### Nanotechnolgy

Top-Down Approach
Lithographic, Manipulation, Industrial process

Bottom-Up
Self-assembly, natural process

## **Building Block**

Log, Brick
High energy physicist –quark
Physicist-proton, neutron, electron

periodic table

Chemist- molecule

Biologist- cells

#### How to assemble them

**Thermodynamic** 

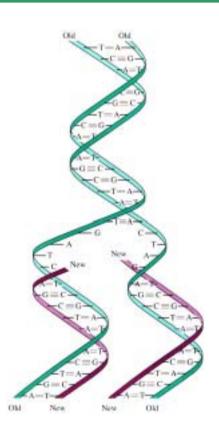
Strong-Weak interaction

Chemical bond

Hydrogen bond

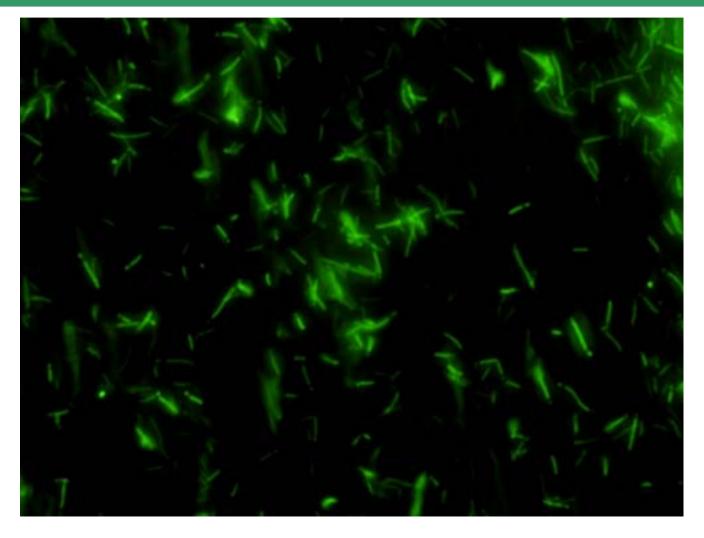
Other interaction

### Self-Assembly Process in Nature





# Cell Factory E-Coli



**Figure 1** Assembly of branched DNA molecules. **a**, Self-assembly of branched DNA molecules into a two-dimensional crystal. A DNA branched junction forms from four DNA strands; those strands coloured green and blue have complementary sticky-end overhangs labelled H and H', respectively, whereas those coloured pink and red have complementary overhangs V and V', respectively. A number of DNA branched junctions cohere based on the orientation of their complementary sticky ends, forming a square-like unit with unpaired sticky ends on the outside, so more units could be added to produce a

two-dimensional crystal. **b**, Ligated DNA molecules form interconnected rings to create a cube-like structure. The structure consists of six cyclic interlocked single strands, each linked twice to its four neighbours, because each edge contains two turns of the DNA

double helix. For example, the front red strand is linked to the green strand on the right, the light blue strand on the top, the magenta strand on the left, and the dark blue strand on the bottom. It is linked only indirectly to the yellow strand at the rear.

Figure 2 Two-dimensional DNA arrays. a, Schematic drawings of DNA double crossover (DX) units. In the meiotic DX recombination intermediate, labelled MDX, a pair of homologous chromosomes, each consisting of two DNA strands, align and cross over in order to swap equivalent portions of genetic information; 'HJ' indicates the Holliday junctions. The structure of an analogue unit (ADX), used as a tiling unit in the construction of DNA two-dimensional arrays, comprises two red strands, two blue crossover strands and a central green crossover strand. b, The strand structure and base pairing of the analogue ADX molecule, labelled A, and a variant, labelled B\*. B\* contains an extra DNA domain extending from the central green strand that, in practice, protrudes roughly perpendicular to the plane of the rest of the DX molecule. c, Schematic representations of A and B\* where the perpendicular domain of B\* is represented as a blue circle. The complementary ends of the ADX molecules are represented as geometrical shapes to illustrate how they fit together when they selfassemble. The dimensions of the resulting tiles are about 4 × 16 nm and are joined together so that the B\* protrusions lie about 32 nm apart. d, The B\* protrusions are visible as 'stripes' in tiled DNA arrays under an atomic force microscope.

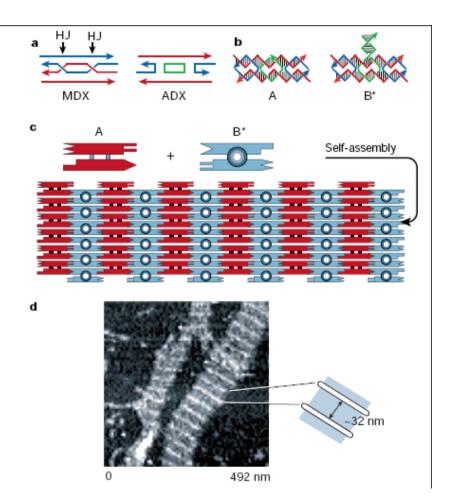


Fig. 1. Tectosquare structure and assembly principles. (A) Assembly scheme. (B) TectoRNA 2D diagram: LT tectoRNAs have stems 6 bp longer than ST tectoRNAs. N, nt positions involved in stems: x and X, nt from the 3' tail (in red) and KL loops (in green and blue) involved in Watson-Crick bp for tail-connectors or KL motif formation. respectively. RA motif consensus sequence is in orange. (C) Tectosquare 3D model (LT). Front and side views are shown. KL loops form four sequencespecific KL motifs (in blue, red, magenta, and green) that adopt collinear topologies (see also fig. S1). (D) Change of 3' tail directionality upon RA motif swapping. (E) Tectosquare cis and trans assembly configurations. (F) The five types of tectosquares used in this study.

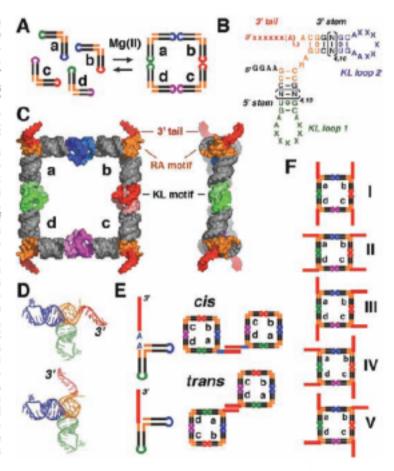
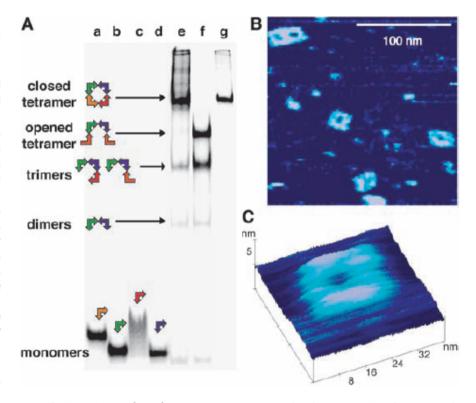
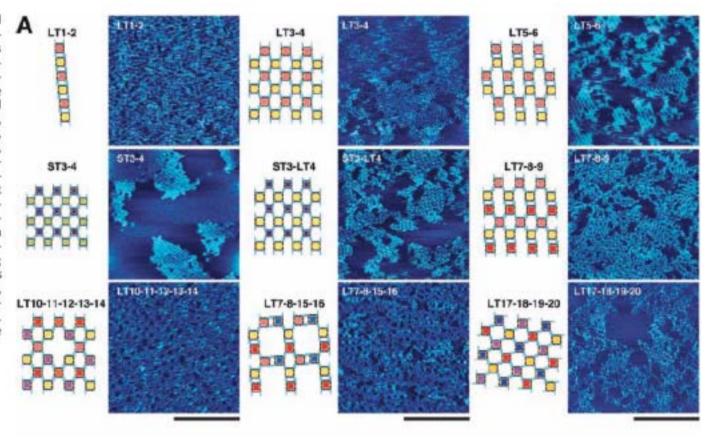


Fig. 2. RNA tectosquares are stable and stiff supramolecular assemblies. (A) Nondenaturing PAGE at 0.2 mM Mg(OAc), of various combinations of LT tectoRNAs. Lanes a, b, c, and d: tectoRNAs, a, b, c, and d, respectively, at a final concentration of 20 nM. Lane e: equimolar mixture of a, b, c, and d (20 nM each). Lane f: equimolar mixture of tectoRNAs a. b. e, and f (20 nM each). Units e and f assemble with a and b, respectively, but prevent the formation of a circular complex. Lane g: tectosquare after nondenaturing PAGE gel purification and elu-



tion at  $4^{\circ}$ C in the presence of 15 mM Mg(OAc)<sub>2</sub>. Tectosquares can be kept at  $4^{\circ}$ C for several days without showing any sign of dissociation or degradation. (B and C) AFM visualization of LT tectosquare in solution on mica surface (B) or in air after precipitation of the RNA on mica coated with poly-L-lysine (C).

Fig. 3. Diagram and AFM images of tectosquare nanopatterns generated from 22 tectosquares. (A) One micrometer square scale AFM images obtained in solution for: LT1-2, ladder pattern; LT3-4, fish net pattern; LT5-6, diamond pattern; ST3-4, striped velvet pattern; ST3-LT4, basket weave pattern; LT7-8-9, lace pattern; LT10-11-12-13-14, polka dot pattern; LT7-8-15-16, tartan pattern; LT17-18-19-20, cross pattern. Scale bars. 500 nm. (B) Magnification of patterns in (A). Scale bar, 20 nm. (See also fig. S3.)



# Review of General & Organic Chemistry

- ♦ Diameter of a nucleus is only about 10<sup>-15</sup> m.
- ♦ Diameter of an atom is only about 10<sup>-10</sup> m.

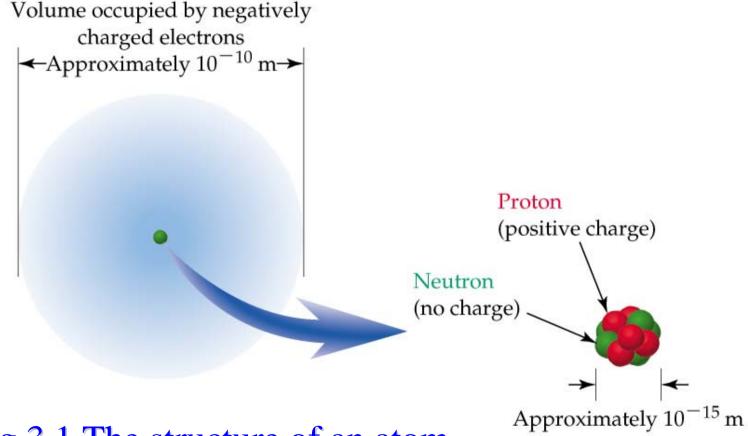


Fig 3.1 The structure of an atom

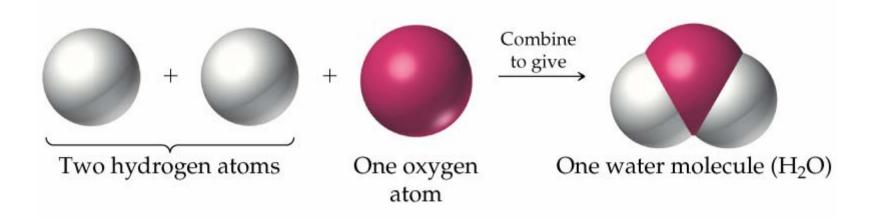
#### 1.6 Elements and the Periodic Table

**Periodic Table,** shown below, is a representation of 113 elements in a tabular format.

1.4																	
1A																	8A
1																	18
1	2A									]		3A	4A	5A	6A	7A	2
H	2																Нe
1.00794										ı		13	14	15	16	17	4.00260
3	4	1	Meta	ls		Metall	oids	N	onmet	als		5	6	7	8	9	10
Li	Be	ı										B	C	N	0	F	Ne
6.941	9.01218	3B	4B	5B	6B	7B		8B		1B	2B	10.81	12.011 14	14.0067 15	15.9994 16	18.9984 17	20.1797 18
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	s	ČΊ	Ar
22.98977	24.305	3	4	3	0	,	0	,	10	11	12	26.98154		30.9738	32.066	35.4527	39948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.0983	_	44.9559	47.88	50.9415		54.9380	55.847	58.9332	58.69	63.546	65.39	69.72	72.61	74.9216	78.96	79.904	83.80
Rb	38 <b>Sr</b>	39 <b>Y</b>	40 <b>Zr</b>	Nb	42 <b>Mo</b>	43 <b>Tc</b>	Ru	45 <b>Rh</b>	Pd	Ag Ag	48 Cd	49 <b>In</b>	50 <b>Sn</b>	51 <b>Sb</b>	52 Te	53 I	54 Xe
85.4678		88.9059	91.224	92.9064	95.94	(98)	101.07	102.9055	106.42	107.8682		114.82	118.710	121.757	127.60	126.9045	131.29
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	At	Rn
132.9054	137.33	138.9055	178.49	180.9479		186.207	190.2	192.22	195.08	196.9665	200.59	204.383	207.2	208.9804	(209)	(210)	(222)
87	88	89	104	105	106	107	108	109	110	111	112		114		116		
Fr (222)	Ra	†Ac	Rf	Db	Sg	Bh (264)	Hs	Mt	(271)	(272)	(277)					ı	
(223)	226.0254	227.0278	(261)	(262)	(266)	(264)	(269)	(268)	(271)	(272)	(277)						
				_													

	58 C <b>e</b> 0.12	59 <b>Pr</b> 140.9077	60 <b>Nd</b> 144.24	PM (145)	Sm 150.36	63 <b>Eu</b> 151.965	Gd 157.25	65 <b>Tb</b> 158.9254	Dy 162 50	67 <b>Ho</b> 164.9304	68 Er 167.26	69 <b>Tm</b> 168.9342	70 <b>Yb</b> 173,04	Lu 174.967
9 T	90 Γ <b>h</b>	91 <b>Pa</b>	92 U 238.0289	93 <b>Np</b>	94 Pu (244)	95 <b>Am</b> (243)	96 Cm (247)	97 <b>Bk</b> (247)	98 Cf (251)	99 <b>Es</b> (252)	100 Fm (257)	101 Md (258)	102 <b>No</b> (259)	103 Lr (262)

Water molecule results when two hydrogen atoms and one oxygen atom are covalently bonded in a way shown in the following picture:



A covalent bond between two hydrogen atoms is shown in this picture.

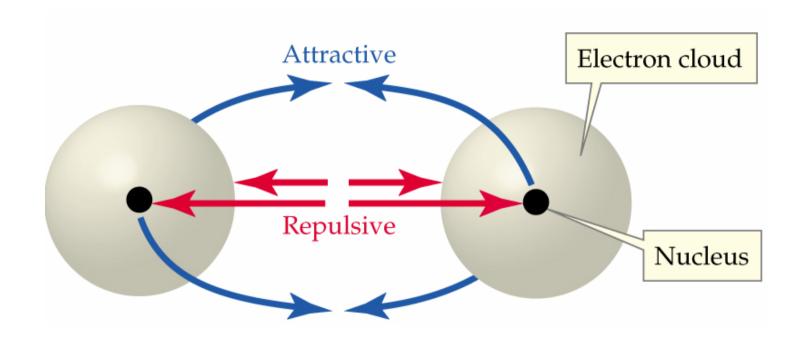
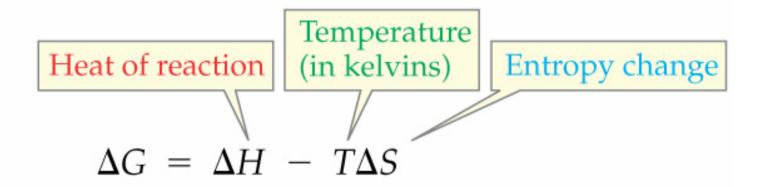


Fig 5.1 A covalent bond is the result of attractive and repulsive forces between atoms.

#### Free-energy change



The value of the free-energy change ( $\Delta G$ ) determines spontaneity.

- $ightharpoonup \Delta G$  is negative; free energy is released; process is exothermic or exergonic.
- ΔG is positive; free energy is added; process is endothermic or endergonic.

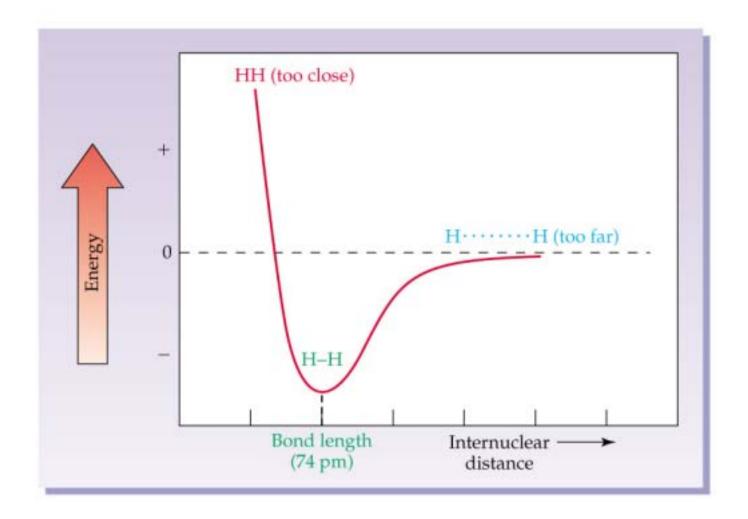
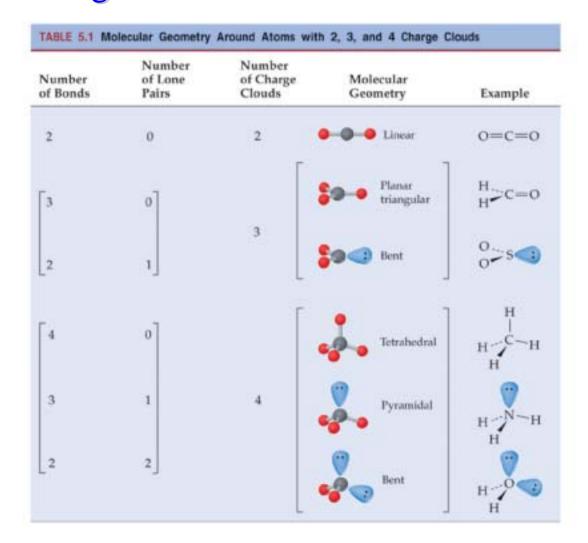


Fig 5.2 A graph of potential energy versus internuclear distance for hydrogen.

# The shape depends on the number of charged clouds surrounding the atom as summarized in Table 5.1



#### 9.1 Mixtures and Solutions

Heterogeneous mixture: A nonuniform mixture that has regions of different composition.

Homogeneous mixture: A uniform mixture that has the same composition throughout.

**Solution**: A homogeneous mixture that contains particles the size of a typical ion or small molecule.

**Colloid**: A homogeneous mixture that contains particles in the range of 2-500 nm diameter.

Solute: A substance dissolved in a liquid.

**Solvent:** The liquid in which another substance is dissolved.

#### 10.4 Water as Both an Acid and a Base

Water is neither an acid nor a base according to Arrhenius acid-base theory since water does not contain appreciable amount of H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup>. However, according to Bronsted-Lowry acid-base theory, water is both an acid and a base.

$$O$$
 $CH_3CO^- + H_2O \iff CH_3COH + OH^-$ 
Acetate ion (base) Water Acetic acid (base) Hydroxide ion (base)

		Acid		Conjugate I	Base		
Increasing acid strength	Strong acids:	Perchloric acid Sulfuric acid	$\begin{array}{c} \mathrm{HClO_4} \\ \mathrm{H_2SO_4} \end{array}$	ClO <sub>4</sub> <sup>-</sup> HSO <sub>4</sub> <sup>-</sup>	Perchlorate ion Hydrogen sulfate ion	Little or	Increasing base strength
	100%	Hydriodic acid	HI	I-	Iodide ion	no reaction	
	dissociated	Hydrobromic acid	HBr	Br-	Bromide ion	as bases	
	***************************************	Hydrochloric acid	HC1	Cl-	Chloride ion	101 101 101 101 101 101	
	Į	Nitric acid	HNO <sub>3</sub>	NO <sub>3</sub> -	Nitrate ion	J	
		Hydronium ion	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	Water		
		Hydrogen sulfate ion	HSO <sub>4</sub> -	SO <sub>4</sub> <sup>2-</sup>	Sulfate ion		
	Weak	Phosphoric acid	$H_3PO_4$	H <sub>2</sub> PO <sub>4</sub>	Dihydrogen phosphate ion	Very weak	
	acids	Nitrous acid	HNO <sub>2</sub>	NO <sub>2</sub> -	Nitrite ion	bases	
		Hydrofluoric acid	HF <sup>2</sup>	F- 2	Fluoride ion		
	ļ	Acetic acid	CH <sub>3</sub> COOH	CH <sub>3</sub> COO-	Acetate ion	J	
	ĵ	Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> -	Bicarbonate ion	)	
	XT.	Dihydrogen phosphate ion	H <sub>2</sub> PO <sub>4</sub> -	$HPO_4^{2-}$	Hydrogen phosphate ion		
	Very	Ammonium ion	NH <sub>4</sub> +	$NH_3$	Ammonia	Weak	
	weak decids	Hydrocyanic acid	HCN	CN <sup>-</sup>	Cyanide ion	bases	
	acids	Bicarbonate ion	HCO <sub>3</sub> -	CO <sub>3</sub> <sup>2-</sup>	Carbonate ion		
		Hydrogen phosphate ion	HPO <sub>4</sub> <sup>2</sup> -	PO <sub>4</sub> 3-	Phosphate ion	J	
		¥47-4	ш.о.	OH-	The description	Strong	
		Water	H <sub>2</sub> O	OH-	Hydroxide ion	J base	•

Table 10.1 Relative strengths of acids and bases

#### 10.8 Dissociation of Water

Like all weak acids, water is slightly dissociated into H<sup>+</sup> and OH<sup>-</sup> ions. The concentrations of the two ions are identical. At 25°C, concentration of each ion is 1.00 x 10<sup>-7</sup>.

Ion product constant for water, k<sub>w</sub>:

$$k_w = k_a[H_2O] = [H_3O^+][OH^-]$$
  
= [1.00 x 10<sup>-7</sup>][1.00 x 10<sup>-7</sup>]  
= 1.00 x 10<sup>-14</sup> at 25°C.

Product of [H<sub>3</sub>O<sup>+</sup>] and [OH<sup>-</sup>] is a constant. Therefore, in an acidic solution where [H<sub>3</sub>O<sup>+</sup>] is large and [OH-] must be small.

# 10.9 Measuring Acidity in Aqueous Solution: pH

A pH value between 0 and 14 is used to indicate concentration of  $H_3O^+$  or  $OH^-$  in solution. Mathematically, the pH of a solution is defined as the negative common logarithm of the  $H_3O^+$  concentration:

$$pH = -log [H_3O^+] or$$
  
 $[H_3O^+] = 10^{-pH}$ 

Acidic solution: pH < 7  $[H_3O^+] > 1.00 \times 10^{-7} M$ 

Neutral solution: pH = 7  $[H_3O^+] = 1.00 \times 10^{-7} M$ 

Basic solution: pH > 7  $[H_3O^+] < 1.00 \times 10^{-7} M$ 

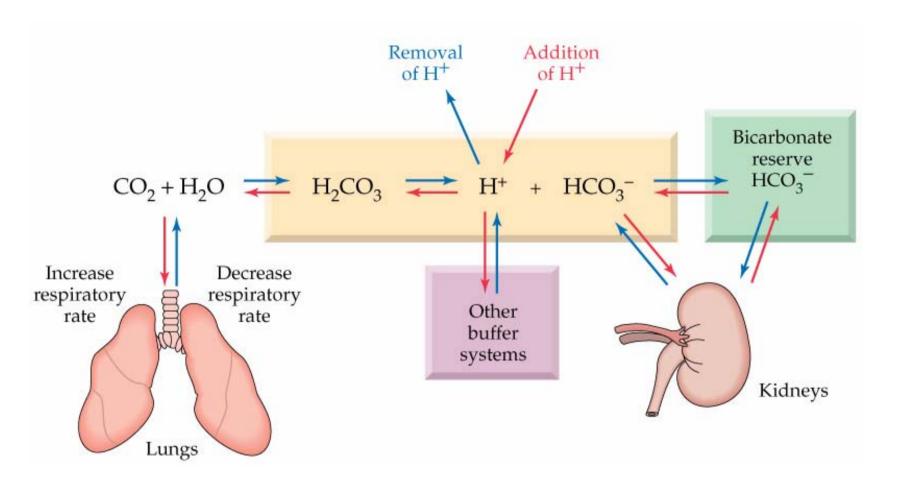


Fig 10.7 Lungs and kidneys relation with the bicarbonate buffer system

# 12.1 The Nature of Organic molecules

Organic chemistry: The chemistry of carbon compounds.

 Carbon is tetravalent; it always form four bonds.

> H—C—H H—Methane, CH<sub>4</sub>

# Organic molecules

CH

CHO, CHS

**CHN** 

C=0

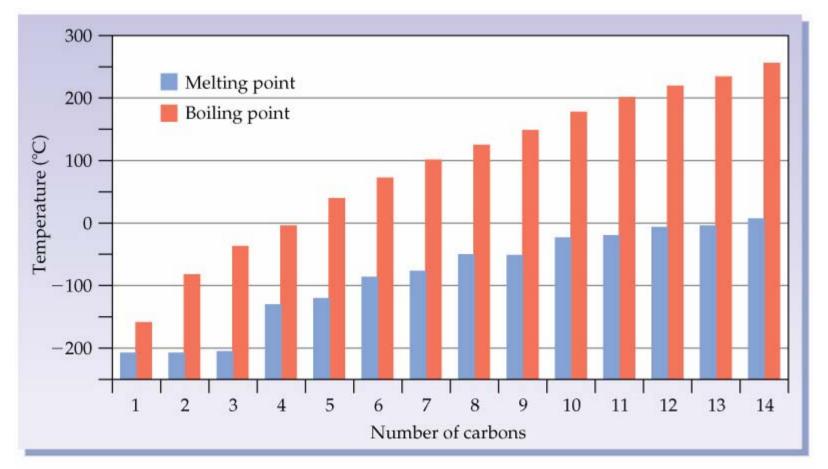
**COO** 

**CON** 

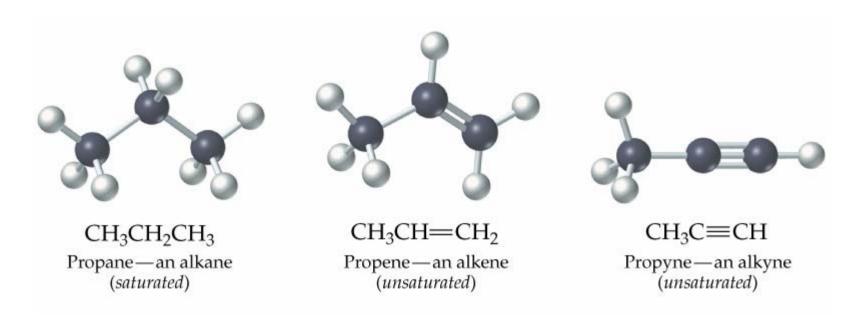
Alkane Alkene Alkyne Aromatic	Contains only C—H and C—C single bonds  C—C  —C—C	CH <sub>3</sub> CH <sub>3</sub> Ethane  H <sub>2</sub> C=CH <sub>2</sub> Ethylene  H—C=C—H Acetylene (Ethyne)  H H	-ane -ene -yne
Alkyne	)c=< -c=c )c=<		
300 <b>*</b> 000)	-c=c	H—C=C—H Acetylene (Ethyne)	-101AP
Aromatic	)c-c	\ /	3
	- C C-	H—————————————————————————————————————	None
Alkyl halide	——————————————————————————————————————	CH <sub>3</sub> —Cl Methyl chloride	None
Alcohol	-c-о-н	CH <sub>3</sub> —OH Methyl alcohol (Methanol)	-ol
Ether	-c-o-c-	CH <sub>3</sub> —O—CH <sub>3</sub> Dimethyl ether	None
Amine	-C-N	CH <sub>3</sub> —NH <sub>2</sub> Methylamine	-amine
Aldehyde	-c-с-н	O    CH <sub>3</sub> —C—H Acetaldehyde (Ethanal)	-al
Ketone		CH <sub>3</sub> —C—CH <sub>3</sub> Acetone	-one
Carboxylic acid	он	CH <sub>3</sub> —C—OH Acetic acid	-ic acid
Anhydride	-c-c-c-c-	$CH_3$ $C$	None
Ester		CH <sub>3</sub> —C—O—CH <sub>3</sub> Methyl acetate	-ate
Amide	-С-NH <sub>2</sub> , -С-С-N-H,	CH <sub>3</sub> —C—NH <sub>2</sub> Acetamide	-amide
	-c-c-n-	ned to carbon or hydrogen atoms in the rest of the molecule	

### 12.7 Properties of Alkanes

Melting points and boiling points of straight chain alkanes increases with molecular size.



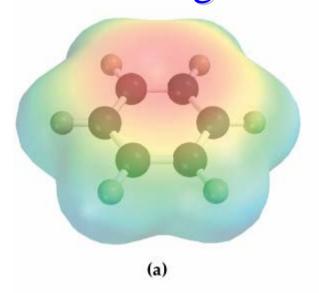
- Alkenes are hydrocarbons that contain carbon-carbon double bonds.
- Alkynes are hydrocarbons that contain carbon-carbon triple bonds.

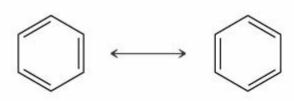


# 13.4 Properties of Alkenes and Alkynes

- Nonpolar, insoluble in water, soluble in nonpolar organic solvents.
- Less dense than water as a result floats on water.
- Flammable
- Nontoxic
- Alkenes display cis-trans isomerism whereas alkynes do not.
- Both alkenes and alkynes are chemically reactive.

- Unlike alkenes, benzene does not undergo addition reactions.
- Benzene's relatively lack of chemical reactivity is due to its structure.
- ◆ There are two possible structures with alternating double and single bonds.







Two equivalent structures, which differ in the position of their double-bond electrons. Neither structure is correct by itself.

(b)

(c)

#### 14.1 Alcohols, Phenols, and Ethers

Alcohol: A compound that has an –OH group bonded to a saturated, alkane like carbon atom, R-OH.

Phenol: A compound that has an -OH group bonded to an aromatic, benzene like ring, Ar-OH.

Ether: A compound that has an oxygen bonded to two organic groups, R-O-R.

#### 14.9 Thiols and Disulfides

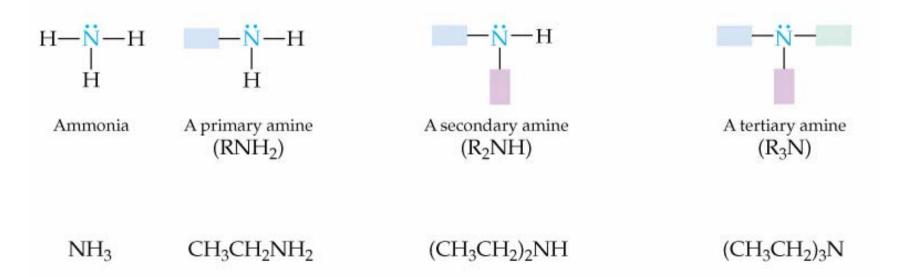
- Thiols (R-SH) are sulfur analog of alcohols (R-OH).
- The systematic name of a thiol is formed by adding -thiol to the parent hydrocarbon name.

Thiols have characteristic foul smell.

- ◆ Thiols (R-SH) react with mild oxidizing agents such as Br₂ in water to yield disulfide (R-S-S-R).
- ♦ The reverse reaction (RS-SR  $\rightarrow$  2RSH) occurs when a disulfide is treated with a reducing agent.
- ◆ S-S bonds between two amino acid cysteines gives protein molecules their required shapes in order to function.
- ◆ Hair protein is rich in S-S and −SH groups. When hair is 'permed' some of the disulfide bonds are broken and new ones are formed giving hairs a different shape.

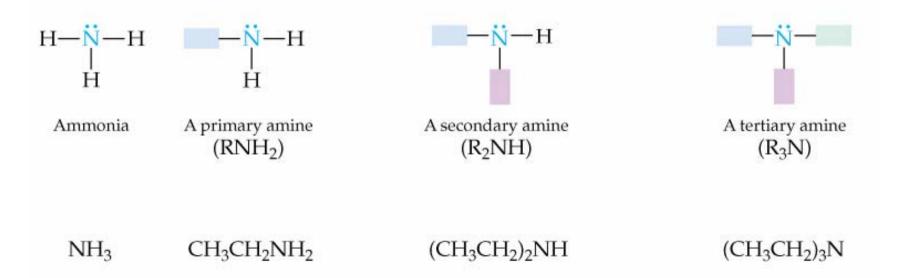
#### 15.1 Amines

Amines are compounds that contain one or more organic groups bonded to nitrogen. They are classified a primary, secondary, and tertiary according to how many organic groups are bonded to the nitrogen atom.



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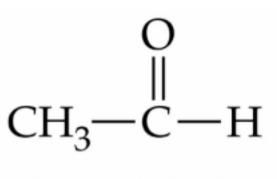
**TABLE 16.1** Some Kinds of Carbonyl Compounds

Family Name	Structure	Example	
Aldehyde	O    R—C—H	O    H <sub>3</sub> C—C—H	Acetaldehyde
Ketone	R-C-R'	$H_3C-C-CH_3$	Acetone
Carboxylic acid	O ∥ R−C−O−H	О    Н <sub>3</sub> С—С—О—Н	Acetic acid
Ester	R-C-O-R'	$H_3C-C-O-CH_3$	Methyl acetate
Amide	R-C-N	$H_3C-C-NH_2$	Acetamide

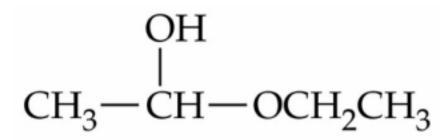
 The reaction is reversible. Hemiacetals rapidly revert back to aldehydes or ketones by loss of alcohol.

#### **Acetal Formation**

◆ In the presence of a small amount of acid catalyst, hemiacetals are converted to acetals. Acetals have two −OR groups attached to what was the original carbonyl carbon.



Acetaldehyde



Acetaldehyde hemiacetal with ethanol

Acetaldehyde acetal with ethanol

Fig 16.3 Acetaldehyde and its hemiacetal and acetal

# 17.1 Carboxylic Acids and Their Derivatives: Properties and Names

- Caboxylic acids have an -OH group bonded to a carbonyl group. In their derivatives, OH is substituted by other group. Such as,
- ♦ Esters have a −OR group bonded to a carbonyl group.
- Amides have an -NH<sub>2</sub> group bonded to a carbonyl group.

OH OR NH<sub>2</sub>
Carboxylic acid Ester Amide

Functional Group	Structure	Type of Biomolecule
Amino group	-NH <sub>3</sub> +, -NH <sub>2</sub>	Amino acids and proteins (Sections 18.3, 18.7)
Hydroxyl group	-ОН	Monosaccharides (carbohydrates) and glycerol: a component of triacylglycerols (lipids) (Sections 22.4, 24.2)
Carbonyl group	-c-	Monosaccharides (carbohydrates); in acetyl group (CH <sub>3</sub> CO) used to transfer carbon atoms during catabolism (Sections 22.4, 21.4, 21.8)
Carboxyl group	О О 	Amino acids, proteins, and fatty acids (lipids) (Sections 18.3, 18.7, 24.2)
Amide group	0 -c-n-	Links amino acids in proteins; formed by reaction of amino group and carboxyl group (Section 18.7)
Carboxylic acid ester	0  -  -  -  -  -  -  -  -  -	Triacylglycerols (and other lipids); formed by reaction of carboxyl group and hydroxyl group (Section 24.2)
Phosphates, mono-, di-, tri-		ATP and many metabolism intermediates (Sections 17.8, 21.5, and throughout metabolism sections)
	-ç-o-p-o-p-o-	
	-C-O-P-O-P-O-P-O-	
Hemiacetal group	-c-oh or	Cyclic forms of monosaccharides; formed by a reaction of carbonyl group with hydroxyl group (Sections 16.7, 22.4)
Acetal group	-C-OR OR	Connects monosaccharides in disaccharides and larger carbohydrates; formed by reaction of carbonyl group with hydroxyl group (Sections 16.7, 22.7, 22.9)

#### Biochemical Building Block

Protein ---- Amino Acid

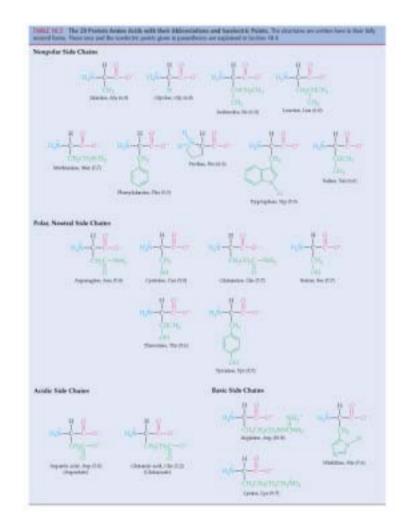
Lipid ---- fatty acid

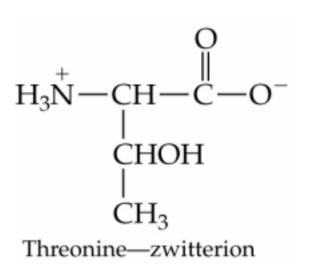
Carbohydrate ---- sugar

- All amino acids present in a proteins are  $\alpha$ amino acids in which the amino group is bonded to the carbon next to the carboxyl group.
- ◆ Two or more amino acids can join together by forming amide bond, which is known as a peptide bond when they occur in proteins.

#### 18.2 Amino Acids

20 amino acids nature uses to build all amino acids in living organisms presented in the Table 18.3





Because they are zweitterion, amino acids have many properties that are common for salts. Such as

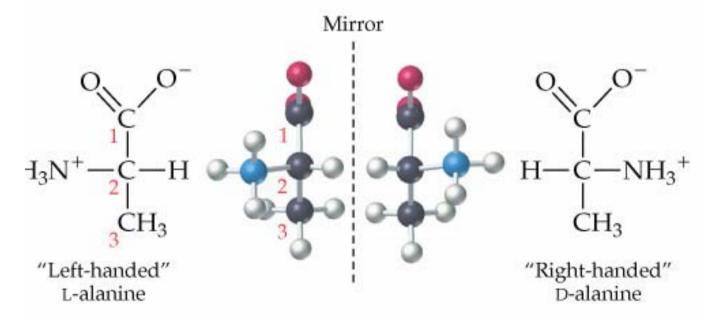
- amino acids crystalline
- amino acids have high melting points
- amino acids are water soluble.

- The charge of an amino acid molecule at any given moment depends on the identity of the amino acid and pH of the medium.
- ◆ The pH at which the net positive and negative charges are evenly balanced is the amino acid's *isoelectric point* the overall charges is zero.

## 18.6 Molecular Handedness and Amino Acids

 Like objects, organic molecules can also have handedness, that is they can be chiral.

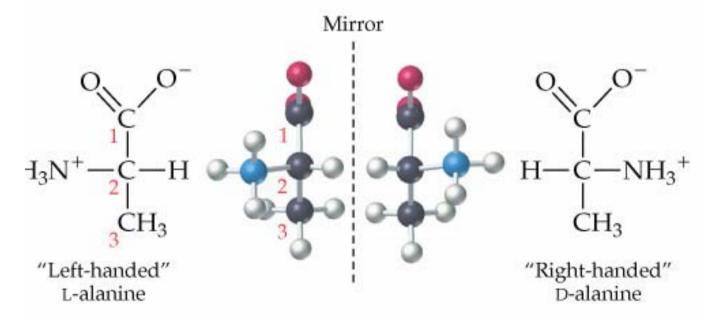
Alanine, a chiral molecule



## 18.6 Molecular Handedness and Amino Acids

◆ Like objects, organic molecules can also have handedness, that is they can be chiral.

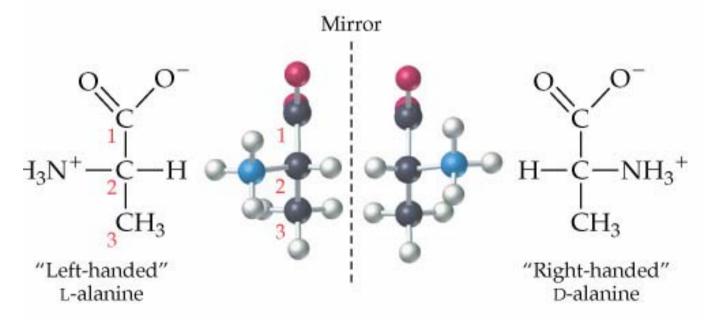
Alanine, a chiral molecule



## 18.6 Molecular Handedness and Amino Acids

◆ Like objects, organic molecules can also have handedness, that is they can be chiral.

Alanine, a chiral molecule



# 24.1 Structure and Classification of Lipids

- Lipids are naturally occurring molecules from plants or animals that are soluble in nonpolar organic solvents.
- Lipid molecules contain large hydrocarbon portion and not many polar functional group, which accounts for their solubility behavior.

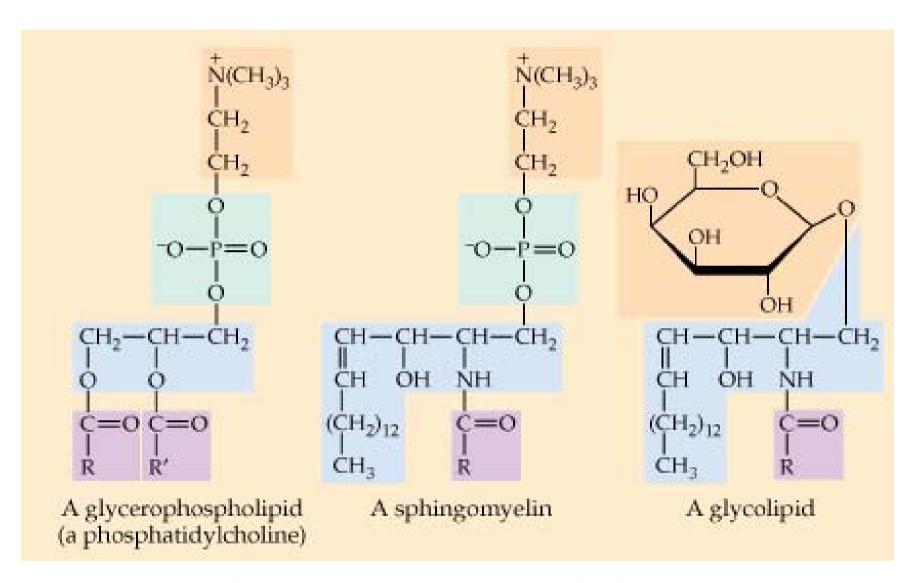
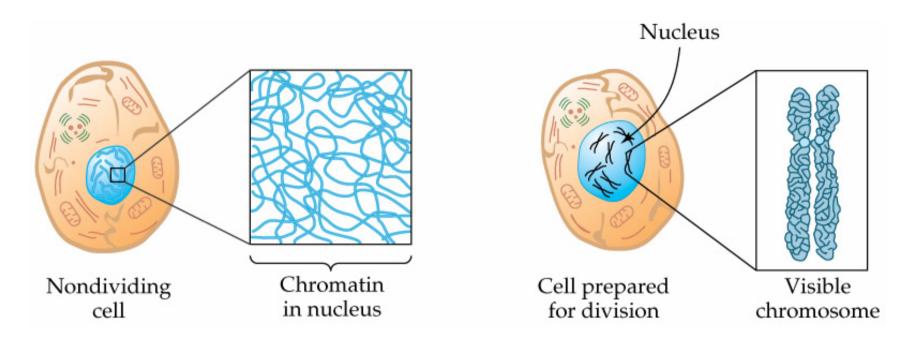
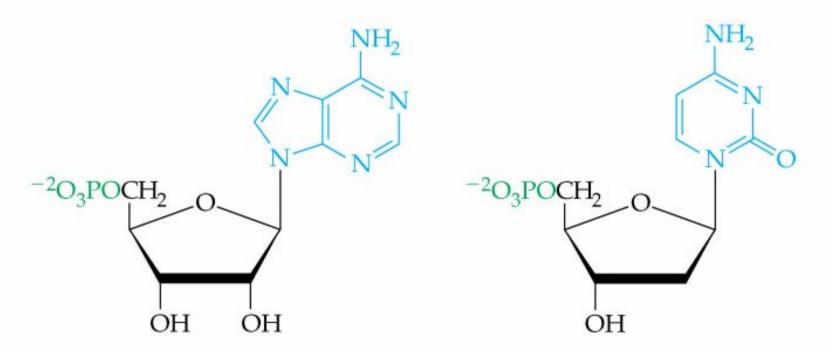


Fig 24.4 Membrane lipids



#### In RNA, the sugar is ribose. In DNA, the sugar is deoxyribose.



Adenosine 5'-monophosphate (AMP) (a ribonucleotide)

Deoxycytidine 5'-monophosphate (dCMP) (a deoxyribonucleotide)

#### Bond formation in DNA replication

