



Inorganic Chemistry

Programme Code- MSCCH-17/18/19

Course Code-CHE-501

**Unit- I Stereochemistry and
Bonding in Main Group
Compounds**

Presented by-

Dr. Charu C. Pant

Department of Chemistry

Uttarakhand Open University, Haldwani

Topics of the syllabi

- ❖ Objectives
- ❖ Introduction
- ❖ VSEPR theory
- ❖ Walsh Diagram
- ❖ d- p bond
- ❖ Bent's rule and energetics of hybridization
- ❖ Some simple reactions of covalently bonded molecules
- ❖ Summary
- ❖ Terminal Questions
- ❖ Answers

❖ *Objectives:*

Objective of this unit is to introduce you with important basic concepts to understand the bonding and structure of inorganic substances. Prerequisites to understand the offerings of this chapter are the concepts of valence, dot structures of inorganic molecules, hybridization and general understanding of structural representation and chemical reactions. At the end of this chapter student should be able to understand and explain the rather difficult bonding and structures of inorganic molecules.

➤ *Introduction:*

There are several models and theories that explain shapes and geometries of molecules. Importantly, there are early models such as one due to G. N. Lewis that provide with the knowledge of electronic structures of molecules. Many subsequent theories build upon the foundation laid by the Lewis theory of electronic structures of molecules. *Valence Shell Electron Pair Repulsion* (VSEPR) theory is a model used to predict the geometry of a molecule from the number of electron pairs surrounding their central atoms. The theory is also called as Gillespie-Nyholm theory after Ronald Gillespie and Ronald Nyholm who were the main contributors to this theory.

❖ Objectives:

Objective of this unit is to introduce you with important basic concepts to understand the bonding and structure of inorganic substances. Prerequisites to understand the offerings of this chapter are the concepts of valence, dot structures of inorganic molecules, hybridization and general understanding of structural representation and chemical reactions. At the end of this chapter student should be able to understand and explain the rather difficult bonding and structures of inorganic molecules.

❖ Introduction

There are several models and theories those explain shapes and geometries of molecules. Importantly, there are early models such as one due to G. N. Lewis those provide with the knowledge of electronic structures of molecules. Many subsequent theories build upon the foundation laid by the Lewis theory of electronic structures of molecules. *Valence Shell Electron Pair Repulsion* (VSEPR) theory is a model used to predict the geometry of a molecule from the number of electron pairs surrounding their central atoms. The theory is also called as Gillespie-Nyholm theory after Ronald Gillespie and Ronald Nyholm who were the main contributors to this theory.

❖ *Valence Shell Electron Pair Repulsion (VSEPR) theory:*



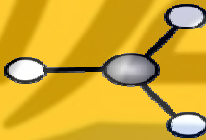



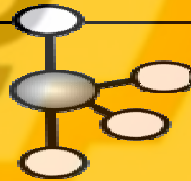
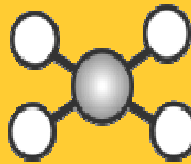
The VSEPR model to explain shapes and geometries of polyatomic molecules is based on Lewis model of molecular structures. This theory predicts the shape of molecule from the knowledge of Lewis dot structures. In fact, the VSEPR theory relies on the tendency of the valence electron pairs surrounding an atom to exert repulsion among each other and thereby adoption of geometrical arrangement to minimize this repulsion. It is important to note that repulsion between two lone pairs is stronger than that between a lone pair and a bonding pair, which in turn is stronger than the repulsion between two bonding pairs of electrons.

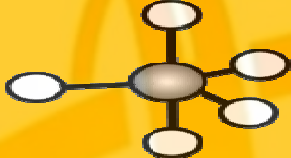
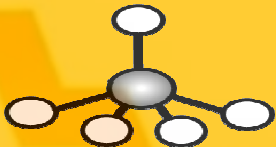
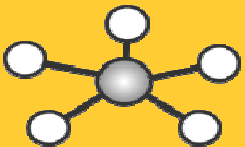
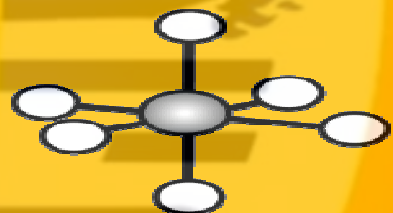
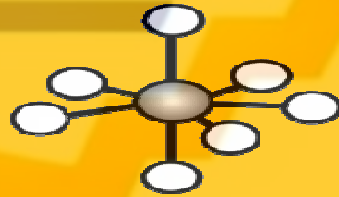
Hence, the VSEPR theory makes use of positions of different atoms and electrons around a central atom. Complete positioning of bonded and lone electron pairs of electrons determine the shape of the molecule. The final shape is deduced by ignoring the position of lone electron pairs. Although, the VSEPR theory can be applied for a variety of compounds; nevertheless, it excellently explains geometry of simple halides of the p block elements. It is also important to note that the VSEPR models do not take steric factors, i.e., bulkiness of substituent around the central atom into account. Following are the general rules for determining VSEPR geometries of a given molecule.

1. Draw the Lewis structure of the molecule for which geometry has to be evaluated.

2. Place the lone pairs (lp) and bonding pairs (bp) of electrons around the central atom.
3. Electron–electron repulsions decrease in the sequence: lone pair–lone pair ($lp-lp$) > lone pair–bonding pair ($lp-bp$) > bonding pair–bonding pair ($bp-bp$).
4. If the central atom is connected to a surrounding atom by multiple bond, then the electron–electron repulsions decrease in the order: triple bond–single bond > double bond–single bond > single bond–single bond.
5. Possible common shapes for a molecule or ion, AB_n comprising of central atom A surrounded by n atoms of B, are presented in **Table 1**

Table:1

	Molecular formula	Coordination number	Geometry (Bond Angle)		
1	AB ₂	2	 Linear (180°)	 Bent	
2	AB ₃	3	 Trigonal Planar (120°)	 T shaped (180° / 90°)	 Trigonal pyramidal
3	AB ₄	4	 Tetrahedral (109.5°)	 See-saw shaped	 Square planar (90°)

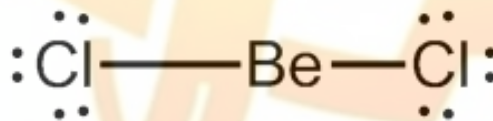
4	AB_5	5	<div>    </div> <div> <p>Trigonal bipyramidal ($120^\circ / 90^\circ$)</p> <p>Square pyramidal</p> <p>Pentagonal planar (72°)</p> </div>
5	AB_6	6	<div>  </div> <p>Octahedral (90°)</p>
6	AB_7	7	<div>  </div> <p>Pentagonal bipyramidal ($90^\circ / 72^\circ$)</p>

Some of the examples:

► ***Structure of beryllium chloride (BeCl_2):***

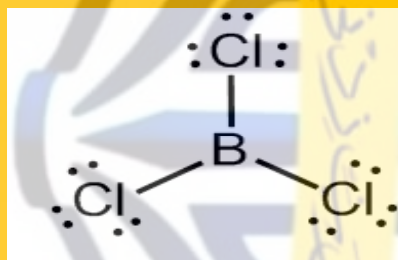
Beryllium chloride is a white coloured hygroscopic solid substance with chemical formula BeCl_2 . Beryllium chloride has two bonding pairs and no lone pair of electrons around the beryllium atom as depicted in **Figure 1**. In order to minimize mutual repulsion, the between bonding pairs of electron orient as far from each other as possible which results in the **linear geometry** of the molecule. As per VSEPR considerations, the Cl-Be-Cl bond angle is 180° .

Figure 1.

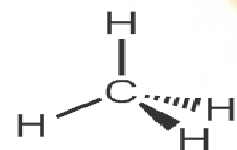


► *Structure of boron trichloride (BCl_3):*

Boron trichloride is a colourless gas with chemical formula BCl_3 . This molecule has three bonding pairs of electrons around boron atom; hence, the molecule assumes **trigonal planar geometry** with Cl-B-Cl bond angle of 120° (**Figure 2**).



► *Structure of water (H_2O), ammonia (NH_3) and methane (CH_4):*



4 bp, 0 lp
Tetrahedral
(109.5°)



3bp, 1 lp
trigonal pyramidal
(107°)



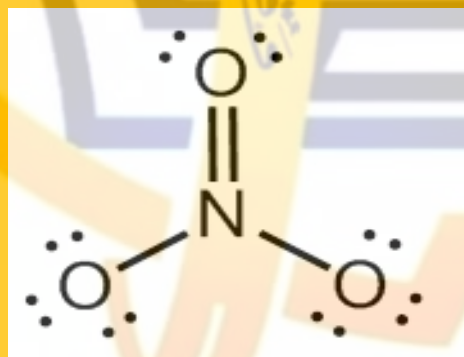
2 bp, 2 lp
bent
(104°)

Explanation:

Each of the water, ammonia and methane molecules has four electron pairs around the respective central atom (**Figure 3**). However, the number of bonding and lone pairs of electrons is different. Methane with four bonding pair of electrons has a tetrahedral geometry (H-C-H bond angle = 109.5°). Ammonia has three bonding pairs and a lone pair of electrons; therefore, the geometry reduces to trigonal pyramidal. Since, the *lp-lp* repulsion is stronger than the *bp-lp* repulsion; therefore, H-N-H bond angles of ammonia are contracted to 107° . In case of water there are two lone pairs and two bonding pairs of electrons are there around the oxygen atom. Therefore, the geometry of molecule reduces to bent shape with H-O-H bond angle of 104° .

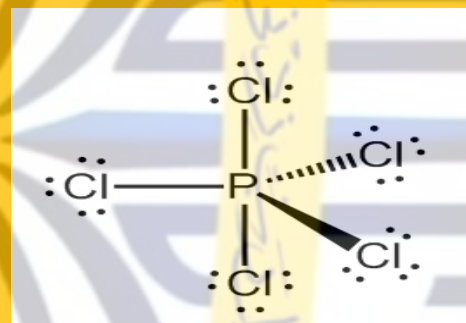
► *Structure of nitrate anion (NO_3^-):*

The Lewis structure of nitrate anion is presented in Figure 4 in which formal charge on anion is not depicted for the sake of clarity. Central nitrogen atom has one double bonded and two single bonded oxygen atoms around it. There is no lone pair of electron present around nitrogen atom. Hence, VSEPR theory suggests a trigonal planar geometry (**Figure 4**).



➤ *Structure of phosphorous pentachloride (PCl_5):*

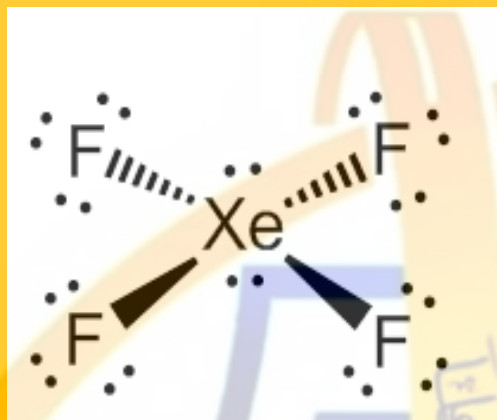
Phosphorous pentachloride molecule has five bonding pairs of electrons around phosphorous atom and there is no lone pair of electrons on central atom. Therefore, VSEPR theory suggests the structure of PCl_5 to be trigonal bipyramidal (**Figure 5**).



➤ *Structure of xenon tetrafluoride (XeF_4):*

The Lewis structure of xenon tetrafluoride suggests four bonding pairs and two lone pairs of electrons around central Xenon atom. Hence the octahedral geometry for six coordinated central atoms reduces to square planar in case of XeF_4 (**Figure 6**).

➤ **Figure 6:**



❖ **Limitations of VSEPR theory:**

The VSEPR theory makes general statements about molecular geometry which is very useful in predicting the geometries of most of the molecules and ions. However, there are limitations to the theory as the predicted structures does not corroborate with those established by physical characterizations in some cases as discussed as follow.

1. Structures of IF_7 and TeF_7^- are *isoelectronic* with seven bonding pairs of electrons around the respective central atoms. Hence, VSEPR predicts pentagonal bipyramidal geometry for both of these structures. VSEPR theory does not predict different bond distances for axial and equatorial positions in pentagonal bipyramidal geometry. Physical characterization establishes that the axial bonds of these structures are slightly shorter than the respective equatorial bonds. Additionally the geometry of TeF_7^- in their crystallographically characterized salts seems much distorted from the predicted pentagonal bipyramidal geometry as the equatorial fluorine atoms are not coplanar.

2. VSEPR theory successfully predicts the geometry of simple p-block molecules but it is not appropriate to predict structures of the d-block derivatives.

3. VSEPR theory does not take inert pair effect into account. Hence, it does not explain structures of molecules derived from heavy elements of periodic table. Crystallographic analyses has revealed that the species such as $[\text{SeCl}_6]^{2-}$, $[\text{TeCl}_6]^{2-}$ and $[\text{BrF}_6]^-$ possess regular octahedral geometry which is not justifiable using VSEPR theory.

❖ ***Walsh diagrams:***

Walsh diagrams were first introduced by Prof. A.D. Walsh to rationalize the shapes adopted by polyatomic molecules in the ground state as well as in excited states. Walsh diagrams are graphical representation depicting calculated orbital binding energies of a molecule plotted against bond angles. These diagrams predict geometries of small molecules and explain why a given molecule is more stable in certain geometry than the other. Walsh's rule states that a molecule will assume a structural geometry which provides most stability to its highest occupied molecular orbital (HOMO).

Walsh diagram is used to explain the regularity in the structures of related molecules having identical number of valence electrons. For example, water (H_2O) and sulphur dioxide (H_2S) exhibit similar structures. Walsh diagram also explains the change in geometry of molecules with the change in their number of electrons or their spin state.

➤ *Walsh diagram for tri-atomic molecules*

Simplified Walsh diagram for a triatomic molecule is depicted in **Figure 7**, which is energy versus bond angle plot. It should be noted that the depicted energy levels are qualitative and for actual system should be calculated by a suitable simulation. MO levels drawn on the left are for the bent configuration with bond angle of 90° whereas those on right are for the linear configuration with bond angle 180° .

➤ **Figure 7:**

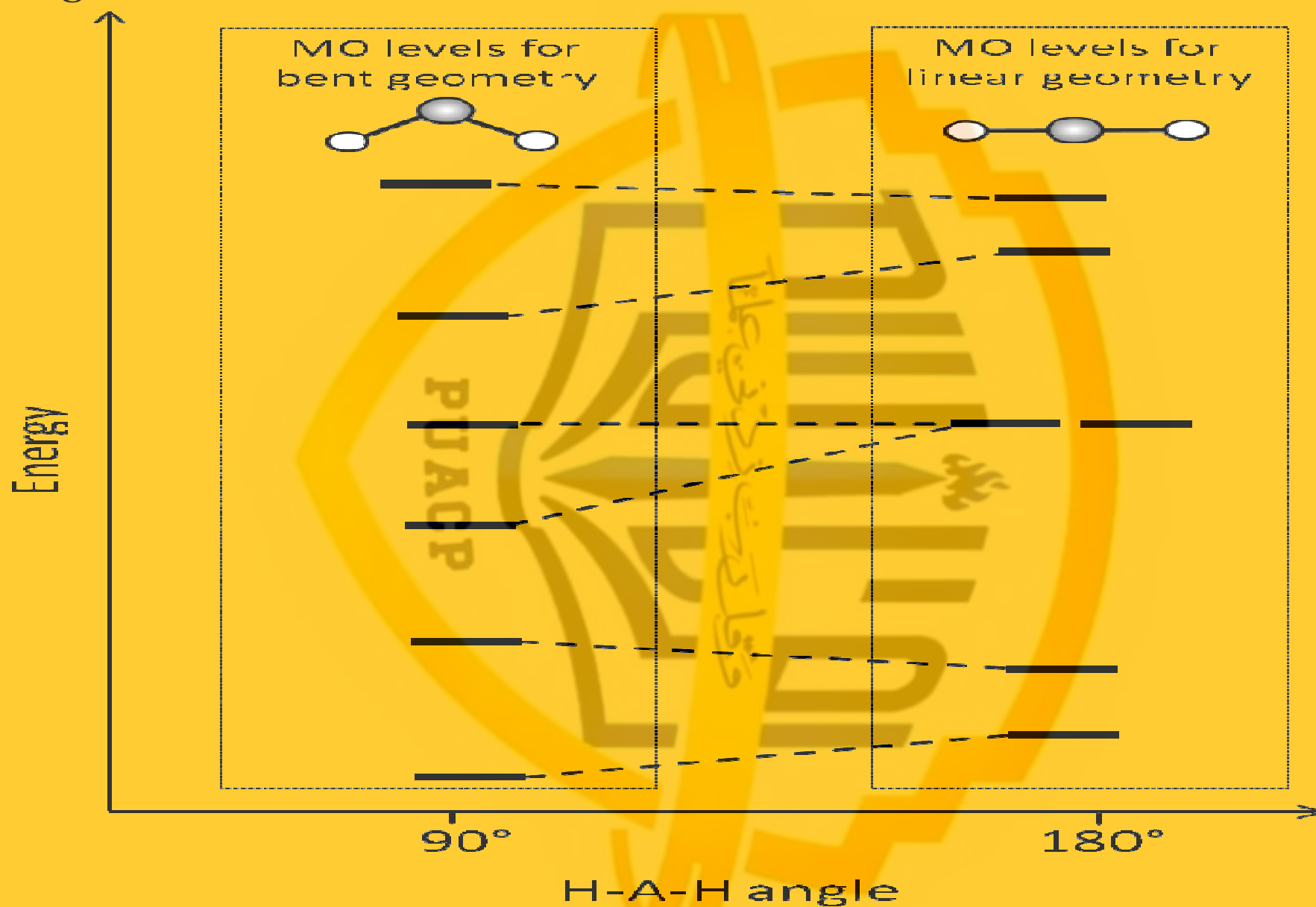
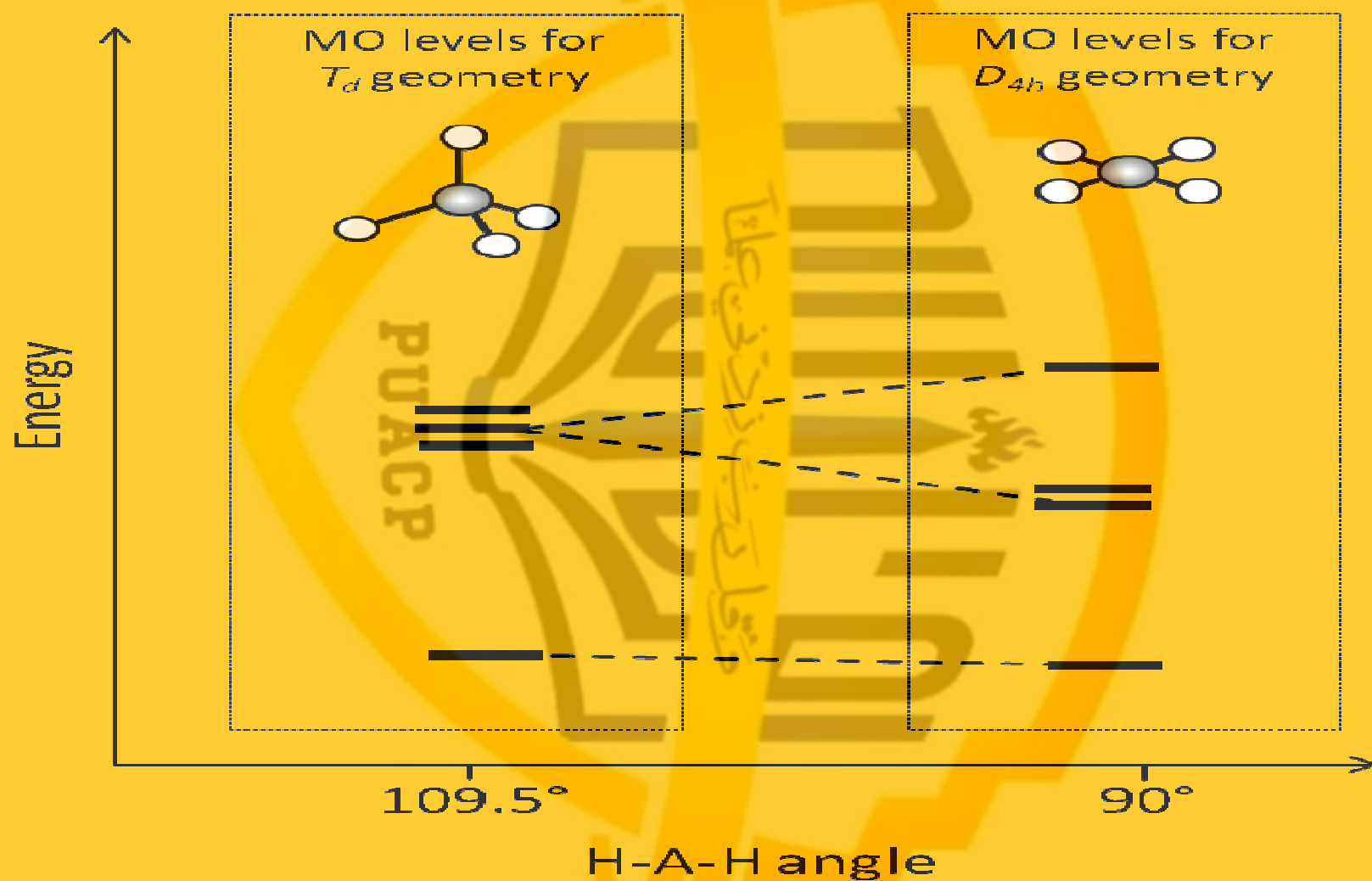


Figure 7. Simplified Walsh diagram for a tri-atomic molecule, AH_2

➤ Walsh diagram for penta-atomic molecules:

For penta-atomic molecule, an imaginary model AH_4 can be considered which can assume a tetrahedral or square planar geometry. Methane (CH_4) and sulfur tetrafluoride (SF_4) are the real examples for such categories. For instance, for the formation of methane molecule one 2s and three 2p orbitals of carbon and four 1s orbitals, one from each hydrogen atoms get involve in bonding. Abovementioned eight orbitals result in four bonding and four antibonding orbitals out of which bonding orbitals occupy all eight electrons involved in formation of molecule. In case of tetrahedral geometry significant overlap between the orbitals of carbon and hydrogen is possible which reduces the energy of bonding orbitals whereas in the square planar configuration the extent of overlap is very low which in turn results in orbitals of considerably high energy as depicted in the **Figure 8**. Hence, the CH_4 molecule prefers the tetrahedral geometry rather than the square planar or the intermediate distorted geometries.

Figure 8. Simplified Walsh diagram for a methane like penta-atomic molecule, AH_4



❖ *$d\pi$ - $p\pi$ bond:*

Formation of inorganic molecules is different than that of organic molecules in many aspects, one of which is the occurrence of $d\pi$ - $p\pi$ bonds. Generally π bonds, as in case of organic molecules, form by lateral overlapping of p orbitals present on two atoms such as carbon, nitrogen or oxygen. Bonding interactions between two d orbitals resulting in δ bonds in inorganic molecules are also prevalent. However, bonding interactions in inorganic molecules can also make use of suitably available d and p orbitals at once. When a bond forms by lateral overlapping of p (or p^*) and d orbitals present on two different atoms, it is called $d\pi$ - $p\pi$ bond. Such bonds are frequently observed in metal complexes such as carbonyls and nitrosyls.

A simple example is sulfur trioxide (SO_3). Main group compounds such as phosphine oxides and disiloxane can also feature the $\text{d}\pi\text{-p}\pi$ bonds. Presence of $\text{d}\pi\text{-p}\pi$ bonding interactions usually result in shortening of bond length and planar configuration of involved atoms. However, observing such molecular features should not always be attributed to $\text{d}\pi\text{-p}\pi$ bonds as several other factors may also be playing role. Hence, a careful evaluation of electronic and orbital symmetries must be made.

Phosphine Oxide ($\text{R}_3\text{P}=\text{O}$) offers an example of $\text{d}\pi\text{-p}\pi$ bond in molecules comprising of nonmetallic elements (**Figure 9**). In this case all the p orbitals present on phosphorous are utilized in hybridization and hence not available for lateral overlapping.

Empty d orbital on phosphorous accepts electron density from filled p orbital available with oxygen atom. This $d\pi-p\pi$ bond causes tighter binding of both involved atoms which is reflected in short bond distance (150 pm) and stability (bond energy 544 kJ/mol) of the bond.

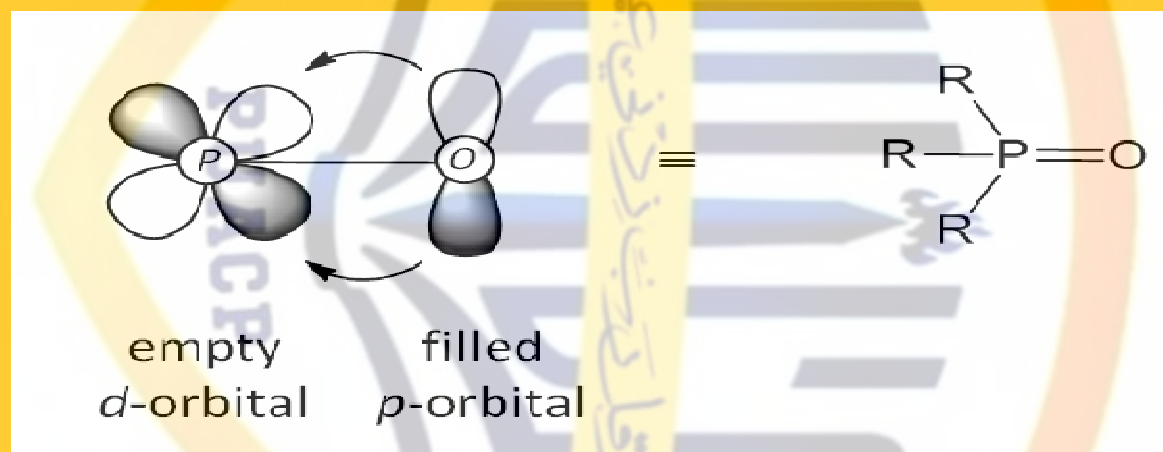
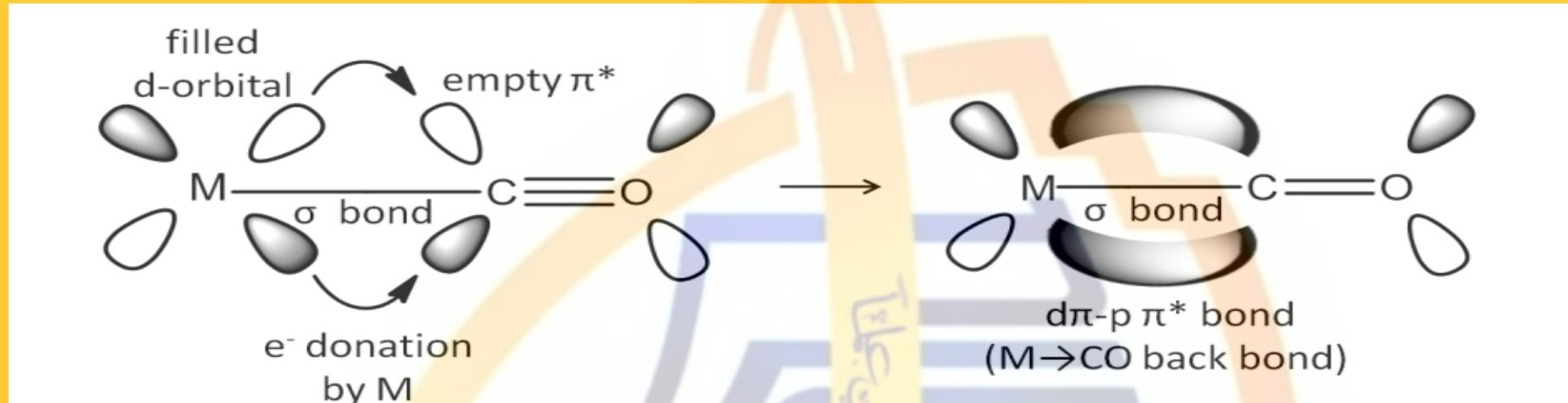


Figure 9. $d\pi-p\pi$ bond in phosphine oxide.

Bonding in metal carbonyls is classical example of $d\pi-p\pi$ bond, where empty π^* orbital present of oxygen atom accepts electron density from the filled d orbital of metals which results in the increase in bond order of metal-carbon bond (**Figure 10**).

Figure 10. $d\pi$ - $p\pi$ bond in a typical metal carbonyl system.



❖ 1.6 Bent's Rule and Energetic of Hybridization:

Hybridization is the concept of mixing atomic orbitals of different energy and shape to form same number of new hybrid orbitals of equal energies. Hence, hybridization is the energy redistribution of atomic orbitals realized by linear combination of atomic orbitals. As the orbital energies are of the order of magnitude of bond energies, hence it is important tool to determine the structure of molecules.

Bent's rule relates the orbital hybridization of central atom in a molecule with the electronegativities of substituents and was originally stated by Henry Bent as "Atomic s character concentrates in orbitals directed toward electropositive substituents". Learners, you must recall that the 's' orbital has lower energy than the 'p' orbital. Moreover, a hybrid orbital having higher 's' character has lower energy and 's' orbital like shape. On the other hand higher 'p' character results in higher energy and 'p' orbital like shape of the hybrid orbital. As the 's' orbitals are closer to the atomic nuclei, it stabilizes the lone pair of electron than the 'p' orbital does. Hence, it is logical to say that more stable molecular model would allow the orbitals rich in 'p' character for bonding purpose and those rich in 's' character for accommodating the lone pairs of electrons.

It can also be stated that, electron density available on 's' rich orbital is closer to the nuclei hence, less available for bonding. Therefore, electronegative substituent would withdraw electron density from 'p' rich orbitals than the 's' like orbitals. We can illustrate this using structure and bonding in PCl_3F_2 . Formation of this molecule involves mixing of one s, three p and one d orbitals to form five sp^3d orbitals. The five hybrid orbitals are not identical but can be grouped in set of two (axial) and three (equatorial) orbitals (**Figure 11**). The equatorial set is resulted by s, p_x and p_y orbitals whereas axial set is resulted by p_z and d orbitals. Experimental evidences indicate that the fluorine and chlorine atoms in PCl_3F_2 molecule are situated at axial and equatorial positions respectively, which is in agreement with Bent's rule.

Figure 11. Position of substituent in PCl_3F_2 molecule (left) and the geometry of p -orbitals on phosphorous (right).



Important implication of Bent's rule and energetic of hybridization can be seen in the significant difference in the bond angles of hydrides of group 15 or 16 elements. As presented in **Table 2**, ammonia (hydride of first element in group 15) features a bond angle of 107.2° , whereas the hydrides of subsequent elements down the group, *i.e.*, P, As and Sb feature bond angles closer to 90° . Similar trend can be observed for the group 16 hydrides.

Table 2. Formula and bond angles for group 15 and 16 hydrides.

S.No.	Group 15 hydride	Bond angle	Group 16 hydride	Bond angle
1	NH ₃	107.2°	OH ₂	104.5°
2	PH ₃	93.8°	SH ₂	92°
3	AsH ₃	91.8°	SeH ₂	91°
4	SbH ₃	91.3°	TeH ₂	89.5°

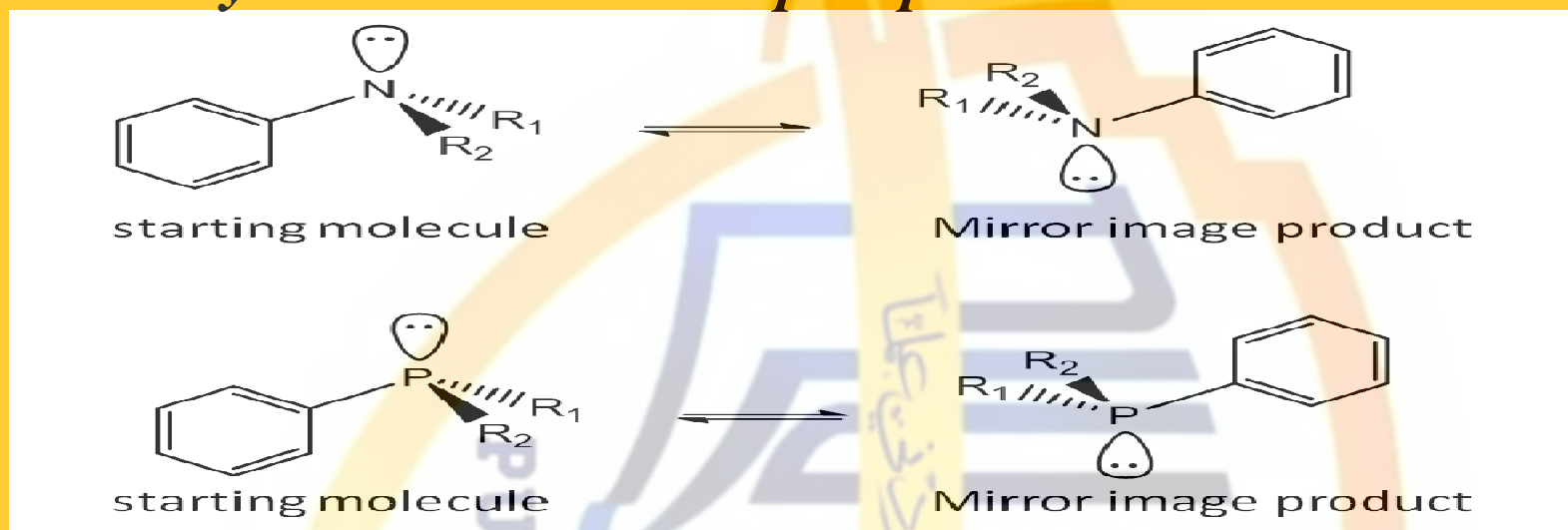
❖ Some simple reactions of covalently bonded molecules:

Inorganic reactions are different than the organic ones in many aspects including the structural features. Organic reactions primarily involve sp , sp^2 and sp^3 hybridized carbon centres, therefore, organic reactions usually deal with linear, trigonal planar and tetrahedral geometries. On the contrary, inorganic molecules feature a variety of structural diversity. This poses much concerns pertaining to the structural, configurational and dynamic changes in case of inorganic reactions. Therefore, this section discusses two transformations involving structural changes in inorganic molecules. Subsequent reactions are of environmental and industrial importance.

A. Atomic Inversion:

Atomic inversion in molecules is spatial rearrangement of atoms giving rise to the mirror image products. Usually, the molecules involving tri-substituted N and P atoms, *i.e.*, amines and phosphines show such a phenomenon (**Figure 12**). It should be noted that the atomic inversion in non-chiral molecules yield product identical to the starting substance. However, a dissymmetric molecule, gives rise to a product with a molecular configuration that is a mirror image of that of the original molecule. The energy barrier for atomic inversion in case for amines is usually so small that the isolation of enantiomers cannot be effected.

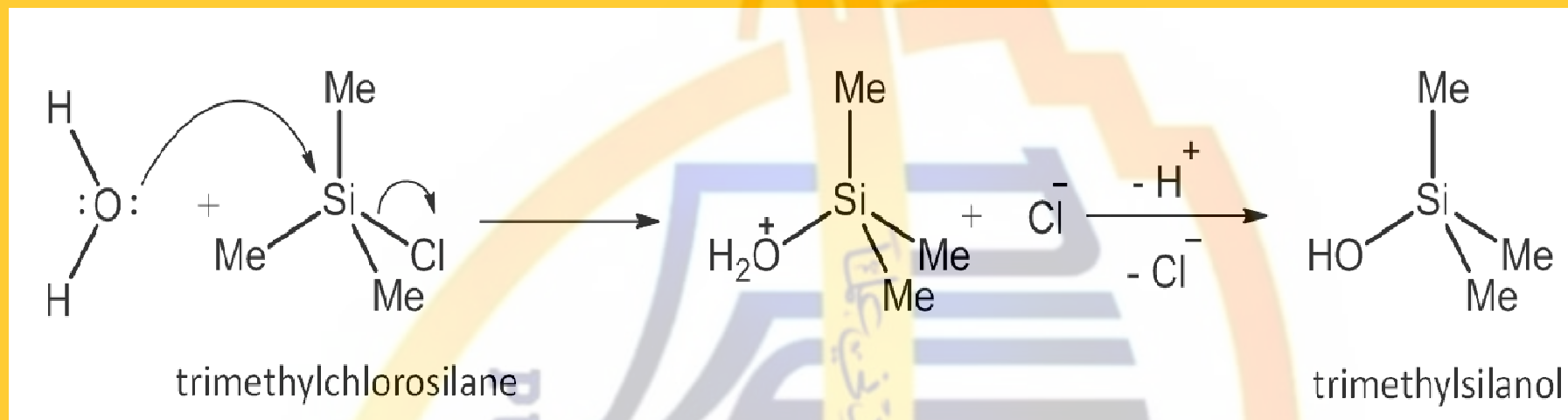
Figure 12. Atomic inversion around nitrogen and phosphorous atoms in dissymmetric amine and phosphine molecules.



B. Nucleophilic Substitution Reaction:

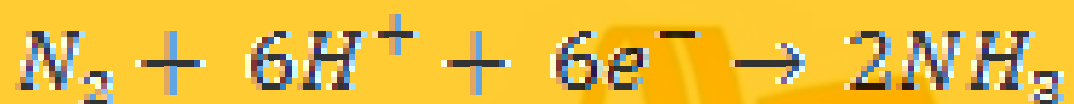
Hydrolysis or solvolysis is a common reaction of inorganic substances which involves nucleophilic substitution reactions. Hydrolysis of trimethylchlorosilane to yield trimethylsilanol is presented below as an example (**Figure 14**). Note that the hydrolysis of a related bifunctional compound, dimethyldichlorosilane is used to synthesise a polymeric

Figure 14. Synthesis of trimethylsilanol by hydrolysis of trimethylchlorosilane.



1.7.5 Nitrogen Fixation

Nitrogen fixation is a very important reaction involving the conversion of natural nitrogen, N_2 (which has a triple bond between two nitrogen atoms) into ammonia. The reaction takes place at ambient temperature and 0.8 atm pressure of nitrogen in the Rhizobium bacteria found in the nodules on some plant roots. The reaction can be presented as follows:



The process of nitrogen fixation involves enzymatic catalysis which is not discussed in this book. However, it should be noted that enzymatic processes are highly energy efficient chemical reactions in which various enzymes act as catalysts. It is important to note that the Haber process, the industrial procedure to synthesize ammonia requires high temperature, high pressure and an iron catalyst. Qualitative comparison of nitrogen fixation and Haber process would allow you to assess the superiority of enzymatic processes which are not yet completely understood. The ammonia produced in above reaction is used by plants for formation of essential building blocks of life such as amino acids.

❖Summary:

This chapter discussed some important concepts to understand the bonding and structure of inorganic molecules. VSEPR theory offers a simple yet very useful concept to understand the geometry of simple molecules. Walsh diagram and Bent's rule are relatively intricate topics that complement VSEPR theory towards complete understanding of structures of inorganic molecules. Lastly, some important reactions of inorganic compounds are discussed. The discussion on selected reactions not merely presents the chemical transformations but also touch upon the structural, environmental and industrial importance of the same.

1.9 Terminal Questions

Multiple choice type questions

1. Identify the shapes of the following molecules using concepts of VSEPR.



2. Draw the Lewis Dot Structures for each of the following species.



3. Arrange following in the decreasing order of bond angles:

4. What is the molecular geometry of NCl_3 ?

5. Which one of the following is the correct bond angle between atoms adopting a trigonal planar geometry?



Short answer type questions

1. Write the statement of Bent's rule.
2. Write the name of geometry for a molecule with central atom having seven substituents.
3. Write full form of acronym, VSEPR.
4. Central atom in a molecule has two substituents and two lone pair of electrons. Discuss the bond angle that you expect for molecule in question.
5. What are solvolysis reactions?

Long answer type questions

1. Discuss energetic of hybridization with suitable examples.
2. Discuss structure of tetrachloromethane (CCl_4) in light of the VSEPR theory.
3. Discuss the $d\pi$ - $p\pi$ bonding in case of a sulfur compound.
4. Why phosphine oxide exhibits shorter $\text{P}=\text{O}$ bond length and high stability, explain.
5. Draw and discuss Walsh diagram for methane.

THANK YOU

