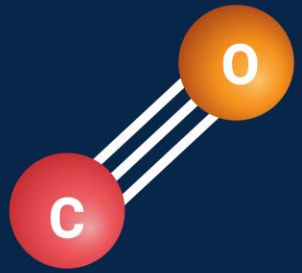
CHEMICAL BONDING - L7



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Bond Parameters

$sp = 180°$
$sp^2 = 120$
$sp^3 = 109.28$

sp^3d — 90, 120, 180.
sp^3d^2 — 90, 180.
sp^3d^3 — 72, 90, 180.

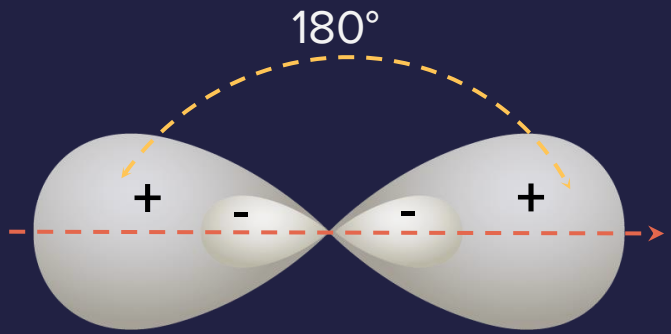
Bond Parameters

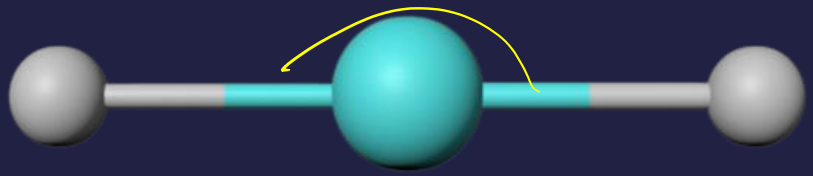
- Bond angle
- Bond length
- Bond energy
- Bond order

C – C C = C C ≡ C
1 2 3

Bond Angle

Angle between the orbitals containing **bonding electron pairs** around the **central atom** in a **molecule/complex ion**

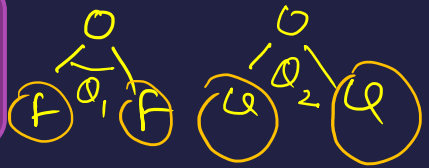




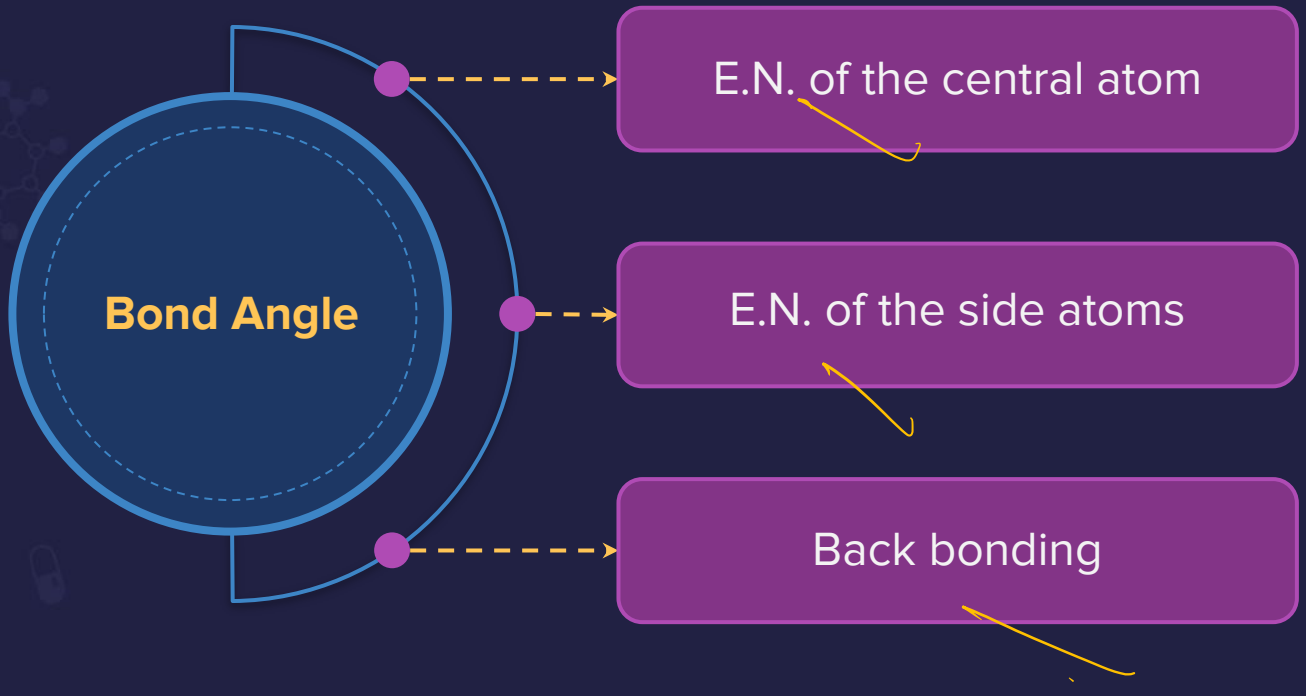
Factors Affecting Bond Angle

Bond Angle

- Hybridization
- Steric repulsions
- Number of lone pairs on central atom



Factors Affecting Bond Angle



Factors Affecting Bond Angle

1 Hybridization

As % s character	↑
Bond angle	↑

BA ∝ S%.

	sp	sp^2	sp^3
S%	50%	33.33%	25%
BA	180	120	109.28

Hybridization Index (n)

If the **angle** between two hybrid orbitals having hybridization sp^n is α

$$\cos \alpha = -\frac{1}{n}$$

Hybridization Index (n)

For hybridization: sp^n

sp^1

sp^2

sp^3

$$\cos^{-1}\left(-\frac{1}{n}\right) = \alpha$$

Angle between hybrid orbitals	α
Hybridization index	n

Hybridization Index (n)

sp	$\cos^{-1}\left(-\frac{1}{1}\right)$	=	180^{o}
sp^2	$\cos^{-1}\left(-\frac{1}{2}\right)$	=	120^{o}
sp^3	$\cos^{-1}\left(-\frac{1}{3}\right)$	=	109.5^{o}

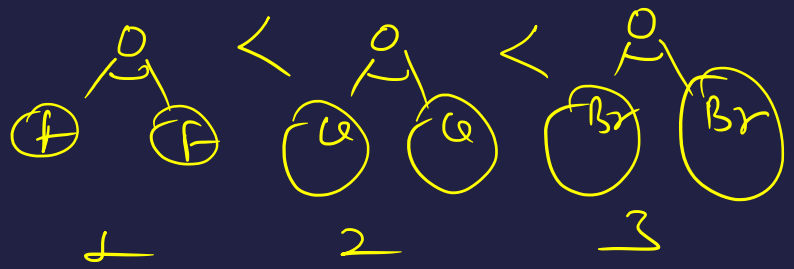
Factors Affecting Bond Angle

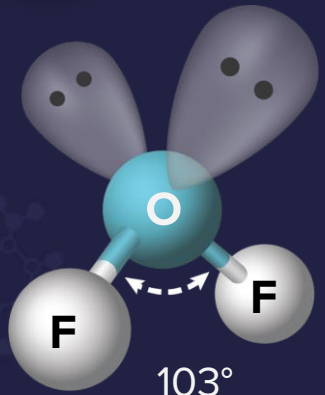
2 Steric Repulsions

Steric repulsions	↑
Bond angle	↑

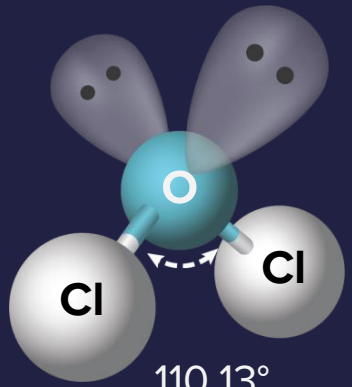
Same **central atom (2nd period)**, same **hybridization (sp^3)** & side atoms are of **3rd period & onwards**

Compare the bond angles of F_2O, Cl_2O, Br_2O.

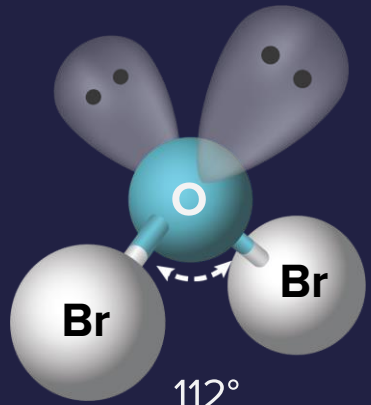




103°



110.13°



112°

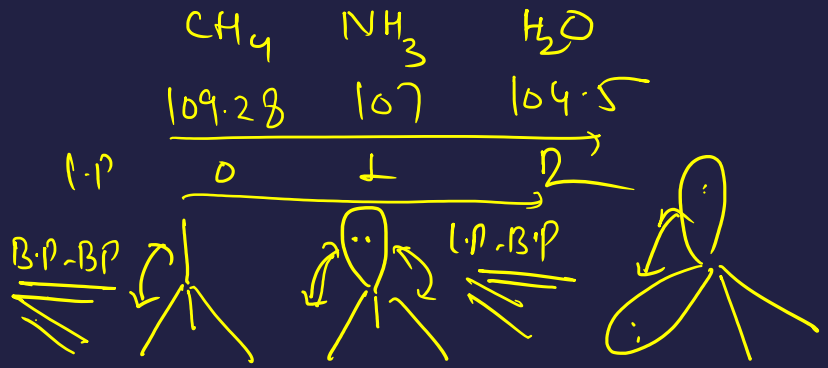
Factors Affecting Bond Angle

3 Number of lone pairs on the central atom

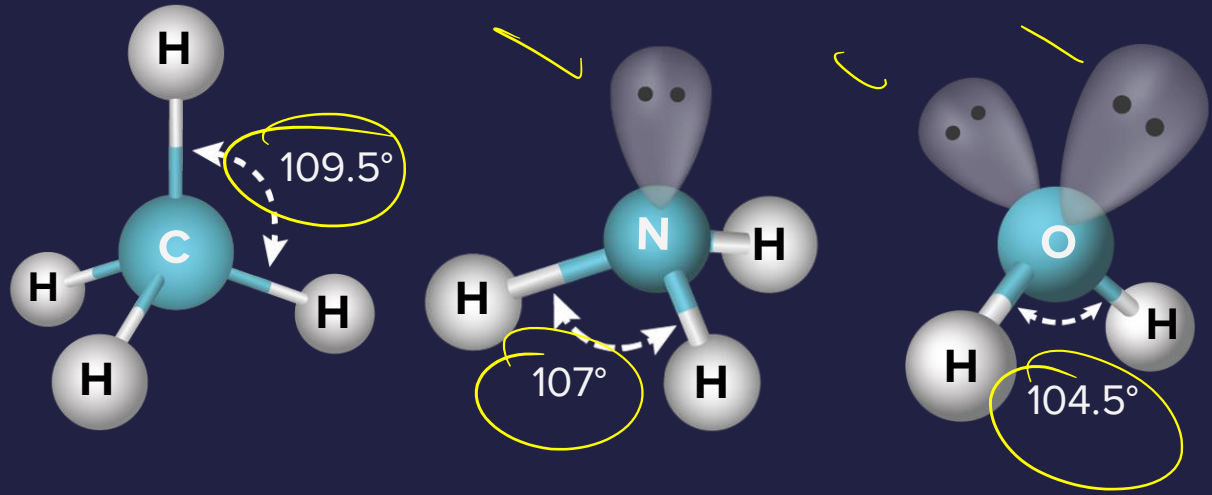
sp3

As number of **lone pairs** ↑

Bond angle ↓



Same hybridization of the central atom



Number of lone pairs ↑ → Bond angle ↓

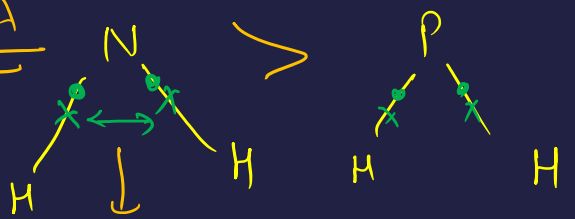
Factors Affecting Bond Angle

4 Electronegativity of the central atom

E.N. of central atom	↑
Bond angle	↑

EN N > P

BA



Same **hybridization** and number of **lone pairs** on central atom

Arrange the following in the increasing order of their bond angles: Cl_2O, Cl_2S, Cl_2Se.

$Cl_2O > Cl_2S > Cl_2Se$

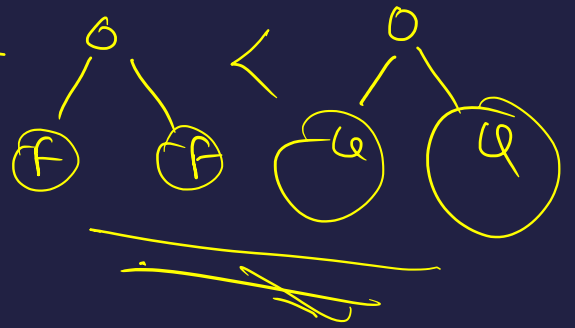
Factors Affecting Bond Angle

5 Electronegativity of the side atoms

E.N. of side atom ↑

Bond angle ↓

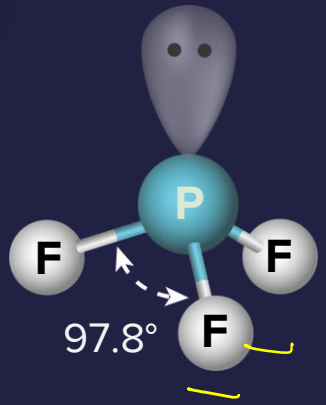
B.A

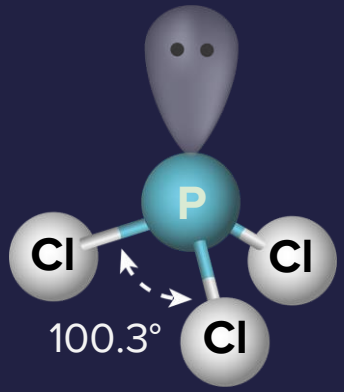


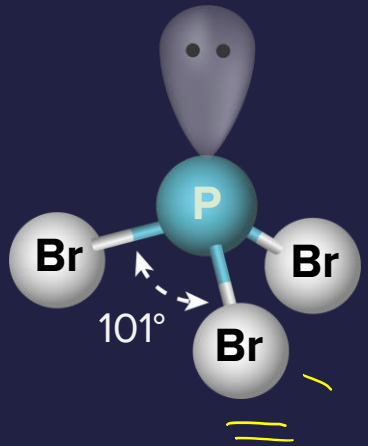
Same **central atom**, same **hybridization** & **same number of lone pairs**

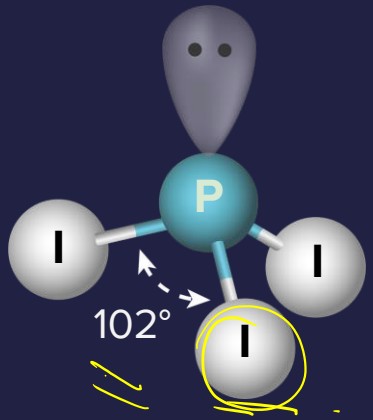
Arrange the following in the increasing order of their bond angles: PF_3, PCl_3, PBr_3 & PI_3.

$PF_3 < PCl_3 < PBr_3 < PI_3$


P
F
F
F
97.8°


P
Cl
Cl
Cl
100.3°


P
Br
Br
Br
101°


P
I
I
I
102°

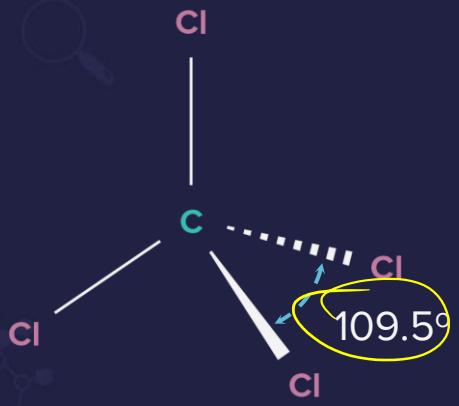
Remember!!

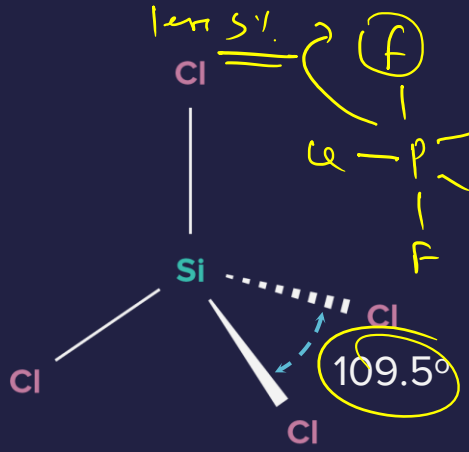
sp³ ol·p + 4σ = 4

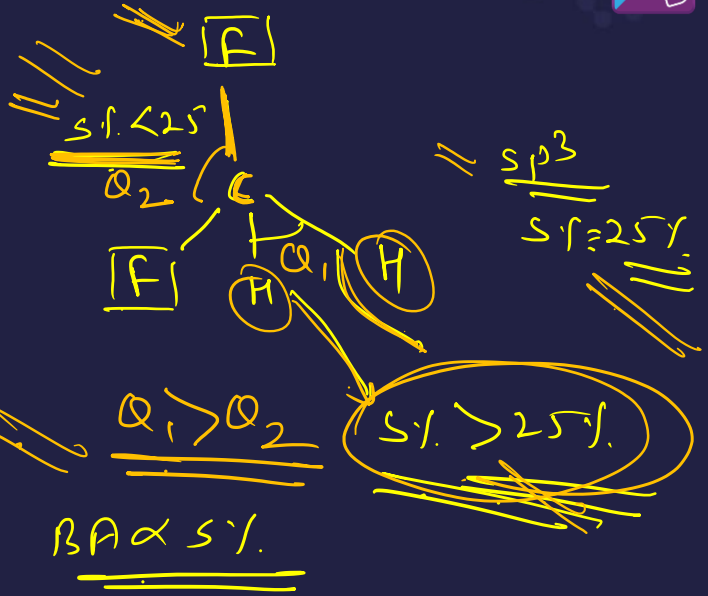
CH_4 CH_3Cl CH_2Cl_2 $CHCl_3$

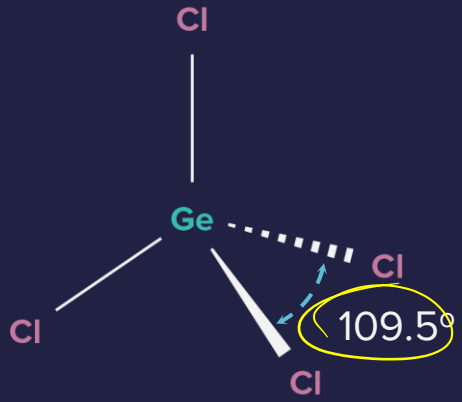
109.28

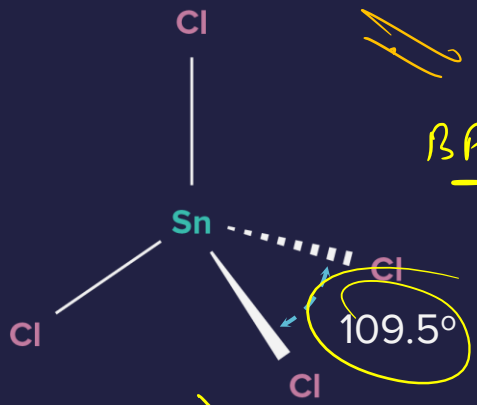
- Regular geometry
- All the **side atoms** are **identical** and **no lone pair** on central atom
- Bond angle **not affected** by **electronegativity**











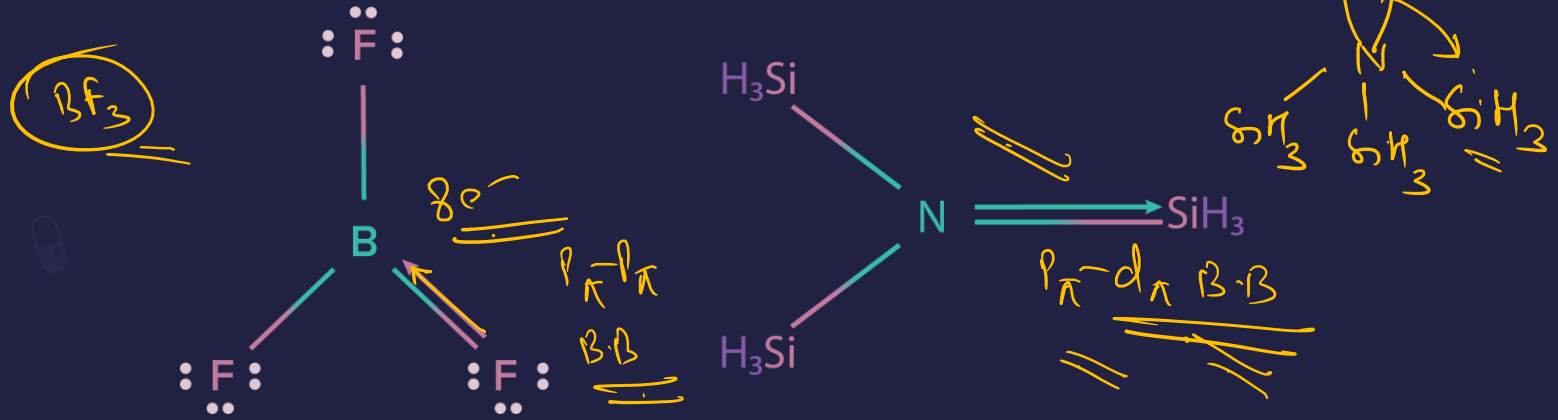
CCl_4 = $SiCl_4$ = $GeCl_4$ = $SnCl_4$

Factors Affecting Bond Angle

6 Back Bonding

Side atom ⟶ Central atom

Central atom ⟶ Side atom

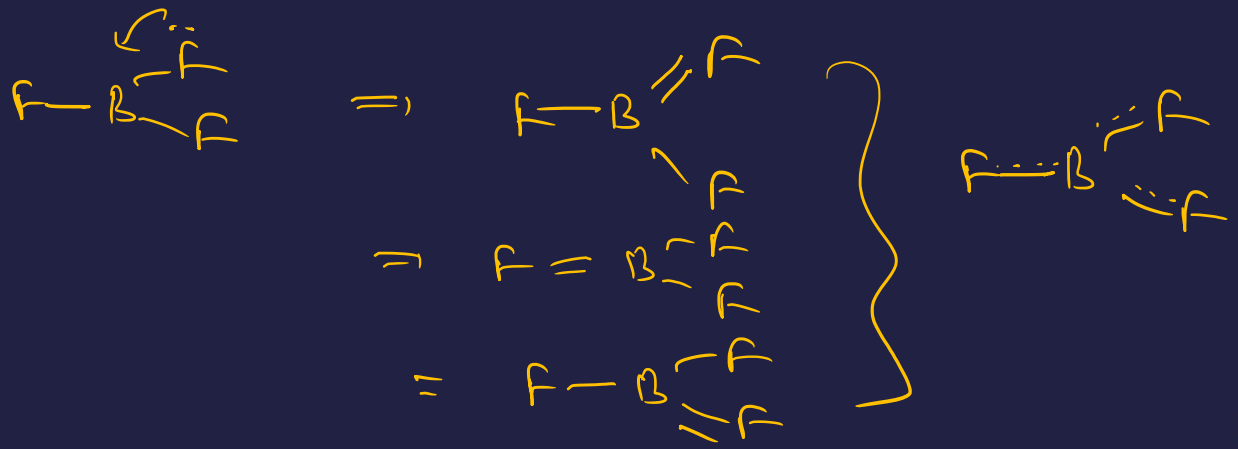


Factors Affecting Bond Angle

BF_3

Bond angle = 120°

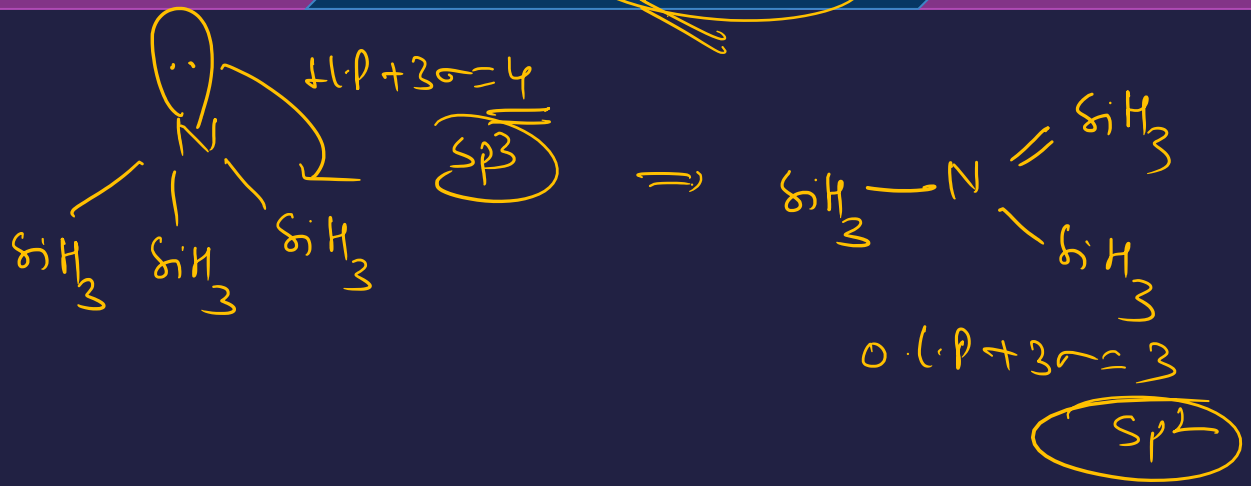
Due to back bonding → Bond order ↑ → But net effect in repulsion is **zero**



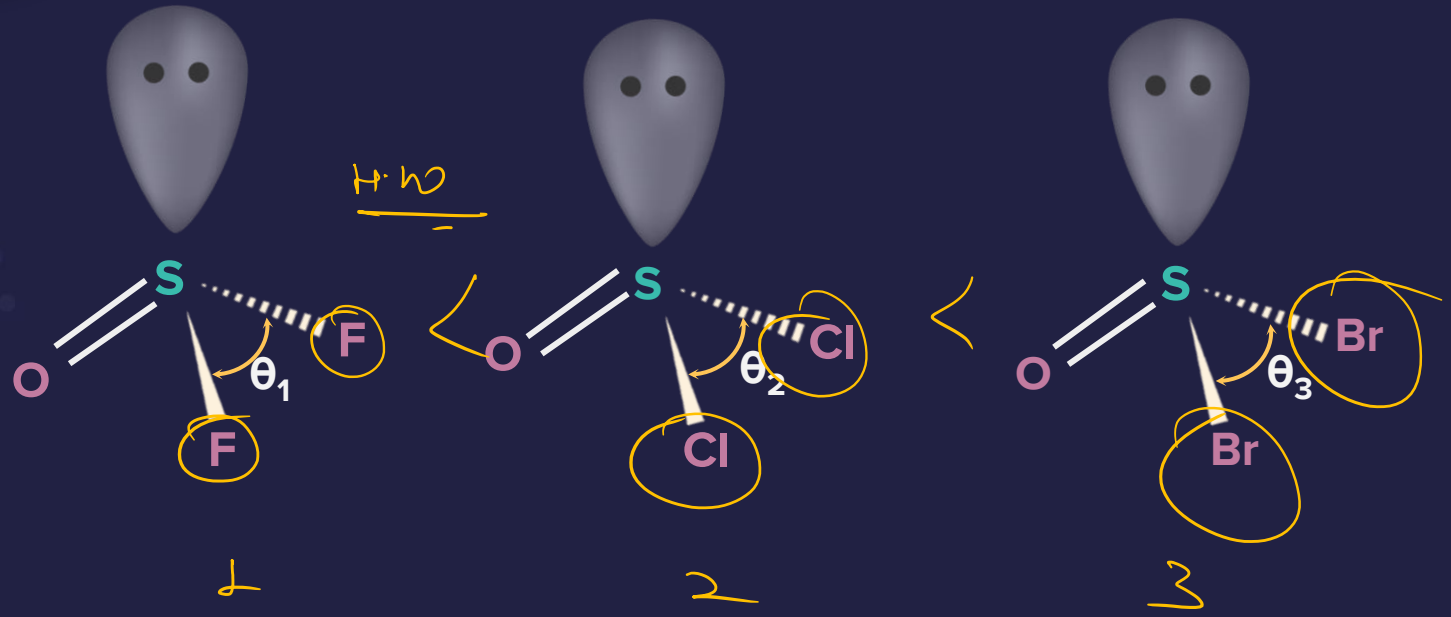
Factors Affecting Bond Angle

$N(SiH_3)_3$

Due to back bonding → Hybridization changes from sp^3 to sp^2 → Bond angle ↑



Compare the bond angles in thionyl halides.



% s - character

Hybrid Orbitals

BA ∝ S %

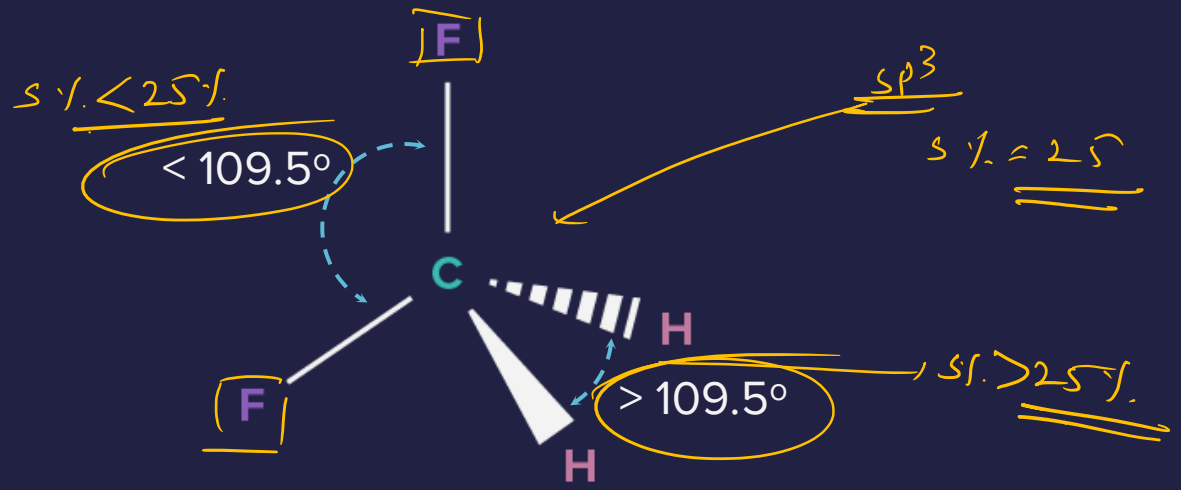
% s - character ↑

Occupied by **Electropositive** side atom

% s - character ↓

Occupied by **Electronegative** side atom

% s - Character



C - H bond	More % s character
C - F bond	Less % s character

If the ∠H-C-F bond angle in CHF_3, CH_2F_2 and CH_3F are θ_1, θ_2 and θ_3 respectively, then which of the following is correct:

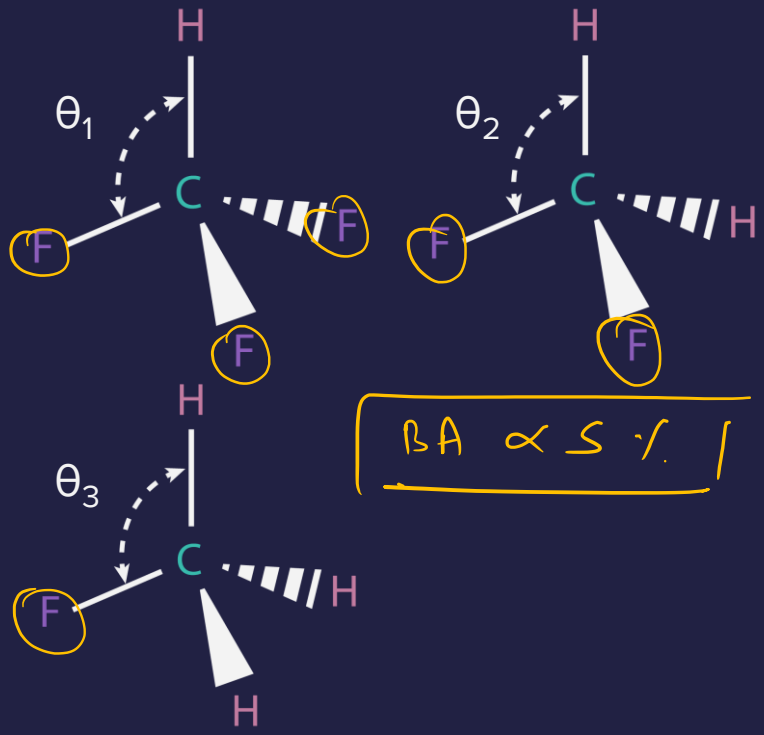
H·no

a) $\theta_1 > \theta_2 > \theta_3$

b) $\theta_1 > \theta_3 > \theta_2$

c) $\theta_3 > \theta_2 > \theta_1$

d) $\theta_1 = \theta_2 = \theta_3$



BA ∝ S·C

Bond Length

Equilibrium distance between the **nuclei of two bonded atoms** in a molecule

Factors Affecting Bond Length

- Size of the bonded atom
- Number of lone pairs on bonded atoms
- Multiplicity of bonds
- Electronegativity difference
- % s-character

Factors Affecting Bond Length

1 Size of the bonded atom

Size of bonded atom ↑ → Bond length ↑

H - F < H - Cl < H - Br < H - I

F - F < Cl - Cl < Br - Br < I - I

Factors Affecting Bond Length

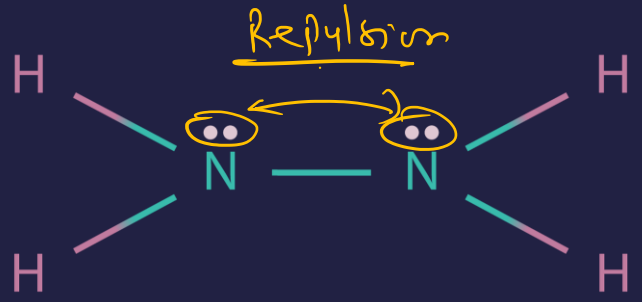
2 Number of lone pairs on the bonded atoms

For atoms in same period

Number of lone pairs ↑ → Bond length ↑

Example

Unexpected N–N **bond length** in hydrazine



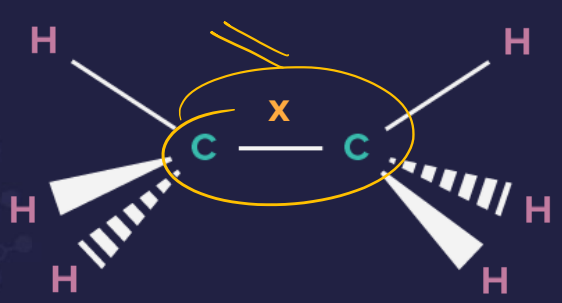
Because of **l.p. – l.p. repulsions**

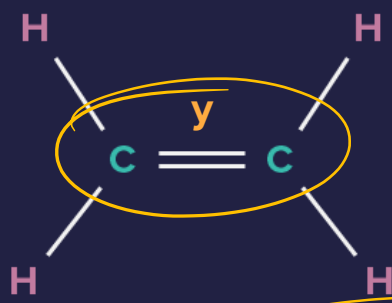
Factors Affecting Bond Length

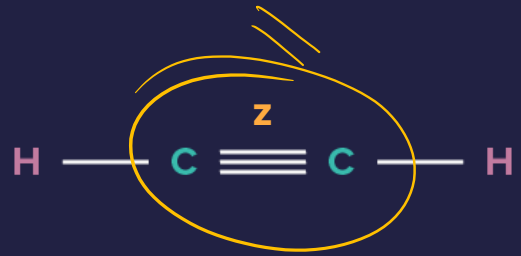
3 Multiplicity of Bonds

Multiplicity ↑ **Bond length** ↓

Factors Affecting Bond Length







$BL \propto \frac{1}{B.O}$

z < y < x

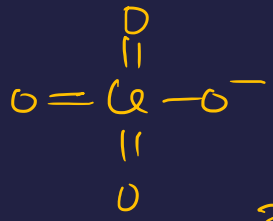
Arrange the following molecules in the increasing order of their bond lengths:

(a) F_2 , N_2 , O_2

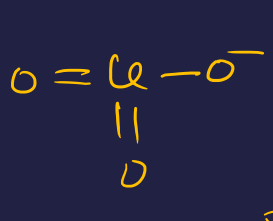
F–F > O=O > N≡N

(b) ClO_4^- , ClO_3^- , ClO^- (Cl - O bond length)

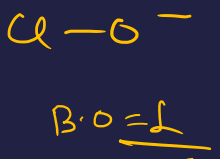
$BL \propto \frac{1}{B.O}$



B.O = 7/4



B.O = 5/3



B.O = 1

Factors Affecting Bond Length

4 Electronegativity Difference

ΔE.N. between the atoms ↑ → **Bond length** ↓

Bond Length

C - H	>	N - H	>	O - H	>	F - H
0.4		0.9		1.4		1.9

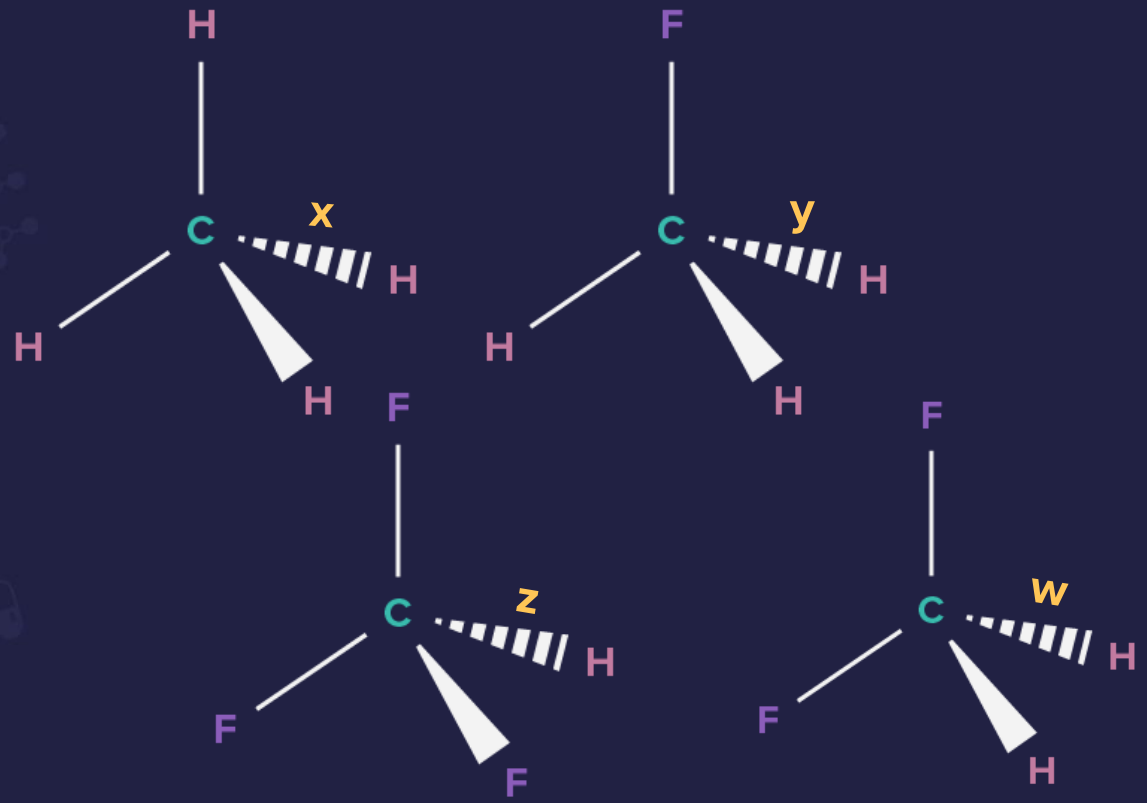
E.N. difference

Factors Affecting Bond Length

5 Percentage s-character

% s - character in hybrid orbitals ↑ **Bond length** ↓

Compare the C-H bond lengths for the following compounds: CH_4, CH_3F, CH_2F_2, CHF_3



Bond Energy

Amount of **energy** required to **break** **1 mole** of **particular** type of **bonds** between two atoms in **gaseous state**

Unit: **$kJmol^{-1}$**

Bond Energy

Multiplicity of bond ↑ → Magnitude of bond energy ↑

Bond	Energy ($kJmol^{-1}$)
C—C	347
C=C	611
C≡C	837

Factors Affecting Bond Energy

Bond length (for same bonded atom) ↓ → Bond energy ↑

Bond	Bond length (pm)	Energy ($kJmol^{-1}$)
Cl - Cl	199	243
Br - Br	228	192
I - I	267	151

Examples

Bond energy order

C – F > C – Cl > C – Br > C – I

C – C > Si – Si > Ge – Ge

Remember!!

Heavier the isotope, **stronger** is the bond

C - H < C - D < C - T

Bond Order

The **number of bonds** between the two atoms in a molecule

Bond Order

Shared pairs of electrons

Lone pair of electrons

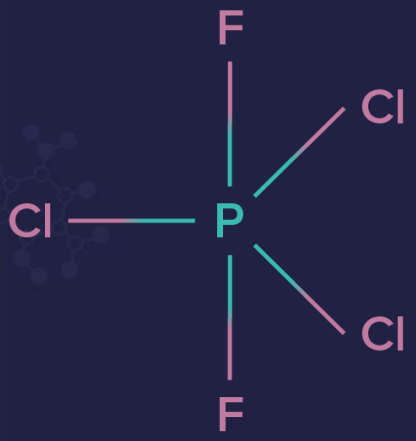
Bond order = 2

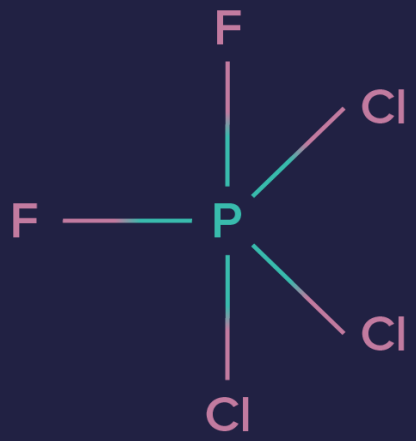
Bent's Rule

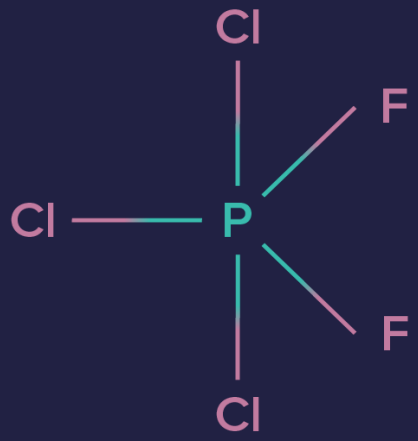
In T.B.P. geometry

Equatorial position	**High %s character**	Occupied by **lone pair**, **multiple bond**
Axial position	**Low %s character**	Occupied by more **electronegative** element

Bent's Rule







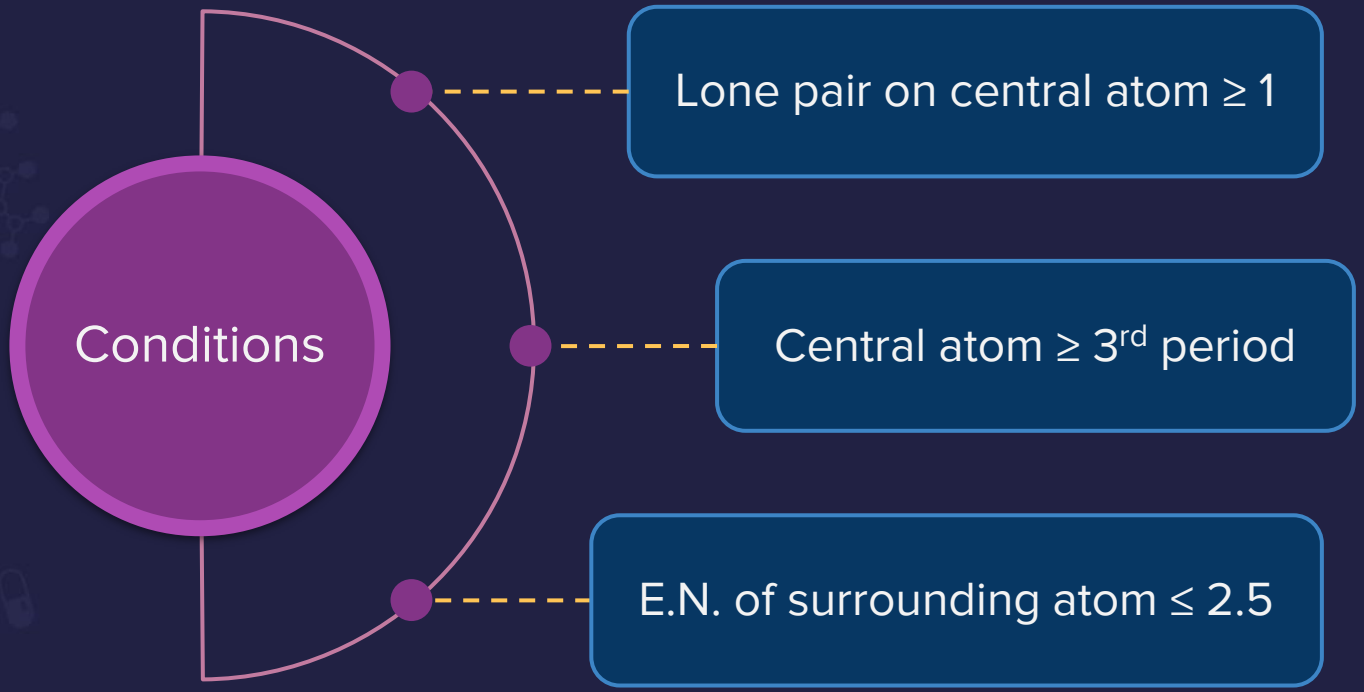
Most stable

Drago's Rule

Hybridization does not take place for **compounds** of elements of **3rd period & onwards,** which are bonded to a **less electronegative element** like **hydrogen.**

Energy difference between the **participating orbitals** is **very high**

Drago's Rule


Conditions
Lone pair on central atom ≥ 1
Central atom ≥ 3rd period
E.N. of surrounding atom ≤ 2.5

Drago's Rule

Pure atomic p orbitals take part in bonding with bond angle ≃ 90°

In case of **PH_3**

Orbitals of **P** do not come to **similar energy level**

Cannot participate in hybridization

Drago's Rule

In case of PF_3

↓

δ+ is created on the **P** atom by the **3 F** atom

↓

Orbitals of P atom contract to attain similar energy level & gets hybridized

The Cl—C—Cl angle in 1, 1, 2, 2-tetrachloroethene and tetra chloromethane respectively will be about

AIPMT 2002

a) 120° and 109.5°

b) 90° and 109.5°

c) 109° and 90°

d) 109.5° and 120°

Which one of the following has the smallest bond angle?

AIPMT 2001

a) OH_2

b) SH_2

c) NH_3

d) NO_2

Which one of the following has the largest bond angle?

AIPMT 2001

a) BBr_3

b) BCl_3

c) BF_3

d) None of these

Which one of the following has the largest 'C-C' bond length?

AIPMT 2005

a) CH_2CHCCH

b) $HCCCCH$

c) CH_3CHCH_2

d) $CH_2CHCHCH_2$

Find out total number of molecules that exists among the following:

HFO_4, PH_5, SCl_6, SF_6, IF_7, H_4Xe.

Molecule	Exist or not	Reason
HFO_4	Does not exist	Absence of d-orbital
PH_5	Does not exist	No orbital contraction
SCl_6	Does not exist	Steric crowding
SF_6	Forms	
IF_7	Forms	
H_4Xe	Does not exist	No orbital contraction

Stay Positive. Work Hard. Make It Happen!

THANK YOU