

# **Engineering Chemistry BAS102**

## **UNIT -1 Atomic and Molecular Structure**

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## Molecular orbital theory

### Postulates of Molecular Orbital Theory

Molecular Orbital Theory was given by *R.S. Mulliken* and *F. Hund*.

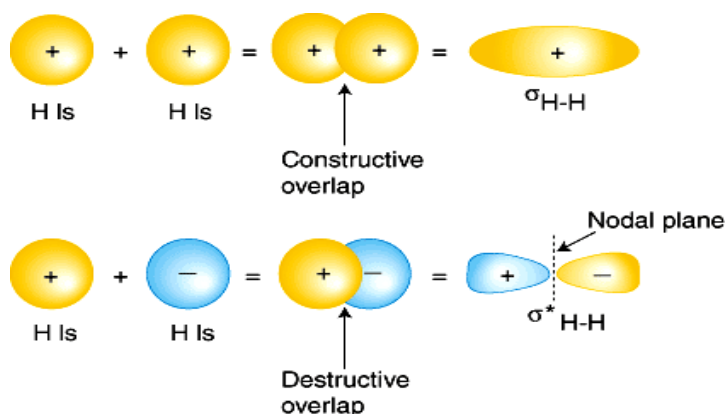
According to MOT the valence electrons are associated with all the nuclei in the molecule.

1. Atomic orbitals with same energy & symmetry combine to form molecular orbitals by *LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)*

- If  $\Psi_A$  &  $\Psi_B$  are wave functions of atoms A & B then according to LCAO:  $\Psi_{M.O} = \Psi_A \pm \Psi_B$
- Two types of molecular orbitals are formed: bonding and anti bonding molecular orbitals.
- Molecular orbitals formed the *additive overlap* of two atomic wave functions is known as *Bonding Molecular orbital*. i.e.  $\Psi_b = \Psi_A + \Psi_B$
- Molecular orbitals formed by *subtractive overlap* of two atomic orbitals wave function is called *Anti-bonding molecular orbital* i.e.  $\Psi_a = \Psi_A - \Psi_B$

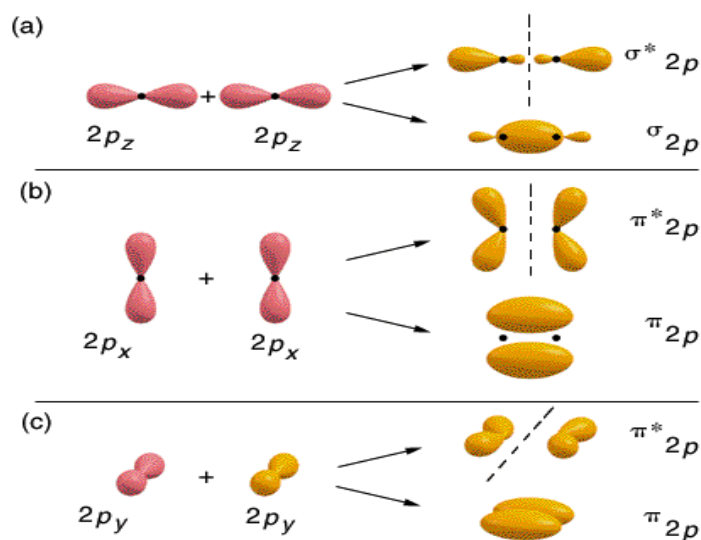
### Linear combination of atomic orbitals

#### S-orbital linear combination

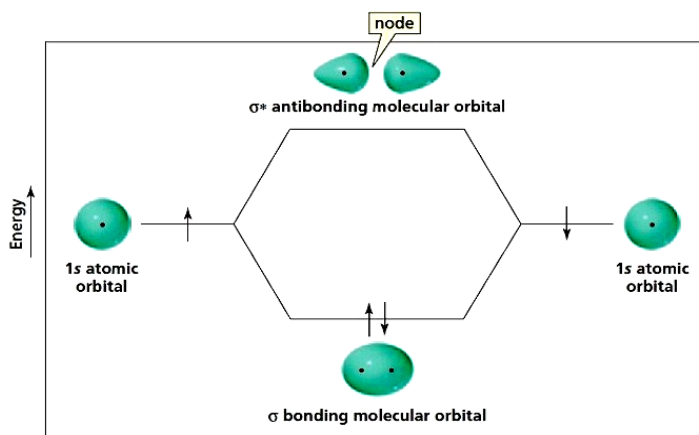


### Linear combination of atomic orbitals

#### P-orbital linear combination



2. The no. of molecular orbitals formed is always equal to the number of atomic orbitals taking part in bond formation.



3. Energy level of bonding M.O. is less than that of individual atomic orbitals. So, electrons present in bonding M.O. stabilize the molecule.

4. Energy level of anti-bonding M.O. is more than that of individual atomic orbitals. So electrons present in anti-bonding M.O. destabilize the molecule.

5. Molecular orbitals that do not participate in bonding are called non-bonding M.O. & their energy is equal to that of individual atomic orbitals.

6. Molecular orbitals are *polycentric*.

7. The atomic orbitals involved in the formation of M.O. completely lose their identity after the formation of molecular orbitals.

8. Electrons filling in the molecular orbitals follow *Aufbau principle, Pauli's exclusion principle & Hunds rule of maximum multiplicity*.

9. The electrons are filled in the molecular orbitals according to the following order:

From  $H_2$  to  $N_2$ :  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \pi 2px = \pi 2py, \sigma 2pz, \pi^* 2px = \pi^* 2py, \sigma^* 2pz$

From  $O_2$  to  $Ne_2$ :  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2pz, \pi 2px = \pi 2py, \pi^* 2px = \pi^* 2py, \sigma^* 2pz$

10. Molecules or ions with *one or more unpaired  $e^-$*  in molecular orbitals are *paramagnetic* while those with all paired electrons in M.O. are called *diamagnetic*.

11. Stability & strength of a chemical bond is expressed in terms of bond order.

12. Bond Order – Bond order is equal to one half of the difference between the number of electrons in bonding M.O & the no. of  $e^-$  is anti-bonding M.O.

$$B.O. = \frac{1}{2} (N_b - N_a)$$

$N_b$  = electrons in B.M.O.

$N_a$  = electrons in anti B.M.O.

**Significance of bond order:**

- Zero B.O.: Molecule does not exist.
- Negative bond order is not possible.
- Positive value of B.O.: Molecule exists & is stable.
- Bond order of +1, +2, +3 indicates the molecule has single, double or triple bond respectively.
- Bond order  $\propto$  Bond stability  $\propto$  1/ Bond length

### Differences between bonding and antibonding molecular orbitals.

BONDING MOLECULAR ORBITALS	ANTIBONDING MOLECULAR ORBITALS
They are formed by additive overlapping of atomic orbitals.	They are formed by subtractive overlapping of atomic orbitals.
$\psi_b = \psi_A + \psi_B$ (A and B are two atomic orbitals)	$\psi_a = \psi_A - \psi_B$ (A and B are two atomic orbitals)
Electrons contribute to the formation of bond.	Electrons do not contribute to the formation of bond.
They have low energy and high stability.	They have high energy and low stability.
They are shown as $\sigma, \pi$ etc.	They are shown as $\sigma^*, \pi^*$ etc.
Maximum electrons are located in between the two nuclei.	Electrons are scattered.
Electron density is higher.	Electron density is lower.

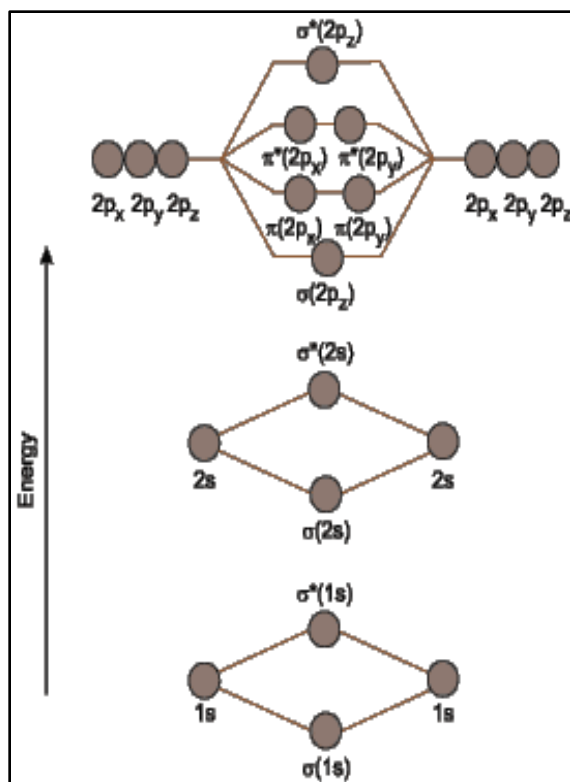
### Molecular Orbital Diagrams of some homo-diatomic molecules

**Homodiatomic Molecules:** These are the molecules formed of the same atoms. Example:  $O_2, H_2$  etc.

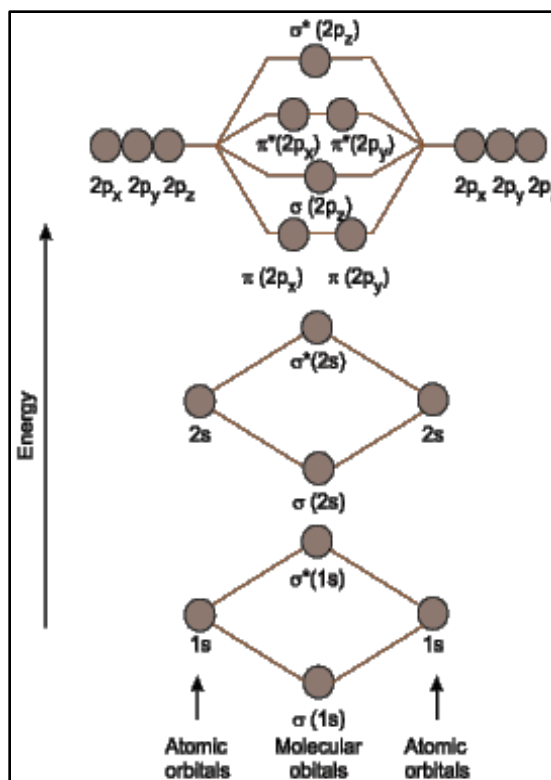
Following order of configuration is followed for various molecules:

From  $H_2$  to  $N_2$ :  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \pi 2p_x = \pi 2p_y, \sigma 2p_z, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$

From  $O_2$  to  $Ne_2$ :  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_x = \pi 2p_y, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$



From H<sub>2</sub> to N<sub>2</sub>



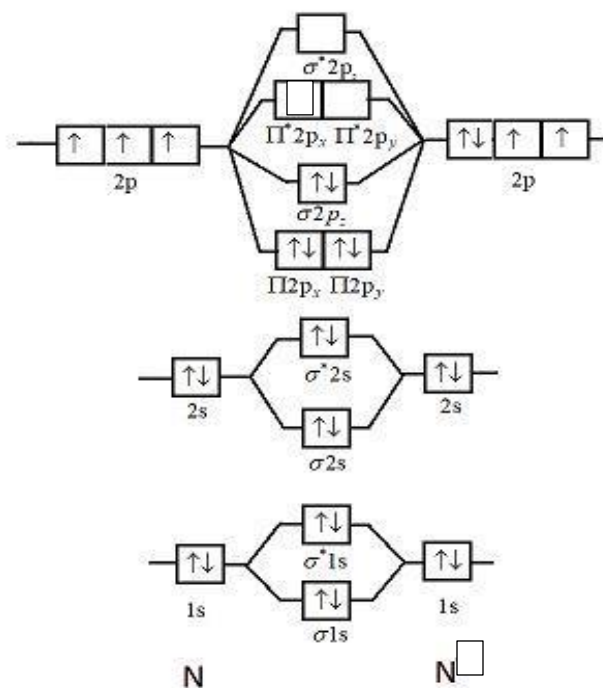
From O<sub>2</sub> to Ne<sub>2</sub>

**N<sub>2</sub> (14 e<sup>-</sup>):**  $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

$$\text{B.O.} = \frac{1}{2} (N_b - N_a)$$

$$= \frac{1}{2} (8 - 2)$$

$$= \frac{1}{2} \times 6 = 3$$



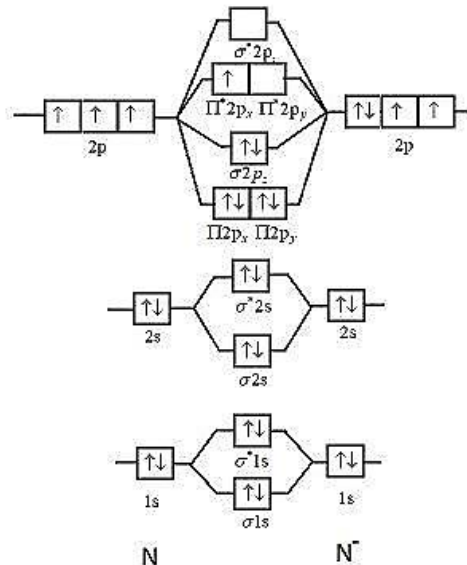
Magnetic Behaviour: It is diamagnetic in nature.

**N<sub>2</sub><sup>-</sup> (15 e<sup>-</sup>):**  $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$

$$B.O. = \frac{1}{2}(N_b - N_a)$$

$$1/2 (10-5) = 2.5$$

**Magnetic Behaviour:** It is paramagnetic in nature.



**N<sub>2</sub><sup>+</sup> (13 e<sup>-</sup>):**  $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x = \pi^* 2p_y, \sigma^* 2p_z$

$$B.O. = \frac{1}{2}(N_b - N_a)$$

$$1/2(9-4) = 2.5$$

Since, ***B.O.  $\propto$  stability.***

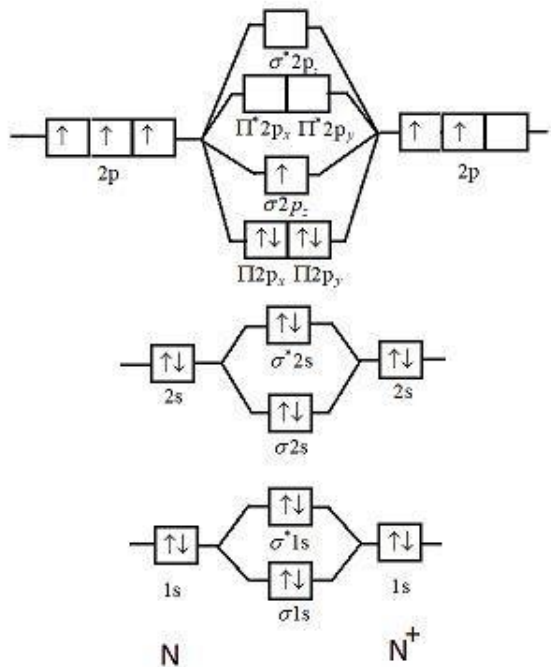
So, the order of stability will be:

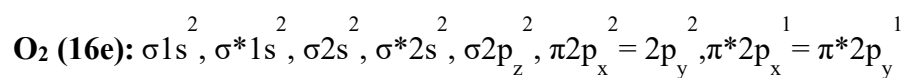
$$N_2 > N_2^- = N_2^+$$

***Also, B.O.  $\propto$  1 / Bond Length***

So, the order of bond length will be:

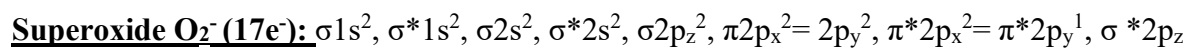
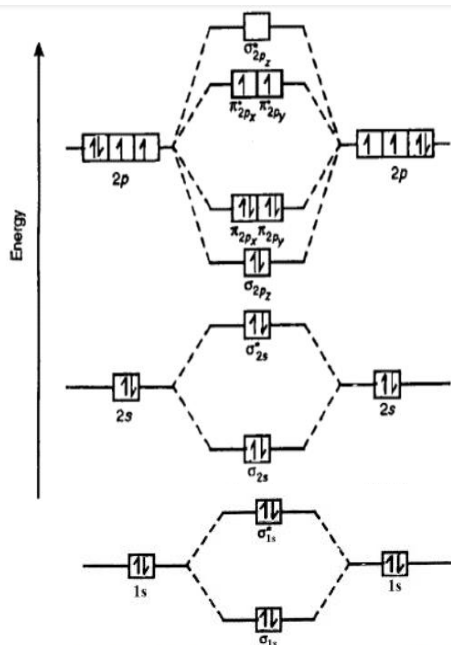
$$N_2^- = N_2^+ > N_2$$





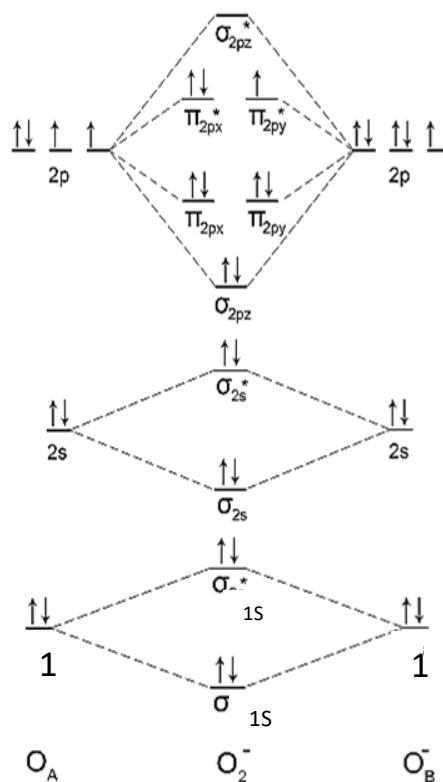
$$\text{B.O. of O}_2 = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (8 - 4) = 2$$

Magnetic Behaviour: It is paramagnetic in nature.



$$\text{B.O. of O}_2^- = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 7) = 1.5$$

Magnetic Behaviour: It is paramagnetic in nature.



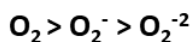


Peroxide  $\underline{\underline{O_2^{2-}}}$  (18e<sup>-</sup>):  $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$

$$\text{B.O. of } O_2^{2-} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 8) = 1$$

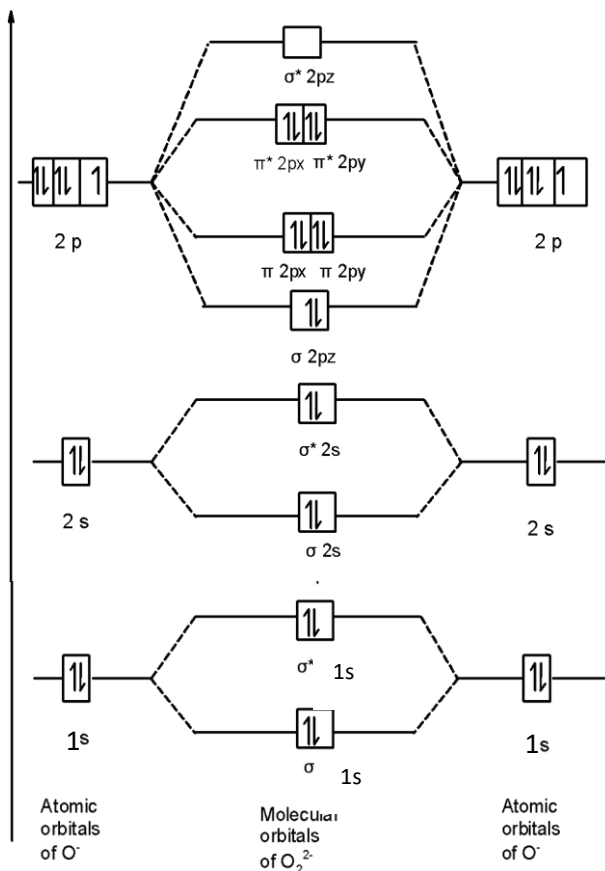
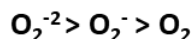
Since, **B.O.  $\propto$  stability.**

So, the order of stability will be:



Also, **B.O.  $\propto$  1 / Bond Length**

So, the order of bond length will be:



## Application of Molecular orbital theory to Hetero-nuclear diatomic molecules

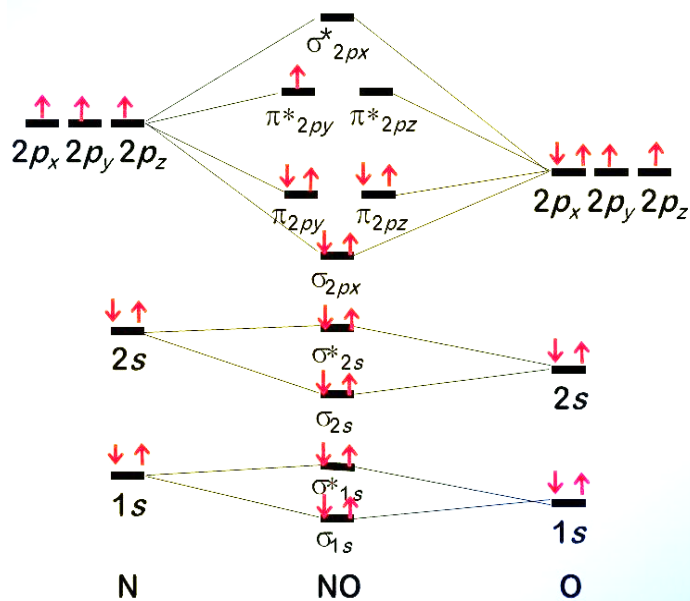
### Hetero-diatomic molecules

- Molecules that contain two different atoms.
- Molecular orbital energy level diagram is always skewed towards the more electronegative atom.
- More electronegative atomic orbital lies closer to bonding M.O. and less electronegative atomic orbital lies closer to antibonding M.O.

**MO Diagram of NO (15 e<sup>-</sup>):**  $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2 = \pi 2p_y^2 < \pi^* 2p_x^1 = \pi^* 2p_y^0$

$$\begin{aligned} B.O. &= \frac{1}{2}(N_b - N_a) \\ &= \frac{1}{2}(8 - 3) \\ &= 5/2 = 2.5 \end{aligned}$$

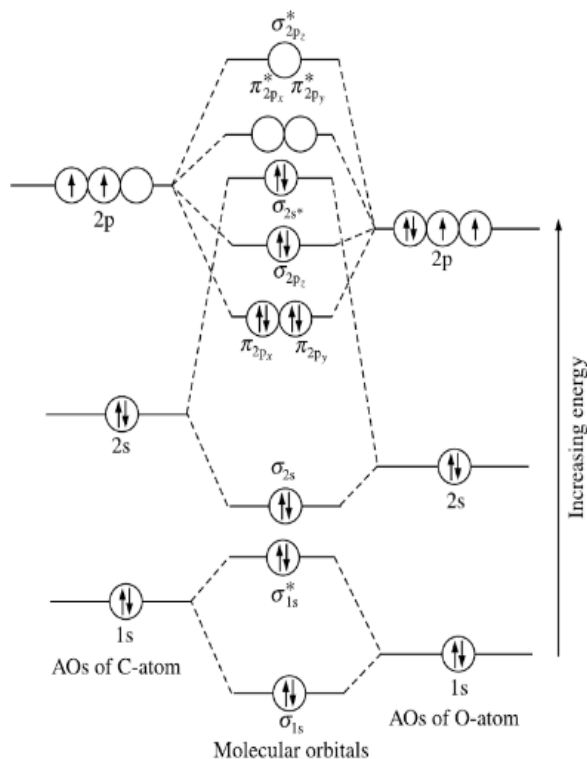
NO molecule is **paramagnetic** in nature due to an unpaired electron in  $\pi^* 2p_x$  orbital.



**MO Diagram of CO (14 e<sup>-</sup>):**

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 = \pi 2p_y^2 < \sigma 2p_z^2$

$$\begin{aligned} B.O. \text{ of } NO &= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 2) \\ &= 6/2 = 3 \end{aligned}$$



**Diamagnetic** in behaviour as it does not contain any unpaired electron.

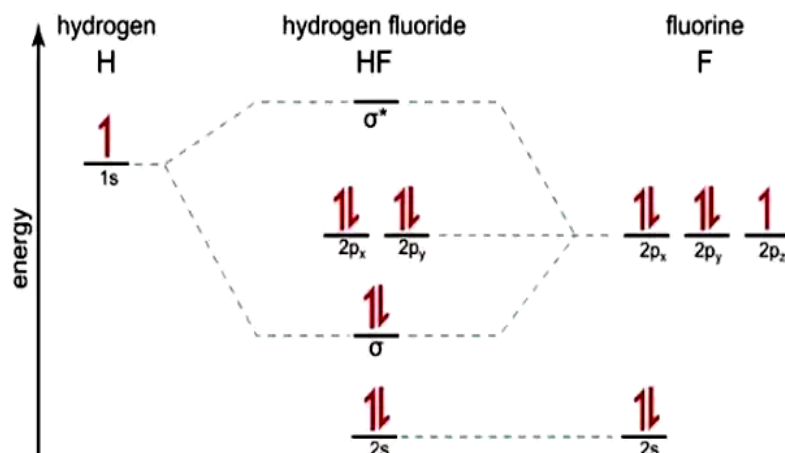
**HF (10 e<sup>-</sup>):** 1s and 2s electrons as well as 4 electrons of p orbital of fluorine do not participate in the formation of molecular orbital of HF and exist as lone pairs. 1s of hydrogen pairs up with 2p unpaired electron of fluorine to form  $\sigma_{sp}$  molecular orbital.

$$B.O. \text{ of } HF = \frac{1}{2}(N_b - N_a)$$

$$= \frac{1}{2}(2 - 0) = 1$$

It is a stable molecule as the bond order is 1.

HF is **diamagnetic** in nature.

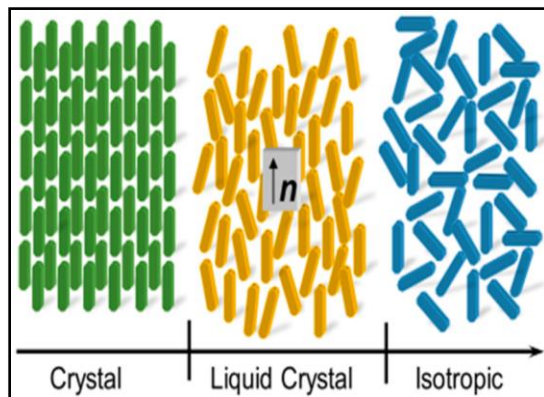


## Liquid crystals: Classification, Properties and Applications

Liquid Crystals are state of matter which has properties between those of conventional liquids and solid crystals. For example, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.

The liquid-crystalline state is often called **mesomorphic state** (mezos meaning "intermediate"), and the liquid crystals are called **mesophase**.

**Friedrich Reinitzer**, Austrian botanist studied about it first in 1888 in a material known as **cholesteryl benzoate**.



### Following character describe the crystalline structure:

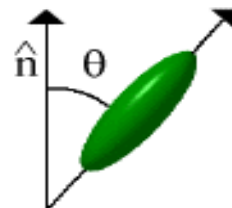
**Positional order:** The extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows).

**Orientalional order:** Represents a measure of the tendency of the molecules to align along the director on a long-range basis.

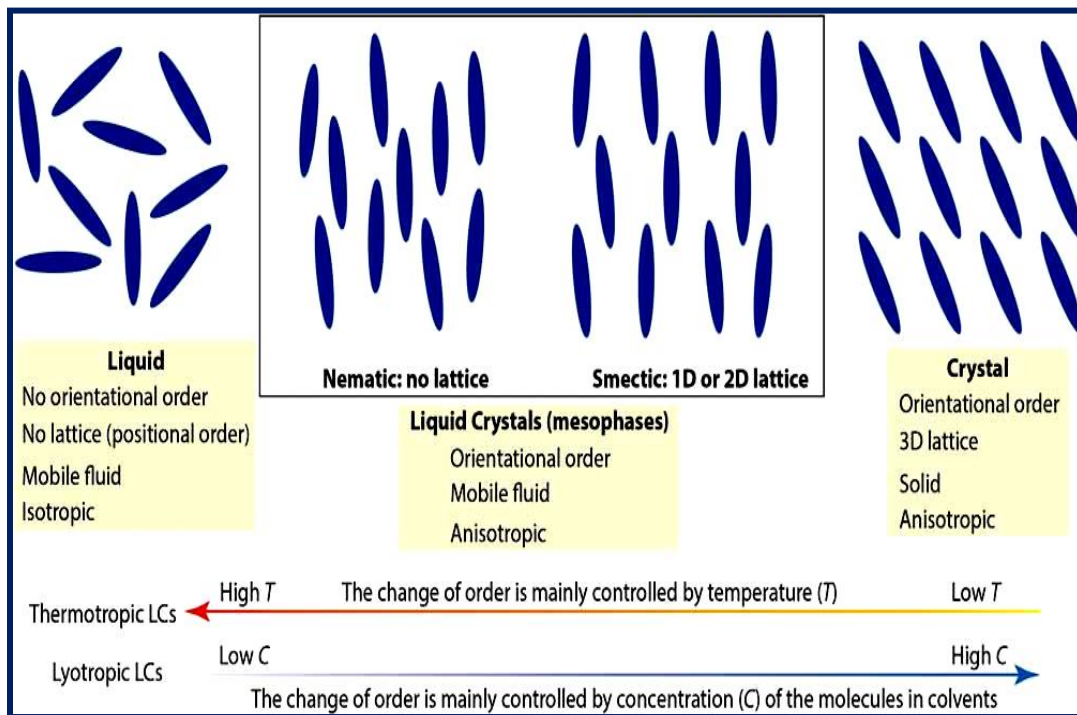
**Bond Orientalional Order:** describes a line joining the centres of nearest neighbour molecules without requiring a regular spacing along that line.

Positional order + Orientalional order = crystal phase

Varying Positional order + Orientalional order = LC phase

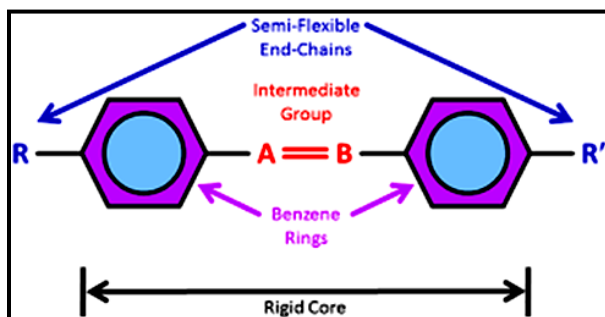


- Positional order + Orientalional order = Crystal Phase
- Positional order + No Orientalional order = Plastic Phase
- Varying Positional order + Orientalional order = Liquid crystalline Phase
- No positional order + No Orientalional order = Isotropic (Liquid) Phase



### Properties of liquid crystals

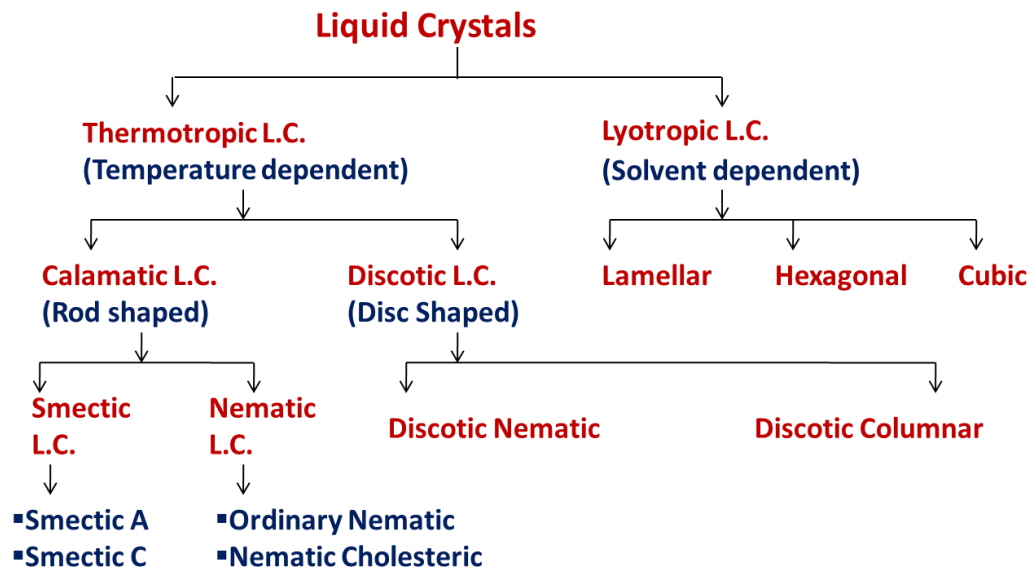
- The molecules are *rod shaped or disc shaped*.
- All liquid crystals are mesogens but all mesogens are not liquid crystals.
- Molecules are *anisotropic* in nature.
- Assuming that the direction of preferred orientation in a liquid crystal (LC) is  $\uparrow$ , this direction can be represented by an arrow, called the *director of the LC*.
- Each molecule is orientated at some angle to the director.
- These molecules possess *very strong dipole moment*.
- The liquid crystal molecules prefer to align *parallel to each other* because of the strong intermolecular attraction ( *$\pi$ - $\pi$  interaction*).
- A typical Liquid Crystal molecule is represented by *a central rigid part*, known as *mesogen* (generally aromatic) and the *flexible ends* (generally aliphatic groups).
- It consists of *two or more ring systems connected by a central linkage group*.



### Essential requirements for a molecule to be a liquid crystal

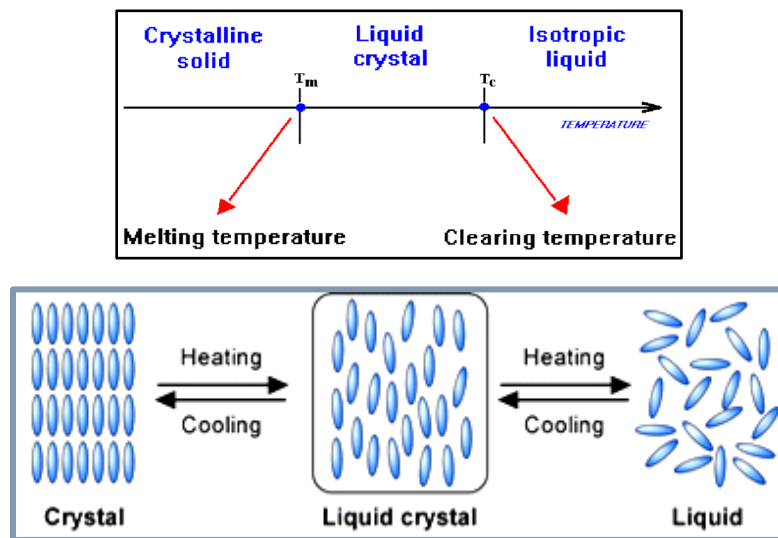
- Shape of the molecule must be *rod like or disc like*.
- Molecule must be *anisotropic* in nature.
- Molecule must have some *rigidity in its central region and the ends must be flexible*.
- Although LC's combine the properties of a crystalline solid and an isotropic liquid, they exhibit very specific electro-optical phenomena, which have no equivalent analogues in solids or in liquids.

## Classification of liquid crystal:



### 1. Thermotropic liquid crystals:

They are formed by change of temperature. They occur as liquid crystals over a certain temperature range between the solid and liquid phase. *Example – LCD TV's, alarm clocks.*



Thermotropic liquid crystals are further classified into:

- Colamatic Liquid Crystals (Rod like or elongated molecules)
- Discotic Liquid Crystals (Disc shape molecules)

Colamatic liquid crystals are elongated, rod shaped molecules. They are further classified as Nematic and Smectic liquid crystals.

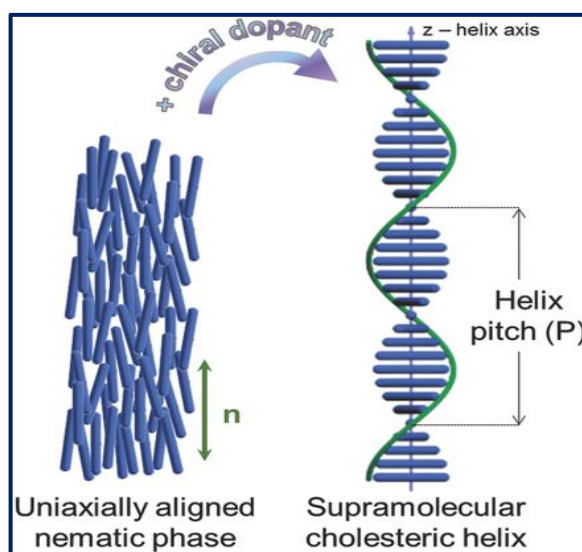
### Nematic liquid crystal:

- Word Nematic derived from Greek word *Nema* which means "thread".
- No positional order but possess orientational order.
- The molecule have elongated rod like shape and are thread like.
- Do not have layered structure.
- Flow like normal liquids.
- They have low viscosity.
- Formed at relatively higher temperature.
- Can be aligned by the application of electric or magnetic field.
- Molecules are free to move in all the directions.
- Flow in all directions & not in layers.
- E.g.- p-azoxy anisole (first synthetic liquid crystal to be produced).
- Nematic liquid crystals can be further classified as:
  - a) **Ordinary nematic phases**: These molecules possess ordinary nematic phase characteristics as discussed earlier.
  - b) **Cholesteric nematic phases**: This phase is also known as chiral nematic phase. The molecules are essentially chiral and resemble nematic molecules in nature.

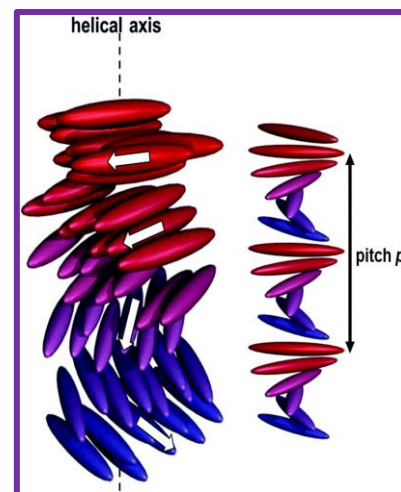


### Cholesteric Liquid Crystals (Chiral Nematic)

- This phase is usually observed from cholesterol derivatives.
- The molecules are essentially chiral.
- The molecules are arranged in layers.
- These are formed by adding chiral twisting agent to the nematic liquid crystals.



- Each layer in Cholesteric liquid crystal is tilted with respect to the other one, and hence the molecules take a one complete turn of 360 degrees to make a helix.
- The distance covered by the director in making one complete turn is known as pitch.
- Cholesteric Liquid crystal reflects light approximately equal to pitch.
- Pitch is inversely proportional to the temperature.
- Pitch is affected by temperature, pressure as well as by electric and magnetic fields.



### Smectic Liquid Crystals:

- Molecules are cigar shaped.
- Have short range orientational as well as positional order.
- These are arranged in layers i.e. have layered structure.
- They do not flow like normal liquids and has limited mobility.
- They have high viscosity.
- Not affected by external electric or magnetic field.
- Molecules are free to move within the layers, but not from one layer to another.
- Flow in layers and different layers can slide over one another.
- Are of two types: Smectic A and C.
- E.g.: Ethyl-para-azoxy phenetole.

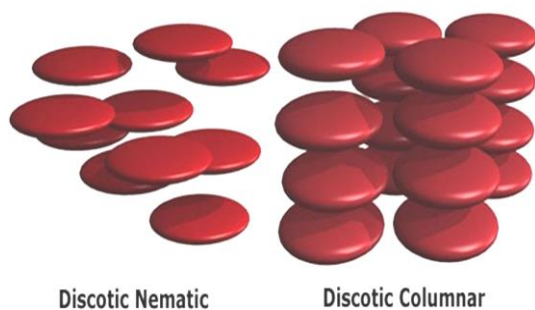


### Discotic Liquid Crystals:

- Molecules are *essentially disc shaped*.
- Discotic mesogens are typically composed of an *aromatic core surrounded by flexible alkyl chains*. Disc-shaped molecules have a tendency to lie on top of one another forming either *discotic nematic phases* (with discs oriented similar to that of nematic phase i.e. not having position order but having orientation order) or *columnar phases* (have column-like structure).

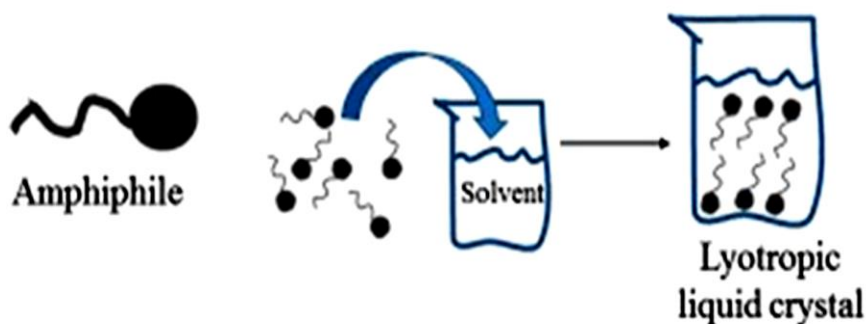


- The aromatic cores allow charge transfer in the stacking direction through the  $\pi$  conjugate systems. The charge transfer allows the discotic liquid crystals to be electrically semi conductive along the stacking direction.
- They are of two types: ***Discotic nematic Phase and Columnar Phase.***



### **Lyotropic Liquid Crystals:**

- Lyotropic liquid crystals are two component systems, where an amphiphile is dissolved in a solvent.
- Thus, lyotropic mesophases are solvent and concentration dependent.
- The amphiphilic compounds are characterized by two different moieties, a hydrophilic polar head and a hydrophobic tail.
- LLC are made by adding solvent to the solid until critical micelle concentration (CMC) is reached. On further addition of solvent LLC changes into liquid phase.
- **Examples:** molecules of soaps, phospholipids (present in cell membranes), toothpaste, many proteins and cell membranes, tobacco mosaic virus.

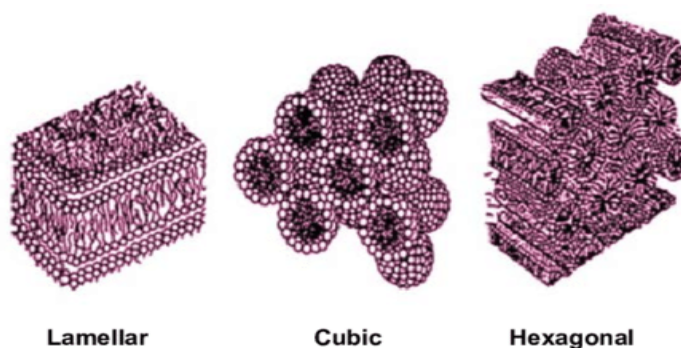


Three types of lyotropic liquid crystals are well known. These are: **lamellar, hexagonal and cubic phases.**

i) The simplest liquid crystalline phase that is formed by spherical micelles is the ‘micellar cubic’, denoted by the symbol  $I_1$ . This is a highly viscous, optically isotropic phase in which the micelles are arranged on a cubic lattice.

ii) At higher amphiphile concentrations the micelles fuse to form cylindrical aggregates of indefinite length, and these cylinders are arranged on a long-ranged hexagonal lattice. This lyotropic liquid crystalline phase is known as the ‘*hexagonal phase*’, and is generally denoted by the symbol  $H_1$ .

iii) At higher concentrations of amphiphile the ‘*Lamellar Phase*’ is formed. This phase is denoted by the symbol  $L_a$ . This phase consists of amphiphilic molecules are arranged in bilayer sheets separated by layers of water.



### Applications of liquid crystals:


- Liquid crystals are used for decorative purpose in cosmetics.
- LLC's based delivery system such as cream, ointment, transdermal patches etc have been used in pharmaceutical.
- Thermotropic Cholesteric liquid crystals are used in body care cosmetics.
- Due to their colour effect Cholesteric liquid crystals are used in nail paints, eye shadows etc.
- Discotic liquid crystals are used in photovoltaic devices, organic light emitting diodes (OLED), and molecular wires.
- Liquid crystals are used for displays in LCD's, Calculator, wrist watches etc.
- Have Medical applications like localized drug delivery.
- To detect radiations& pollutants in atmosphere.
- Used in non-destructive testing.
- Cholesteric liquid crystals are used in coloured thermometers.
- Used to locate tumours, veins, arteries, infections, foetal placenta etc.

## Structure and Applications of Graphite and Fullerenes

### Graphite: An allotrope of Carbon

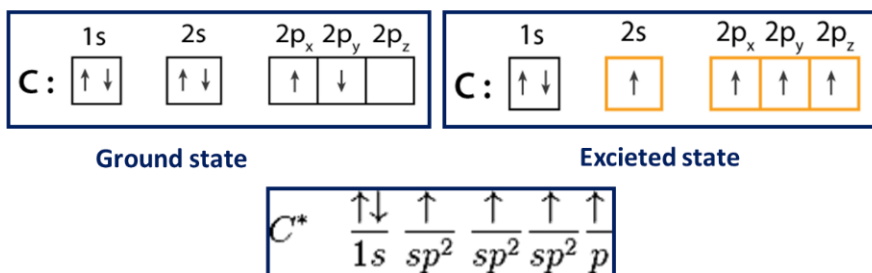
- Graphite is an allotrope of carbon (it is made up of only pure carbon atoms).
- Each carbon atom in graphite is *sp<sup>2</sup> hybridised*.
- 6 such carbon atoms join with the covalent bonds to form hexagons.
- In hexagons each carbon atom forms three covalent bonds (C-C distance is 1.42 Å) with other carbon atoms.
- Fourth electron of each carbon atom is free to move within the layer.
- Various hexagons join together to form a plane or sheet called *graphene*.
- Various sheets (graphene) are arranged one above the other.
- Different layers of graphite are attached to each other with *weak Vander Waals forces*.
- Distance between two successive sheets is 3.41 Å.
- Graphite has *planar, two dimensional* structure.

Name of the Molecule	Graphite
Molecular Formula	C
Hybridization Type	sp <sup>2</sup>
Bond Angle	120°
Geometry	Trigonal Planar

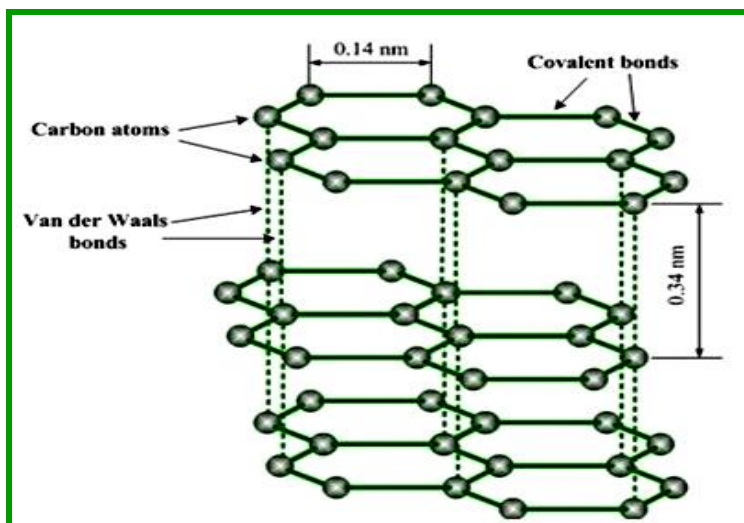


trigonal planar  
carbon in graphite  
with p orbital

### Hybridisation of C in graphite:



### Structure of Graphite



### Properties of Graphite:

- It is greyish **black and greasy** substance.
- Has **metallic luster** and is **opaque to light**.
- **High Melting point** because the strong covalent bonds take long time to break.
- **Slippery nature** / Layers can slide one another due to weak Vander Waal forces of attraction between the two layers.
- **Low coefficient of friction**.
- Ineffective in vacuum conditions.
- Thermodynamically more stable than diamond.
- Graphite exists in two forms:  $\alpha$ -graphite and  $\beta$ -graphite.
- In spite of being non-metal, graphite is a **good conductor of electricity** due to the presence of free electron in  $p_z$  orbital of each carbon.
- **Density  $1.25\text{g/cm}^3$**

### Applications of Graphite:

- **Used as a lubricant** as layers can slide over one another due to **weak vanderwaals forces**.
- **Used in pencil leads** due to soft, slippery nature and it leaves a black mark on paper when rubbed against it.
- It is used in the **preparation of electrodes** as it conducts electricity due to presence of free electron on each carbon atom.
- Due to high melting point it is used **to prepare crucible** for making high grade steel.
- It is used as **moderator in nuclear reactors** as it absorbs fast moving neutrons.

- Used as *conductive ink for screen printing*.

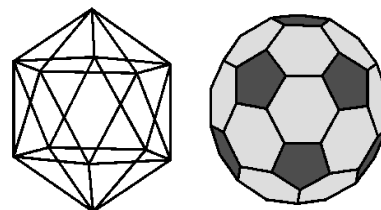
## Fullerene

### (Discovered by Kroto & Smalley)

- It is an allotrope of carbon, also called *Buckminster fullerene or Bucky Ball*.
- Fullerenes exist as  $C_{60}$ ,  $C_{70}$ , etc. The canonical structure,  $C_{60}$ , has *icosahedral symmetry* and an electronic structure similar to that of graphene.
- $C_{60}$  is the most stable & widely used member of the fullerene family.

### Structure of $C_{60}$

- Made up of *60 carbon* atoms.
- Each carbon atom is  *$sp^2$  hybridised*, forming three bonds and having one unpaired electron.
- There are *12 pentagons & 20 hexagons* of C atoms.
- No two pentagons touch each other i.e. each pentagon is surrounded by hexagons from all the sides.
- *Diameter* of  $C_{60}$  molecule is  $7\text{\AA}$ ; geometry-*truncated icosahedron or geodesic dome*.
- There are *30 (C=C) double bonds* in  $C_{60}$ .
- There are *60 vertices, 32 faces*.
- C-C single bond length- $1.45\text{\AA}$ ; C=C double bond length= $1.38\text{\AA}$
- It is highly symmetrical molecular & is said as *zero dimensional*.
- Has tendency to avoid double bonds in pentagon rings.
- Fullerene crystal structure is *FCC*.
- Its density is  *$1.65\text{ gm/cc}$* .



### Preparation of Fullerene:

- Fullerenes are prepared by *Arc Discharge Method*.
- In this the *graphite rods* are vaporized in an *inert atmosphere of helium gas*.
- Graphite rods evaporate to form a mixture of fullerenes ( $C_{60}$ ,  $C_{70}$  etc).
- From this mixture pure  $C_{60}$  is isolated by column chromatography.

Graphite rods kept in an inert atmosphere (He gas)  
at .05 to .1 atm pressure.

↓ *Electric current*

Rods evaporate to give fullerene soot (light and fluffy dust)  
Containing 5 to 15 % fullerenes.

↓ *Sublimation*

Fullerene mixture

↓ *Chromatography using alumina  
hexane*

$C_{60}$

### **Properties of Fullerene:**

- Mustard colored solid and looks brown and black as its thickness increases.
- Basically, semiconductors but on doping with alkali metals can be converted into conductor or super conductor.
- Shows poor aromatic nature.
- Strongest known material to man.
- Exists as discrete molecule unlike graphite or diamond.
- The pentagon of a fullerene is more strained than the hexagon, so at higher temp., fullerene molecule break at pentagon sites.
- It is possible to trap some ions inside fullerene cage or attach some functional molecules to fullerene from outside.
- Can be compressed to lose 30% of its original volume, without destroying the carbon edge structure.

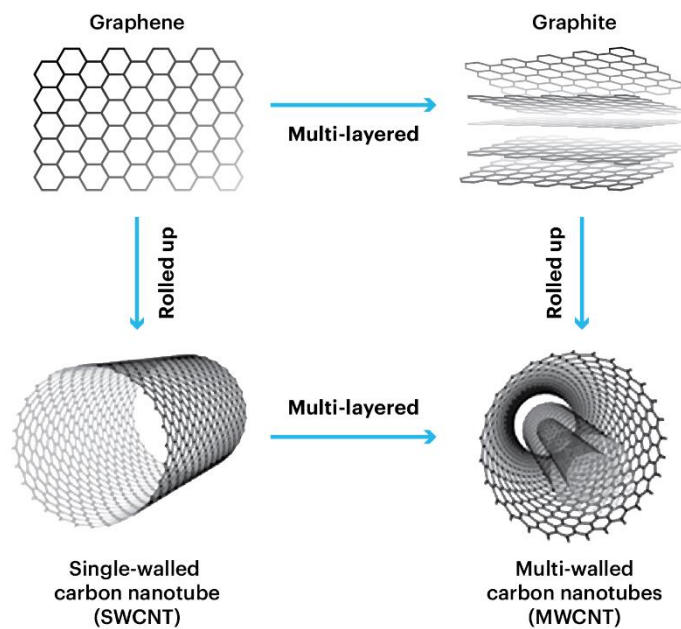
### **Uses of Fullerene**

- Have powerful antioxidant properties, so used in health & personal care areas.
- $C_{60}$  shows catalytic process.
- Act as drug delivery agent.
- $C_{60}$  derivatives act as potential inhibitors to HIV.
- Used in preparation of superconductors.
- In optical devices.

- In preparation of soft Ferro magnets.
- Used in batteries as charge carriers.

### **Carbon nanotubes**

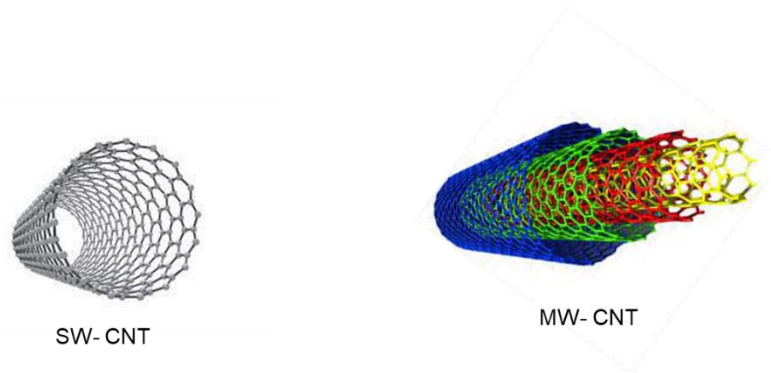
CNT is one of the most important nanomaterial at present time. Before 1991, only 2 allotropes of carbon were known namely Diamond and Graphite. But in 1991, Japanese physicist Sumio Iijima discovered another allotrope of carbon called carbon nanotube. When we roll up 2D graphite (*Graphene*) sheet into a cylindrical tube, we get CNT. The diameter of CNT is about 1-3 nm and can have length up to few micrometers. CNT exhibit extraordinary mechanical properties.



### **Silent feature of CNT**

- They are stiff as diamond.
- They are light weight.
- Their density is  $1/4^{\text{th}}$  of that of steel and thermal opacity is 20 times more than steel.
- In CNT each carbon atom is bounded to 3 other carbon atoms through covalent bonds and forms a lattice in the shape of hexagons
- Outer diameter: 2-20 nm
- Inner diameter: 1-3 nm
- Length: 1-6  $\mu\text{m}$

- MWCNT are different from carbon nanofibre (CNF). CNF have diameter of 200 nm and they are not hollow from inside.
- CNF have been in use for several decades to strengthen compound, but their lattice is different from CNT.
- CNT is improved version of CNF.



### **Properties of CNT**

- CNT as elastic-tensile strength of CNT is about 200 Giga Pascal and therefore CNT can be stretched 20% of their rest length and can be bent and even tied a knot with no resulting effect.
- CNT are good conductor of heat- they have very high thermal capacity. So thermal expansion produced in CNT is very small.
- CNT have good electrical conductivity – CNTs have very few defects so they can carry billion amperes of current /cm.
- CNT are very strong- CNTs are 10 times stronger than steel.
- Chemically stable- They are resistant to corrosion.

### **Type of CNT**

#### **Single Walled Carbon Nanotube (SW-CNTs)**

- Diameter 0.5-2.5 nm, length 2  $\mu\text{m}$
- Aspect ratio is typically greater and often goes up to 10,000.
- It posses 1-D structure and is called Nanowire. Eg. Armchair and Zig Zag SWCNT
- SWCNT is used in electronics.
- Their band gap is from 0 to 2 eV and they can exhibit both metallic and semiconducting behavior.

#### **Multi Walled Carbon Nanotube (SW-CNTs)**

- It consist of several nested coaxial single walled CNTs. E.g. Chiral MW-CNT
- Aspect ratio is typically between 50 and 4,000.



## **Preparation of CNT**

### 1. synthesis of CNTs by Electric arc discharge method

In this method, a potential of 20–25 V is applied across the pure graphite electrodes separated by 1 mm distance and maintained at 500 torr pressure of flowing helium gas filled inside the quartz chamber.

2. Carbon Nano Tubes (CNTs) are prepared by the catalytic decomposition of Methane ( $\text{CH}_4$ ) at 680 degrees Celsius for 120 minutes, by using Nickel Oxide- Silica binary aerogels as the catalyst.

## **Application of CNT**

1. Composite material containing CNT are being used in sports accessories like bicycle frames, tennis rackets, hockey sticks etc.
2. CNTs are used to make Bullet Proof Jackets
3. CNTs can **reduced the** weight of aircraft and spacecraft upto 30%.
4. CNTs can be used to build high performance transistors to replace silicon based transistors because of semi-conducting properties of SWCNT.
5. CNTs can be used to manufacture biosensors and electrochemical sensors which are used to sense greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ) in environment.
6. CNTs can be used to make electrodes.

## **Concepts, Properties and Applications of Nano- Sciences and Nano- materials**

### **Nanomaterials**

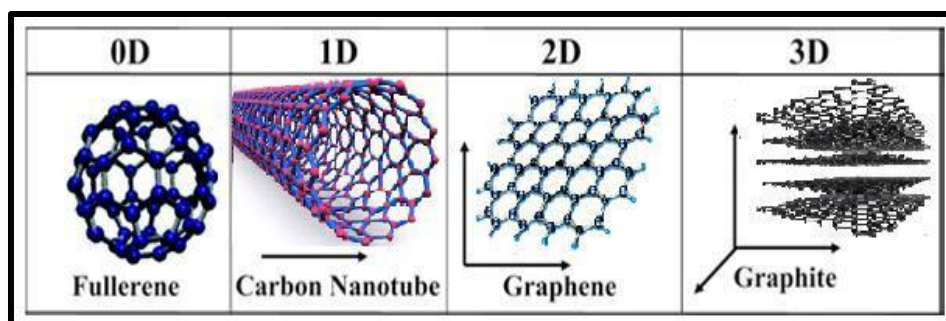
**Nanomaterials**: are materials having at-least one of its dimensions in the nanometer scale ( $1 \text{ nm} = 10^{-9} \text{ m}$ ).

**Nanotechnology**: is the technology of manipulating a material and its properties at the nanoscale (atomic or molecular scale) for target-specific applications.

**Nanostructured materials**: Nanomaterials can be zero, one, two or three dimensional.

### **Various nano materials:**

- Nanoparticles
- Nanowires
- Nanotubes
- Nano-rods
- Nano-porous materials



### Effects of Nano size:

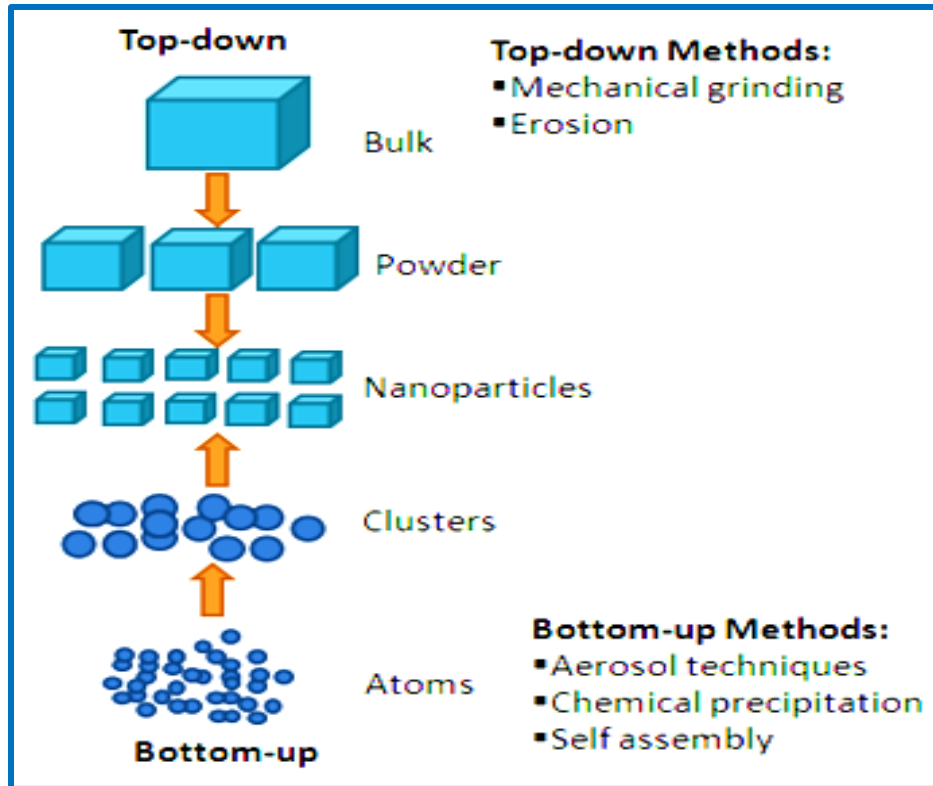
- Properties depend on size, composition, and structure.
- Nano size increases the surface area.
- Change in surface energy (higher)
- Change in the electronic properties.
- Change in optical band gap.
- Change in electrical conductivity.
- Higher and specific catalytic activity
- Change thermal and mechanical stability.

### **Nanomaterials synthesis approach:**

**1. Top down approach:** The synthesis of nano particles using this approach includes built up of the structure by accumulation of each atom or molecule by molecule

**2. Bottom up approach:** This approach includes synthesis of nano particles by breaking down of bulk materials gradually into smaller sizes

- Buildup of material: *Atom → molecule → cluster*



### Applications of nanomaterials:

In major view nanomaterials has found their applications in many major areas:

- Electronics
- Medicine
- Engineering and technology
- Industries
- Environment
- Sensors
- Catalysis
- Nano transistors, Field effect transistors.
- Field emission.
- Nano electrodes.
- Nano medicine, drug delivery systems, disease diagnosis.
- Chemical, bio, pressure, thermal sensors
- Nano devices.

## Green Chemistry

Green chemistry referred to as sustainable chemistry is the branch of chemistry that deals with the design and optimization of processes and products in order to lower, or remove altogether, the production and use of toxic substances. Green chemistry is not the same as environmental chemistry.

### **12 Principles of Green Chemistry**

- **Prevention of waste:** Preventing the formation of waste products is always preferable to the clean-up of the waste once it is generated.
- **Atom economy:** The synthetic processes and methods that are devised through green chemistry must always try to maximise the consumption and incorporation of all the raw materials into the final product. This must strictly be followed in order to minimise the waste generated by any process.
- **Avoiding the generation of hazardous chemicals:** Reactions and processes that involve the synthesis of certain toxic substances that pose hazards to human health must be optimized in order to prevent the generation of such substances.
- **The design of safe chemicals:** During the design of chemical products that accomplish a specific function, care must be taken to make the chemical as non-toxic to humans and the environment as possible.
- **Design of safe auxiliaries and solvents:** The use of auxiliaries in processes must be avoided to the largest possible extent. Even in the circumstances where they absolutely need to be employed, they must be optimized to be as non-hazardous as possible.
- **Energy efficiency:** The amount of energy consumed by the process must be minimized to the maximum possible extent.
- **Incorporation of renewable feedstock:** The use of renewable feedstock and renewable raw materials must be preferred over the use of non-renewable ones.
- **Reduction in the generation of derivatives:** The unnecessary use of derivatives must be minimized since they tend to require the use of additional reagents and chemicals, resulting in the generation of excess waste.
- **Incorporation of Catalysis:** In order to reduce the energy requirements of the chemical reactions in the process, the use of chemical catalysts and catalytic reagents must be advocated.
- **Designing the chemicals for degradation:** When designing a chemical product in order to serve a specific function, care must be taken during the design process to make sure that the chemical is not

an environmental pollutant. This can be done by making sure that the chemical breaks down into non-toxic substances.

- **Incorporating real-time analysis:** Processes and analytical methodologies must be developed to the point that they can offer real-time data for their monitoring. This can enable the involved parties to stop or control the process before toxic/dangerous substances are formed.
- **Incorporation of safe chemistry for the prevention of accidents:** While designing chemical processes, it is important to make sure that the substances that are used in the processes are safe to use. This can help prevent certain workplace accidents, such as explosions and fires. Furthermore, this can help develop a safer environment for the process to take place in.

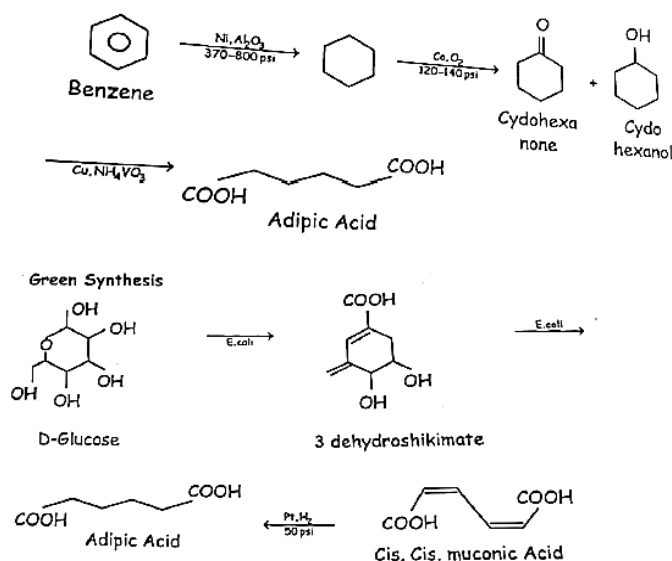
## EXAMPLES

- Green solvents
- Synthetic techniques
- Carbon dioxide as processing agent
- Carpet tile backings
- Transesterification of fats

## Green Chemicals

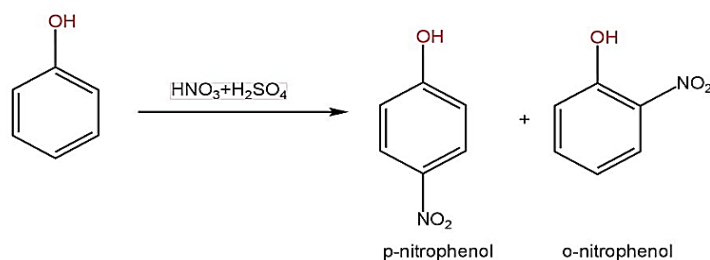
Green chemical is one that provides higher performance and functionality while being more environmentally benign throughout its entire life-cycle. This approach has been codified in the Twelve Principles of Green Chemistry that provide a framework for innovation and design.

### Synthesis of adipic acid by conventional and Green route

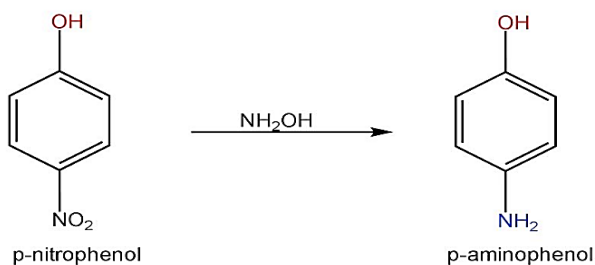


### Synthesis of Paracetamol by conventional route

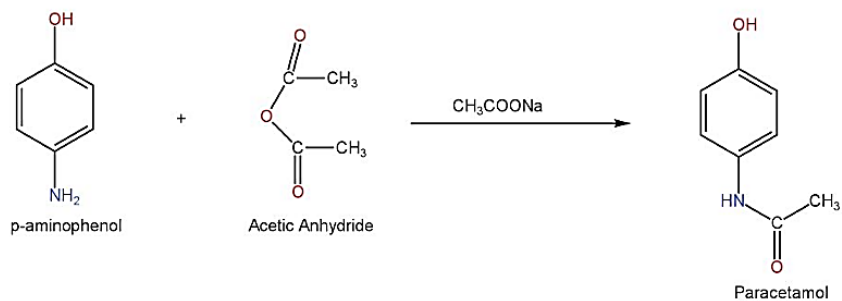
**Step-1:** When nitric acid is added to phenol, phenol undergoes nitration to form Nitrophenol and p-Nitrophenol, p-Nitrophenol is a major product.



**Step -2:** Reduction of Nitro group ( $-\text{NO}_2$ ) to amine group ( $-\text{NH}_2$ ) group

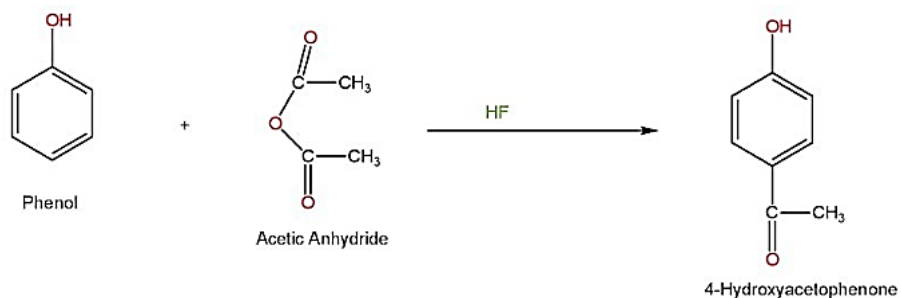


**Step 3:** Nucleophilic addition reaction of p-aminophenol with acetic anhydride ( $\text{CH}_3\text{CO}-\text{O}-\text{OCH}_3$ ) in the presence of sodium acetate ( $\text{CH}_3\text{COONa}$ )

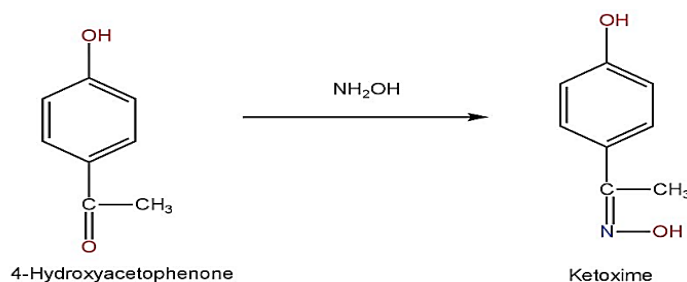


### Green Synthesis of Paracetamol from Phenol

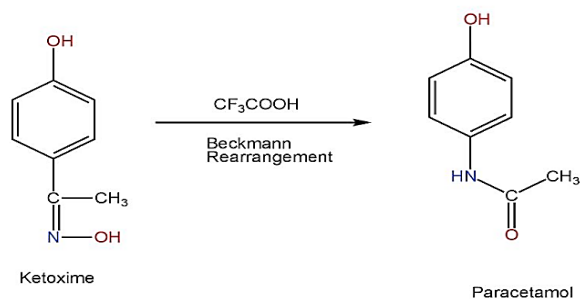
**Step 1:** Phenol reacts with acetic anhydride in the presence of strong acid like HF To undergo acylation reaction to give 4-hydroxy acetophenone.



**Step 2:** Reaction of aldehydes and ketones with hydroxylamine (NH<sub>2</sub>OH) gives oximes. 4-hydroxyacetophenone reacts with hydroxylamine to give corresponding ketoxime.



**Step 3:** Oximes in acidic medium (trifluoroacetic acid, CF<sub>3</sub>COOH) undergoes Beckmann rearrangement to produce substitute amides. Beckmann rearrangement of the above ketoxime gives paracetamol.



### Uses of Paracetamol

- It is used as an antipyretic drug to reduce body temperature in case of high fever.
- It is also used as a weak analgesic to reduce the mild to moderate pain (examples: headache, tooth pain, menstrual pain, etc.)

### Environmental impact of Green Chemistry on Society

Green chemistry is a proactive approach to pollution prevention.

### Advantages of Green Chemistry

1. Plants and animals suffer less harm from toxic chemicals in the environment.
2. Lower potential for Global Warming.
3. Ozone depletion and smog formation.
4. Less chemical disruption of ecosystem.
5. Less use of landfills, especially hazardous waste.

## QUESTIONS

**Marks. 2**

1. Explain homo diatomic molecules and calculate the bond order of hydrogen molecule.
2. Give examples of Industrially important materials used as liquid crystals.
3. Explain why oxygen is paramagnetic in nature.
4. Arrange  $N_2$ ,  $N_2^-$  and  $N_2^+$ , in order of their increasing bond length.
5. Difference between Nematic and Sematic liquid crystals.
6. Why graphite is a good conductor of electricity.
7. Give five applications of nanomaterials.

**Marks. 7**

8. Outline the salient features of MOT on the basis of LCAO principle. Explain BMO and ABMO and differentiate between them.
9. Arrange the following according to their increasing bond length or decreasing stability: a)  $O_2$ ,  $O_2^+$ ,  $O_2^-$
10. Draw a Molecular orbital diagram of CO and  $CO^+$ , and explain the values of bond length for both molecules.
11. Write 12 principal of Green chemistry?
12. Explain the Buckminster fullerene providing the structure and properties.
13. Draw a Molecular orbital diagram of  $O_2$  and on the basis of the diagram prove that Oxygen is paramagnetic in nature.
14. Explain the Graphite providing the structure, properties, and applications.



**Marks. 9**

15. Draw the molecular orbital diagrams of:  $O_2$ ,  $NO$ ,  $CO$ ,  $HF$ . Calculate their bond orders and comment on their magnetic behavior giving reasons for their magnetic behaviour.
16. Draw a Molecular orbital diagram of  $N_2$ ,  $N_2^-$  and  $N_2^+$ , and arrange their bond lengths in ascending order, also comment on their magnetic behaviour giving reasons for their magnetic behaviour.
17. Give the structure, properties and uses of graphite. Explain why graphite is used as lubricant and as a conductor of electricity?
18. Discuss the structure, preparation, properties and application of an allotrope of carbon having truncated icosahedrons geometry (Fullerene or  $C_{60}$ ).
19. What is Liquid crystalline state? Describe the various types of liquid crystals. Give the applications of liquid crystals.
20. What are CNT? Write their types, preparation and application.
21. Describe conventional and non-conventional green synthesis of Paracetamol & Adipic Acid?