	Melting point °C	Solubility in water
o-methoxyphenol	205	27	Slightly soluble
p-methoxyphenol	243	57	Soluble

Chapter 4: Physical Properties and Intermolecular Forces

3. London Dispersion Forces

- **London or Dispersion Forces result when a temporary dipole in a molecule caused by a momentary shifting of electrons induces an opposite and also temporary dipole in an adjacent molecule.**
- **These temporary opposite dipoles cause a weak attraction between the two molecules.**
- **Molecules which rely only on dispersion forces generally have low melting points and boiling points.**
- **Dispersion forces occur in all molecules.**
- **Increasing the molecule size, increases dispersion forces, consequently, increasing the boiling point.**
- **Branching decrease such forces and therefore, decreasing boiling point.**

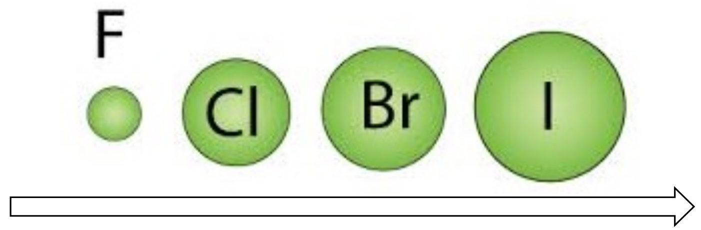




- Polarizability predicts the magnitude of Van der Waals interactions.
- Polarizability is the ability of the electrons on an atom to respond to a changing electric field.
- Atoms with very loosely held electrons are more polarizable.
- Iodine atoms are more polarizable than fluorine atoms because the outer shell electrons are more loosely held.
- Atoms with unshared electrons are more polarizable (a halogen is more polarizable than an alkyl of similar size).
- All things being equal larger and heavier molecules have higher boiling points.
- Larger molecules need more energy to escape the surface of the liquid.
- Larger organic molecules tend to have more surface area in contact with each other and so have stronger van der Waals interactions.
- Methane (CH_4) has a boiling point of -162 °C whereas ethane (C_2H_6) has a boiling point of -88.2 °C.

		Attractive Energies (kJ mol^{-1})			
Molecule	**Dipole Moment (D)**	**Dipole–Dipole**	**van der Waals**	**Melting Point (°C)**	**Boiling Point (°C)**
H_2O	1.85	36[a]	8.8	0	100
NH_3	1.47	14[a]	15	− 78	− 33
HCl	1.08	3[a]	17	− 115	− 85
HBr	0.80	0.8	22	− 88	− 67
HI	0.42	0.03	28	− 51	− 35

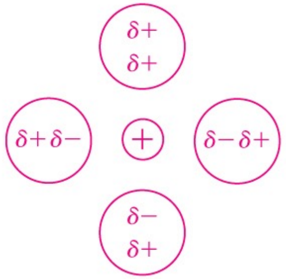
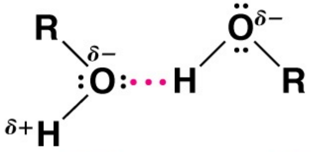
[a] These dipole–dipole attractions are called hydrogen bonds.



Polarizability increases with increasing size

Summary of Attractive Electric Forces

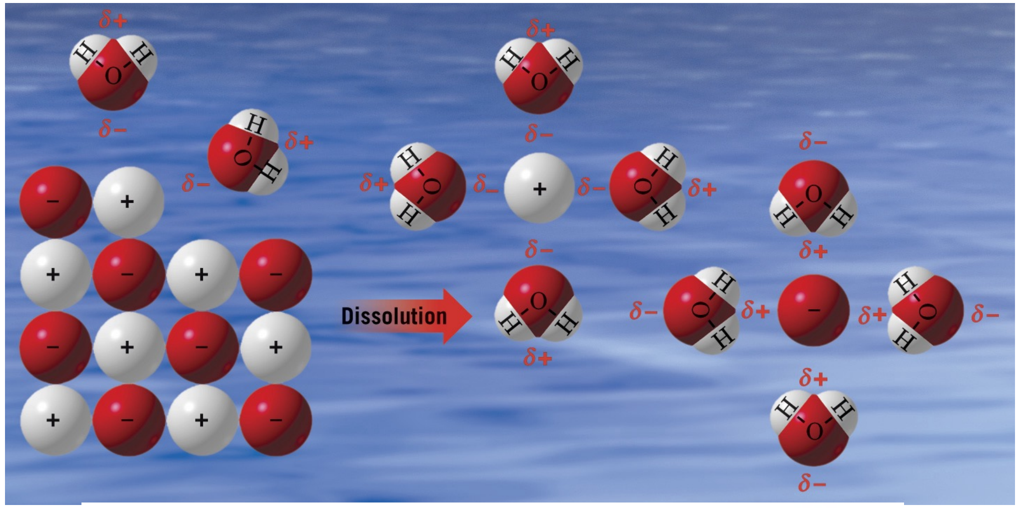
The attractive forces occurring between molecules and ions that we have studied are summarized in the following Table

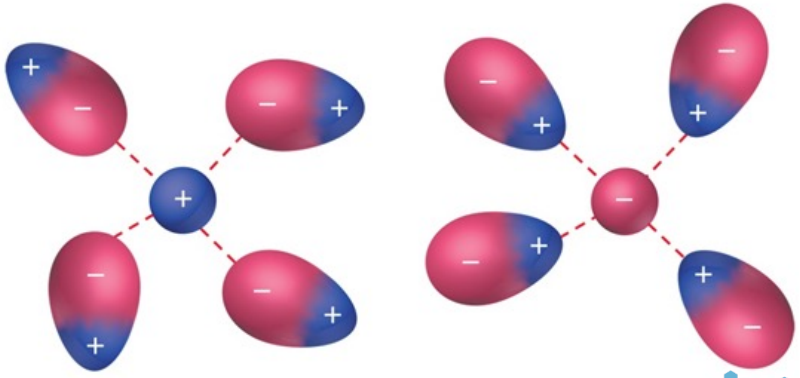
Electric Force	Relative Strength	Type	Example
Cation–anion (in a crystal)	Very strong	⊕ ⊖	Lithium fluoride crystal lattice
Covalent bonds	Strong (140–523 kJ mol^{-1})	Shared electron pairs	H—H (436 kJ mol^{-1}) CH_3—CH_3 (378 kJ mol^{-1}) I—I (151 kJ mol^{-1})
Ion–dipole	Moderate		Na^+ in water (see Fig. 2.9)
Dipole–dipole (including hydrogen bonds)	Moderate to weak (4–38 kJ mol^{-1})	$\overset{\delta-}{—Z}:\cdots\overset{\delta+}{H}—$	 and 
van der Waals	Variable	Transient dipole	Interactions between methane molecules

Chapter 4: Physical Properties and Intermolecular Forces

4.3 Solubility

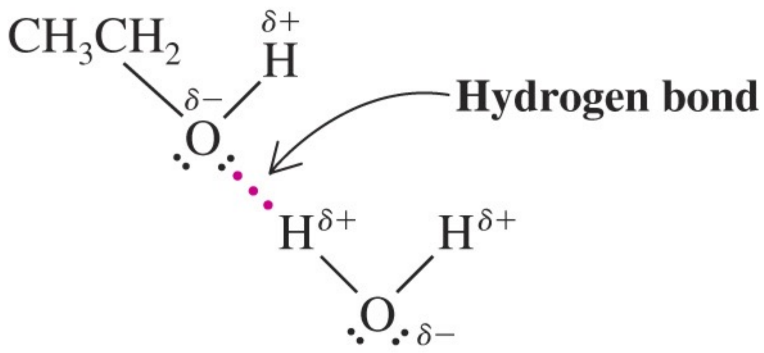
- Solubility of a substance could be explained by the intermolecular forces.
- Water dissolves ionic solids by forming strong dipole-ion interactions.
- A general rule for solubility is that “like dissolves like” in terms of comparable polarities.
  - Polar and ionic solids are usually soluble in polar solvents.
  - Polar liquids are usually miscible.
  - Nonpolar solids are usually soluble in nonpolar solvents.
  - Nonpolar liquids are usually miscible in nonpolar solvents.
  - Polar and nonpolar liquids, like oil and water, are usually not soluble to large extents.





Dipole-ion interactions

- A large alkyl group can overcome the ability of the polar group to solubilize a molecule in water.
- Decyl alcohol is only slightly soluble in water.
- The large alkyl portion is hydrophobic (“water hating”) and overwhelms the capacity of the hydrophilic (“water loving”) hydroxyl.
- Generally one hydrophilic group (e.g. hydroxyl) can make a compound with 3 carbons completely soluble in water.
- One hydrophilic group can make a 5 carbon compound at least partially soluble.



$$\underbrace{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2}OH$$

Decyl alcohol

Guidelines for Water Solubility

- Organic chemists usually define a compound as water soluble if at least 3 g of the organic compound dissolves in 100 mL of water.
- For compounds containing one hydrophilic group—and thus capable of forming strong hydrogen bonds—the following approximate guidelines hold:
  - Compounds with one to three carbon atoms are water soluble.
  - Compounds with four or five carbon atoms are borderline.
  - Compounds with six carbon atoms or more are insoluble.
- In general, increasing the hydrophilic groups in a molecule will increase its solubility in polar solvent.
- In contrast, increasing the hydrophobic groups will decrease the solubility.

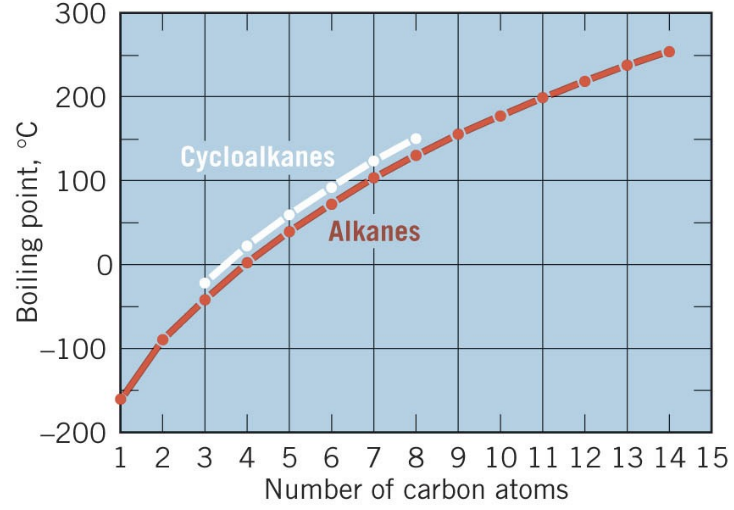
Chapter 4: Physical Properties and Intermolecular Forces

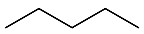
4.4 Physical Properties of some Functional Groups

1. Physical properties of hydrocarbons

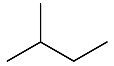
- **C1 – C4 Hydrocarbons are gases, C5 - C17 hydrocarbons are liquids, and hydrocarbons with C18 or higher are wax-like solids.**
- **Hydrocarbons are nonpolar compounds and thus, the dispersion forces controlling their physical properties.**
- **Boiling points of unbranched alkanes increase smoothly with number of carbons (increasing molecular weight).**
- **The boiling point decrease by increasing branching in alkane.**

  This branching decreases the surface area and consequently decreases the dispersion forces.
- **Melting points: increase in an alternating pattern according to whether the number of carbon atoms in the chain is even or odd.**

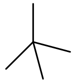




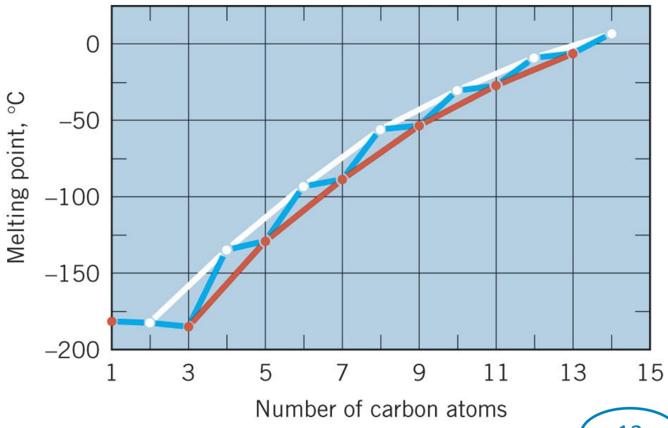
Pentane
B.p. = 36.1 ^oC
M.p. = -129.8 ^oC



Isopentane
B.p. = 27.9 ^oC
M.p. = -159.9 ^oC



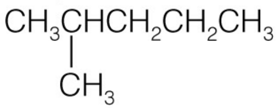
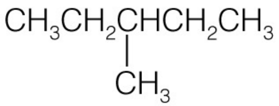
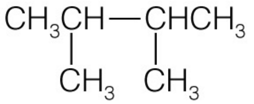
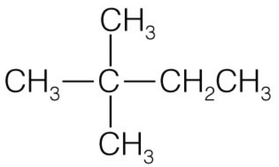
Neopentane
B.p. = 9.5 ^oC
M.p. = -16.6 ^oC



Chapter 4: Physical Properties and Intermolecular Forces

1. Physical properties of hydrocarbons

- **Solubility:** **Alkanes, alkenes, alkynes, and aromatic hydrocarbons are nonpolar compounds and thus, are soluble in nonpolar solvents like carbon tetrachloride CCl_4, and benzene.**
- **They are insoluble in polar solvents like water.**

Molecular Formula	Structural Formula	mp (°C)	bp (°C)[a] (1 atm)	Density[b] (g mL^{-1})	Index of Refraction[c] (n_D 20°C)
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	−95	68.7	0.6594^{20}	1.3748
C_6H_{14}	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_2CH_3$	−153.7	60.3	0.6532^{20}	1.3714
C_6H_{14}	 $CH_3CH_2\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	−118	63.3	0.6643^{20}	1.3765
C_6H_{14}	 $CH_3\underset{\underset{CH_3}{\vert}}{C}H-\underset{\underset{CH_3}{\vert}}{C}HCH_3$	−128.8	58	0.6616^{20}	1.3750
C_6H_{14}	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2CH_3$	−98	49.7	0.6492^{20}	1.3688

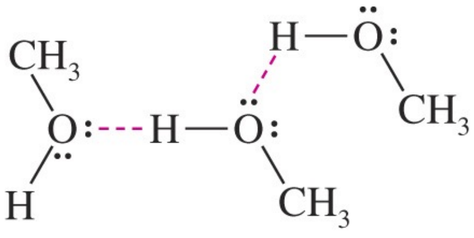
[a] Unless otherwise indicated, all boiling points given in this book are at 1 atm or 760 torr.
[b] The superscript indicates the temperature at which the density was measured.
[c] The index of refraction is a measure of the ability of the alkane to bend (refract) light rays. The values reported are for light of the D line of the sodium spectrum (n_D).

2. Physical properties of alcohols and ethers

- Ethers boiling points are roughly comparable to hydrocarbons of the same molecular weight.
- Molecules of ethers cannot form hydrogen bond to each other.
- Alcohols have considerably higher boiling point than ethers and hydrocarbons due to their ability to hydrogen bond to each other.
- Both alcohols and ethers can make hydrogen bond to water and have similar solubilities of about 8 g per 100 mL in water.
- Solubilities of alcohols in water are gradually decreases as the hydrocarbon portion increases.

Physical properties of some alcohols and ethers

Name	Formula	M.p. (°C)	B.p. (°C)	Water solubility g/100 mL H_2O
Alcohols				
Methanol	CH_3OH	−97	64.7	∞
Ethanol	CH_3CH_2OH	−117	78.3	∞
Propyl alcohol	$CH_3CH_2CH_2OH$	−126	97.2	∞
Isopropyl alcohol	$CH_3CH(OH)CH_3$	−88	82.3	∞
Butyl alcohol	$CH_3CH_2CH_2CH_2OH$	−90	117.7	8.3
Isobutyl alcohol	$CH_3CH(CH_3)CH_2OH$	−108	108.0	10.0
sec-Butyl alcohol	$CH_3CH_2CH(OH)CH_3$	−114	99.5	26.0
tert-Butyl alcohol	$(CH_3)_3COH$	25	82.5	∞
Ethers				
Dimethyl ether	CH_3OCH_3	−138	−24.9	∞
Ethyl methyl ether	$CH_3OCH_2CH_3$	−115.2	10.8	∞
Diethyl ether	$CH_3CH_2OCH_2CH_3$	−116	34.6	7.5
1,2-Dimethoxyethane	$CH_3OCH_2CH_2OCH_3$	−68	83	∞



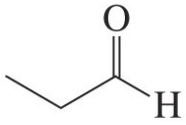
Hydrogen bonding between molecules of methanol

3. Physical properties of aldehydes and ketones

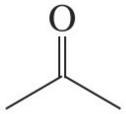
- The type of intermolecular forces in these compounds is dipole-dipole forces.
- Molecules of aldehyde (or ketone) cannot form hydrogen bond to each other.
- They rely only on intermolecular dipole-dipole interactions and therefore have lower boiling points than the corresponding alcohols.
- Aldehydes and ketones can form hydrogen bonds with water and therefore low molecular weight aldehydes and ketones have appreciable water solubility.

Formula	Name	mp (°C)	bp (°C)	Solubility in Water
HCHO	Formaldehyde	−92	−21	Very soluble
CH_3CHO	Acetaldehyde	−125	21	∞
CH_3CH_2CHO	Propanal	−81	49	Very soluble
$CH_3(CH_2)_2CHO$	Butanal	−99	76	Soluble
$CH_3(CH_2)_3CHO$	Pentanal	−91.5	102	Slightly soluble
$CH_3(CH_2)_4CHO$	Hexanal	−51	131	Slightly soluble
C_6H_5CHO	Benzaldehyde	−26	178	Slightly soluble
$C_6H_5CH_2CHO$	Phenylacetaldehyde	33	193	Slightly soluble
CH_3COCH_3	Acetone	−95	56.1	∞
$CH_3COCH_2CH_3$	Butanone	−86	79.6	Very soluble
$CH_3COCH_2CH_2CH_3$	2-Pentanone	−78	102	Soluble
$CH_3CH_2COCH_2CH_3$	3-Pentanone	−39	102	Soluble
$C_6H_5COCH_3$	Acetophenone	21	202	Insoluble
$C_6H_5COC_6H_5$	Benzophenone	48	306	Insoluble

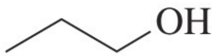

Butane
bp −0.5°C
(MW = 58)



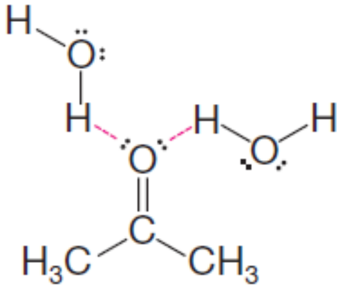
Propanal
bp 49°C
(MW = 58)



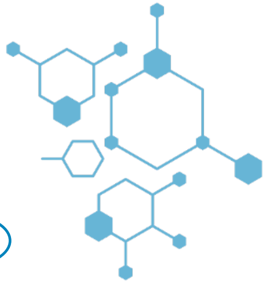
Acetone
bp 56.1°C
(MW = 58)



1-Propanol
bp 97.2°C
(MW = 60)



Hydrogen bonding (shown in red) between water molecules and acetone.



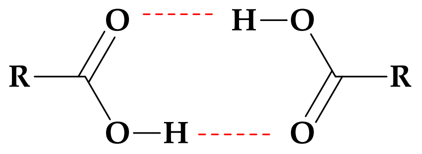
4. Physical properties of carboxylic acids and their derivatives: Carboxylic acids

- Carboxylic acids are polar substances.
- Their molecules can form strong hydrogen bonds with each others and with water.

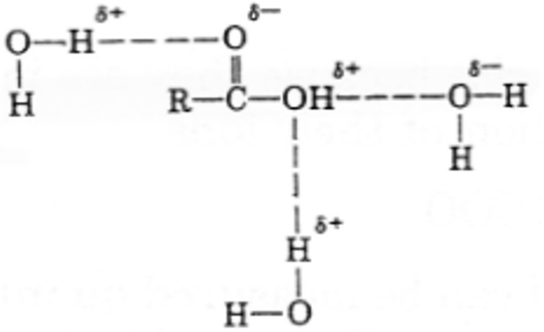
  As a result, carboxylic acids generally have high boiling points than alcohols with comparable molecular weight due to the formation of a dimer of two molecules carboxylic acids by hydrogen bond.
- Carboxylic acids with up to 4 carbons are miscible with water.

  As the length of the carbon chain increases, water solubility decreases.

Structure	Systematic Name	Common Name	mp (°C)	bp (°C)	Water Solubility (g 100 mL^{-1} H_2O), 25°C	pK_a
HCO_2H	Methanoic acid	Formic acid	8	100.5	∞	3.75
CH_3CO_2H	Ethanoic acid	Acetic acid	16.6	118	∞	4.76
$CH_3CH_2CO_2H$	Propanoic acid	Propionic acid	−21	141	∞	4.87
$CH_3(CH_2)_2CO_2H$	Butanoic acid	Butyric acid	−6	164	∞	4.81
$CH_3(CH_2)_3CO_2H$	Pentanoic acid	Valeric acid	−34	187	4.97	4.82
$CH_3(CH_2)_4CO_2H$	Hexanoic acid	Caproic acid	−3	205	1.08	4.84
$CH_3(CH_2)_6CO_2H$	Octanoic acid	Caprylic acid	16	239	0.07	4.89
$CH_3(CH_2)_8CO_2H$	Decanoic acid	Capric acid	31	269	0.015	4.84
$CH_3(CH_2)_{10}CO_2H$	Dodecanoic acid	Lauric acid	44	179^{18}	0.006	5.30



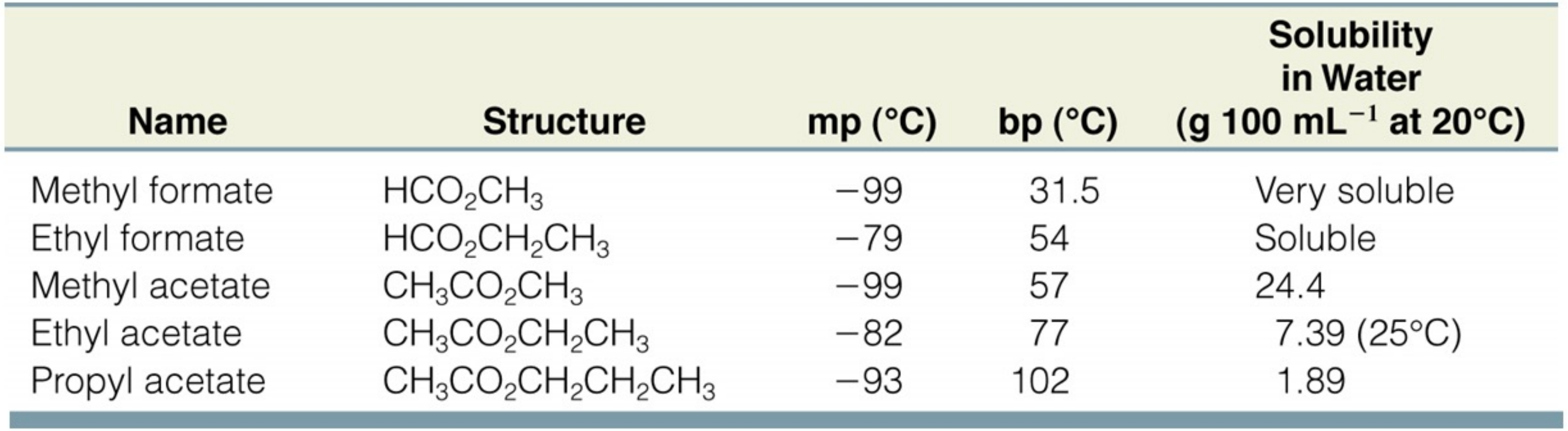
Dimer structure of two carboxylic acids



Hydrogen bond between carboxylic acid and water

4. Physical properties of carboxylic acids and their; Derivatives: Esters

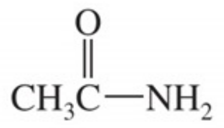
- **Esters are polar compounds, but, lacking a hydrogen attached to oxygen, their molecules cannot form strong hydrogen bonds to each other. As a result, esters have boiling points that are lower than those of acids and alcohols of comparable molecular weights.**
- **The boiling points of esters are about the same as those of comparable aldehydes and ketones.**
- **Esters can make hydrogen bond to water and have appreciable water solubility.**



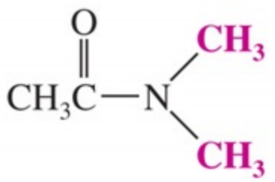
Name	Structure	mp (°C)	bp (°C)	Solubility in Water (g 100 mL^{-1} at 20°C)
Methyl formate	HCO_2CH_3	−99	31.5	Very soluble
Ethyl formate	$HCO_2CH_2CH_3$	−79	54	Soluble
Methyl acetate	$CH_3CO_2CH_3$	−99	57	24.4
Ethyl acetate	$CH_3CO_2CH_2CH_3$	−82	77	7.39 (25°C)
Propyl acetate	$CH_3CO_2CH_2CH_2CH_3$	−93	102	1.89

4. Physical properties of carboxylic acids and their Derivatives: Amides

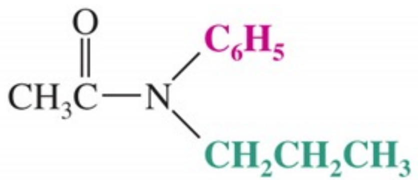
- **Amides with one or two hydrogens on nitrogen form strong hydrogen bonds and have high melting and boiling points.**
- **On the other hand, *N,N*-disubstituted amides cannot form hydrogen bonds to each other and, therefor, have lower melting and boiling points.**
- **Hydrogen bonding between amides in proteins and peptides is an important factor in determining their 3-dimentional shape.**



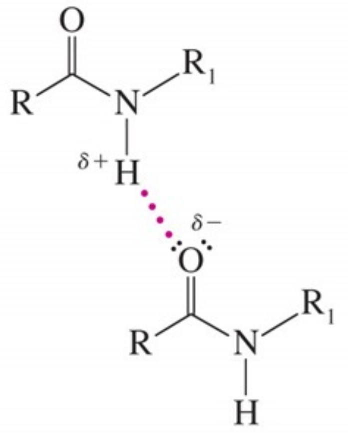
Acetamide
(ethanamide)
mp 82°C; bp 221°C



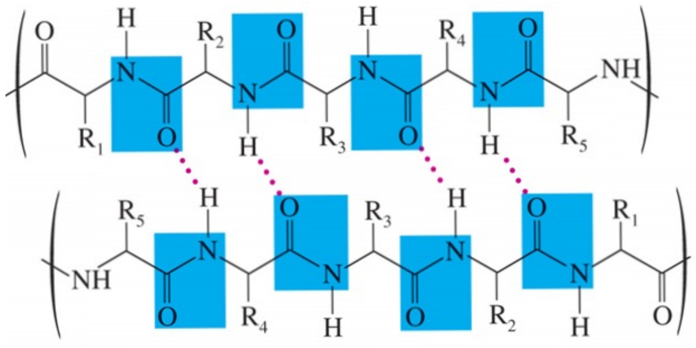
***N,N*-Dimethylacetamide**
mp −20°C; bp 166°C



***N*-Phenyl-*N*-propylacetamide**
mp 49°C; bp 266°C at 712 torr



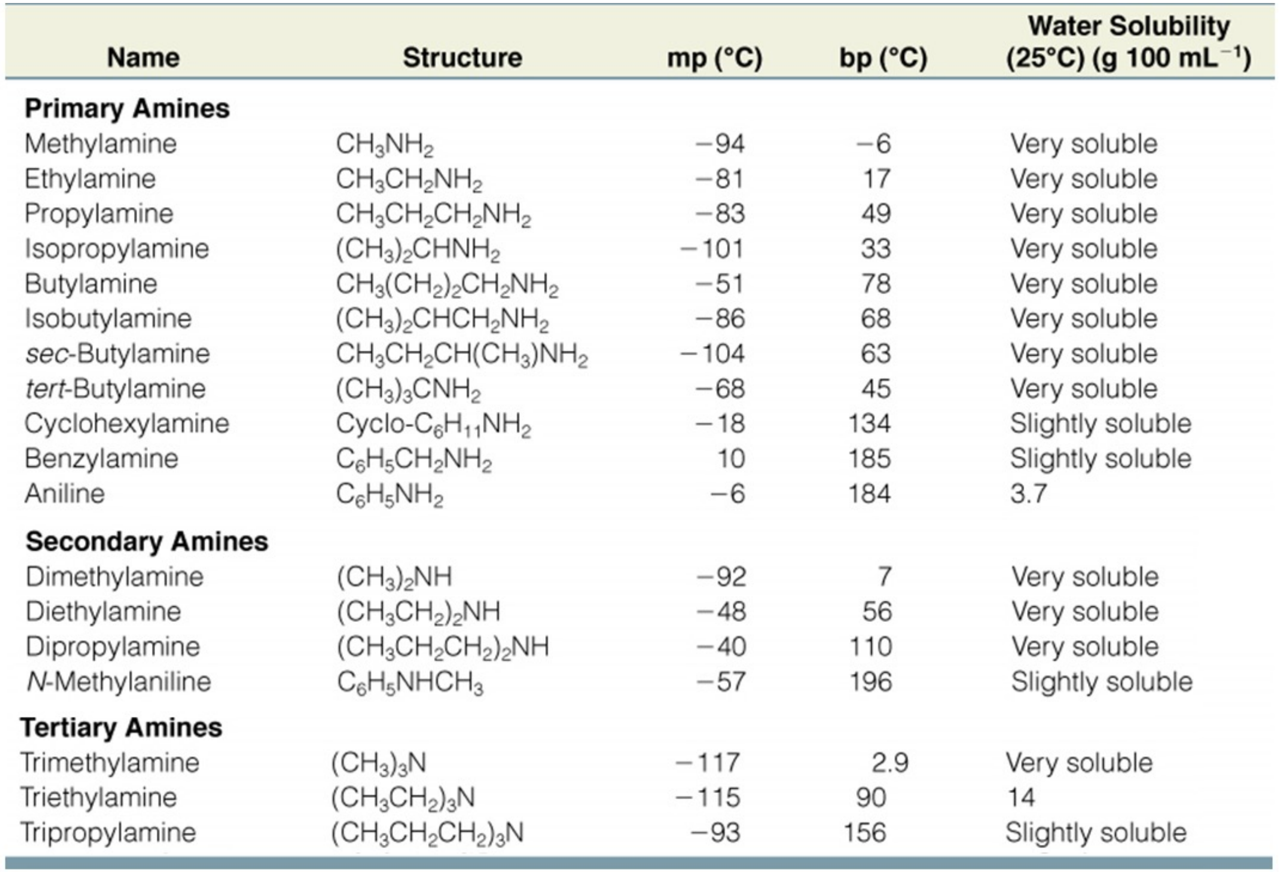
Hydrogen bonding between amide molecules



Hydrogen bonding between amide groups of peptide chains

5. Physical Properties of Amines

- Amines are moderately polar substances, they have boiling points that are higher than those of alkanes, but generally lower than those of alcohols of comparable molecular weight.
- Primary and secondary amines can form hydrogen bonds to each other and water.
- Tertiary amines cannot form hydrogen bonds to each other, but can form hydrogen bond to molecules of water or other hydroxylic solvents.
- Tertiary amines have lower boiling points than primary or secondary amines of comparable molecular weights.
- Low molecular weight amines tend to be water soluble whether they are primary, secondary or tertiary.



Name	Structure	mp (°C)	bp (°C)	Water Solubility (25°C) (g 100 mL^{-1})
Primary Amines				
Methylamine	CH_3NH_2	−94	−6	Very soluble
Ethylamine	$CH_3CH_2NH_2$	−81	17	Very soluble
Propylamine	$CH_3CH_2CH_2NH_2$	−83	49	Very soluble
Isopropylamine	$(CH_3)_2CHNH_2$	−101	33	Very soluble
Butylamine	$CH_3(CH_2)_2CH_2NH_2$	−51	78	Very soluble
Isobutylamine	$(CH_3)_2CHCH_2NH_2$	−86	68	Very soluble
sec-Butylamine	$CH_3CH_2CH(CH_3)NH_2$	−104	63	Very soluble
tert-Butylamine	$(CH_3)_3CNH_2$	−68	45	Very soluble
Cyclohexylamine	Cyclo-$C_6H_{11}NH_2$	−18	134	Slightly soluble
Benzylamine	$C_6H_5CH_2NH_2$	10	185	Slightly soluble
Aniline	$C_6H_5NH_2$	−6	184	3.7
Secondary Amines				
Dimethylamine	$(CH_3)_2NH$	−92	7	Very soluble
Diethylamine	$(CH_3CH_2)_2NH$	−48	56	Very soluble
Dipropylamine	$(CH_3CH_2CH_2)_2NH$	−40	110	Very soluble
N-Methylaniline	$C_6H_5NHCH_3$	−57	196	Slightly soluble
Tertiary Amines				
Trimethylamine	$(CH_3)_3N$	−117	2.9	Very soluble
Triethylamine	$(CH_3CH_2)_3N$	−115	90	14
Tripropylamine	$(CH_3CH_2CH_2)_3N$	−93	156	Slightly soluble