MANZIL

For JEE Aspirants

Legend

Lecture-One Shot

#GOC

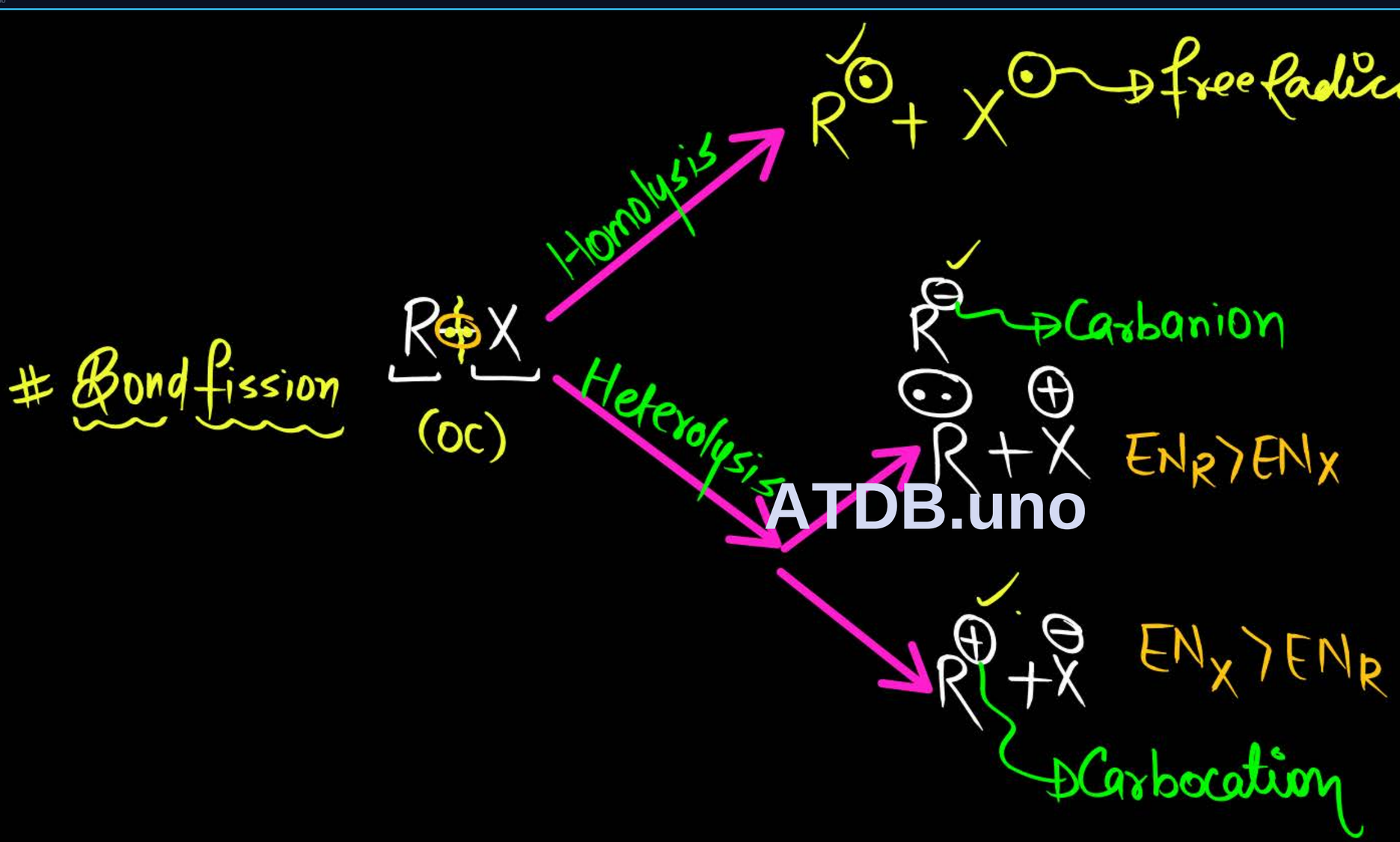
Rohit Agrawal (RA Sir)

TOPICS TO BE COVERED

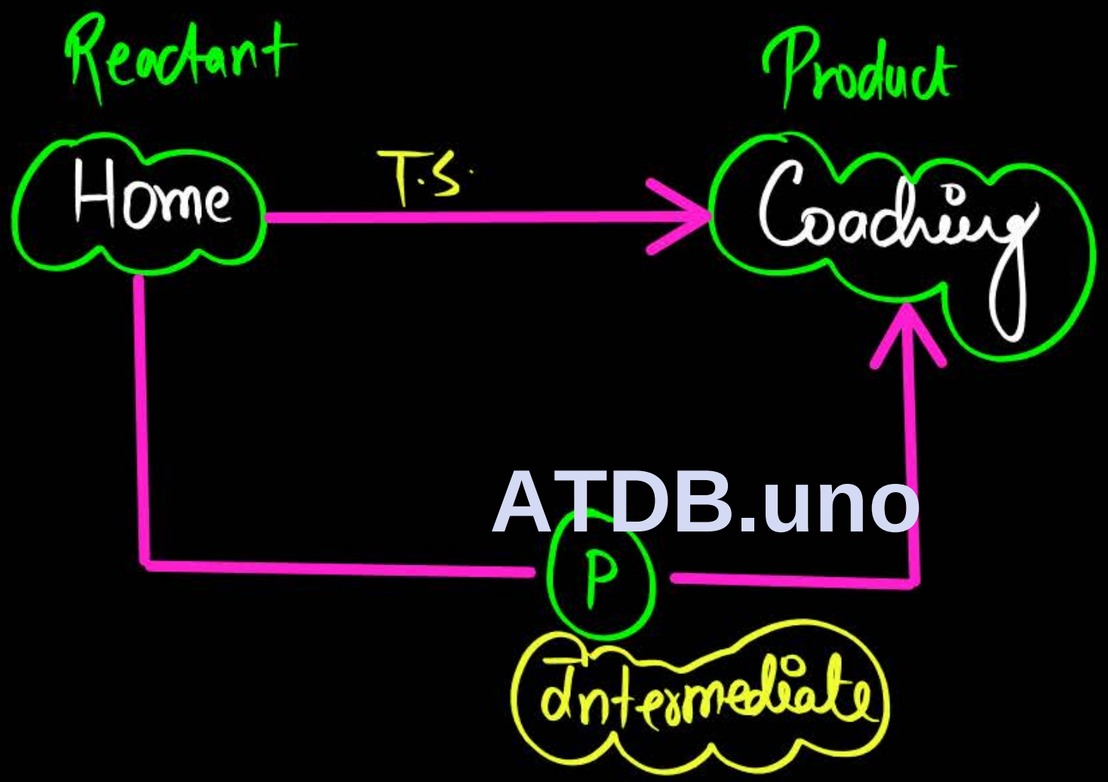
1. Electronic Displacement Effect

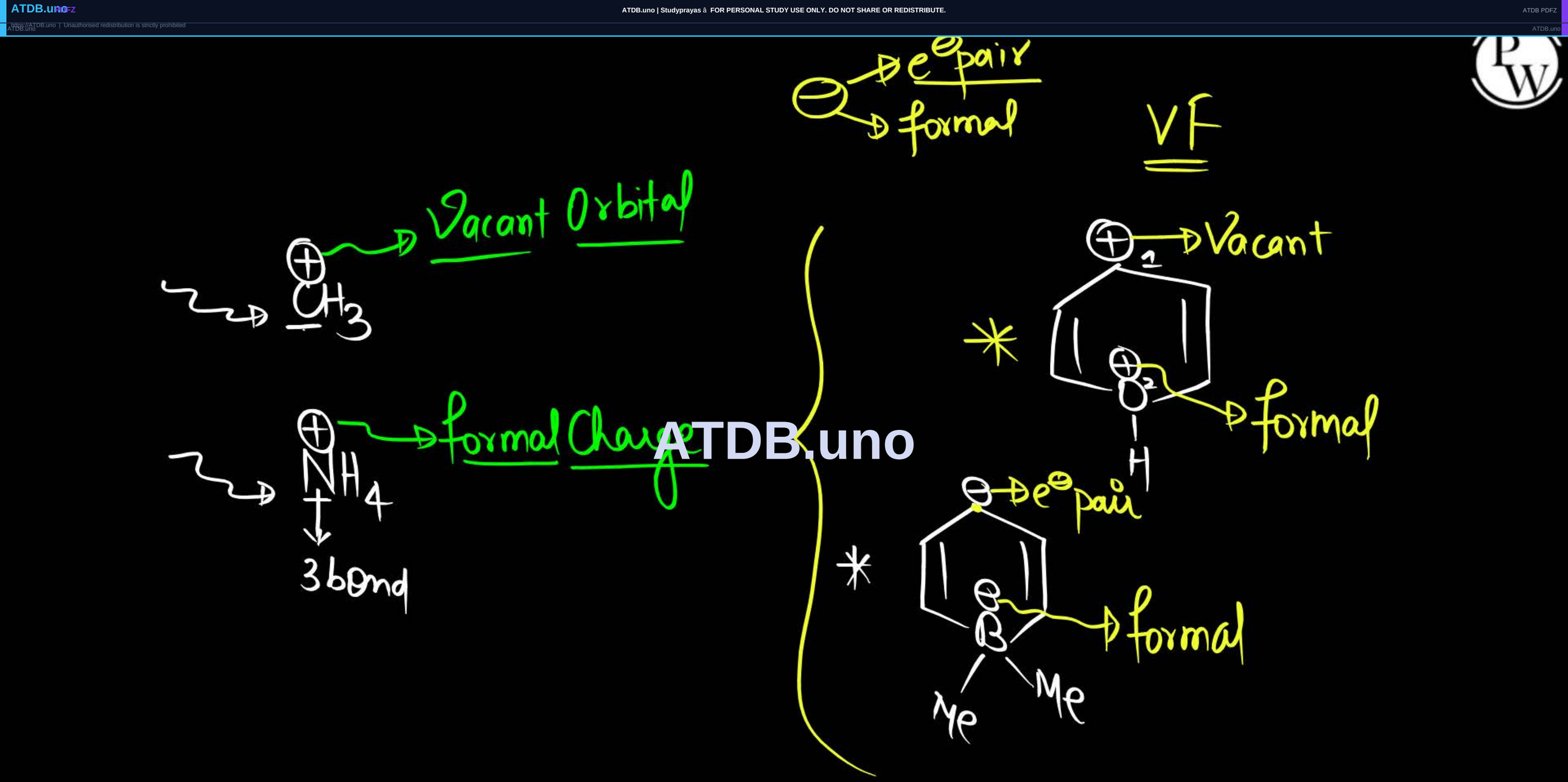
2. Acid and Base

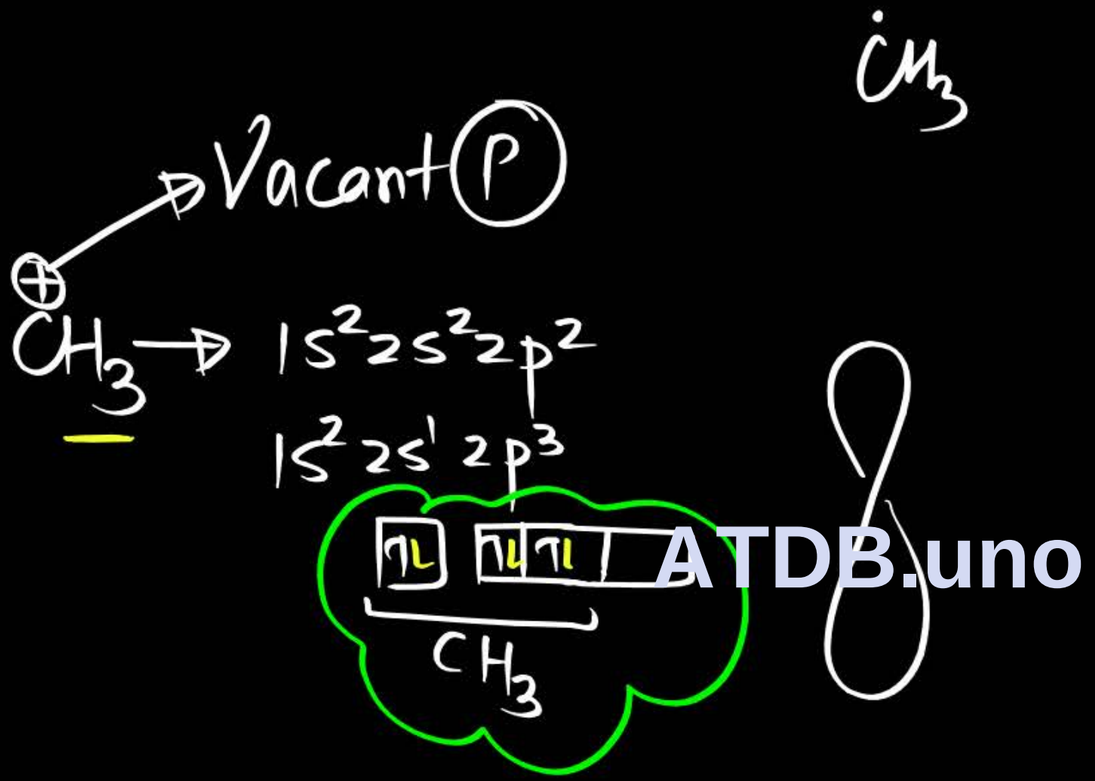
ATDB.uno

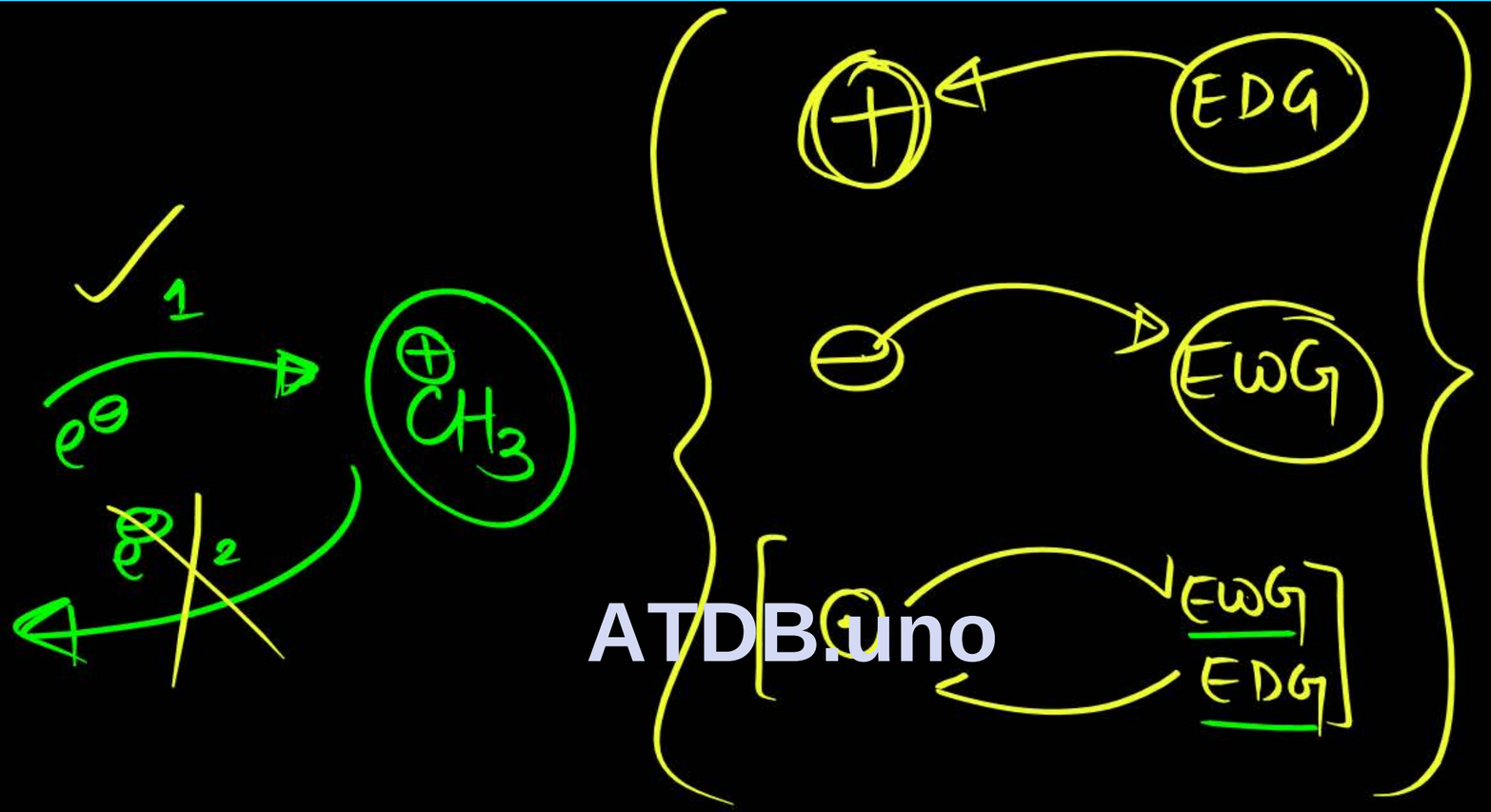


Intermediate









Electronic Displacement Effect

- The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarisation of the bond.

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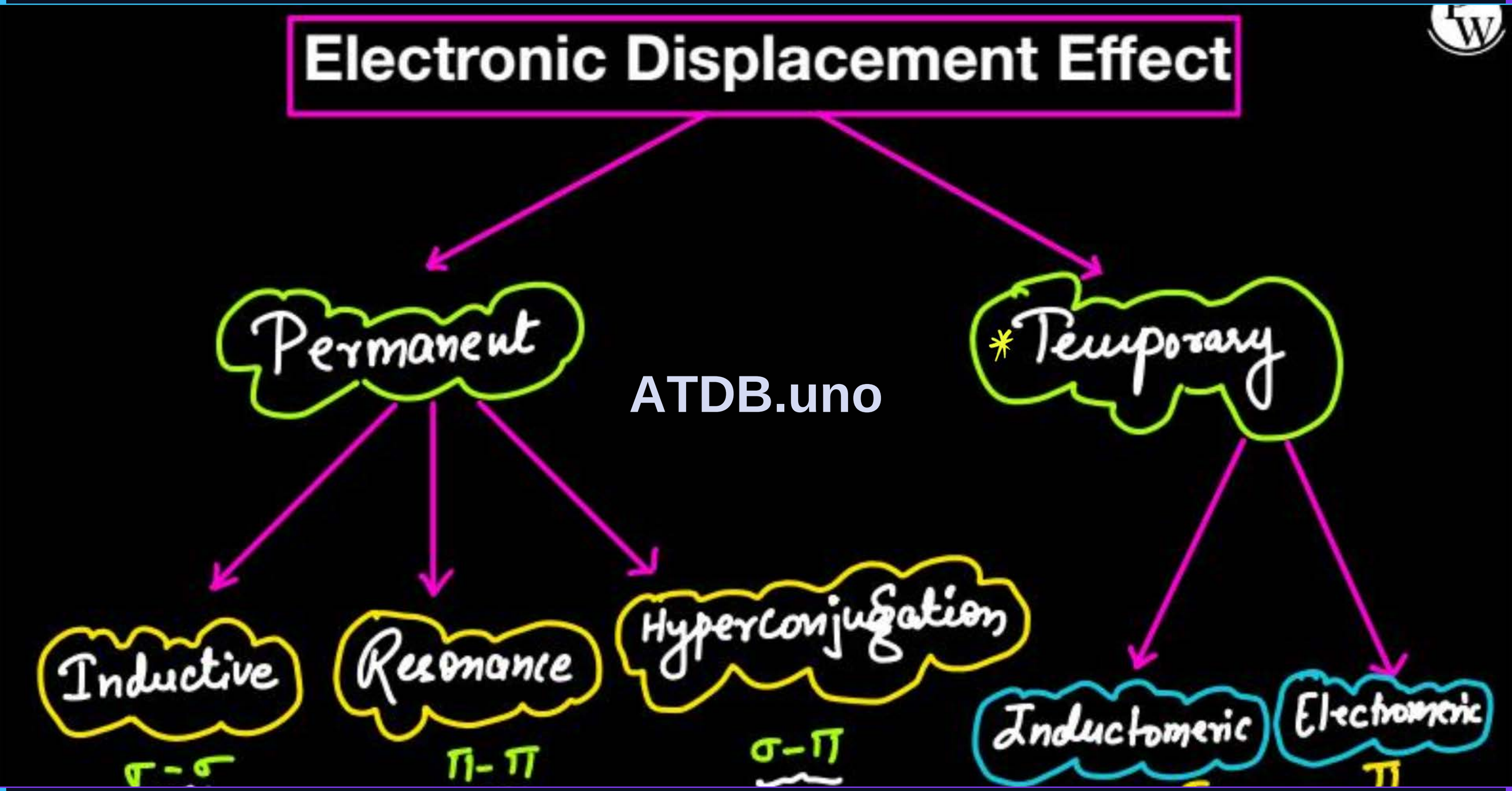
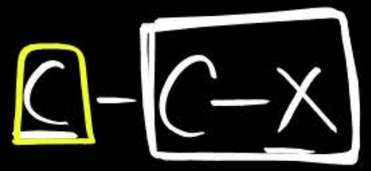
Electronic Displacement Effect



Weakest effect

* Inductive effect



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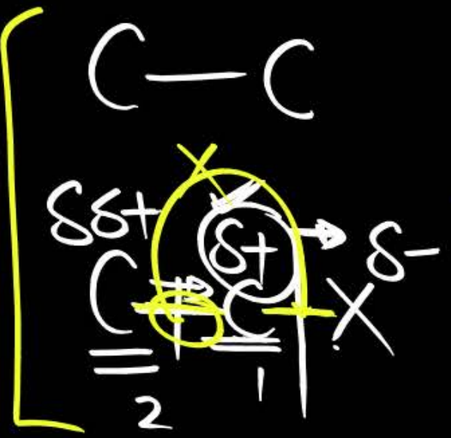


* e⊖ shifting

Inductive Effect

- When a covalent bond is formed between atoms of different electro negativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond.
- This shifting of electron density is known as 'Induction'.
- Due to this induction, adjacent Atom gets effected and developed polarity. This is known as "Inductive Effect"

Properties Of Inductive Effect

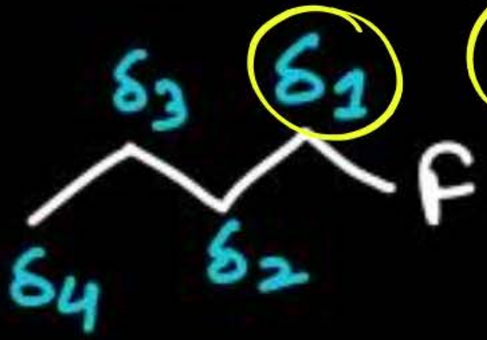
- It is permanent and partial displacement of sigma electrons.
- It is a permanent effect and weak effect.
- Electrons will never changes its atomic orbital.

- Inductive effect is an additive effect.
- It is a distance dependent effect as distance increases inductive effect decreases.
- Only 10% of original charge transfers in each bond and $\delta_4 = 0$.

Find the order of charges ?

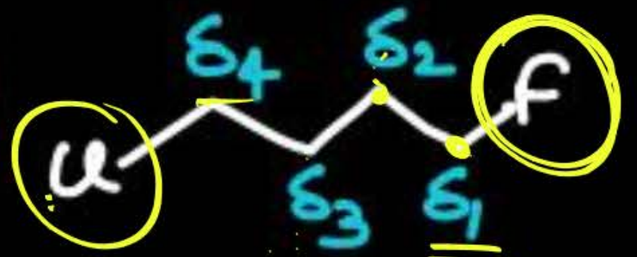
1 > 4 > 2 > 3

(1)



1 > 2 > 7 > 3 > 4

(2)



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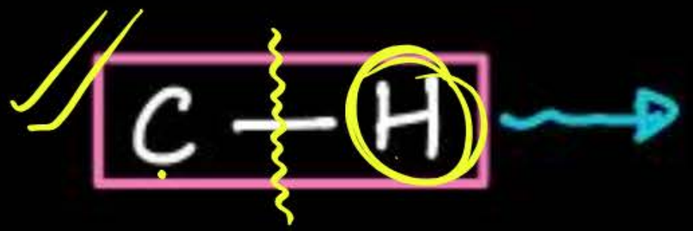
Types Of Inductive Effect

EDG | EWG



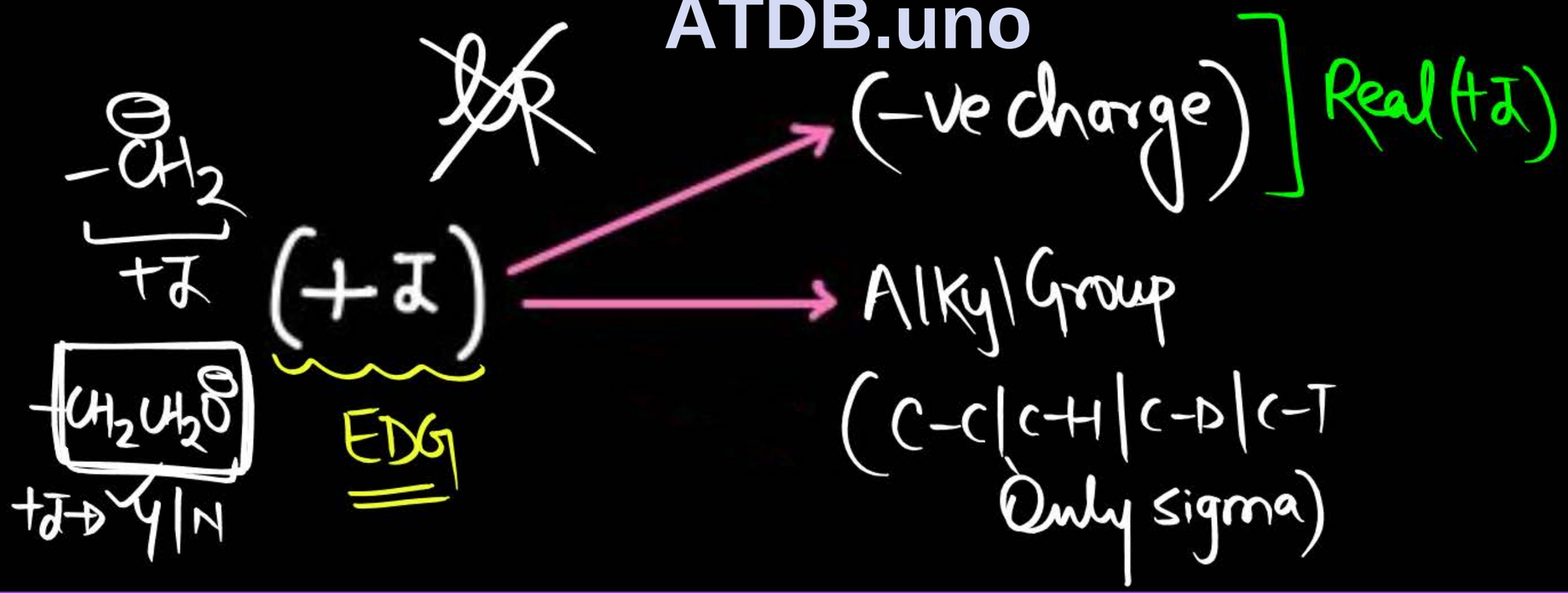
→ Reference

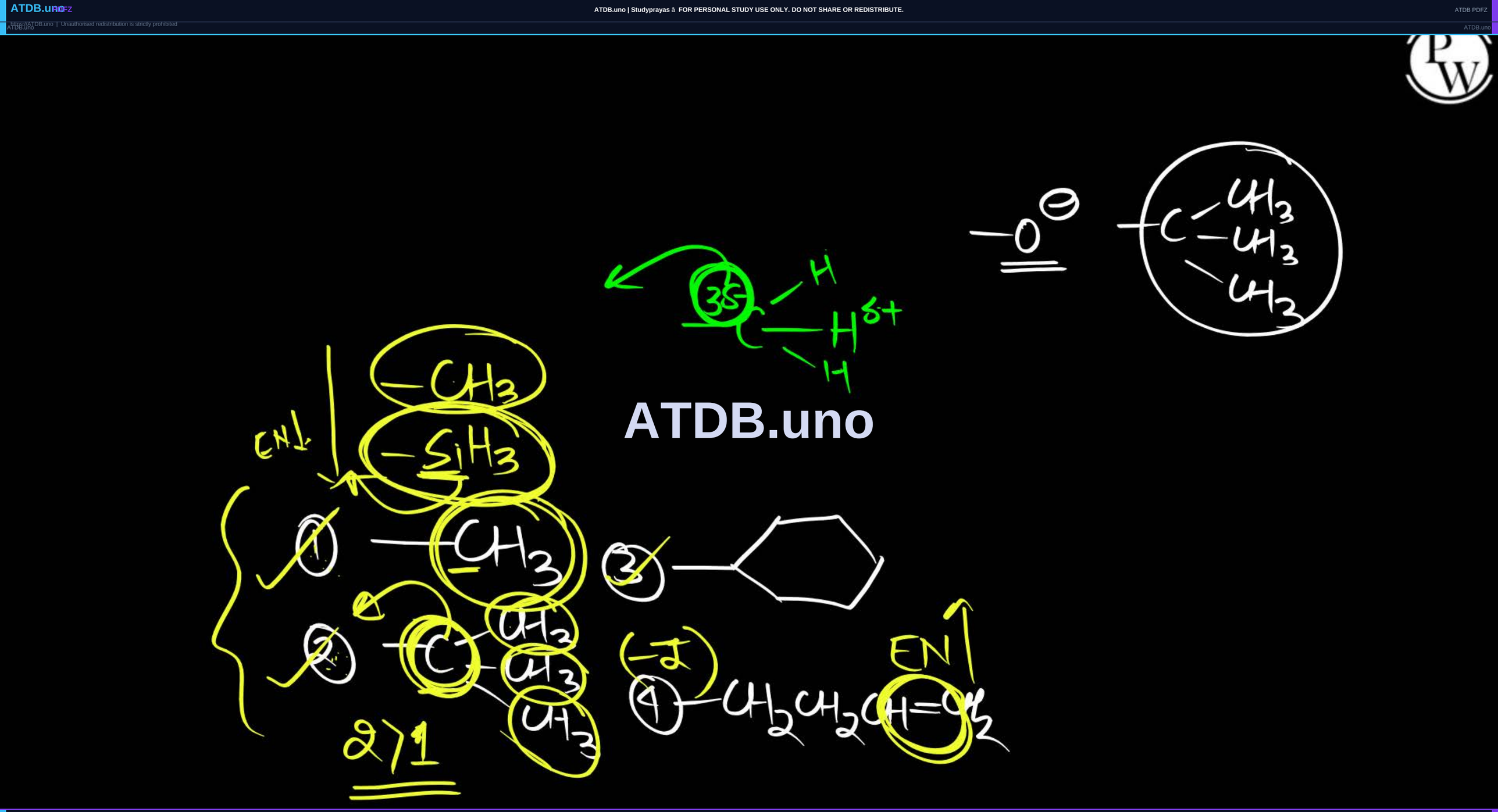
→ A is EWG

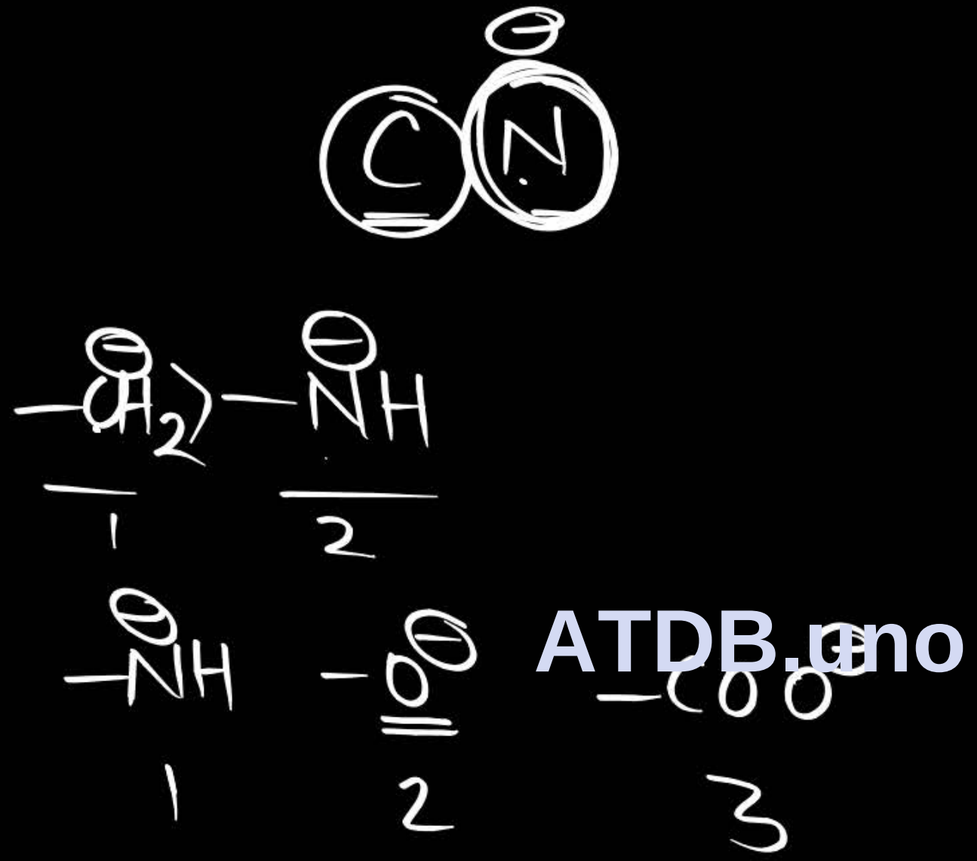
→ B is EDG

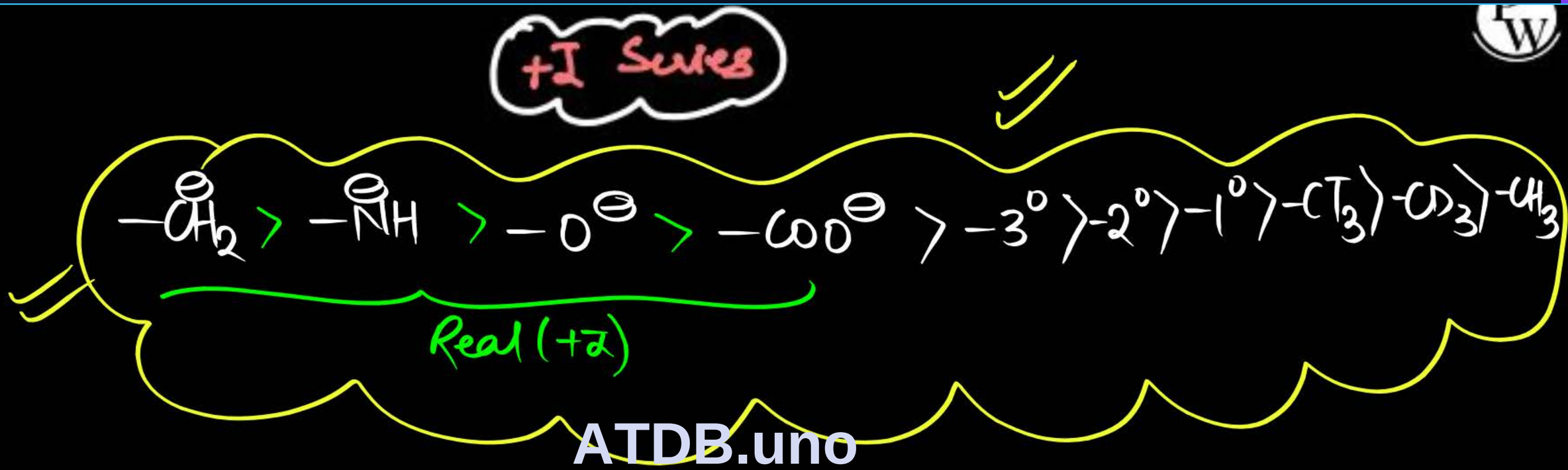
Electron Donating Effect (+I)

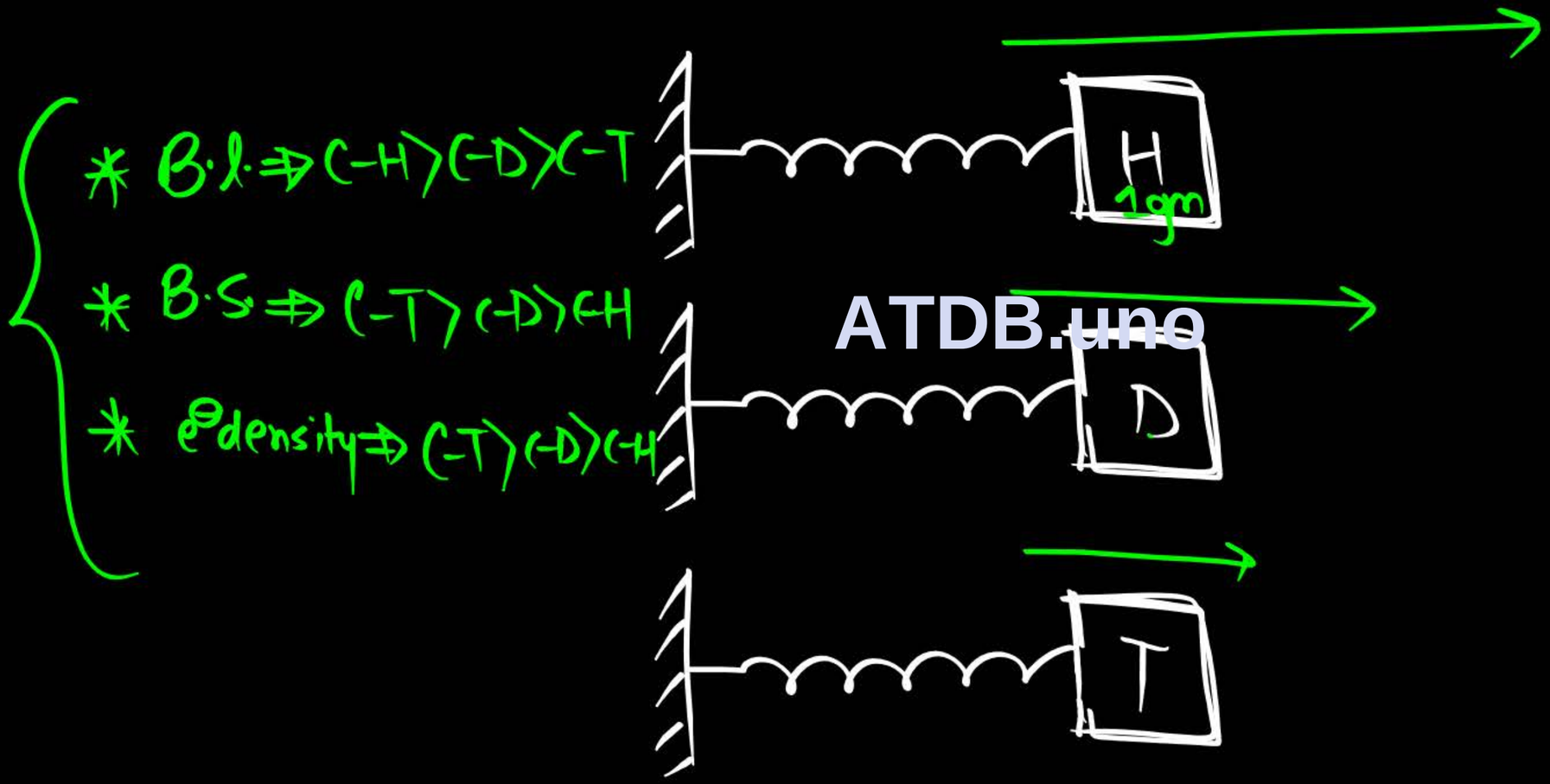
- When bonded pair of electrons are shifted away from any atom or group w.r.t. C—H bond then atom or group shows electron donating effect.











Electron Withdrawing Effect (−I)

- When bonded pair of electrons are shifted towards any atom or group w.r.t. C−H bond then atom or group shows electron withdrawing effect.

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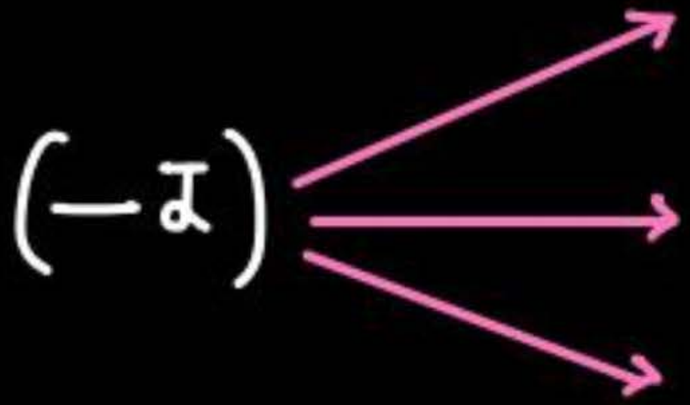

-I Series

$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH$

Positive

3.25 $C(=C$

2.75 1 $C(=O$

3 $C(=C$

$-F > -Cl > -Br > -I > -OR > -OH > -NR_2 > -NH_2$

$-C\equiv CH > -C_6H_5 > -CH=CH_2$

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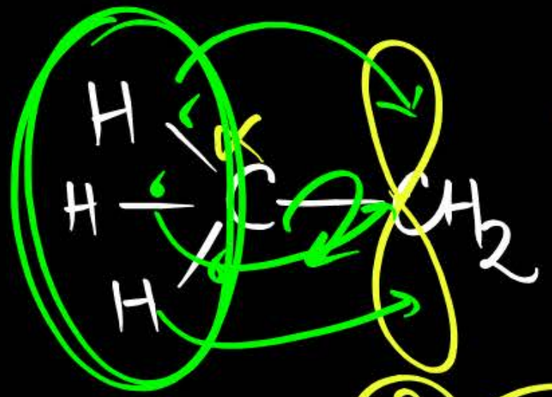
Hyperconjugation

Experiment- Baker and Nathan

∴ Rate of $E^{\oplus}$ ⇒ S > R > Q > P (Expected)

P > Q > R > S (Observed)

Also Known as: Baker-Nathan effect



// Transfer of σ e⊖

Vacant P

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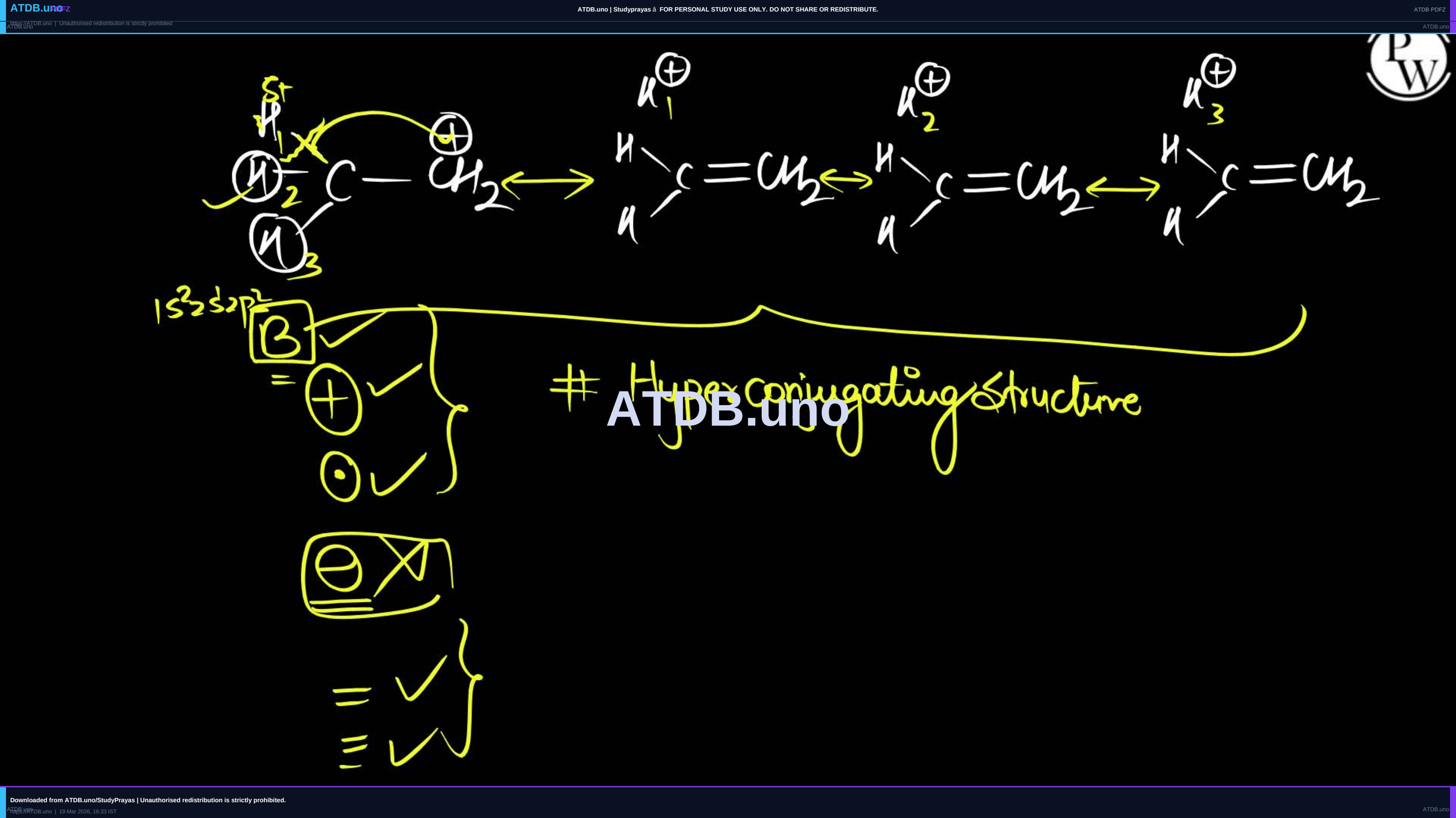
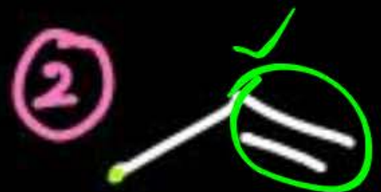


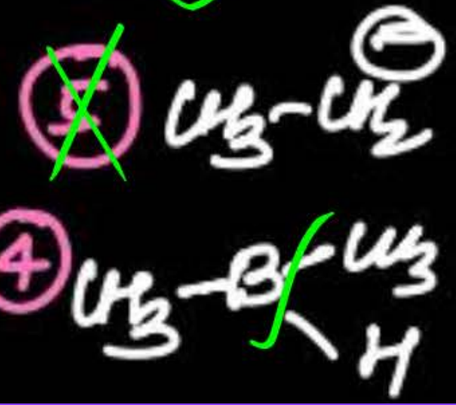
Definition

* When vacant orbital (C^+, B), alkene, Alkyne are present next to σ bond (C-H) then σ-$e^{\ominus}$ of C-H bond delocalised to that vacant orbital. This phenomenon is known as "Hyperconjugation"

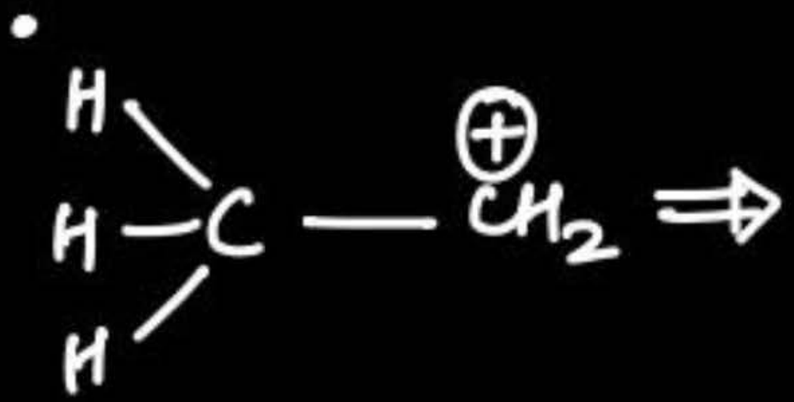
* Delocalisation of σ-electrons (C-H) is known as Hyperconjugation.

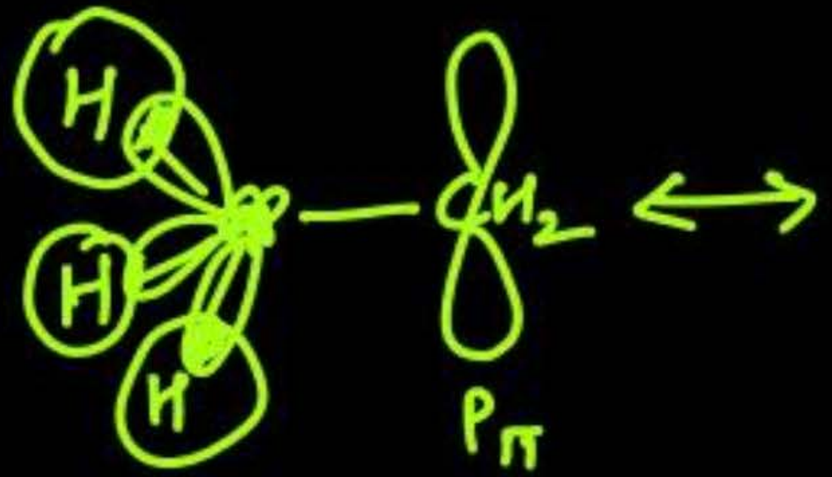
Eg :-

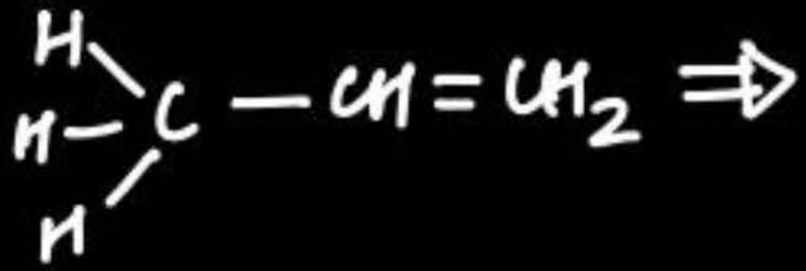


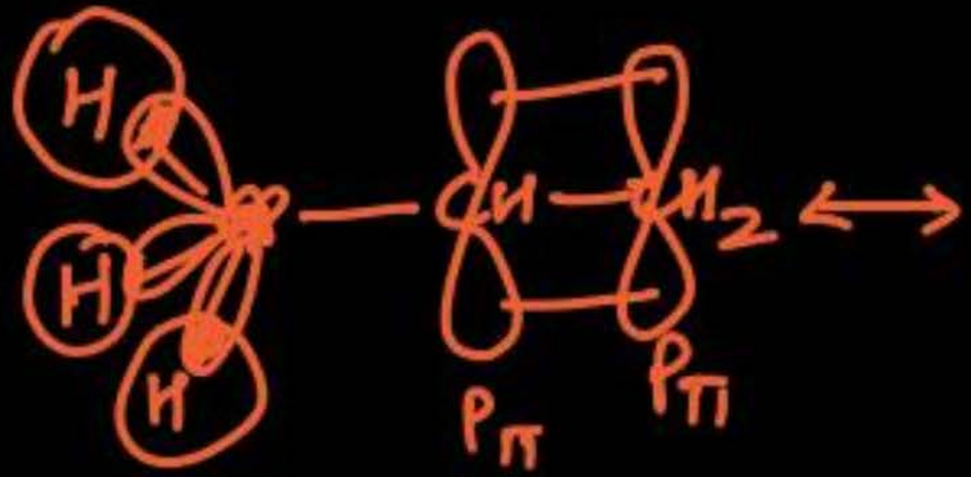


Presentation





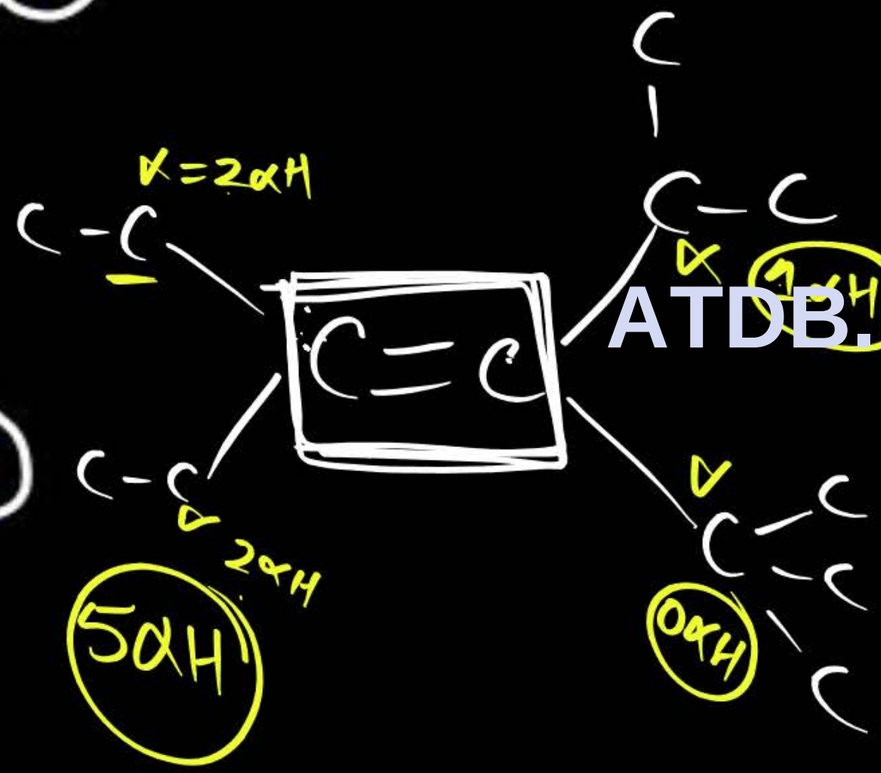




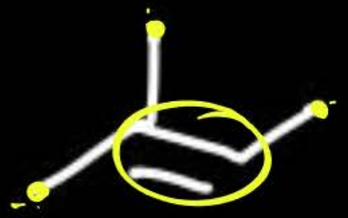
Finding of alpha-H

* Cation

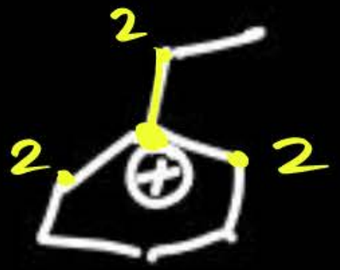
* Alkene

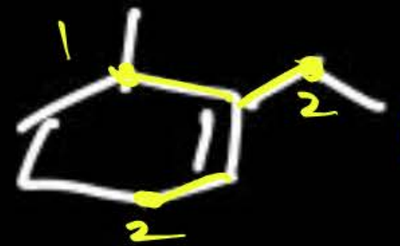


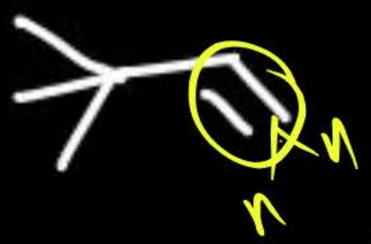
Que Find total alpha H present in following species ?

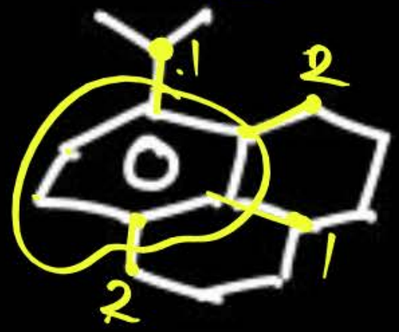
(1)  9αH

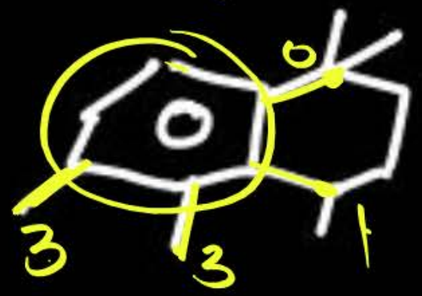
(2) $H_3C-C\equiv C-CH_2CH_3$ (3, 2) 5αH

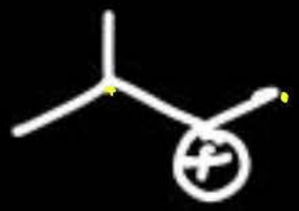
(3)  6αH

(4)  5αH

(5)  0αH

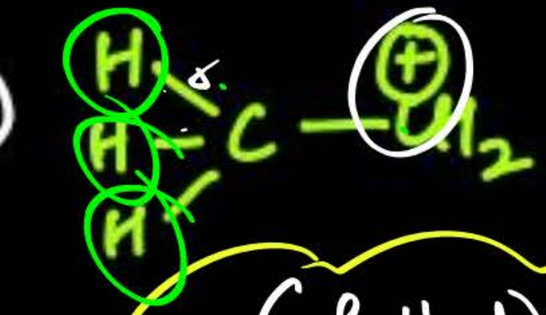
(6)  6αH

(7)  7

(8)  4αH

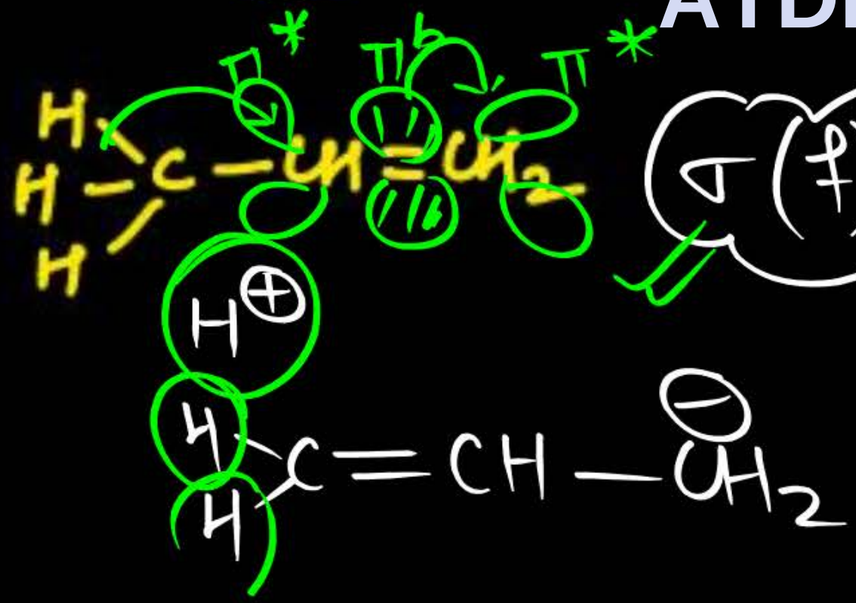
Hyperconjugating Structures

Case-1:



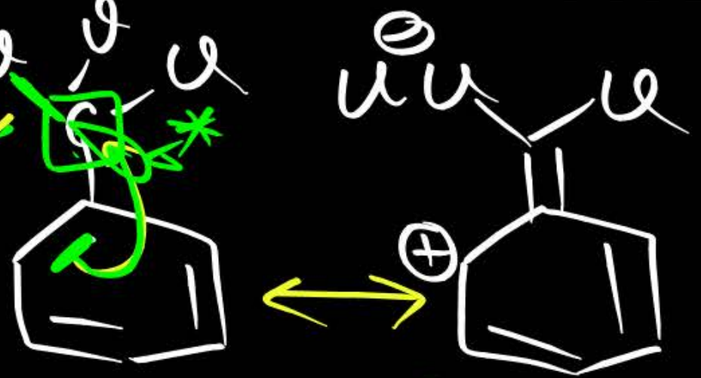
σ (filled) – P (vacant)

Case-2:



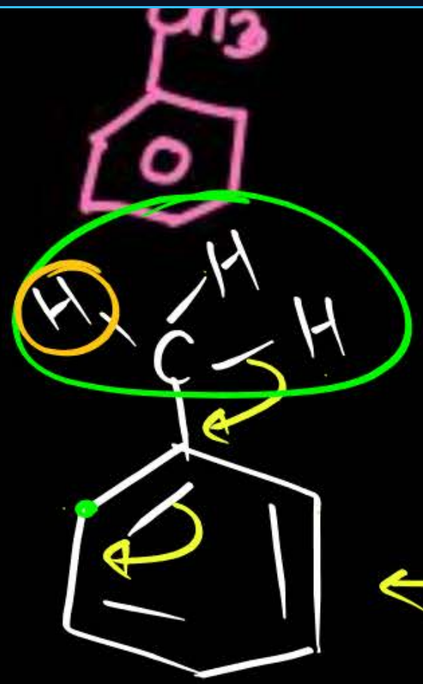
σ (f) – π^* (v)

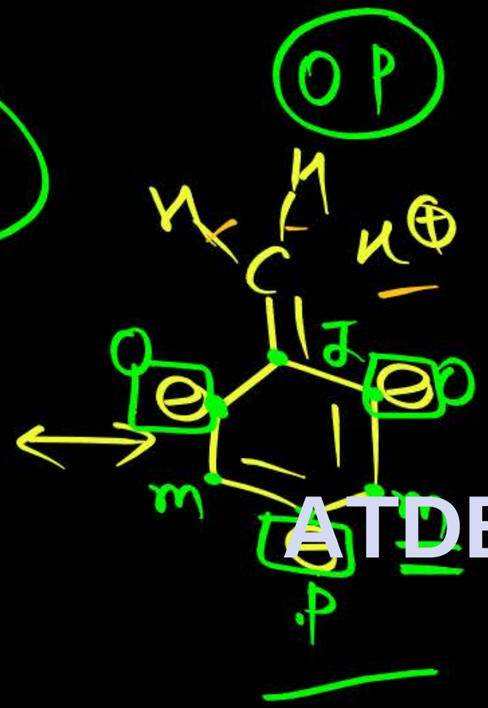
Reverse Hyper (only by $-CCl_3$)



π(filled) – σ^*(vacant)

Case-3:





Hyperconjugation

OP

OP

α-H

Note:

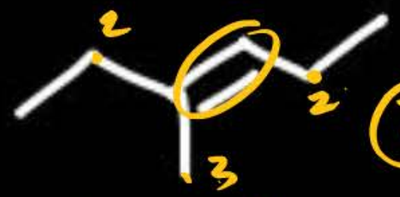
Total H·S· involving C-H bond in benzene = 3 × no·of α-H

* Total hyperconjugating structures involving C-H bond = no·of α-H

* Total hyperconjugating structures = no·of α-H + 1

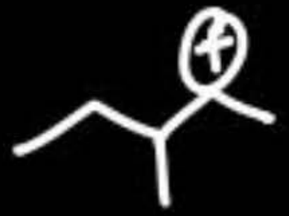
Q. Find total H.S. Involving C-H bond in following compound ?

(1)



7

(2)



(3)

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6

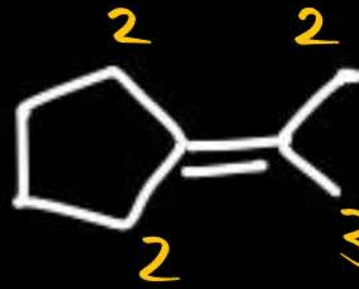
4

(4)

(5)

4

(6)

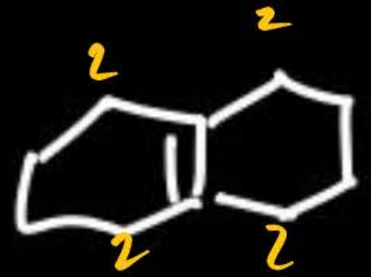


9

(7)

10

(8)



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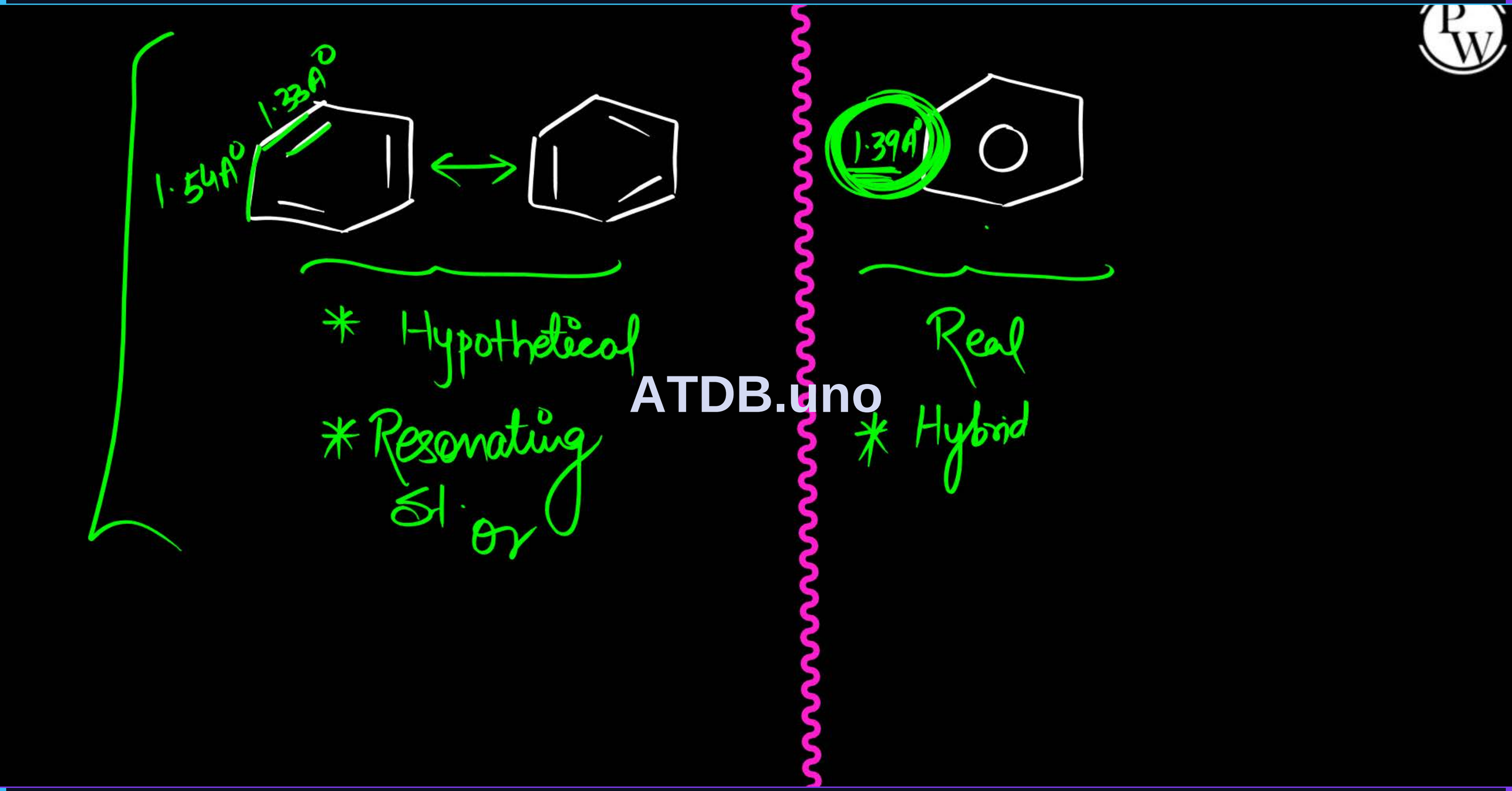


Definitions

- When properties of a compound can't be explained by a single structure then various structures are drawn.

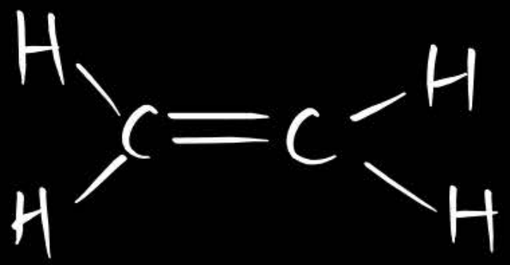
- These structures are known as resonating structures or canonical structures or contributing structures while real compound is known as resonating hybrid.

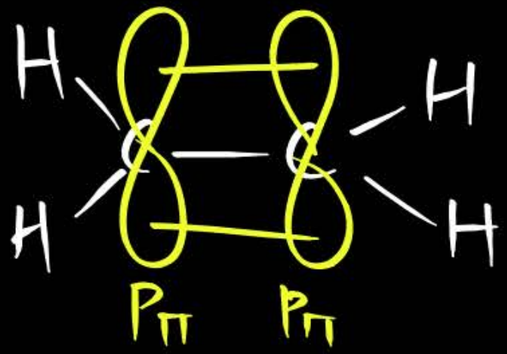
- Ex:

Properties Of Resonance

- It is delocalisation of pi electrons.
- It is a permanent effect and strongest effect.
- It is intramolecular phenomenon.

- Generally most stable RS contribute most.
- It is a distance independent effect.
- Resonating structures are hypothetical and hybrid is real.

① 



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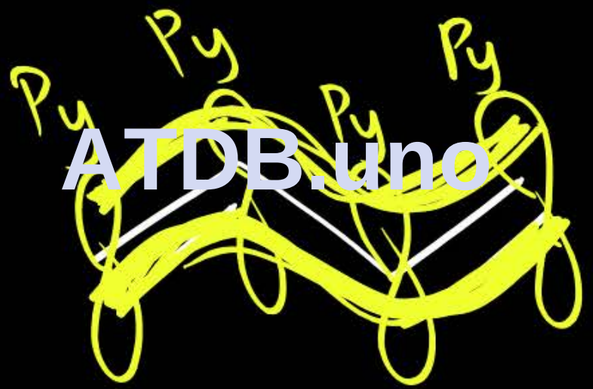
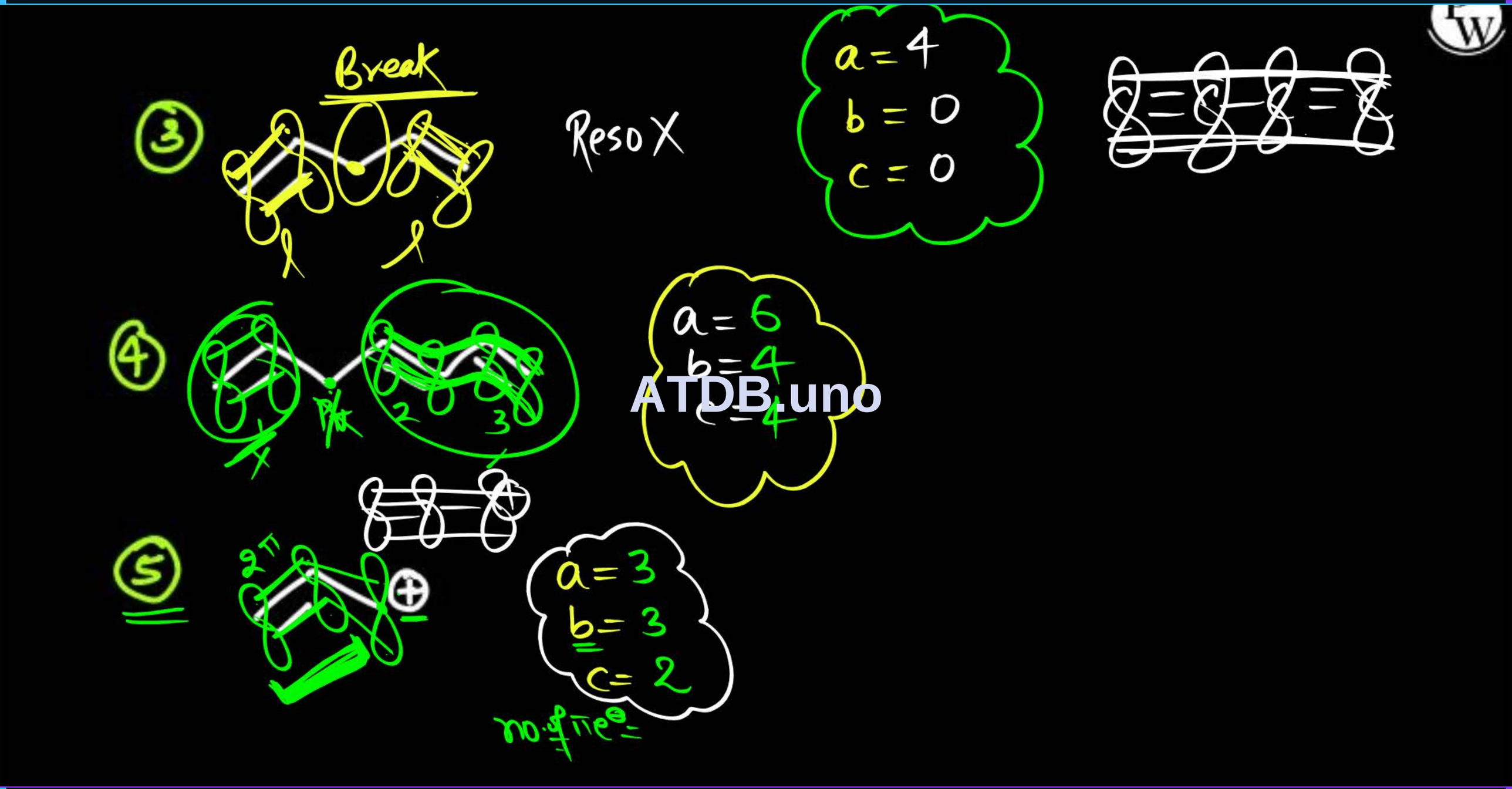


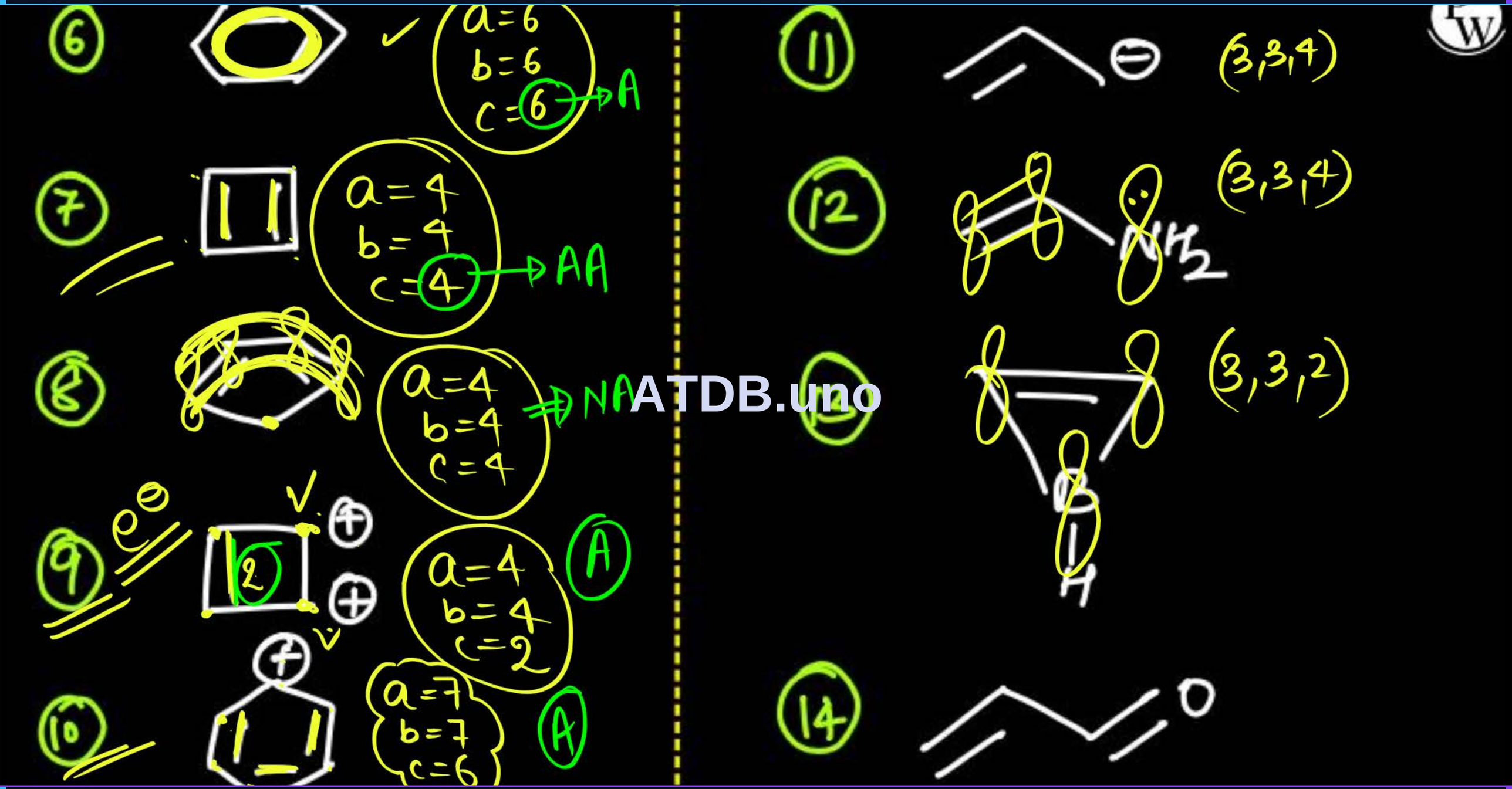
#

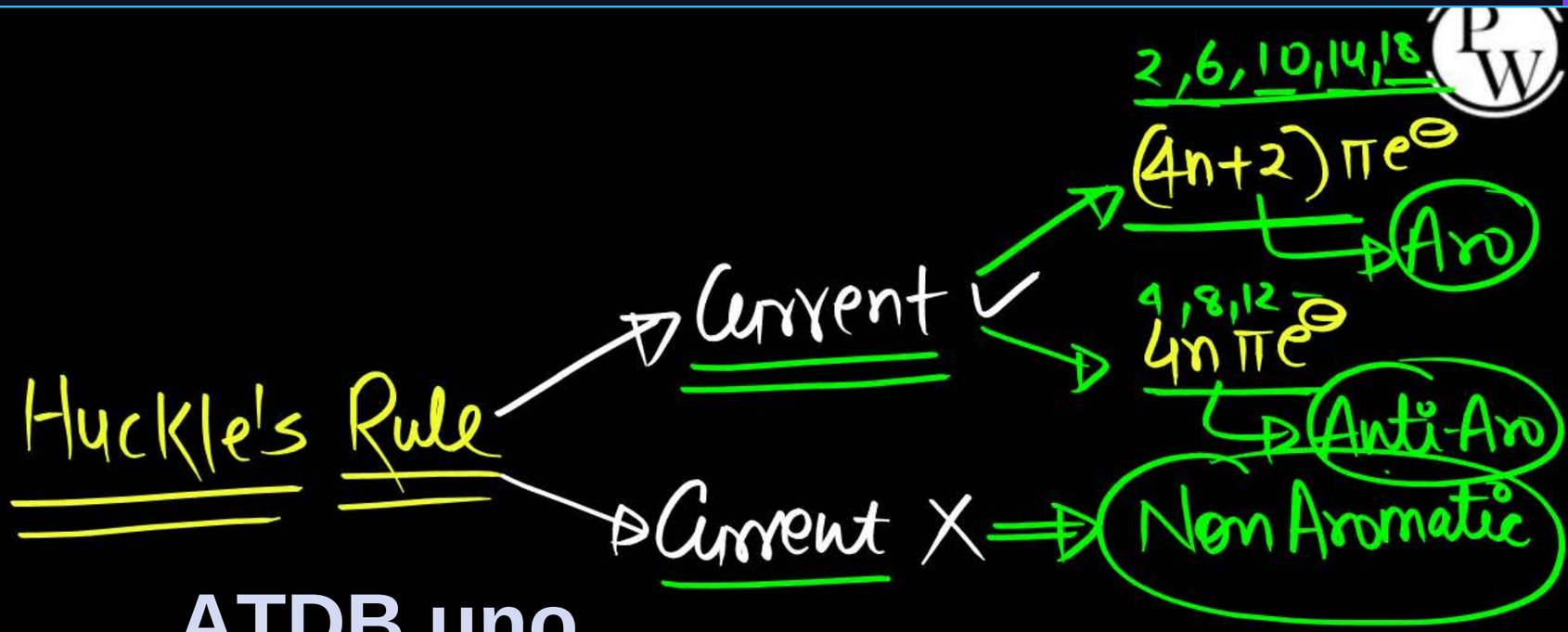
a = no. of P_π = 4

b = no. of P_π in Reso = 4

c = no. of $\pi e^\ominus$ in Reso = 4







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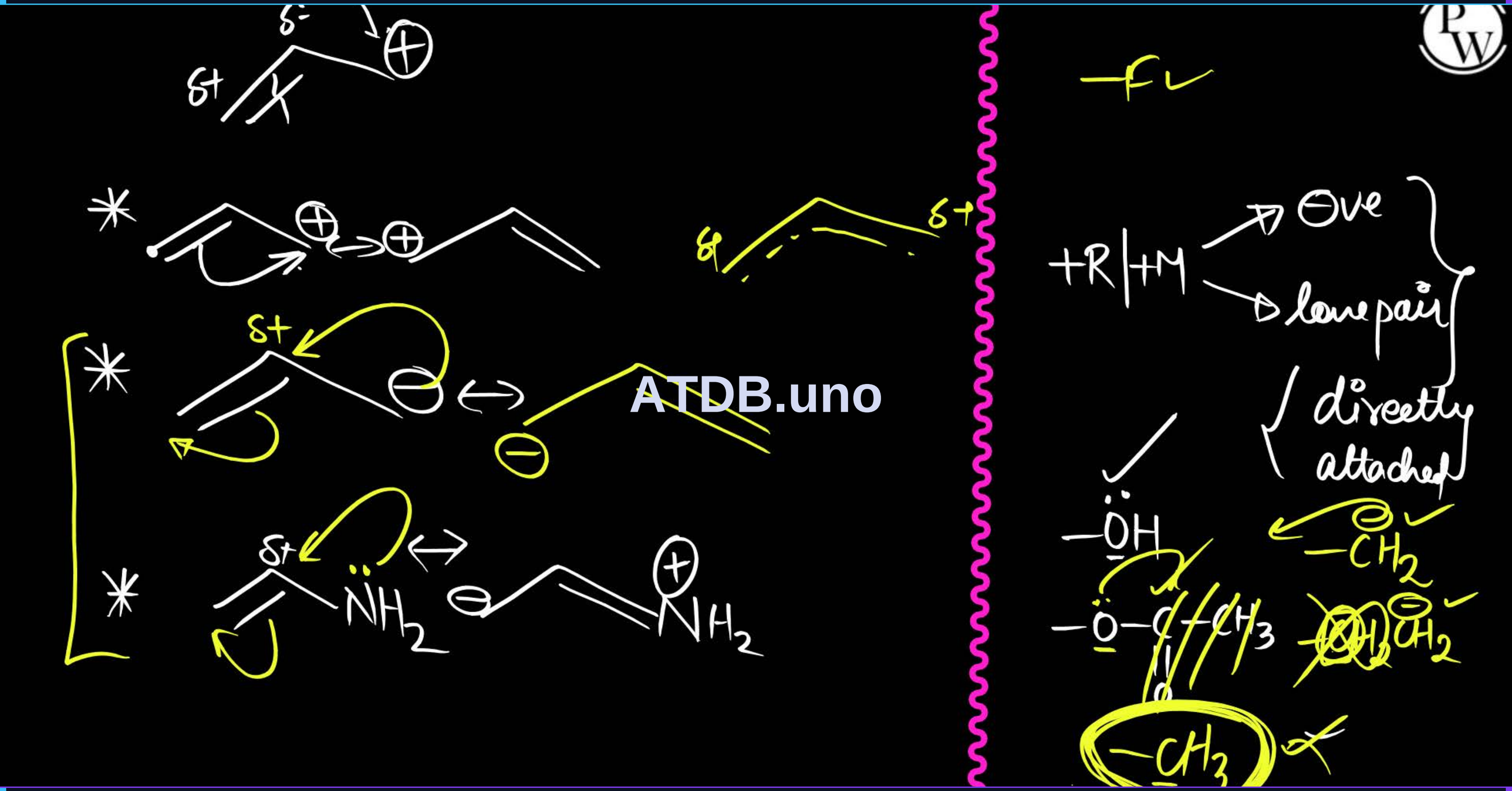
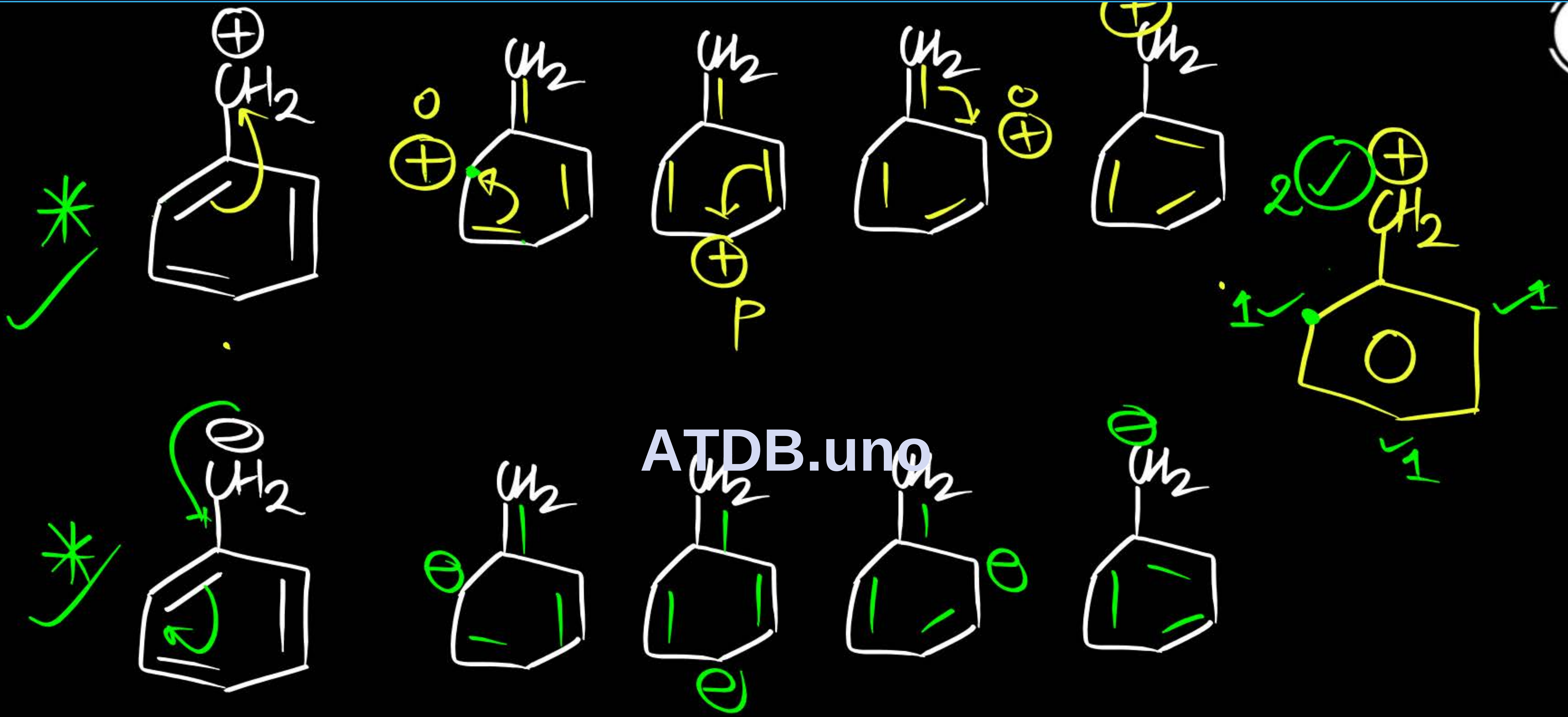
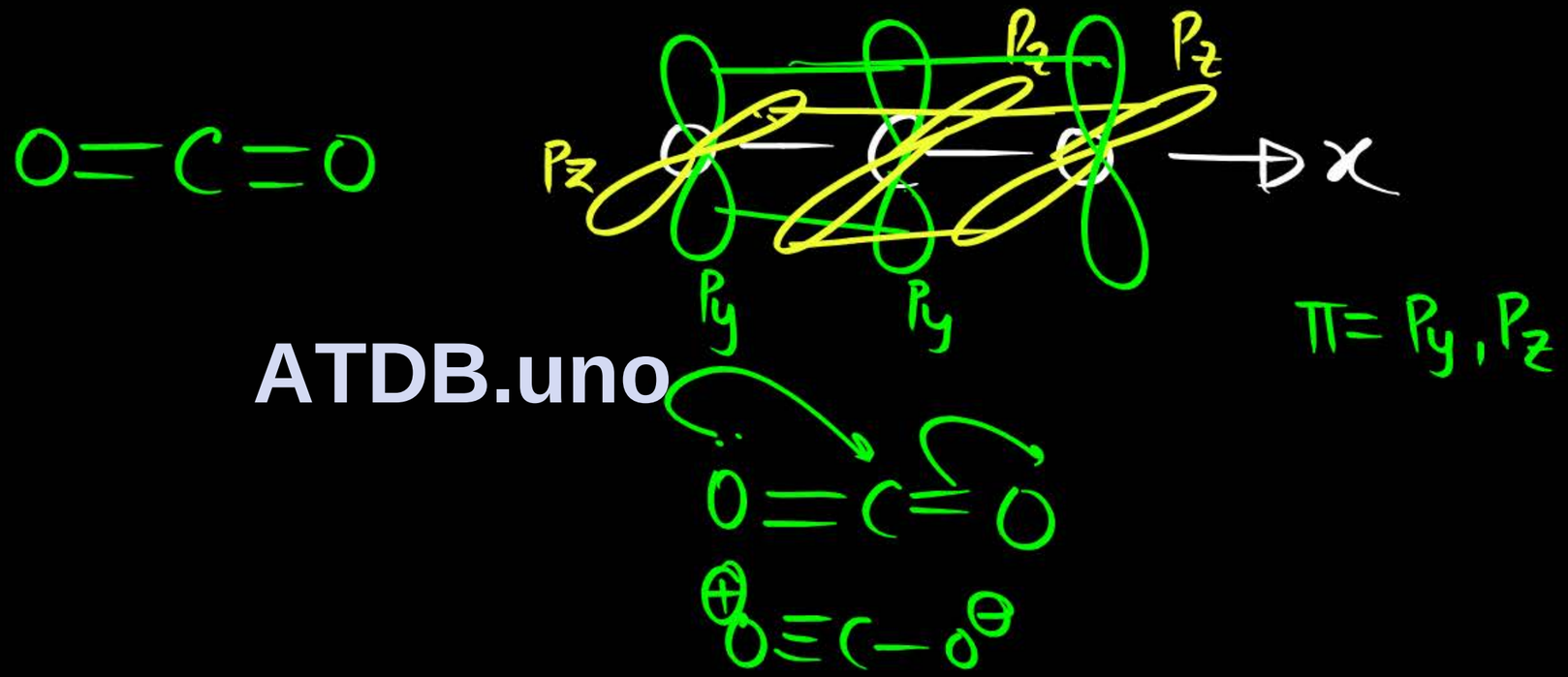


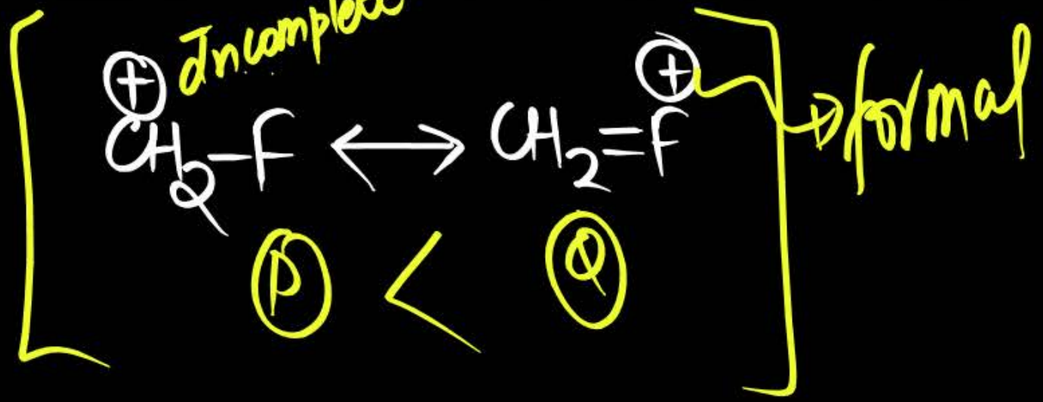




Stability Of RS

Rule-1 Octet

RS having complete octet is more stable



Neutral

Generally Neutral RS is more stable than ionic

ATDB.uno

Rule-3 Electronegative

-ve on More EN atom is more stable and +ve on less EN atom

ATDB.uno

Rule-4 Opposite Charges

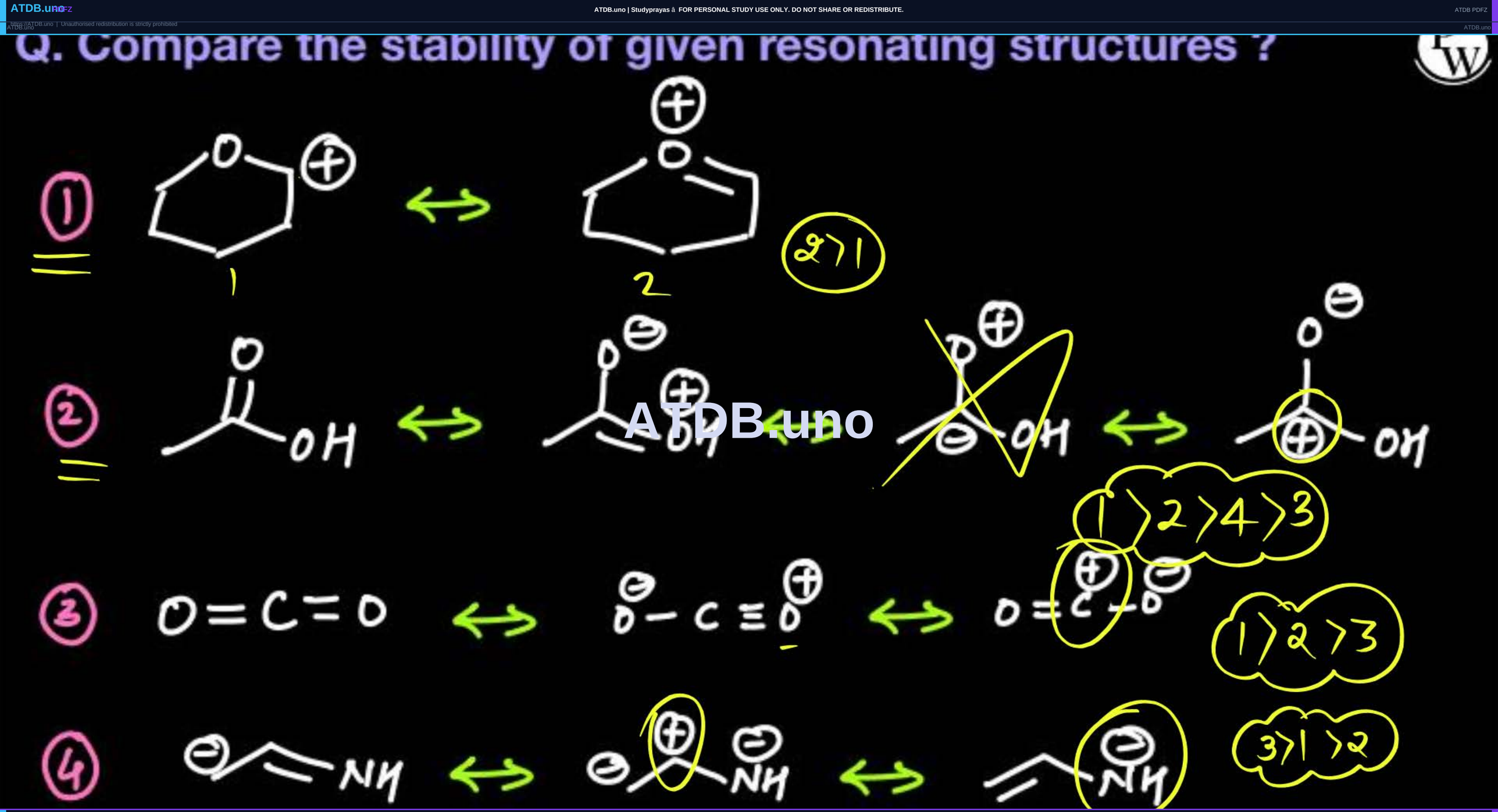
RS having closer opposite charges are more stable as they attract each other

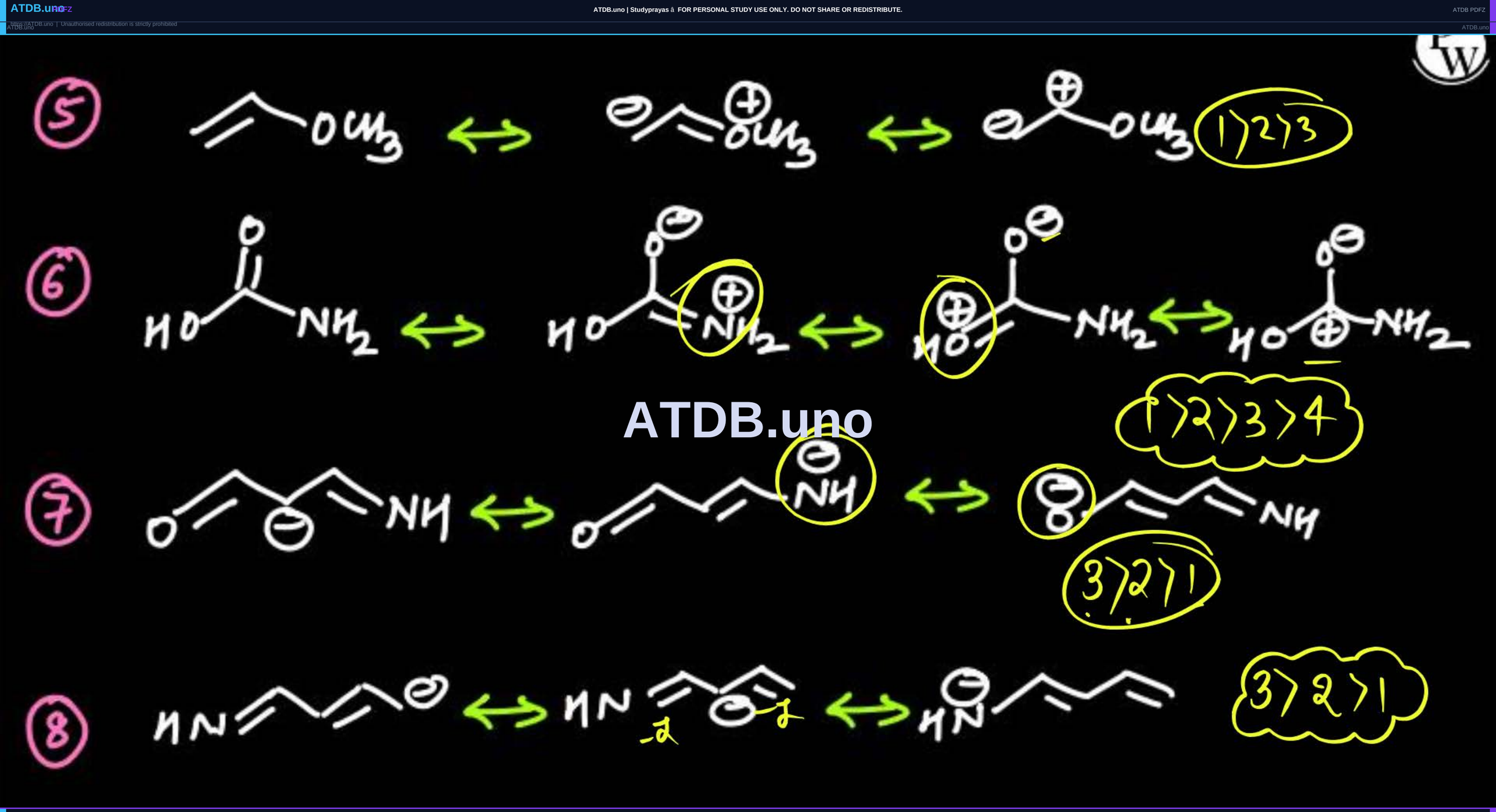
ATDB.uno

RS having more benzene is more stable

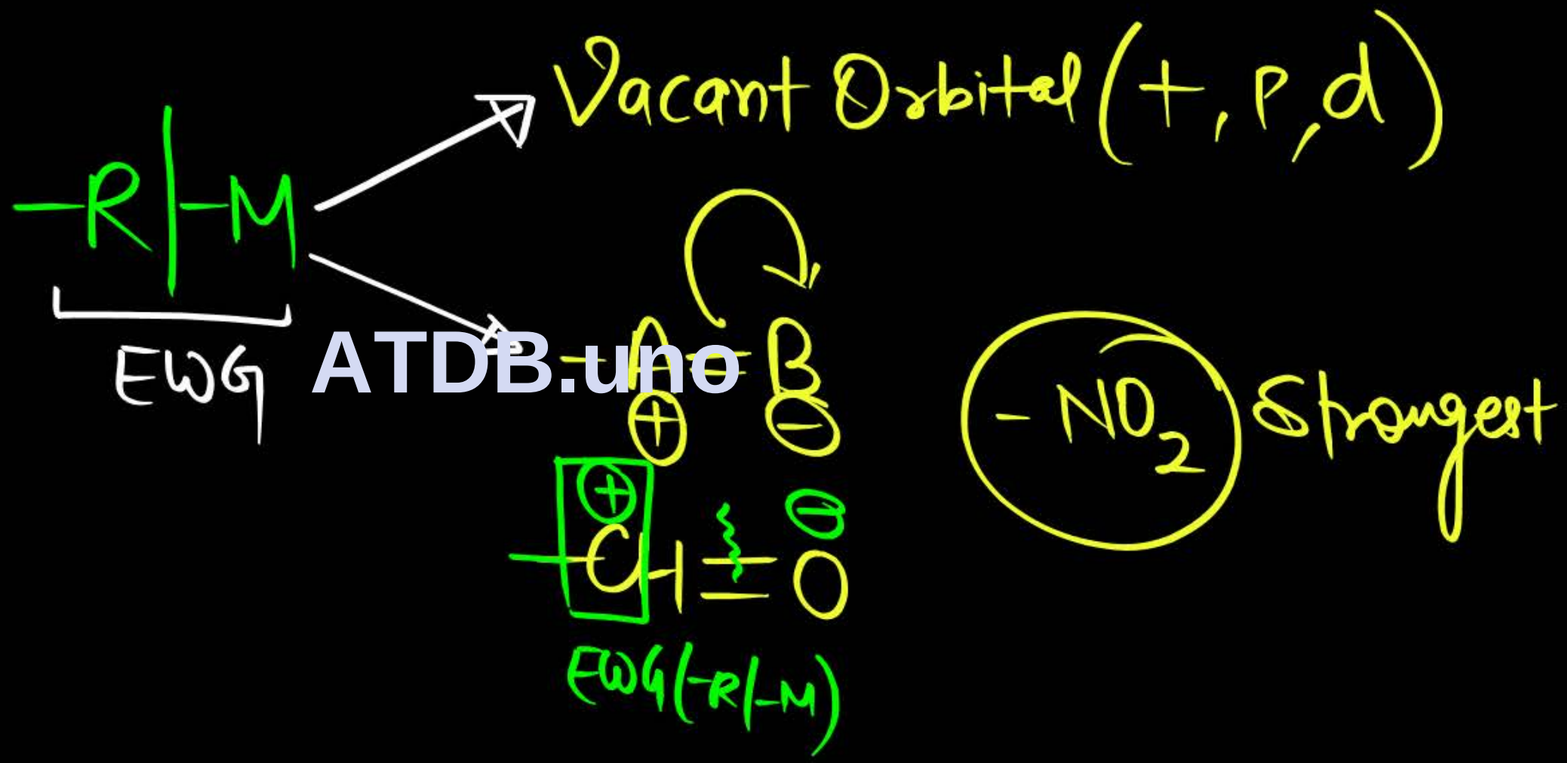
ATDB.uno

Q. Compare the stability of given resonating structures ?





Resonance or Mesomeric Effect

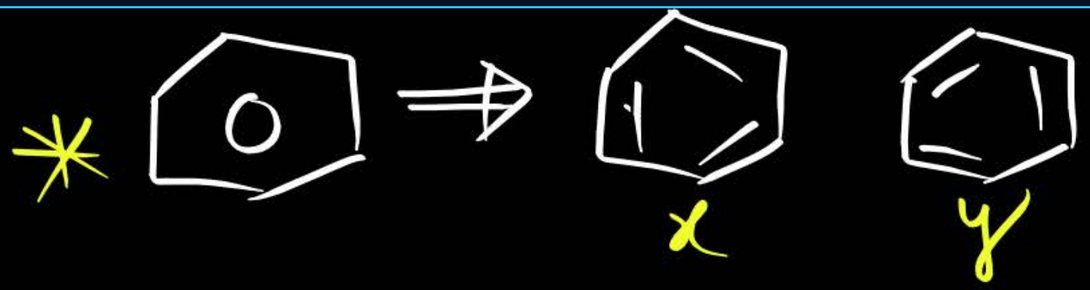


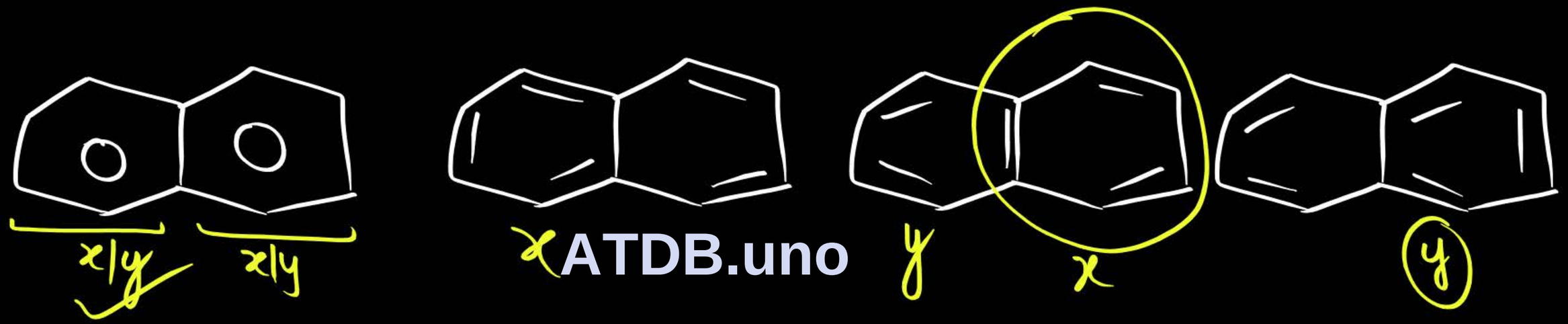
Find Permanent Effects

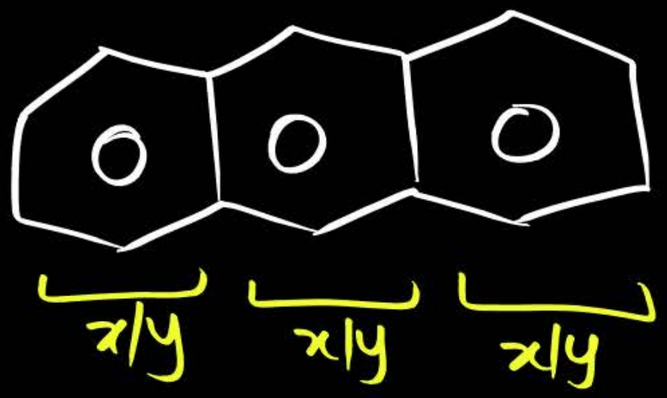
DON'T FORGET Robinhood

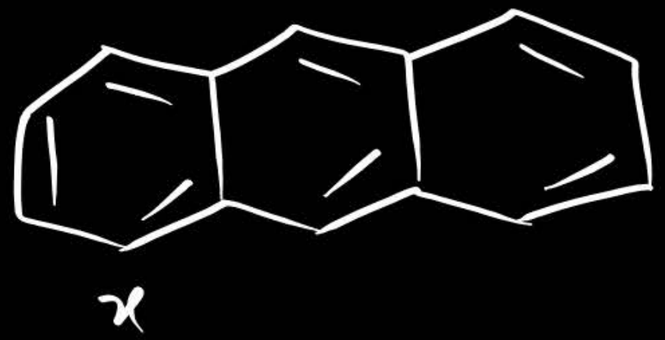
1. $-\ddot{O}H$ ⊕
2. $-\ddot{N}H_2$ ⊕ ⊖
3. $-CH_2$ ⊕
4. $-CH_2OH$ X
5. $-\ddot{N}R_2$ ⊕
6. $-\ddot{F}$ ⊕
7. $-\ddot{N}H-\overset{O}{\overset{\|}{C}}-CH_3$ ⊕

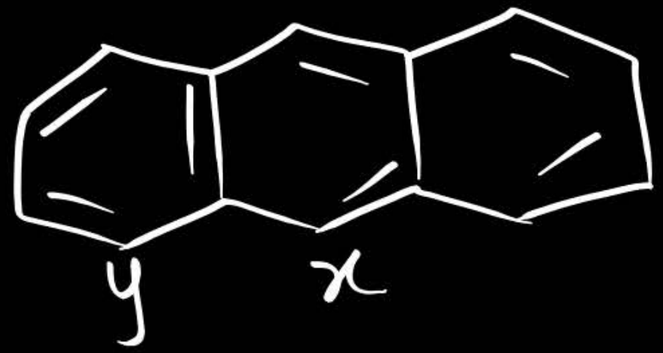
8. $-\ddot{C}l$ [⊕, ⊖ d vacant]
9. $-CHO$ $C \pm O$ ⊖
10. $-Br$ +, −
11. $-\ddot{O}^{\ominus}$ ⊕
12. $-\ddot{N}H^{\ominus}$ ⊕
13. $-CH_3$ X
14. $-CH_2CH_3$ X

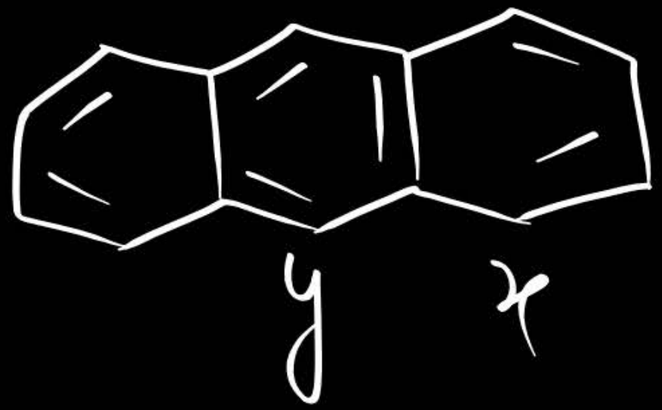


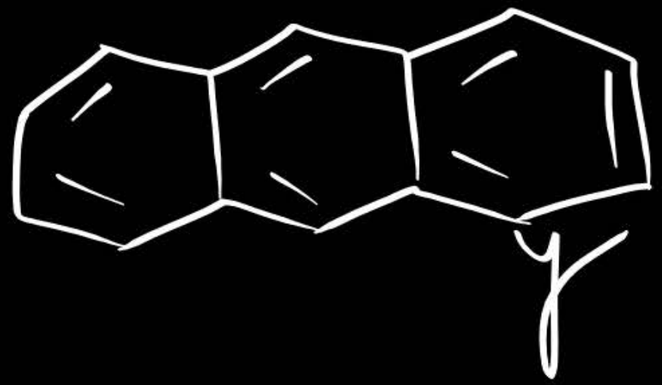


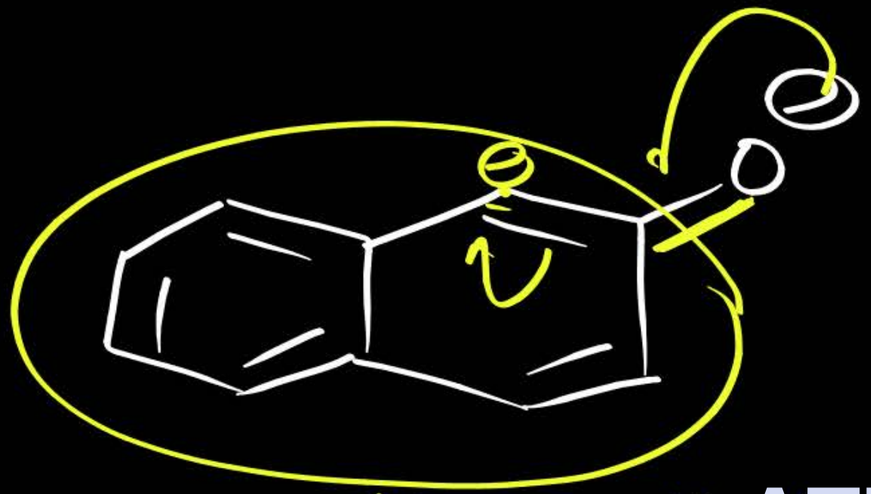


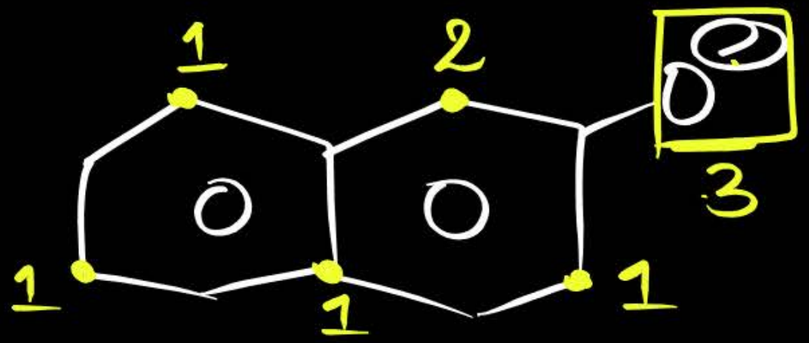






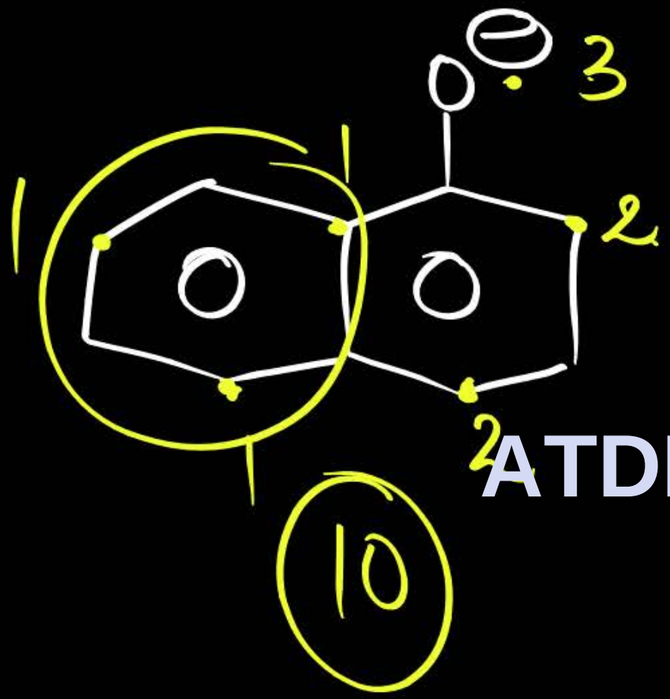


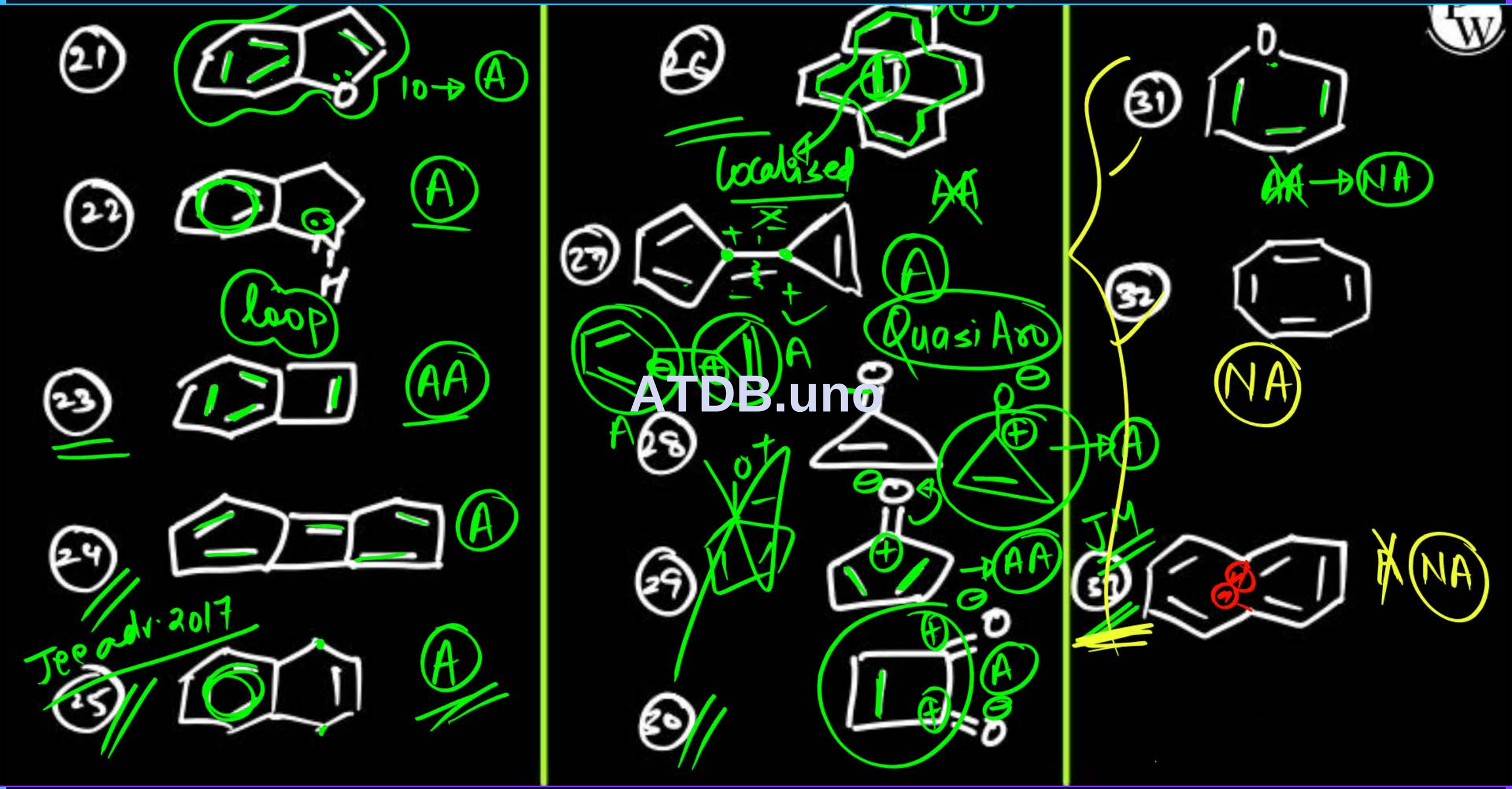


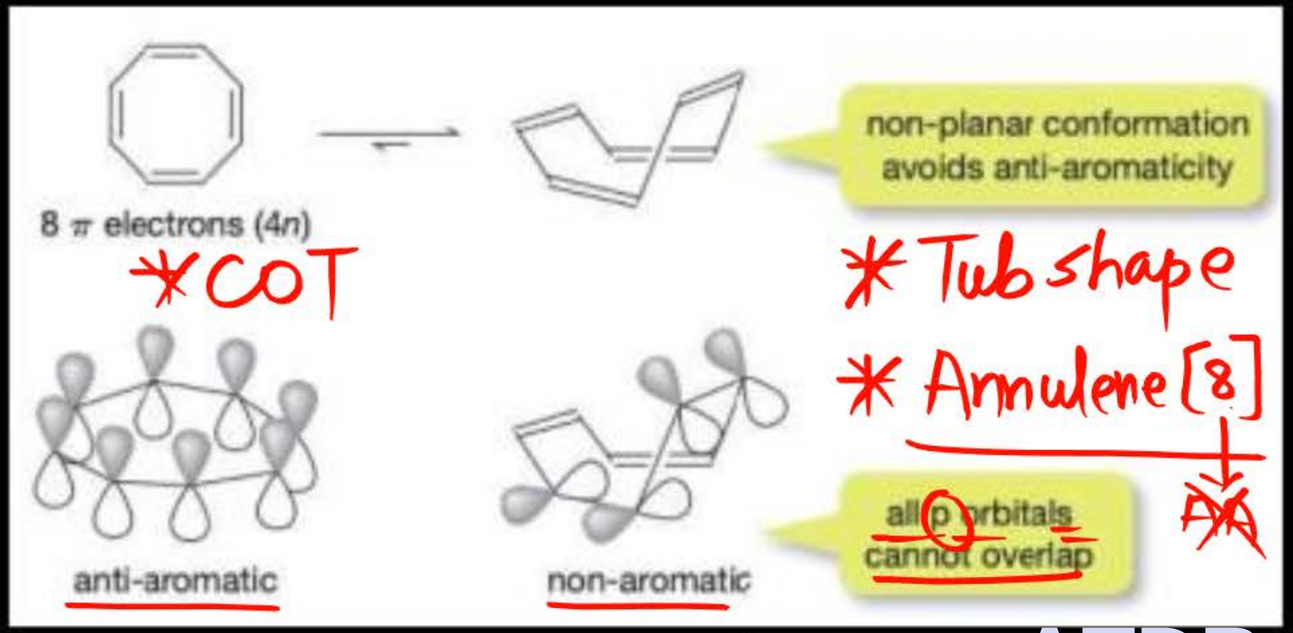


* naphthalene

9 ✓



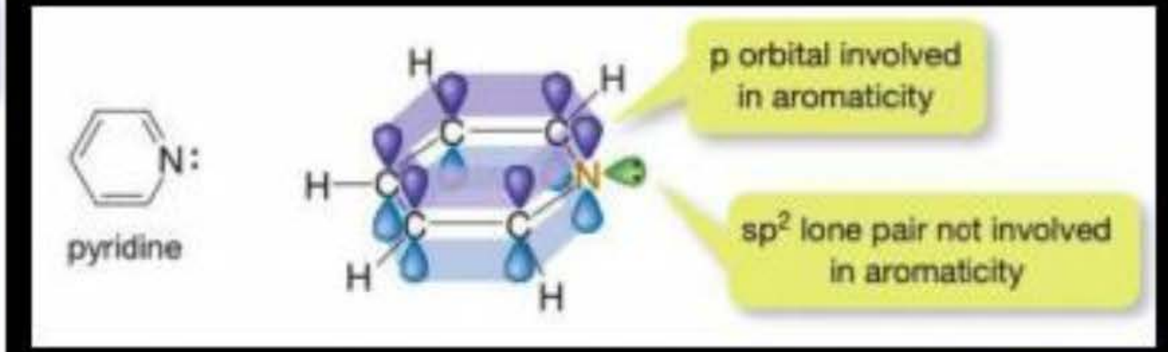


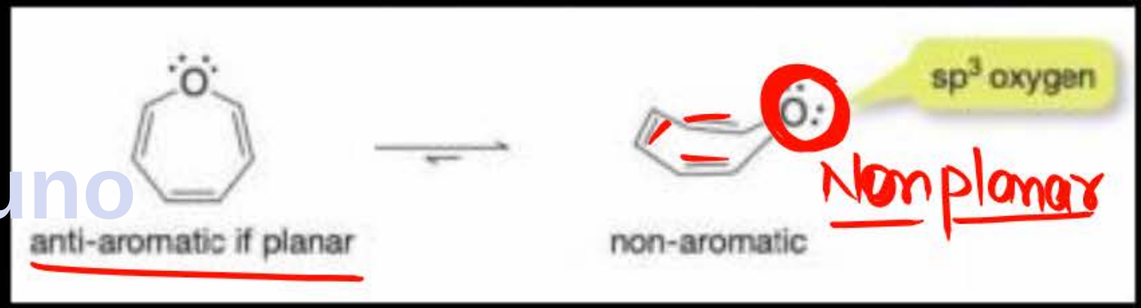


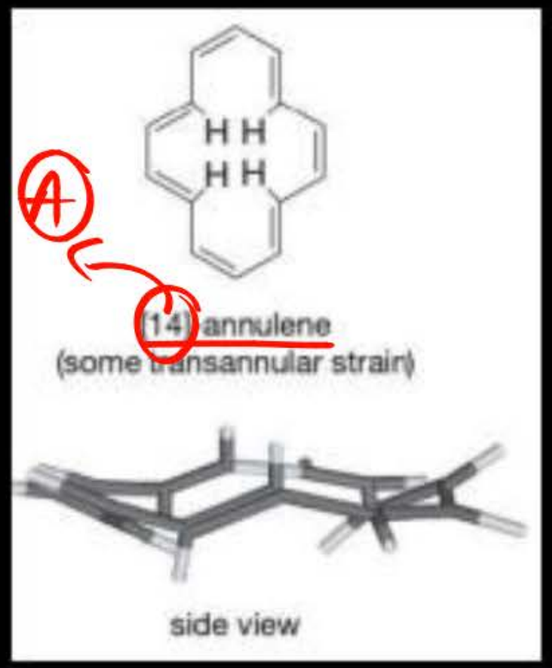
*COT

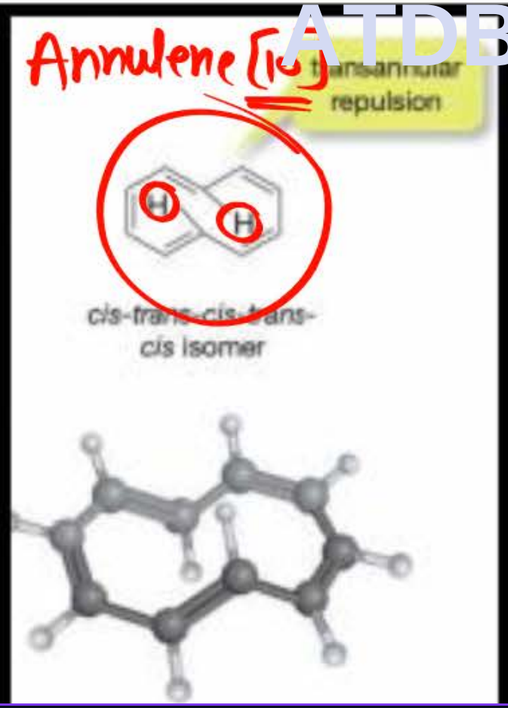
*Tub shape

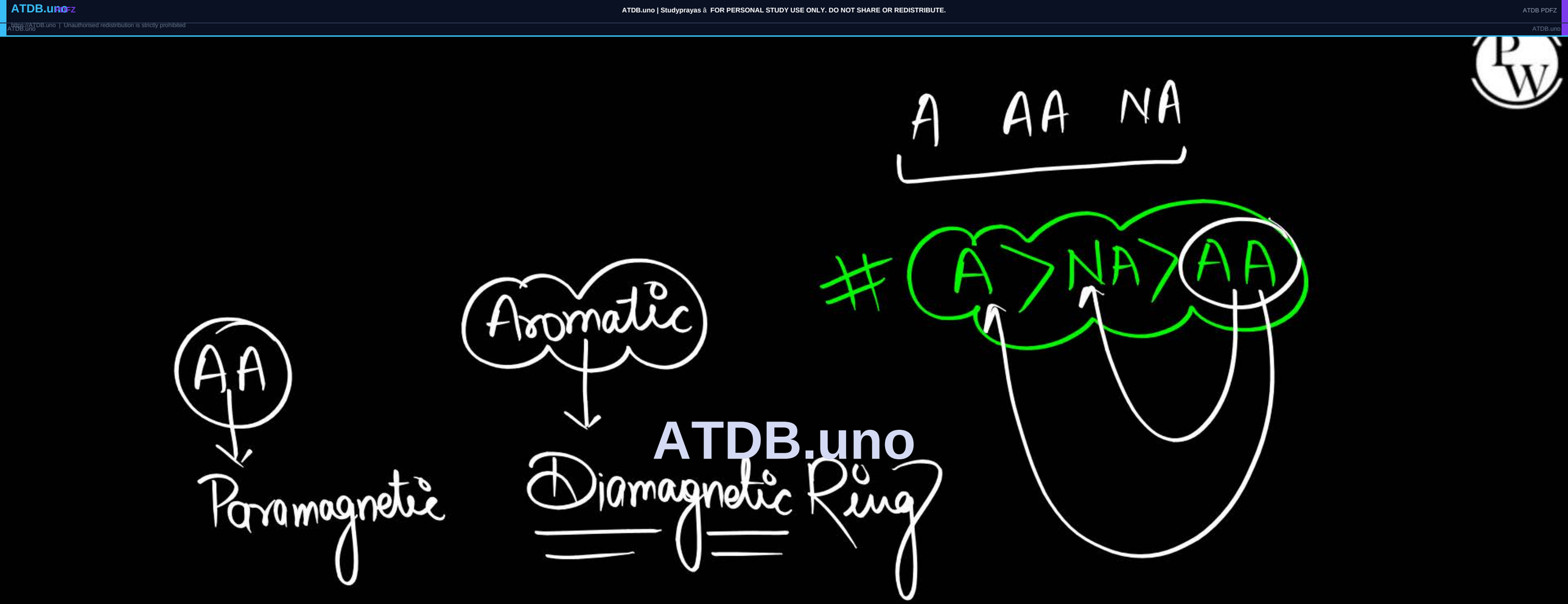
*Annulene [8]

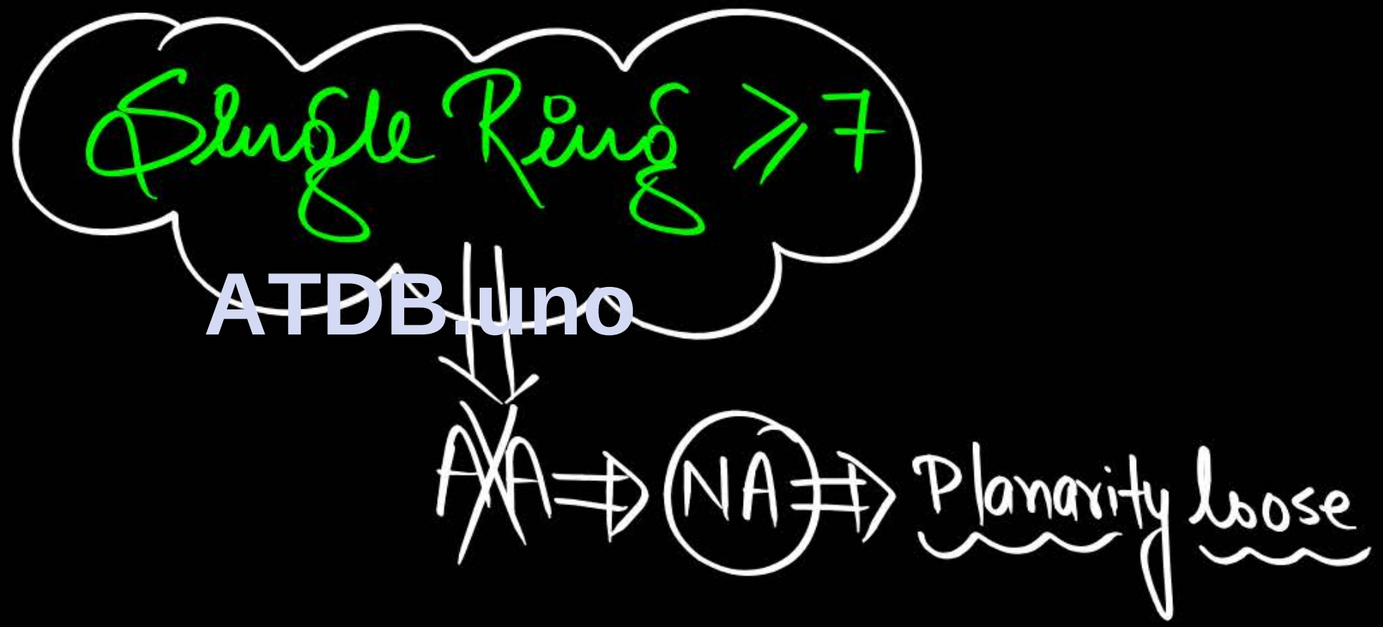




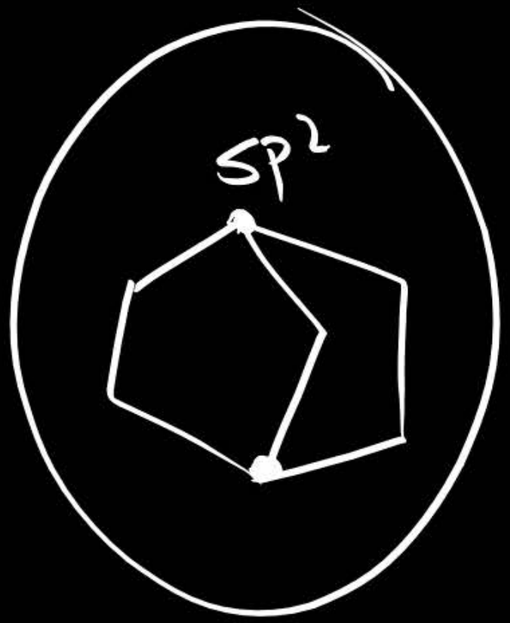








Bredt's Rule



Ring ≤ 8

Bridge atom $\Rightarrow$ Planarity (sp^2)

1. Which of the following species or phenomenon are ?

(1) sp3 ✓ Real

(2)

(3) sp2 Nareal

(4) sp2

(5) Real sp3

(6) N

(7) Real sp3

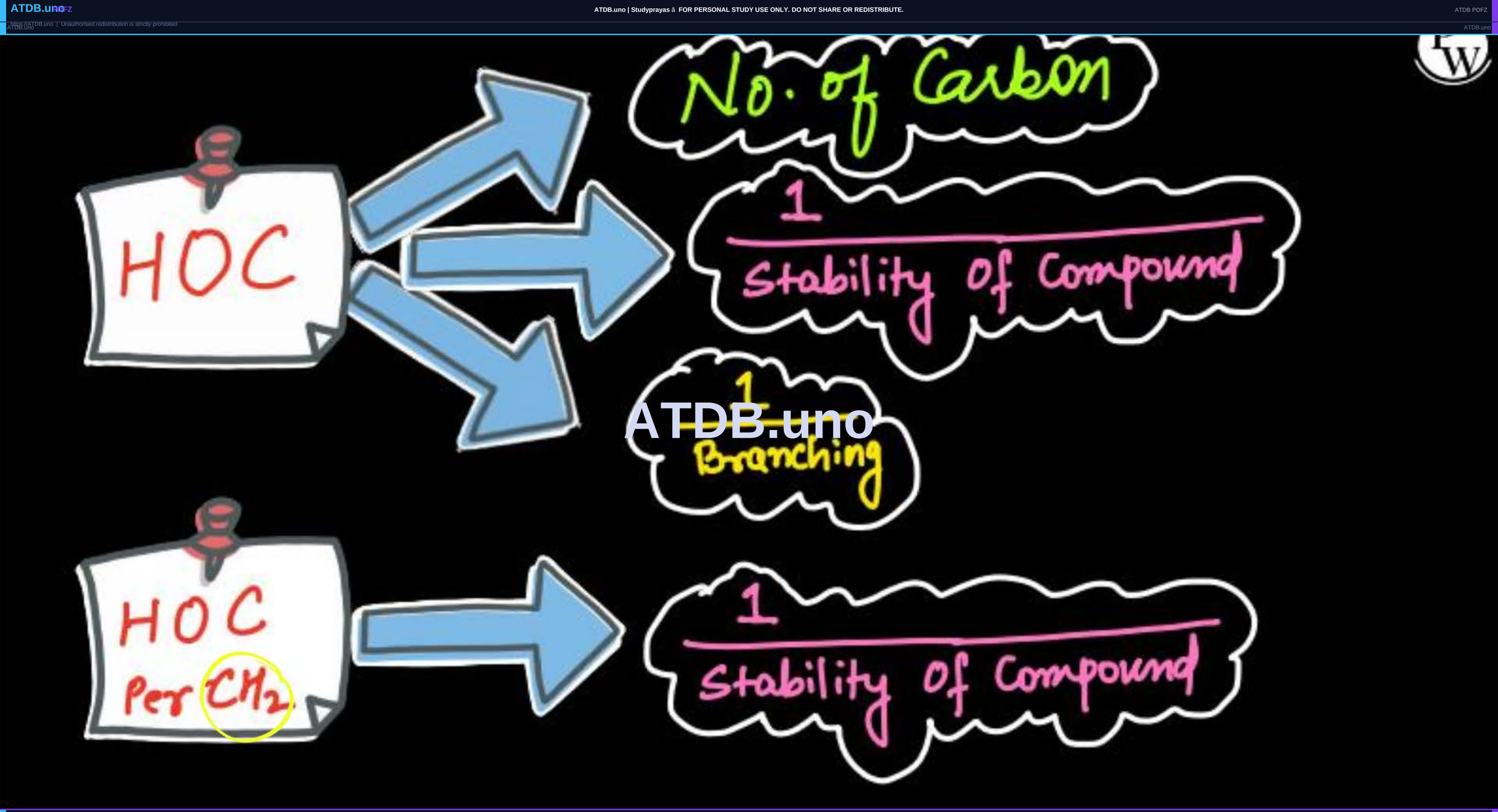
(8) Real sp3

(9) sp2

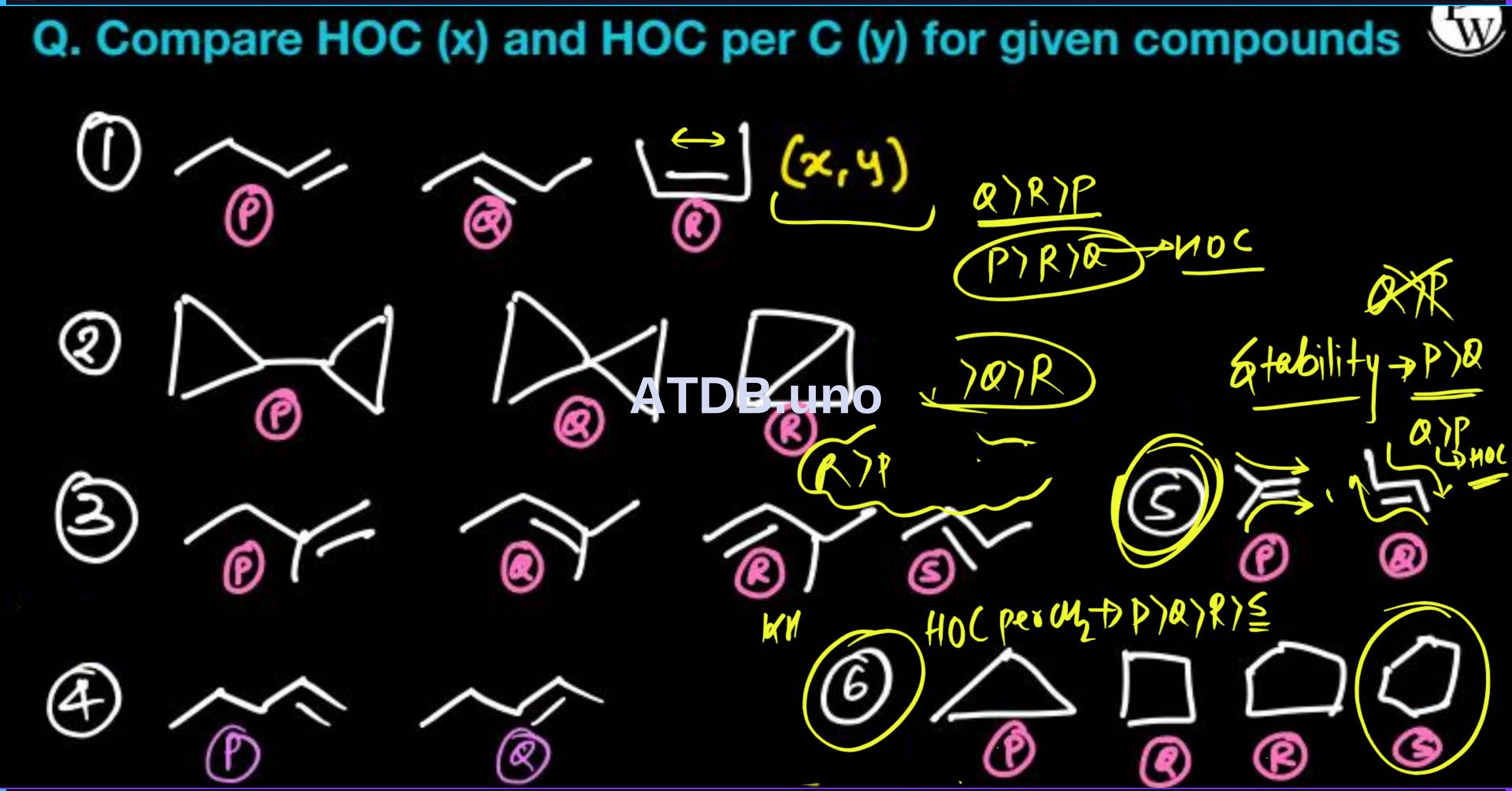
Heat Of Combustion (HOC)

* When one mole of hydrocarbon is fully burned then change in enthalpy is known as 'Heat of Combustion or Enthalpy of Combustion'.

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + y/2\,H_2O \quad [\Delta H_c]$$



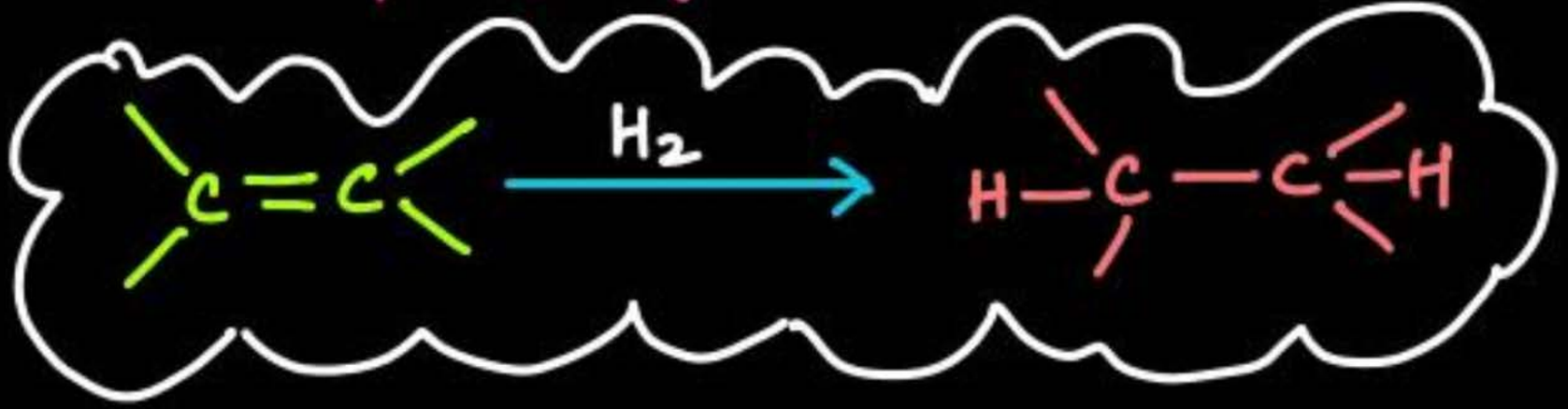
Q. Compare HOC (x) and HOC per C (y) for given compounds



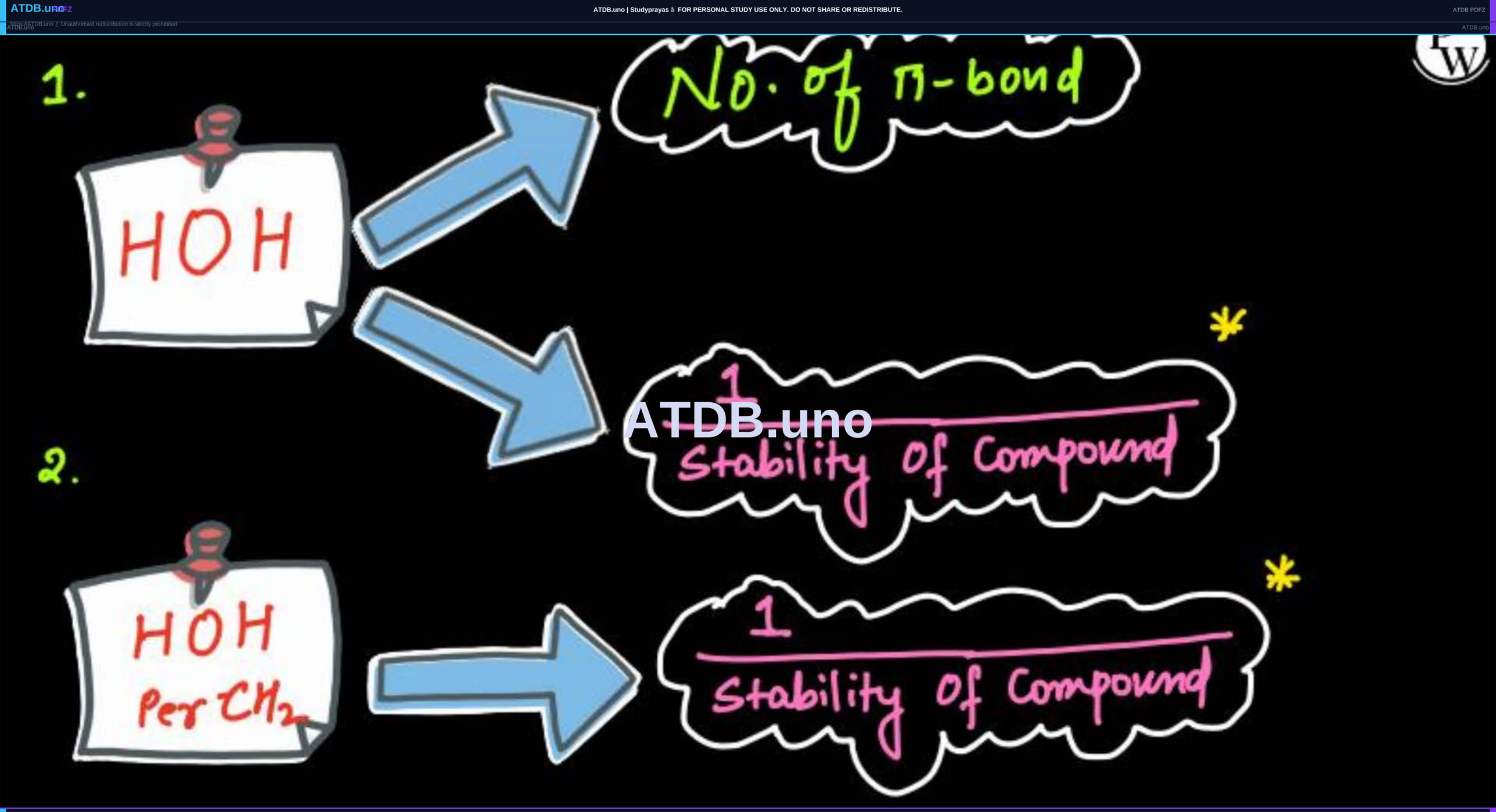
Heat Of Hydrogenation (HOH)

* When 1 mole of a compound completely reacts with 1 mole of Hydrogen (H_2) then change in enthalpy is known as 'Heat of Hydrogenation'.

Ex:

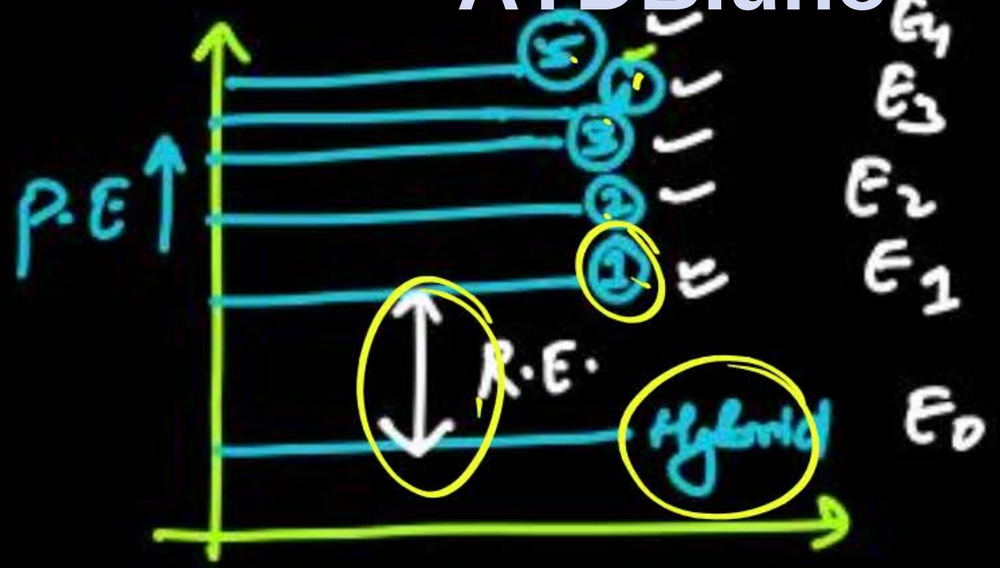


$[\Delta H_H]$



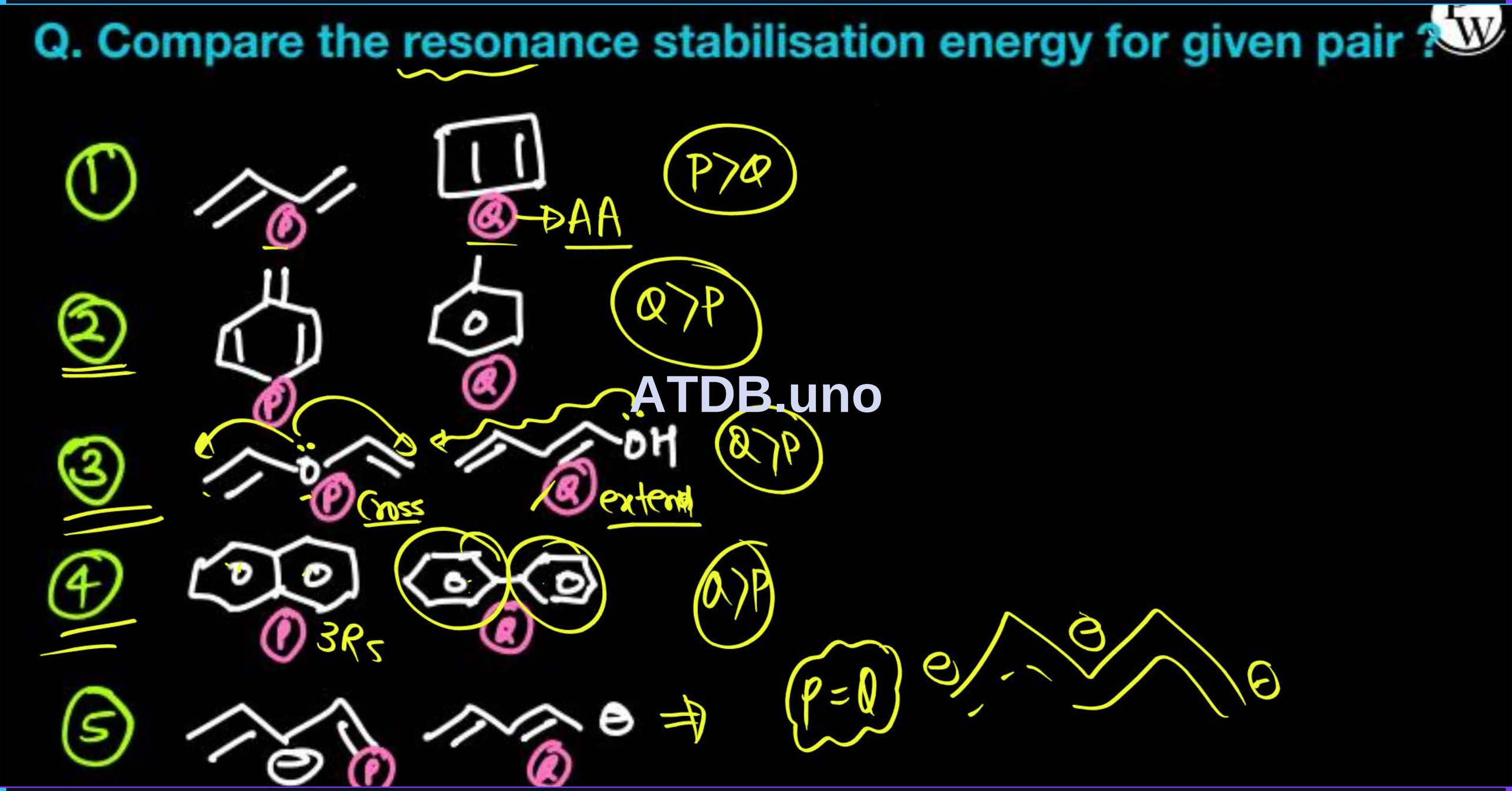
Resonance Stabilisation Energy

* Energy difference b/w most stable resonating structure & Resonance Hybrid is known as Resonance Energy.



$$|R.E| = |(E_1 - E_0)|$$

Q. Compare the resonance stabilisation energy for given pair ?



Calculation of Enthalpy

Q:1

(i)  $+H_2 \longrightarrow$

$\Delta H_H = -28.6$ kCal/mol

(ii)  $+2H_2 \longrightarrow$ 

$\Delta H_H = -54.0$ kCal/mol

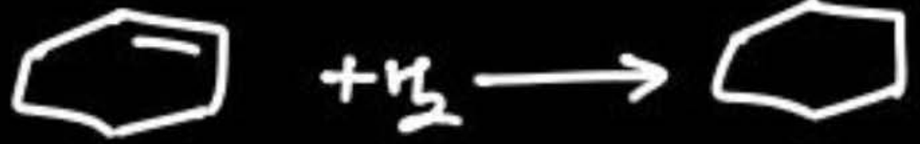
* find the resonance energy?

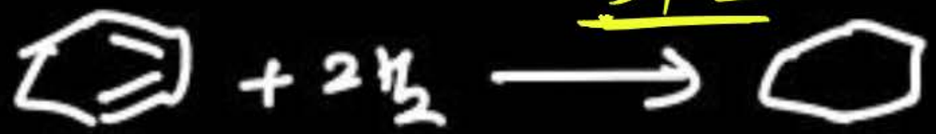
$\Rightarrow -3.2$ kCal/mol

-57.2 - ( )

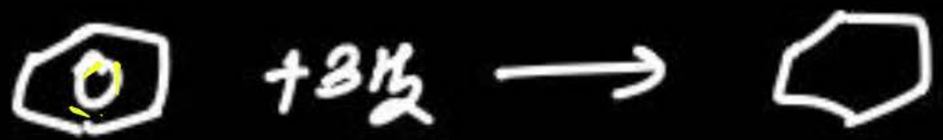
-3.2

Q.2

(i)  ΔH_H = -28.6 kCal/mol

(ii)  -57.2 ΔH_H = -x kCal/mol

-54.2 KC

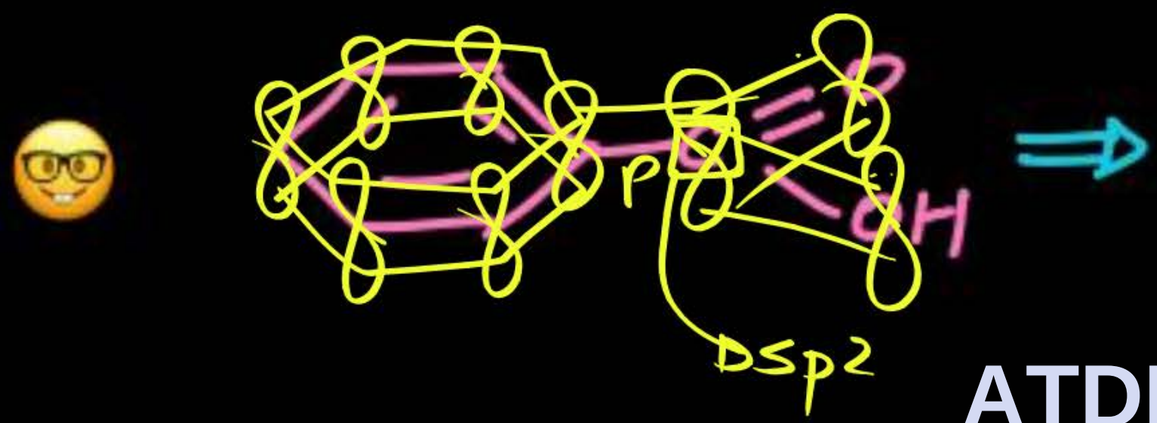
(iii)  ΔH_H = -49.8 kCal/mol

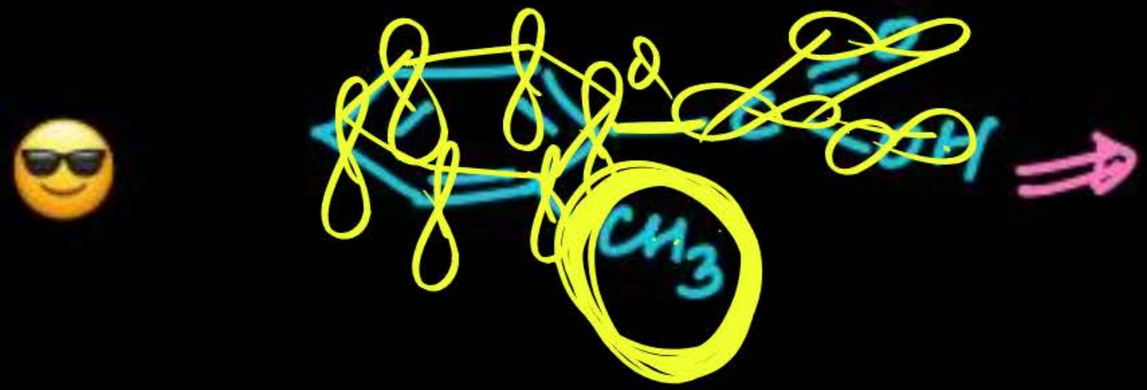
-36

-28.6 x 3 = -85.8

* Find the resonance Stabilization energy of benzene & also find ΔH_H for Cyclohexadiene if R.E. is -3 kCal/mol ?

Steric Inhibition Of Resonance (SIR Effect)





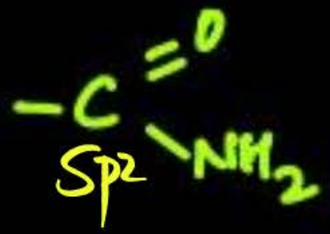
* Due to steric repulsion by group (G) at ortho position, $-sp^2$ group becomes non planar and resonance will inhibit. This Inhibition of resonance is known as S.I.R. effect.

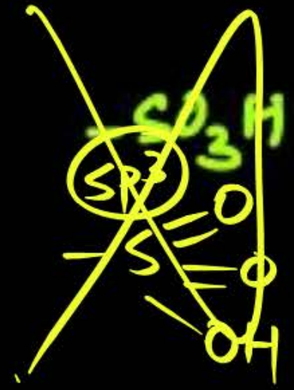
* S.I.R. applied by: All bulky groups except

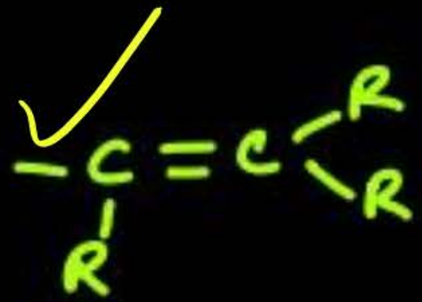
$-OH$, $-OR$, $-NH_2$, $-H$, $-F$ etc.

(2p)

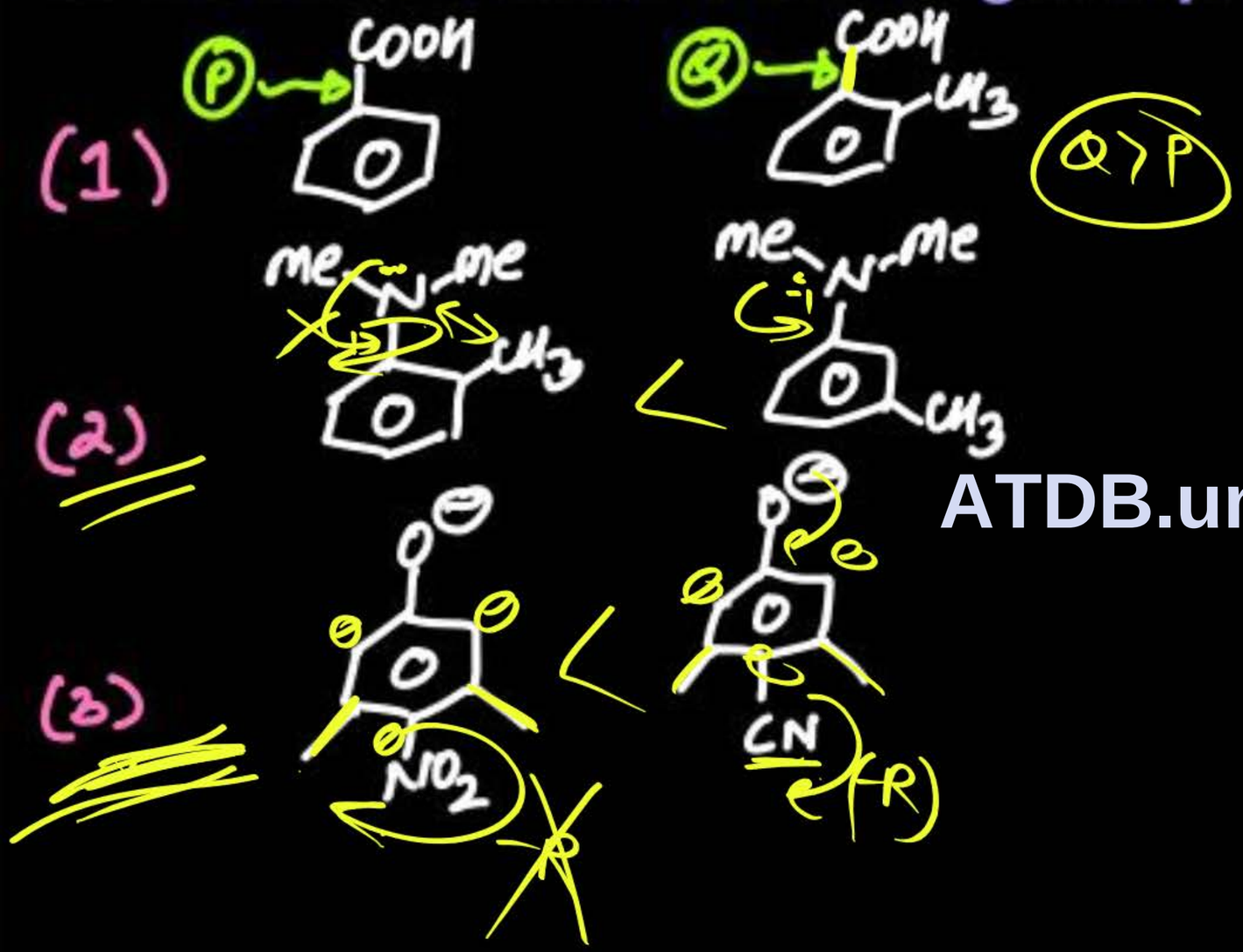
* SIR applied on: [sp^2 group]







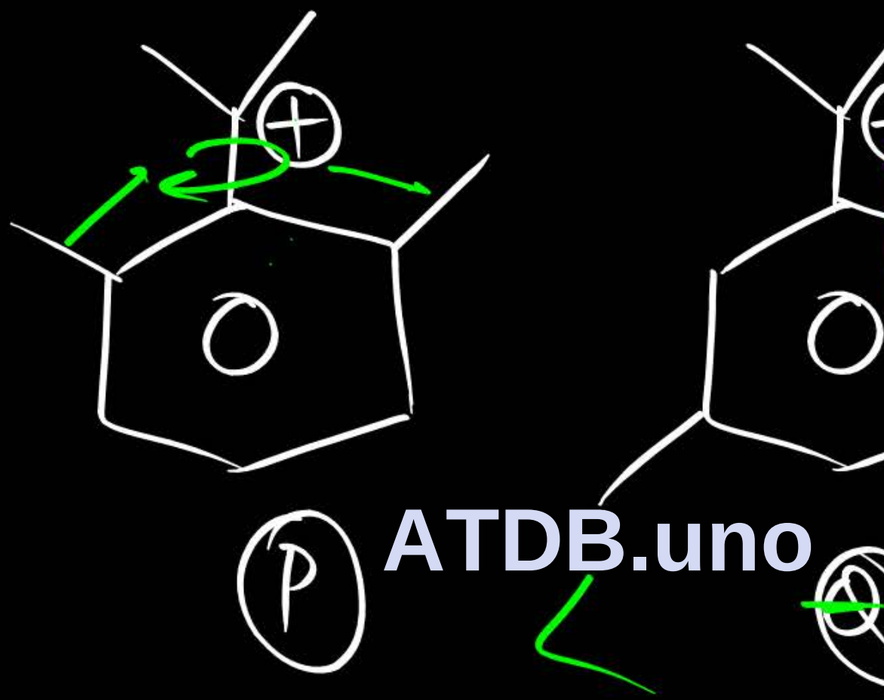
Q. Find the correct order of given properties ?



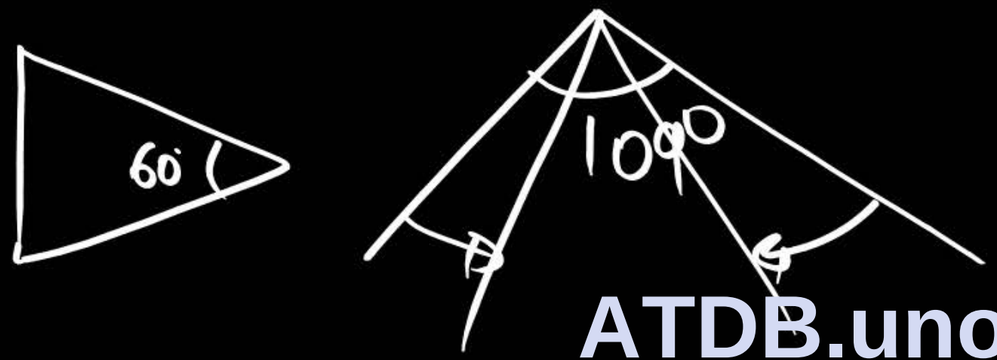
[Bond length]

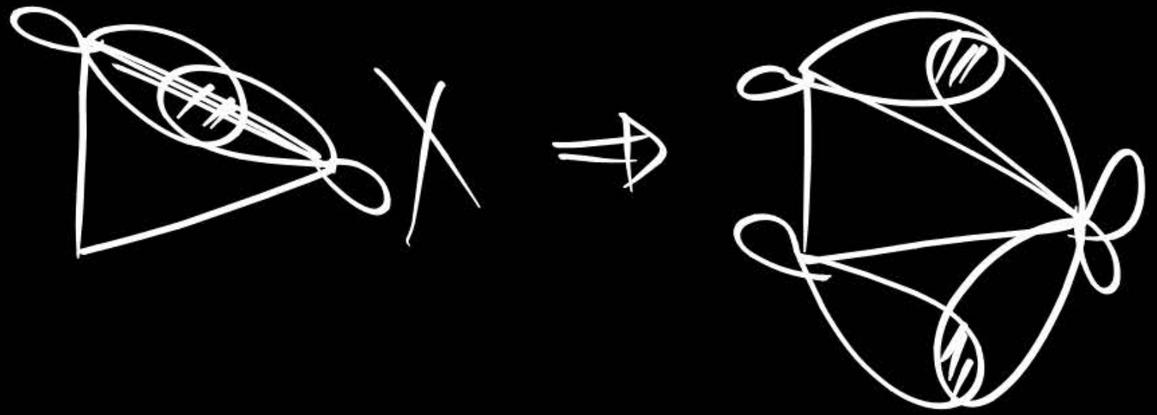
[Resonance Effect]

[Stability of (−) ve]

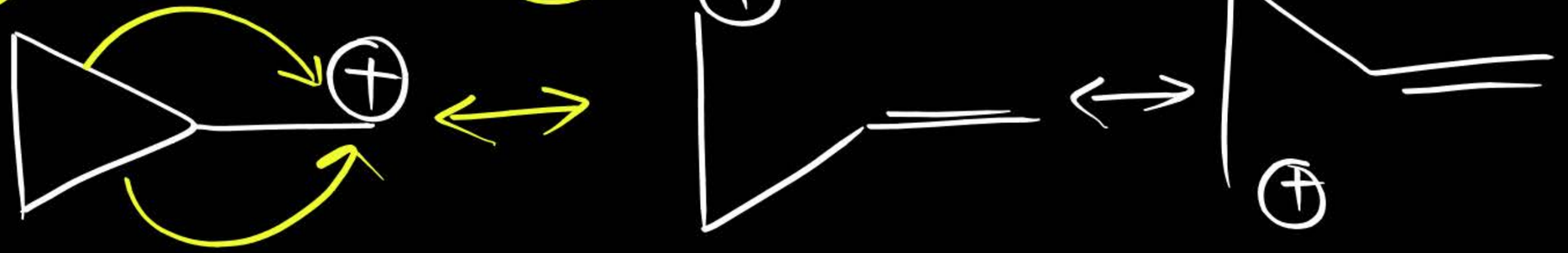


Cyclopropane





Sigma / Lancing



Bond Dissociation Energy ⇒ Homolysis

The amount of energy required to break a bond is same as the amount of energy released when the same bond is formed.

In gaseous state, the energy required for homolytic cleavage of a bond is called Bond Dissociation Energy (BDE) or Bond Strength.

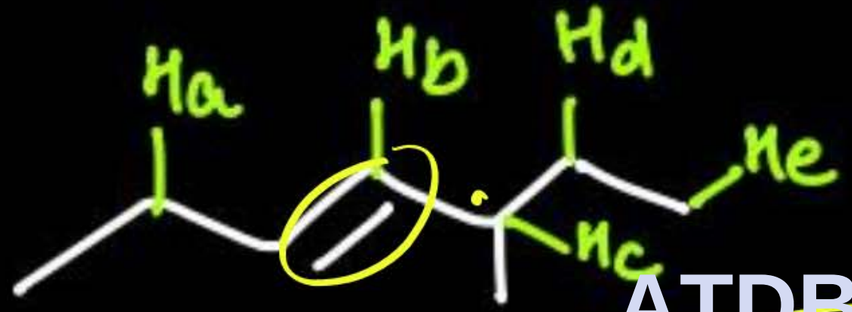
BDE is affected by s-character of the bond and the stability of the radicals formed. Shorter bonds are typically stronger bonds.

$$B.D.E. \propto \frac{1}{\text{Stability of Radical}}$$

Q. Find the bond energy of given bonds ?

(1)

(2)



* 1 > 2 > 3 ⇒ Sta.
* 3 > 2 > 1 ⇒ B·D·E·

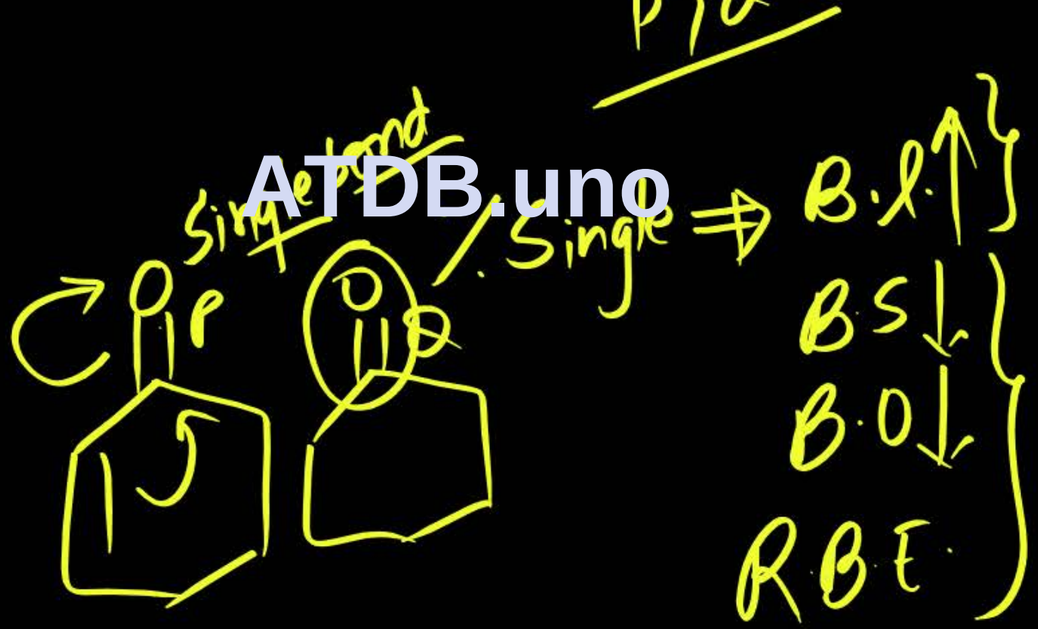
Stabi ⇒ c > a > d > e > b

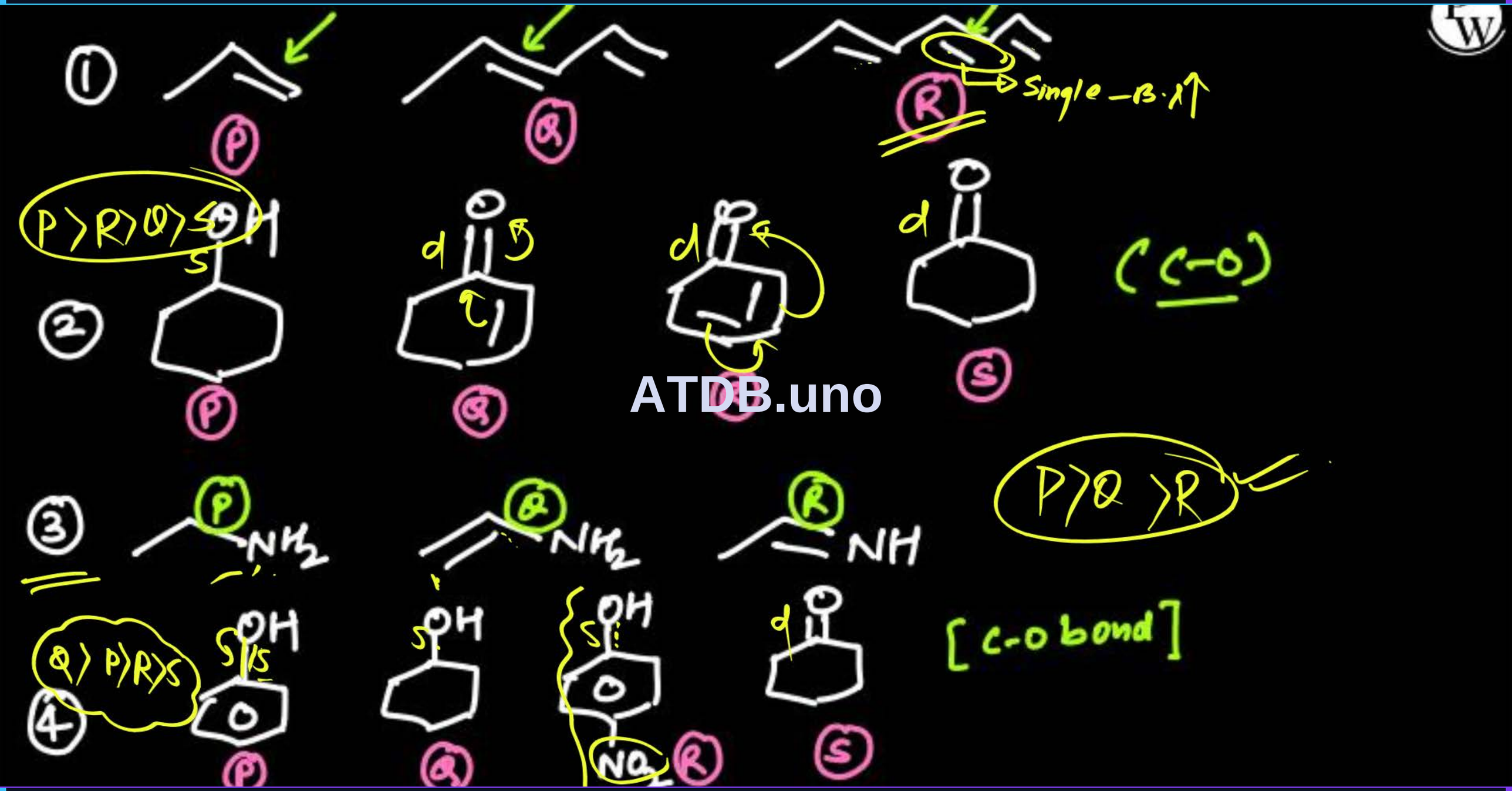
⇓

BDE ⇐ b > e > d > a > c

c a d e b

Bond length





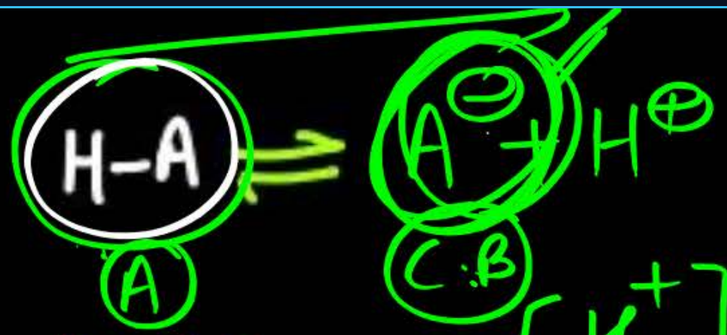
Acid and Base

Arrhenius

Bronsted

Lewis

Acidic Strength



EN

Size

$pK_a = -\log K_a$ $K_a = \frac{[H^+][A^-]}{[HA]}$

$A^\ominus$ Stability $\Rightarrow$ ① EWG

ⓐ $-R, -I$ (EN)

ⓑ $\frac{1}{+R, +M, +I}$

① H-bonding of C.B ↑

② SCR ↑

③ $-R$ ↑

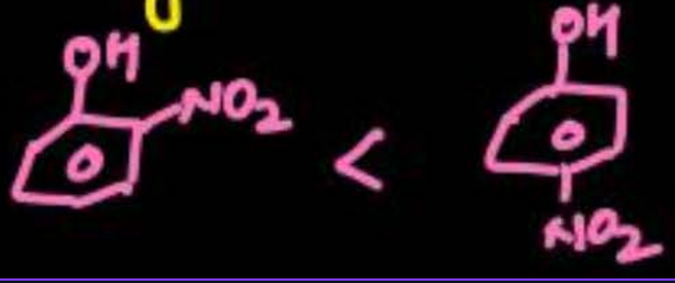
④ H-bonding of acid ↓

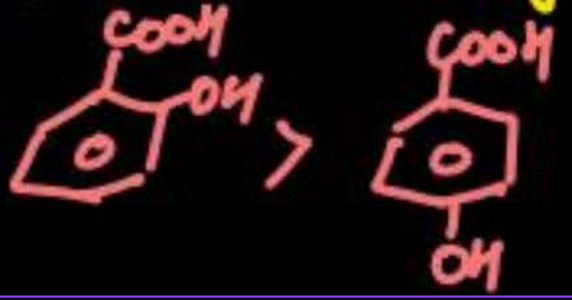
⑤ $-I$

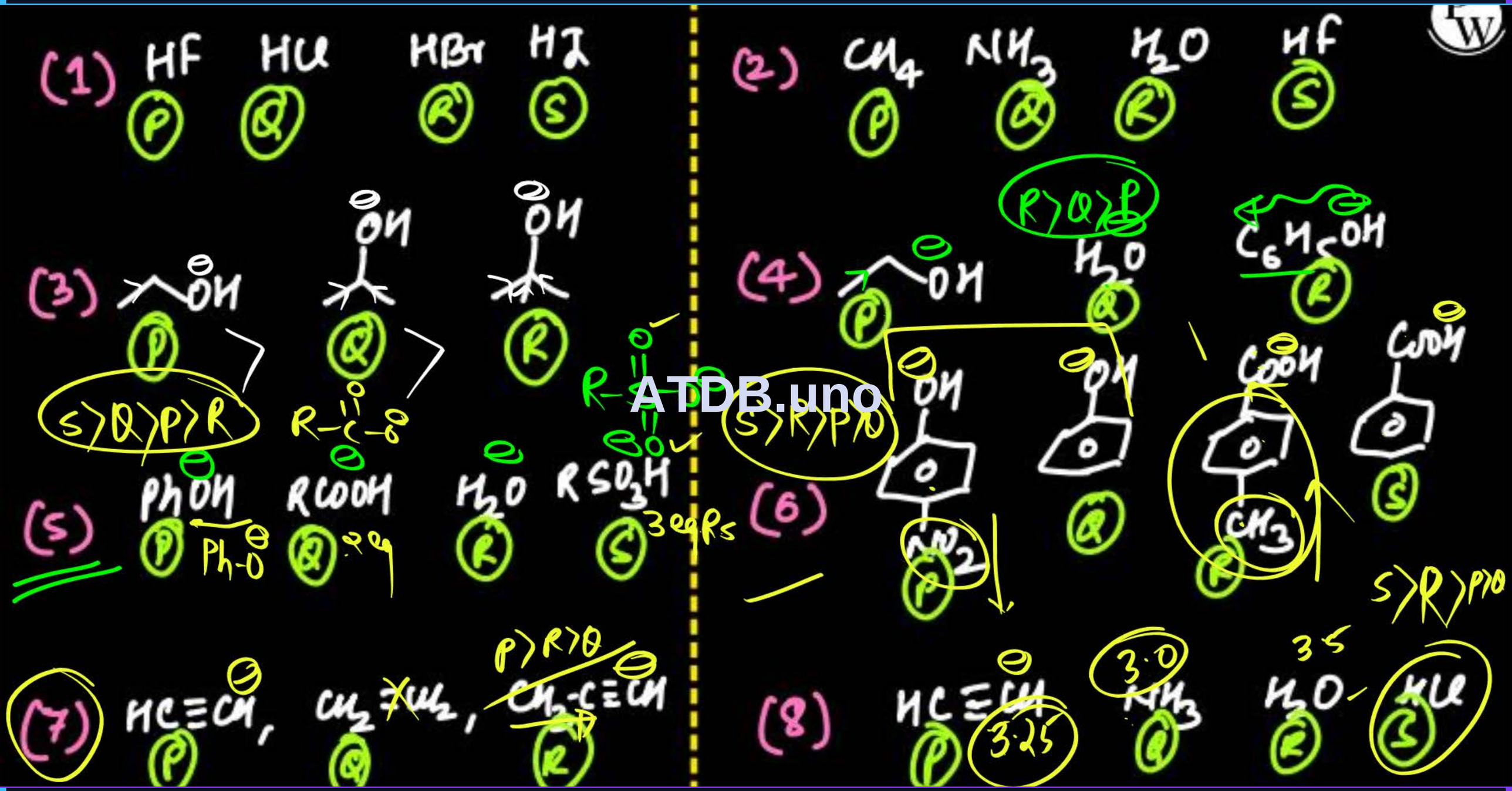
B.T.S.

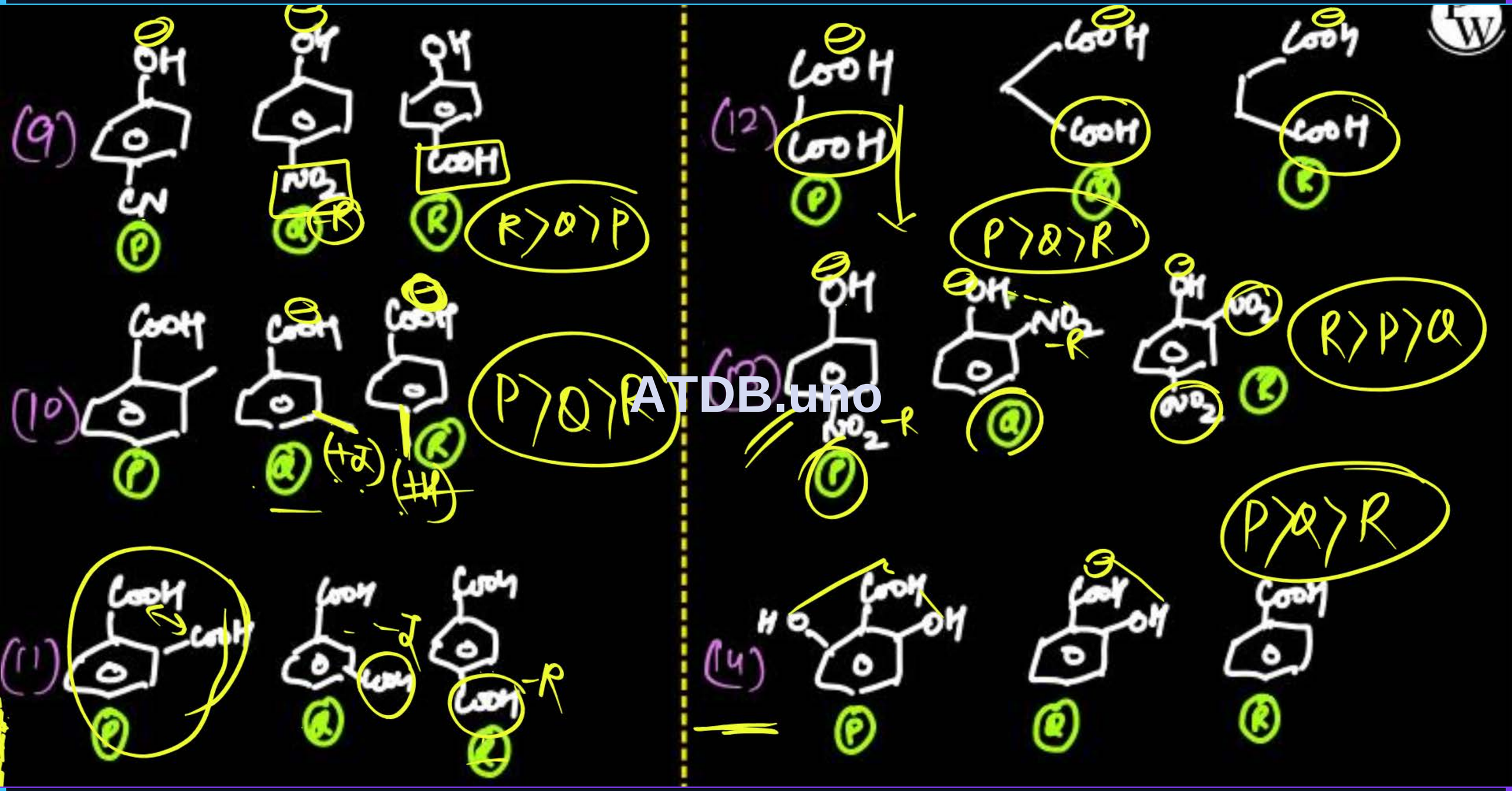
* Ortho substituted carboxylic acid are most acidic among other isomers (o, m, p) due to SIR effect.

* H-bonding in Conjugate base will increase the stability but if H-bonding only occurs in Acid they acidic strength decreases.

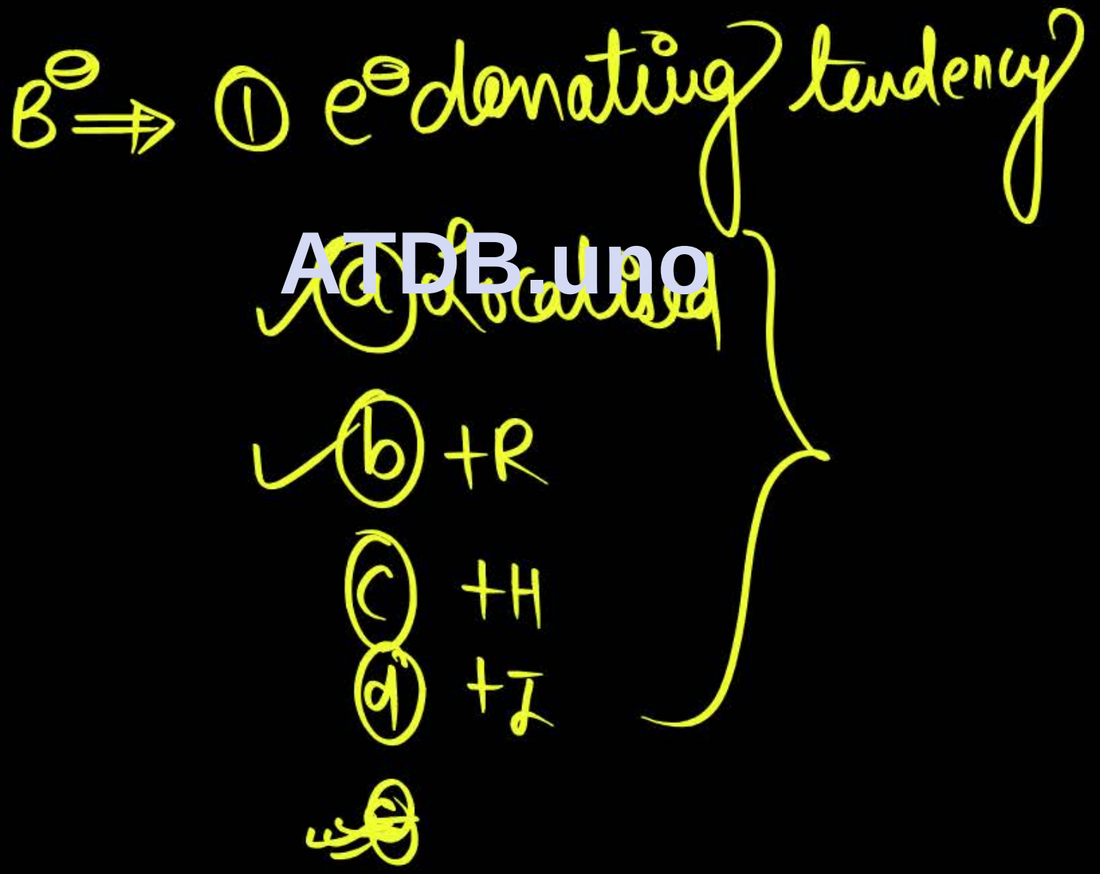
① 

② 





Basic Strength

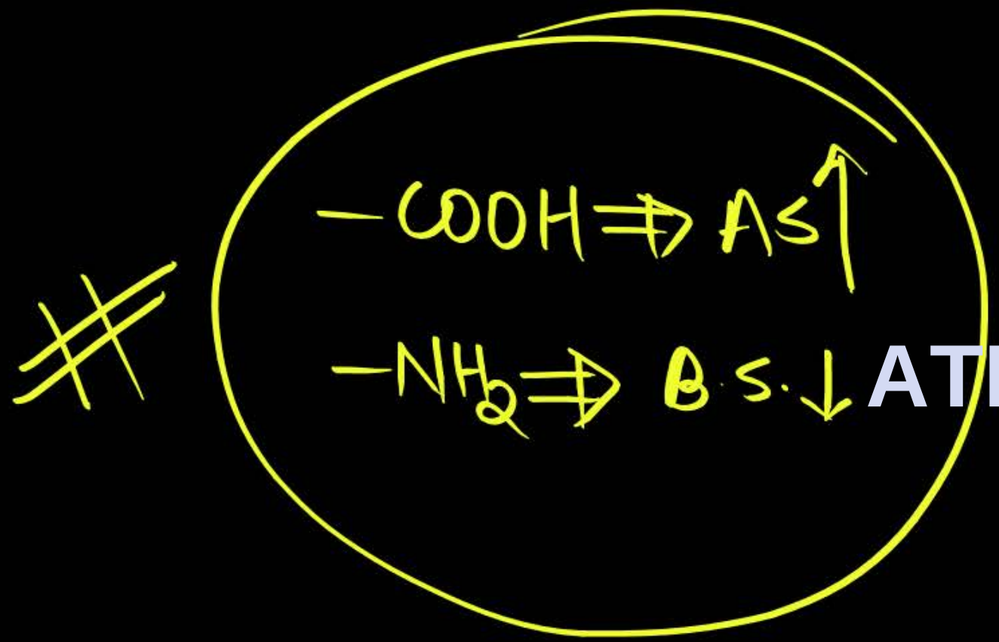


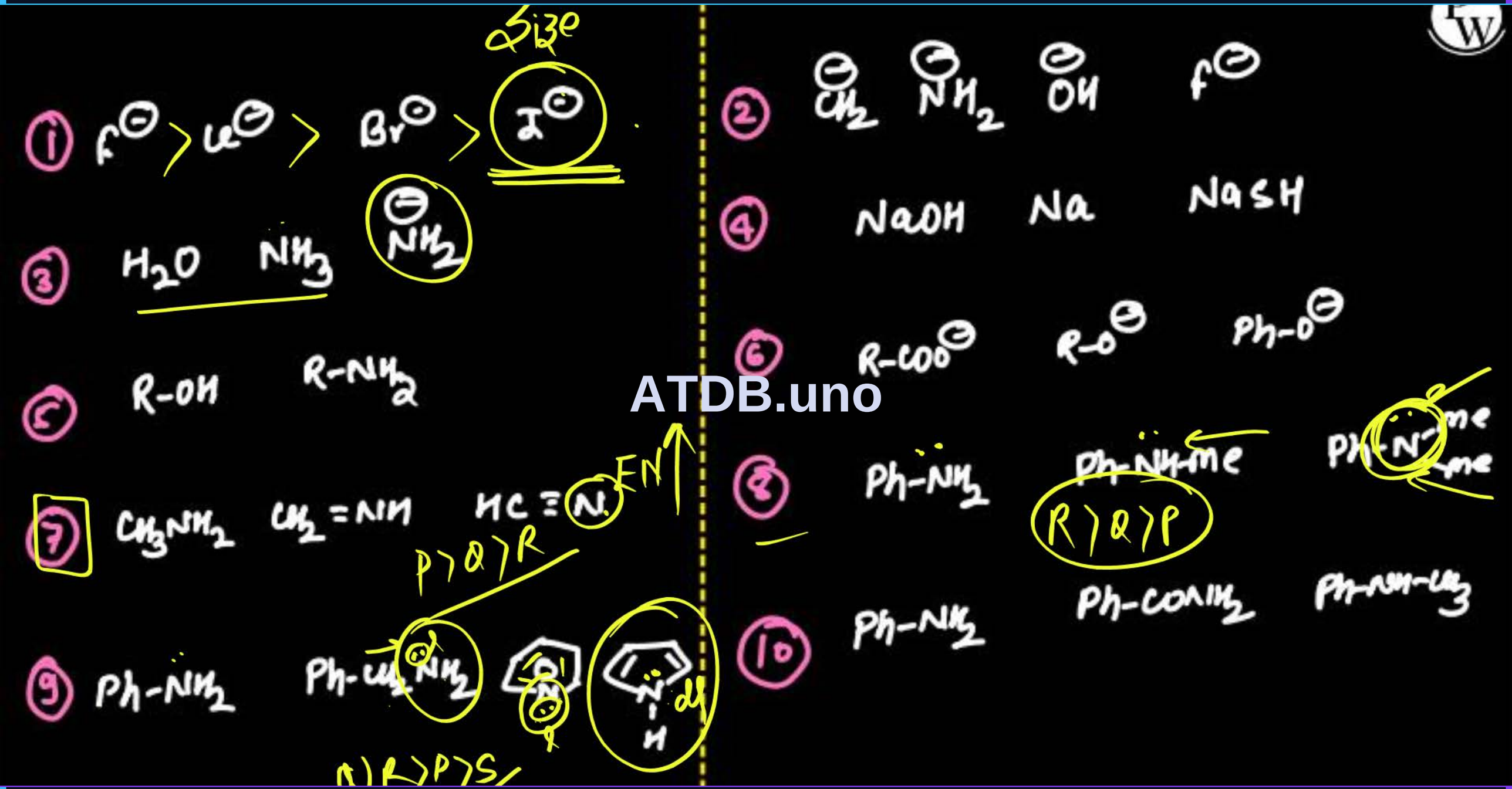
B.T.S.

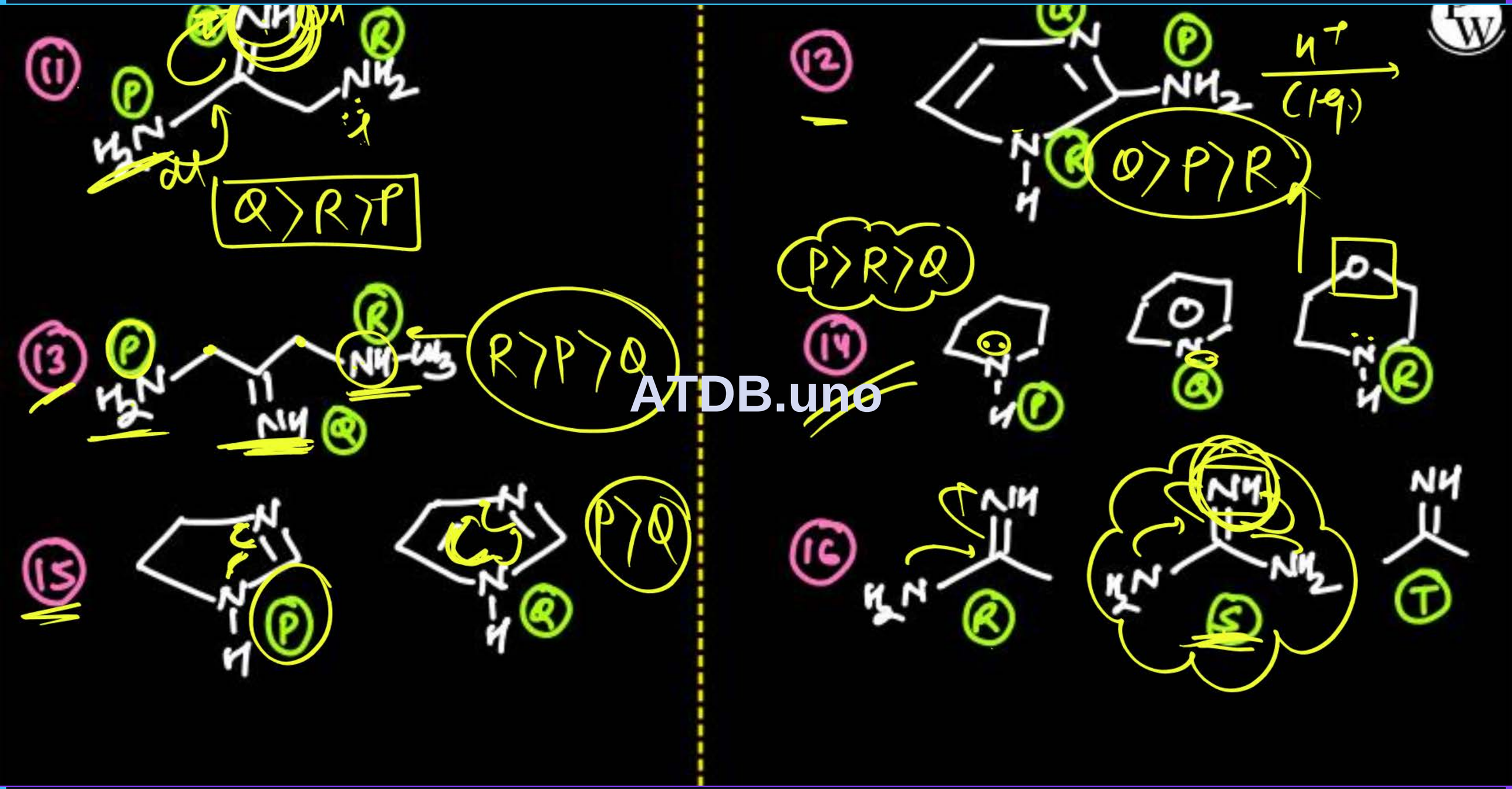
* Ortho substituted aniline are least basic among other isomer. [Solvation Effect]

* As the electron density at donar site increases by +R, +M, +I, Basic strength increases.

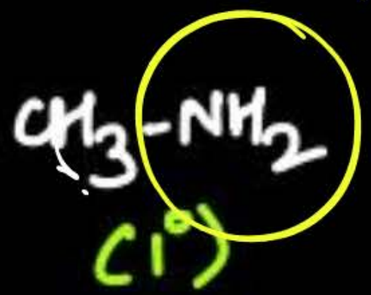
Solvation Effect (SIP)

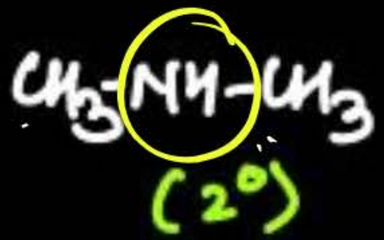


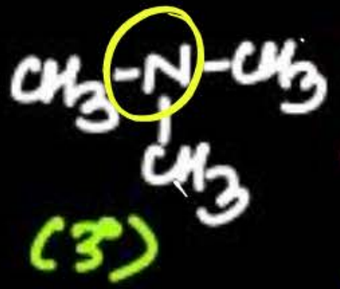




Basic Strength In Water







Gas phase
3 > 2 > 1

Aqueous phase

1° 3°

I ⇒ 3 > 2 > 1

Hbon ⇒ 1 > 2 > 3

⇒ * 2 > 1 > 3 ⇒ Me

* 2 > 3 > 1 ⇒ Et

Practical Organic Chemistry

Solubility Table

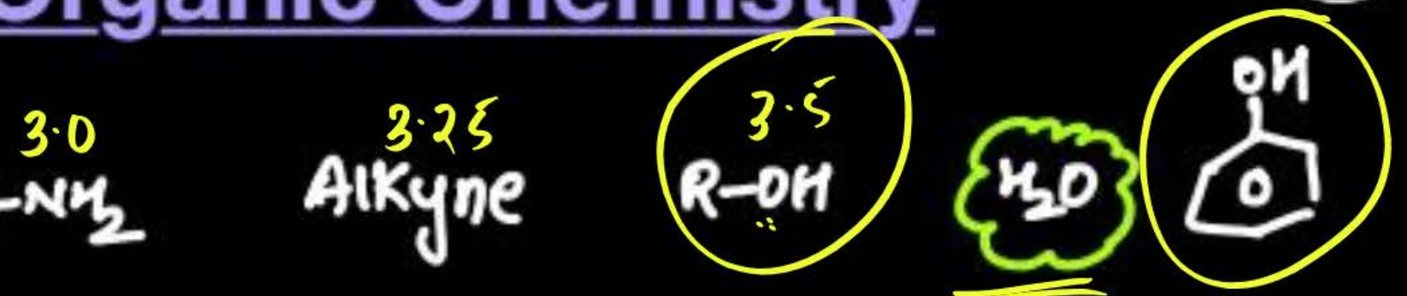
Alkane	Alkene

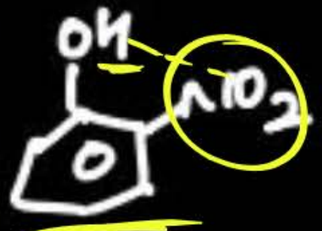
3·0 $R-NH_2$

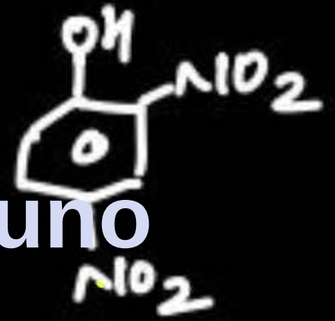
3·25 Alkyne

3·5 R–OH

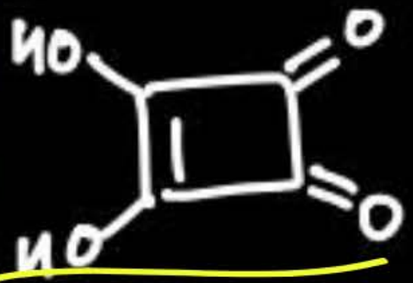
H_2O







R–COOH Ascorbic acid



R–SO_3H Inorganic acids

(HNO$_3$, H_2SO_4, HCl, HBr···)

Solubility in Aq. NaOH

* $HA + NaOH \rightleftharpoons$

* If HA is more acidic than H_2O then reaction will move in forward direction.

* If reaction moves in forward direction then HA will be Soluble in aq. NaOH.

Solubility in Aq. $NaHCO_3$

* $HA + NaHCO_3 \rightleftharpoons$

* If HA is more acidic than H_2CO_3 then reaction will move in forward direction.

* If reaction moves in forward direction then HA will be Soluble in aq. $NaHCO_3$.

Example

Differential Extraction