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CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - I

INORGANIC CHEMISTRY

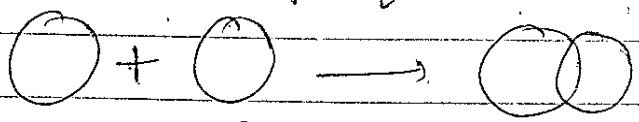
SIERRA INNOVATIONS

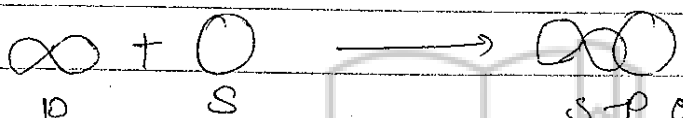
Index

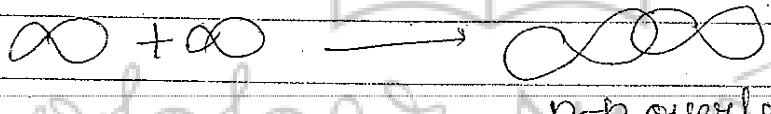
General INORG. CHEM:

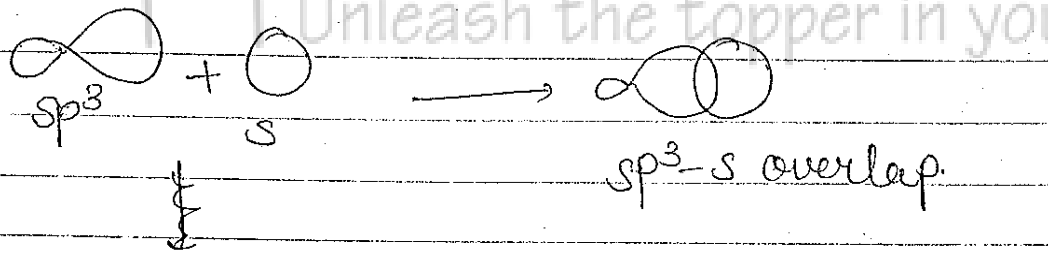
OVERLAPPING

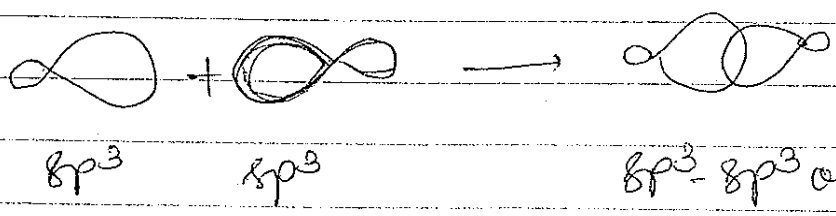
The Intermixing of 2 orb. K/o overlapping.









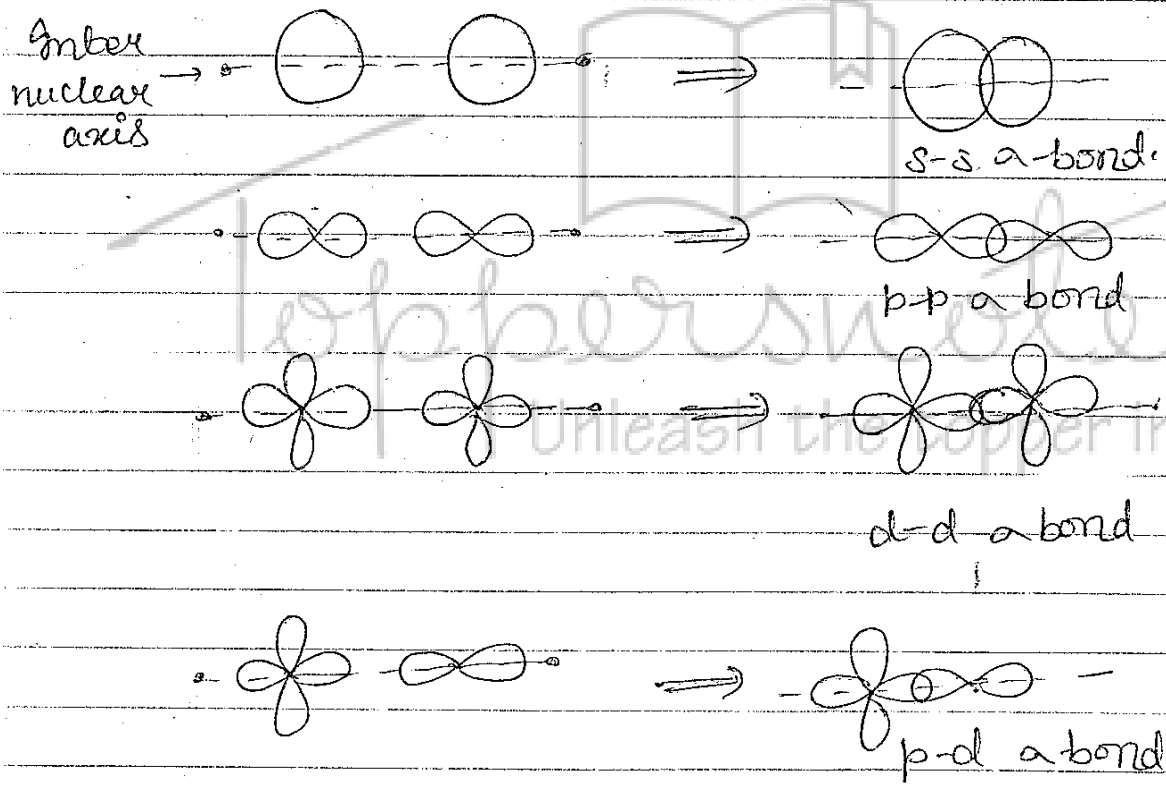


Overlapping
1. Axial → σ bond
2. Lateral → π bond } 3 types overlapping
3. Face-wise → δ bond

* Axial → 1-1 lobe interaction.
* Colateral → 2-2 ← " →
* Face-wise → 4-4 ← " →

AXIAL OVERLAP :-

→ Here intermixing of 2 orb. occurs along the internuclear axis.
→ σ-bond formatn
→ 1-1 lobe interaction.

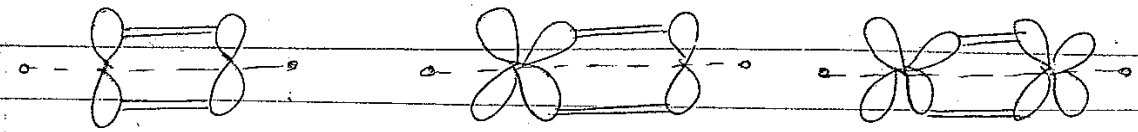


COLATERAL OVERLAPPING

→ side-wise overlap.
Here orb. overlap ⊥ to the INA (inter nuclear axis)
→ 2-2 lobe Interatn.
→ π-bond formtn.

INA by default → Z-axes. (if not given)

t2g → in b/w axis
eg → along the axis lobes ⊕.

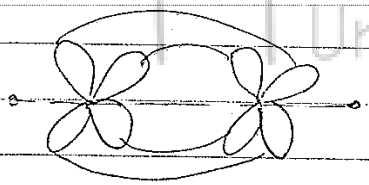


pπ-pπ , dπ-pπ , dπ-dπ

FACE-WISE OVERLAPPING

→ Also occurs ⊥ to the INA
→ δ bond
→ 4-4 lobe interactn.
→ d-orb. are used only.

☆ (δ-bond → eclipsed conformatn)
Ko stable krta h.



Extent of overlap $\propto \frac{1}{\text{size}}$ → Axial & → Colateral

size $\propto \frac{1}{\text{Axial \& Colateral overlap}}$

But d orb size ↑ → face-wise overlap ↑ | size ↑ ∝ facewise overlap

on Moving up to down → pricipal quantum no ↑ → orb size ↑

NOTE: for effective face-wise overlap, size of d-orb. should be large.

3d-3d (δ) 4d-4d (δ) 5d-5d (δ)

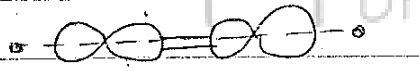
⟶

n ↑, size of d orb ↑, extent of face-wise overlap ↑

strength of δ-bond ↑

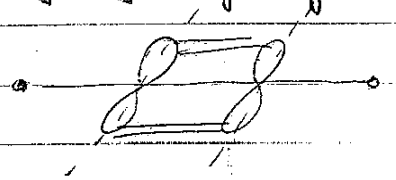
Q. Let INA is x-axis then identify type of bond formed by following interactions?

① px-px



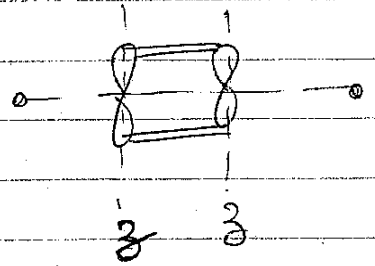
⟶ 1-1 lobe, σ-bond / σ*

② py-py



⟶ 2-2 lobe, π / π*

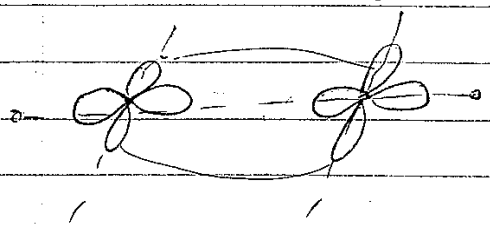
③ pz-pz



⟶ 2,2 lobe, π / π*

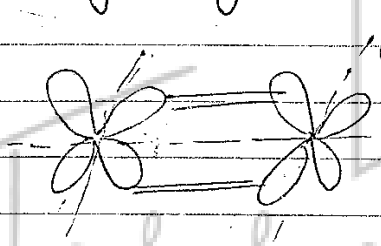
★ If INA is z-axis then dxy, dx^2-y^2 forms δ bond.

④ $dx^2-y^2 - dx^2y^2$ (INA → x-axis given)



π / π^*

⑤ $dxy - dxy$



$\longrightarrow \pi / \pi^*$

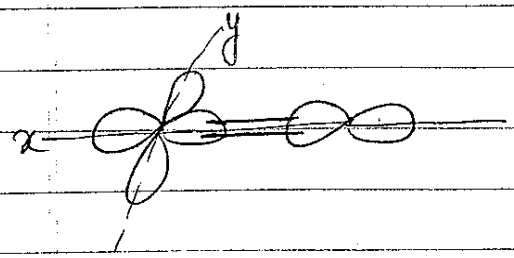
⑥ $dyz - dyz$

$\Longrightarrow \delta / \delta^*$

★★ If INA → x axis ⟶ ~~dyz~~ x coordinate of δ bond bnaye.

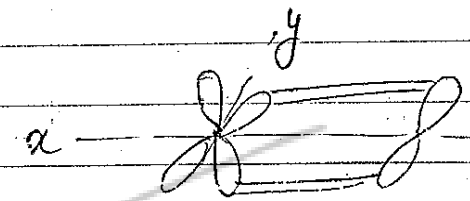
⑦ $dxz - dyz$ ⟶ Non-bonding Interaction.

(8) dx^2-y^2 → px.



$\Longrightarrow \sigma/\sigma^*$

(9) dxy – py



$\Longrightarrow \pi/\pi^*$

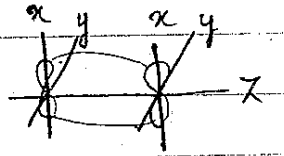
(10) px – py ⟶ Non bonding.

★ If INA ⟶ y ⟶ y coordinate wala ko chadk sb s bond bnaege.

★ If INA ⟶ z ⟶ z chadk ——"——

20. Let INA ⟶ z axis, Identify type of bond formed by the following interaction.

(1) px – px



π bond

② dx^2-y^2 – dx^2-y^2 δ

③ dxy – dxy δ

④ pz – pz ↑

⑤ dyz – dyz ↑

⑥ dxz – dxz. ↑

NOTE: By default INA is z-axes if not given

NOTE: Since a bond is stronger than π-bond so we can say that axial overlap is dominant over colateral overlap. (σ) (π)

EXTENT OF OVERLAPPING

Extent of overlapping depends upon 2 factors :-

① Size of orbital :

→ K/a n

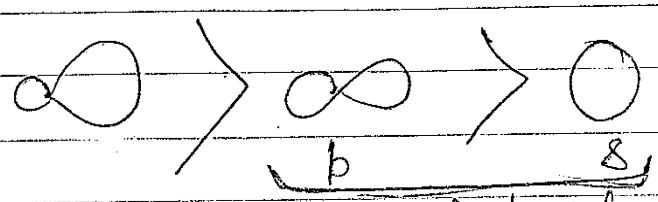
→ Principal quantum no.

→ Directional character of orb.

Extent of overlap $\propto \frac{1}{\text{size of orb.}}$ (or principle quantum no.) $\propto$ Directional characters of orb.

Key points

① All hybrid orb. have more directional character than the unhybrid orb.



Hybrid orb. — unhybrid orb.

(on basis of Directional character)

② Size of unhybrid orb. depends upon principal quantum no.

1s 2s 3s 4s 5s

2p 3p 4p 5p

3d 4d 5d

→

n↑, size of atomic orb.↑ ∴ extent of overlap ↓,

- Bond strength ↓
- Bond Energy ↓

★ dz^2 cannot form δ bond.
(as 4-4 lobe interaction not possible)

③ All hybrid orb. have identical shape, (identical directional character) but diff. size; & their size ~~& the~~ is inversely proportional to the % s character.

		% s	% p
For hybrid orb	sp^3	25%	75%
Size $\propto \frac{1}{\%\ s\ character}$	sp^2	33.33%	66.66%
Size $\propto \frac{1}{EN}$	sp	50%	50%

D: ★ on moving up to down (ऊपर वाले eg में) (shape of orb). directional character are same.
But % s character ↑
size of hybrid orb ↓
extent of overlap ↑
Bond strength ↑
Bond Energy ↑

eg: $-\overset{|}{\underset{|}{C}}-H$ sp^3 • sp Bond strength max.

$=C-H$ sp^2

$\equiv C-H$ sp

• sp Carbon has highest electro-negativity to if H niklega to sp C max. stable hoga.

★ I^- more stable than F^- cz Iodine ka volume or size ↑ Fluorine chota hai Iodine se.

⑤ If both size & directional character vary at the same time then size is dominant over the directional character.

EXTENT OF OVERLAP

eg: 1s–1s > 2s–2s

small size — larger size

2p–2p > 3p–3p

s–s < p–p(σ) (directional character) isliye Direction dekhte h. atomic no given nahi h

1s–1s (small size) > 2p–2p(σ) (large size) (size dominating over directional character)

Extent of overlap :

s–s(σ) > pπ–pπ

bond stronger over bond: 2s–2s(σ) > 2p(π)–2p(π) (Here size samajh nahi aa Directional character dekha gya.)

Extent of overlap → (σ) (π)

Size

D.C.

Q. Arrange in decreasing order of extent of overlap?

① 1s-1s > 2s-2s > 3s-3s > 4s-4s (size)

② sp-sp > sp^2-sp^2 > sp^3-sp^3 (1.s)

③ sp-s > sp^2-s > sp^3-s

④ sp-s < sp-p principle quantum no ↑ ∴ directional C. decrease only

⑤ 50% 33.33% 25%
sp-p > sp^2-p > sp^3-p (size)

⑥ s-s p-p(σ) s-p p-p(π)

2 > 3 > 1 > 4

⑦ 1s-1s 2s-2s 2p-2p(σ) 2s-2p

1 > 3 > 4 > 2 > 5

2p-2p(π)

⑧ $-\overset{|}{\underset{|}{C}}-F$ > $-\overset{|}{\underset{|}{C}}-Cl$ > $-\overset{|}{\underset{|}{C}}-Br$ > $-\overset{|}{\underset{|}{C}}-I$

(smallest size) 1 > 2 > 3 > 4 (max. size).

Size $\propto \frac{1}{\%S} \propto \frac{1}{\text{overlap}}$.

⑨ 3d–3d 4d–4d 5d–5d | size $\propto \frac{1}{\sigma \& \pi \text{ Bonding}}$

Extent of overlap on basis of | size $\propto$ δ bond

σ bond → 1 > 2 > 3
π bond → 1 > 2 > 3
} size ↑, overlap ↓

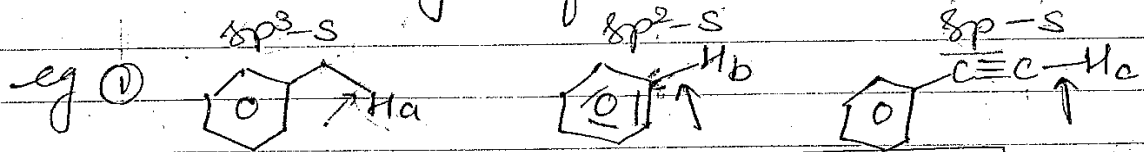
δ bond → 3 > 2 > 1 → size ↑, overlap ↑

⑩ 1s–1s, 2s–2s, 2p–2p(σ), 2s–2p, 3p–3p(σ), 3s–3s, 4s–4s, 4s–4p, 4p–4p(σ)

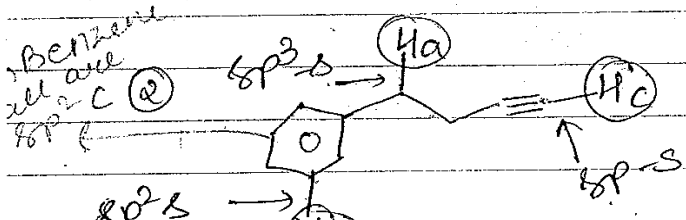
1 > 4 > 3 > 2 > 6 > 5 > 7 > 10 > 9 > 8

Q. Arrange the following in decreasing order of bond strength of indicated bond.

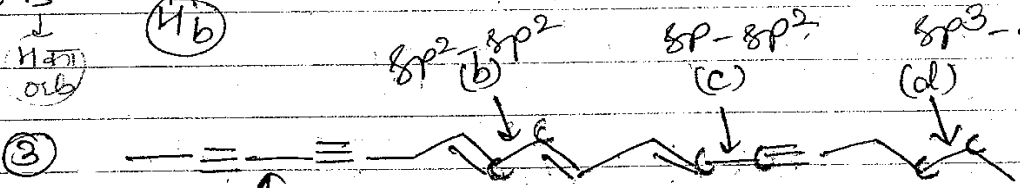
eg ①



Hc > Hb > Ha



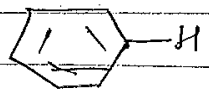
Hc > Hb > Ha



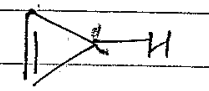
a > c > b > d

★ Stability → Benzylic > Allylic
★ B.S → Allylic > Benzylic

(4)



sp^2 – S



sp^3 – S

3 > 1 > 2

$R-C\equiv C-H$

sp – S

कुल 9 H उनमें 5 degree.

$CH_3-\overset{1^\circ}{CH_2}-(H_a)$ → 1° radical बनेगा after H release

All are sp^3–S overlap ∴ homolytic cleavage करके देखेंगे.

$CH_3-\overset{2^\circ}{CH}(CH_3)-(H_b)$ → 2°

1 > 2 > 3

$H_3C-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{3^\circ}{(H_c)}$ → 3° radical बनेगा. C से most stable ∴ इसे जल्दी E देनी पड़ेगी तोड़ने के लिए. corresponding bond को

★ H के निकलने के बाद 3° radical बनेगा जो इसे stable है इसलिए H के साथ की σ bond easily टूटेगा तभी 3° rad. बनेगा. इसलिए ΔH Energy में σ bond easily टूटेगा.

Stability of free-rad → 3 > 2 > 1 > CH3 > H

Homolytic cleavage करो then sbse strong rad. के corresponding Bond की strength sbse कम।

Order for BS

⑥ $Ph-CH_2-Ha$ $\quad$ $Ph-CH(Ph)-Hb$ $\quad$ $Ph-C(Ph)_2-Hc$

a > b > c

(3° rad bnega : E ↓ hyp ∴ B.S. ↓)

⑦ Ha Hb Hc

a > b > c

reso ↑, St of structure ↑ ∴ less E hyp ∴ BS ↓

⑧ Hb (sp²-s), Hc (benzylic, sp³-s), He (sp³-s, यहां reso लगी है), Hf (sp-s), Hd (यहां से reso हटी है), Ha (allylic, sp³-s)

size ↑; I.S ↓; BE ↓, BS ↓, overlap ↓

sp की size choti hoti h sbse

Hf > Hb > He > Hd > Ha > Hc

(Stability of radical ↑ ∝ 1/E ∝ BS ↓)

⑨ d (sp³-sp²), a (sp²-sp²), b (sp²-sp²), c (sp-sp), e (sp³-sp³)

>b>a>e>d

d और e पे homolytic cleavage krenge. d पे बनने वाला allylic rad stabilised by reso ∴ St ↑ to Bond St. ↓

* Jitna strong rad. utni कम stability of corresponding bond. (BS ↓)

e पे बनने वाला allylic rad less stable ∴ corresponding Bond की Bond strength ↑.

Purpose:
① Directional character aja.
② Bond strength ↑ hoja.

Hybridisation

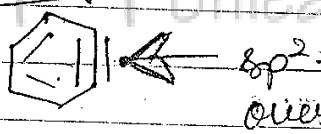
→ Hypothetical concept.

→ The orb. of the atom having almost similar energy intermix, & redistribute their Energy & form new orb. in equal no. having similar shape, size & Energy.

These orb. c/o hybrid orb. & this phenomenon kp so.

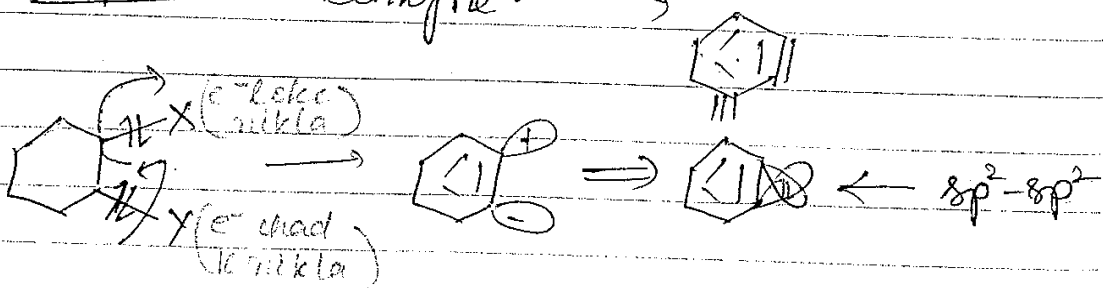
These hybrid orb. are oriented in space in such a way that these feel minimum repulsion.

Benzyne



** Hybrid orb. does not form π-bonds.

Exception → Benzyne →



−Y⊕ e⁻ chad k nikla → c/o electrofuge
−X⊖ e⁻ leke nikla → c/o nucleofuge.