Chapter-15

PREDICTION OF BOND ANGLE OF POLYATOMIC MOLECULES

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The angle between the two covalent bonds of a molecule is called the bond angle. When in covalent bonds, **bond pair electron clouds, are adjacent to each other, then, due to excessive repulsive force between two adjacent bond pair electron clouds, the bond angle increases**. **When bond pair electron clouds move towards the central atom** instead of the peripheral atom, **then, they are adjacent to each other and exhibit much more repulsive force, which increases the bond angle of the molecule (Fig.1)**

So, the mainly responsible repulsive force for bond angle prediction is a bond pair – bond-pair (BP-BP) repulsion. If there is any other repulsive force greater than BP-BP repulsions, such as lone pair-lone pair (LP-LP) or lone pair-bond pair (LP-BP) repulsion, in this particular case, BP-BP repulsion not freely act, hence, bond angle diminishes[1,2,3,4,5,6,7].

The order of repulsive force as per VSEPR theory is a

lone pair-lone pair (LP-LP) > lone pair – bond-pair (LP-BP) > bond pair – bond-pair (BP-BP).

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Factors affecting the bond angle of simple molecules or ions:

i) Different Repulsive force:

The order of bond angle depends on different repulsive forces present in molecules is as follows

bond pair–bond-pair (BP-BP)>lone pair–bond-pair (LP-BP)>lone pair-lone pair (LP-LP)
(LP = 0) (LP = 1) (LP=2)

Thus, with increasing number of lone pair electrons, bond angle decreases.

Ex. The bond angle of methane (CH_4), ammonia (NH_3) & water (H_2O), follows the order: methane (CH_4) > ammonia (NH_3) > water (H_2O). In methane (CH_4), LP on C = 0 and only BP-BP repulsion is there, in ammonia (NH_3), LP of N = 1 and hence, two repulsive forces (LP-BP & BP-BP) are there, in water (H_2O), LP on O = 2, hence, three types of repulsive forces (LP-LP, LP-BP & BP-BP) are there.

ii) Electronegativity of the central atom (when repulsive force and peripheral atoms are same): When a pair of molecules, having the same repulsive force, in which, peripheral atoms are the same but central atoms are different, then, bond angle increases with increasing electronegativity values of the central atom due to much more repulsive interactions between two adjacent bond pair electron clouds, shifted towards higher electronegative central atom. Ex. In between H_2O and H_2S, both exhibit the same repulsive forces (LP-LP, LP-BP & BP-BP). Here, peripheral atoms are same 'H' but central atoms are different 'O' & 'S'. In between oxygen and sulfur, since, central atom 'O' in H_2O is much more electronegative (E.N. of O = 3.5) than central atom 'S' in H_2S (E.N. of S = 2.5), therefore, oxygen attracts bond pair electron clouds towards itself more closely than that of sulfur. As a result of it, bond pair-bond pair repulsion between two bond pair electron clouds will be much more in water, H_2O than that of H_2S. Hence, bond angle of H_2O > H_2S **(Fig.1)**.

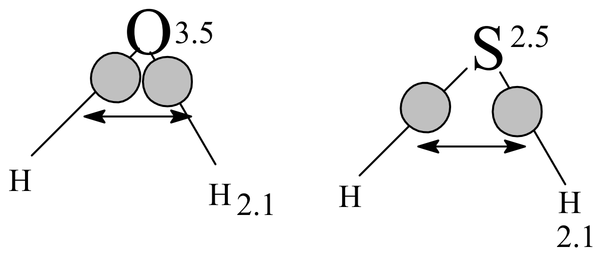

Fig. 1 : Bond angle varies on bp-bp repulsion

iii) Electronegativity of the peripheral atom (when repulsive force and central atoms are same): When, pair of molecules, having same repulsive force, in which, central atoms are same but peripheral atoms are different, then, bond angle decreases with increasing electronegativity values of the peripheral atom due to much less repulsive interactions between two bond pair electron clouds, shifted towards higher electronegative peripheral atom.

Ex. In between NH_3 and NF_3, both have LP =1 and hence, exhibit same repulsive forces (LP-BP & BP-BP). Here, central atoms are same 'N' but peripheral atoms are different 'H' & 'F'. In between fluorine and hydrogen, since, peripheral atom 'F' in NF_3 is much more electronegative (E.N. of F = 4.0) than peripheral atom 'H' in NH_3 (E.N. of H = 2.1), therefore, fluorine attracts bond pair electron clouds towards itself more closely than that of hydrogen. As a result of it, bond pair-bond pair repulsion between two adjacent bond pair electron clouds will be much more in ammonia, NH_3 than that of NF_3. Hence, bond angle of $NH_3 > NF_3$ **.**

iv) Bond angle depends on the hybridization state: Bond angle is directly proportional to the s character of a hybrid orbital as follows:

Bond angle follows the order sp – C (50 % s) > sp^2 – C (33.3 % s) > sp^3 – C (25% s)

Ex. H-C ≡ C-H > $H_2C = CH_2$ > $H_3C - CH_3$

sp $\quad$ sp^2 $\quad$ sp^3

Problems on Bond Angle

Q. Arrange the following into their decreasing order of bond angle

i) BCl_3, BF_3, BBr_3

ii) AsH_3, SbH_3, PH_3, NH_3

iii) $AsCl_3$, $SbCl_3$, PCl_3, NCl_3

iv) CCl_4, $SiCl_4$, H_2O, H_2S, H_2Se

v) CH_4, NH_3, H_2O

vi) NH_3, NCl_3, NF_3

Ans:

i) $BBr_3 > BCl_3 > BF_3$ (E.N. order F > Cl > Br)

ii) $NH_3 > PH_3 > AsH_3 > SbH_3$ (E.N. order N > P > As > Sb)

iii) $NCl_3 > PCl_3 > AsCl_3 > SbCl_3$ (E.N. order N > P > As > Sb)

iv) $CCl_4 > SiCl_4 > H_2O > H_2S > H_2Se$ (E.N. order C > Si & O > S > Se)

LP = 0 0 2 2 2

v) $CH_4 > NH_3 > H_2O$

LP = 0 1 2

vi) $NH_3 > NCl_3 > NF_3$ (E.N. order F > Cl > H)

It may be expected **that these times economic methods would go a long way to help to the students of chemistry at Undergraduate, Senior Undergraduate and Post-Graduate level** to predict bond angle of simple organic and inorganic molecules.