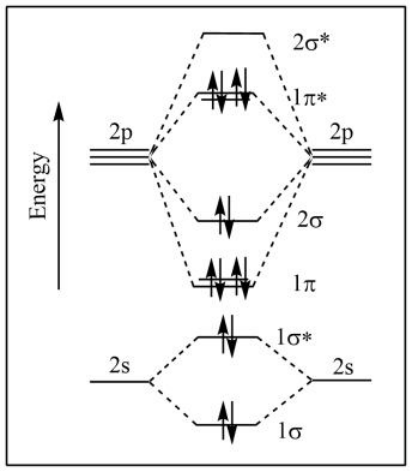
CHEMISTRY

SECTION 1 (Maximum Marks: 12)

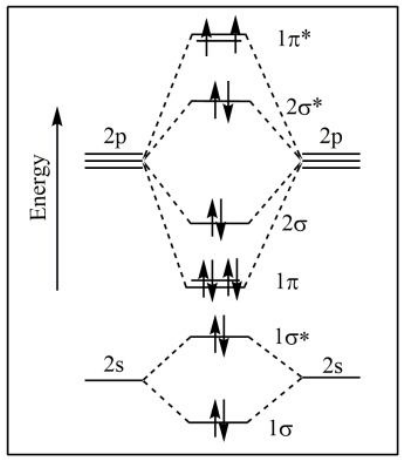
- This section contains **FOUR (04)** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is the
- correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +3 If **ONLY** the correct option is chosen;
  Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered);
  Negative Marks : −1 In all other cases.

*Q. 1 The correct molecular orbital diagram for F_2 molecule in the ground state is

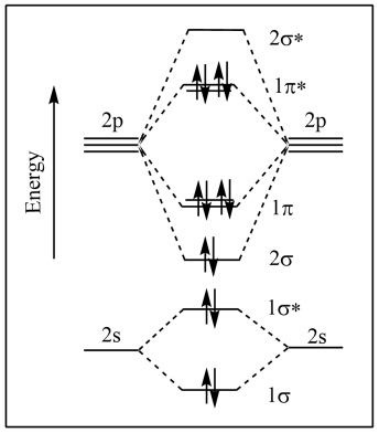
(A)



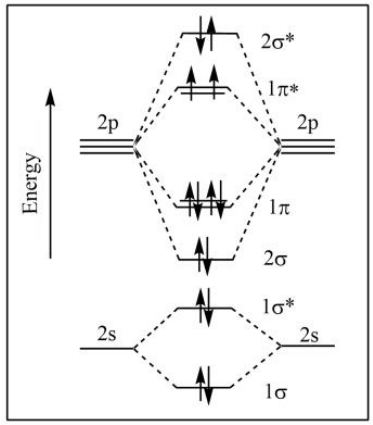
(B)



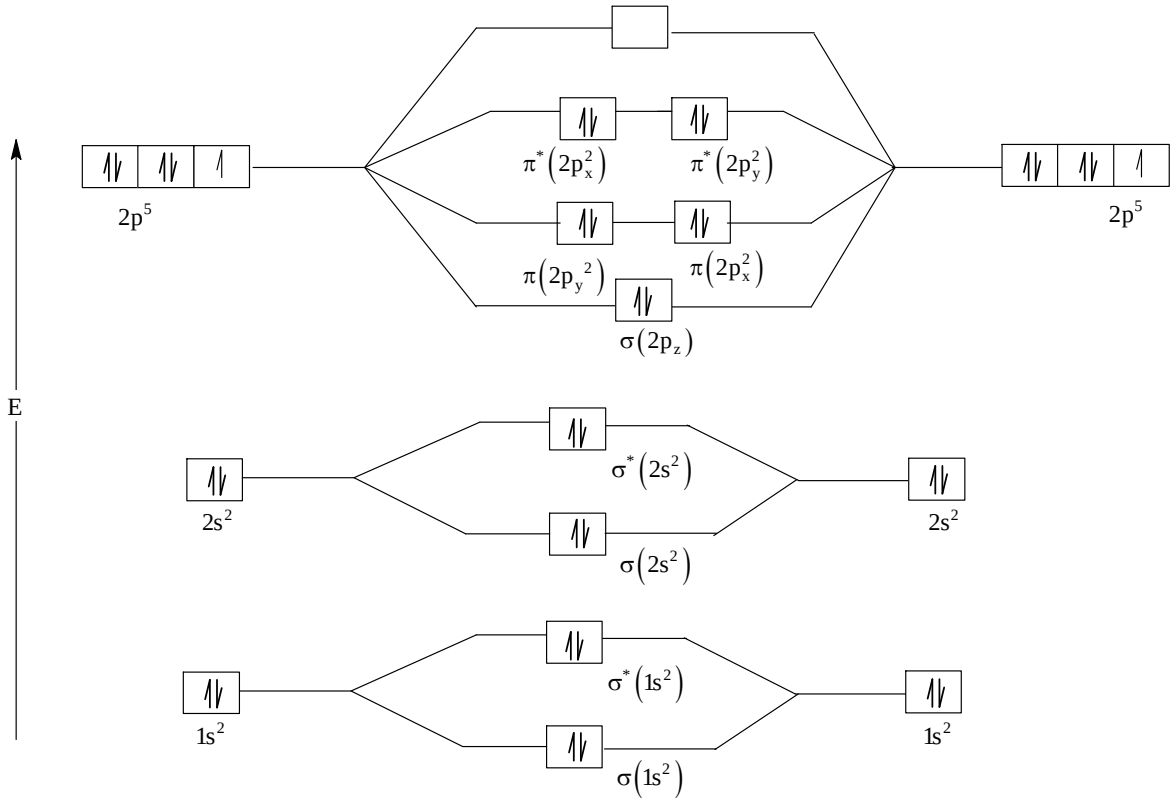
(C)



(D)



Sol. C



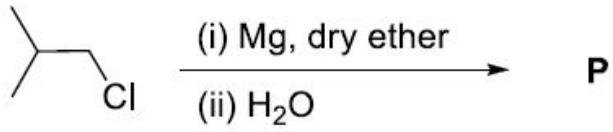
Q. 2 Consider the following statements related to colloids.
(I) Lyophobic colloids are **not** formed by simple mixing of dispersed phase and dispersion medium.
(II) For emulsions, both the dispersed phase and the dispersion medium are liquid.
(III) Micelles are produced by dissolving a surfactant in any solvent at any temperature.
(IV) Tyndall effect can be observed from a colloidal solution with dispersed phase having the same refractive index as that of the dispersion medium.

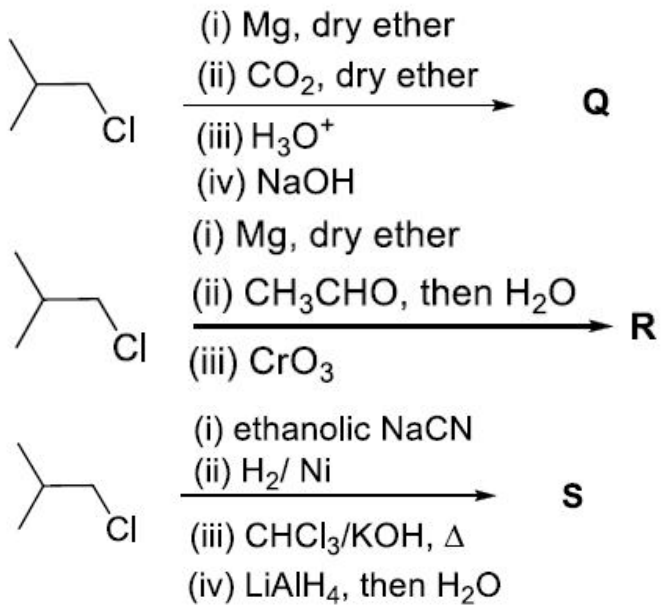
The option with the correct set of statements is

(A) (I) and (II) (B) (II) and (III)
(C) (III) and (IV) (D) (II) and (IV)

Sol. **A**
In tyndall effect, refractive indices of dispersed phase and dispersion medium differ greatly in magnitude.
- Micelles are formed by surfactant at CMC or above CMC and at Kraft temperature or above Kraft temperature.

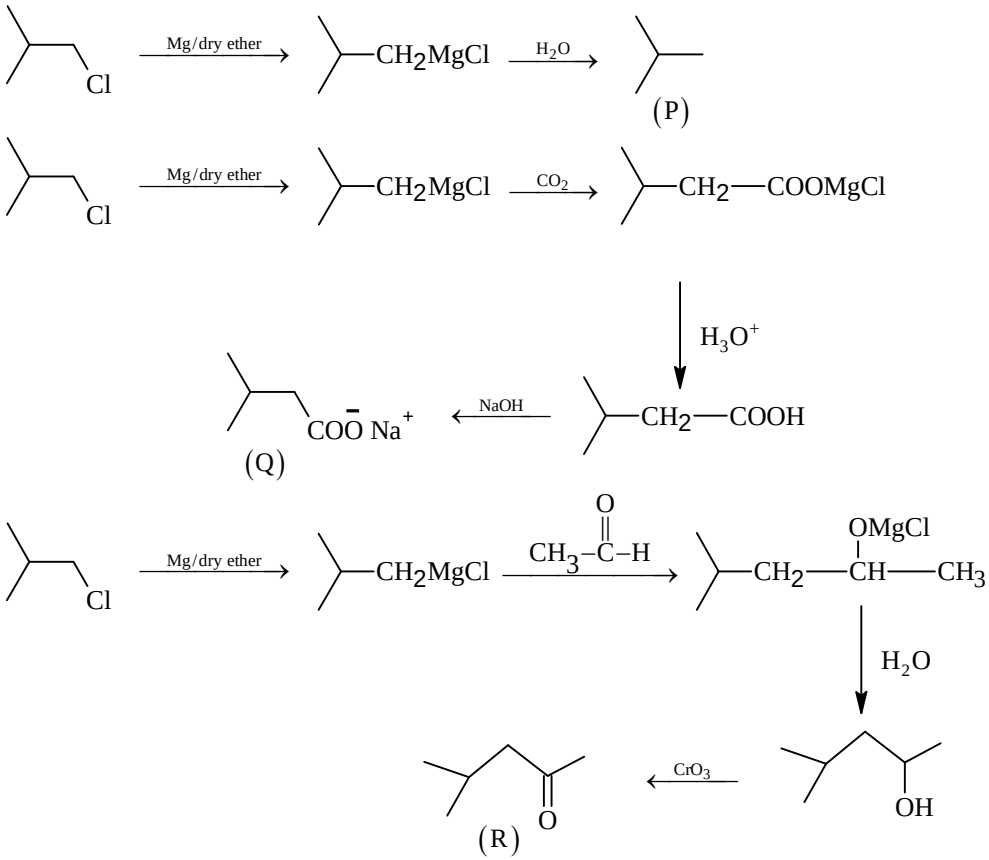
Q. 3 In the following reactions, **P**, **Q**, **R**, and **S** are the major products.

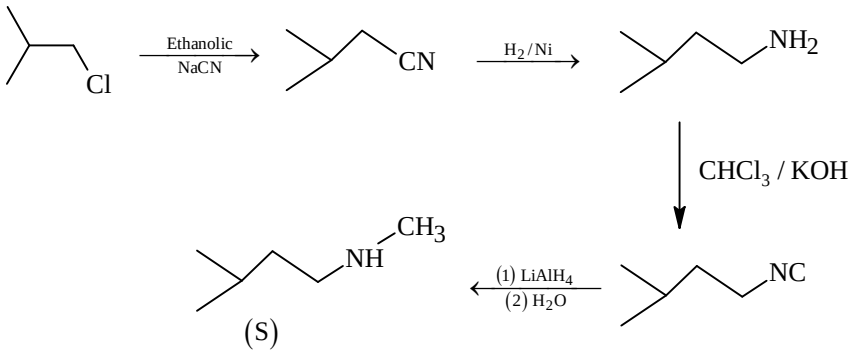




The correct statement about **P**, **Q**, **R**, and **S** is
(A) **P** is a primary alcohol with four carbons.
(B) **Q** undergoes Kolbe's electrolysis to give an eight-carbon product.
(C) **R** has six carbons and it undergoes Cannizzaro reaction.
(D) **S** is a primary amine with six carbons.

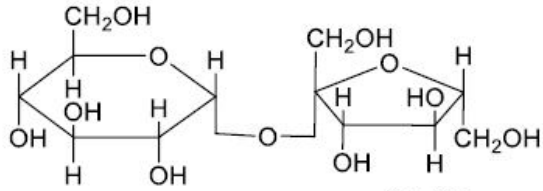
Sol. **B**



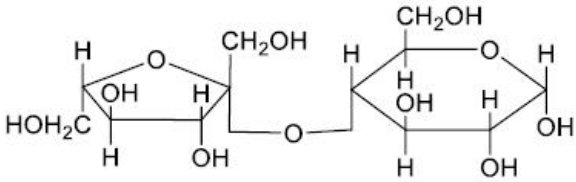


Q.4 A disaccharide **X** cannot be oxidised by bromine water. The acid hydrolysis of **X** leads to a laevorotatory solution. The disaccharide **X** is

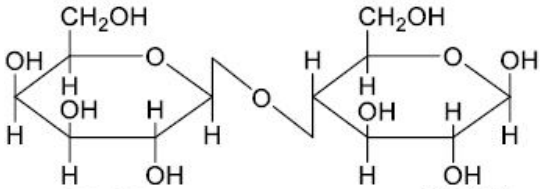
(A)



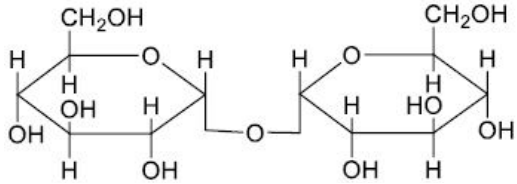
(B)



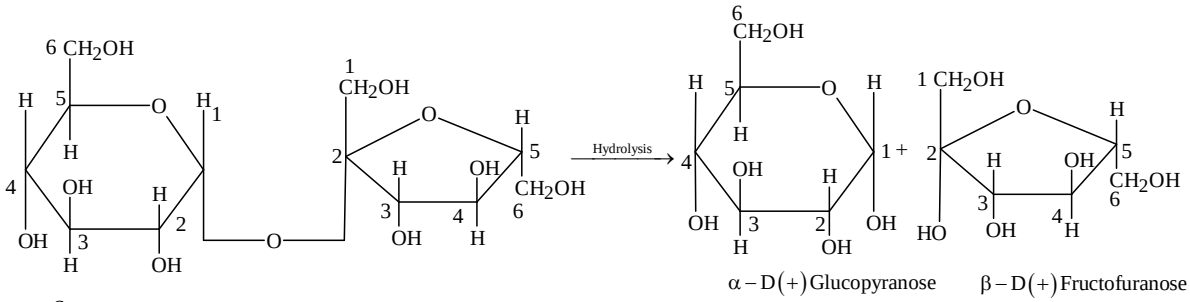
(C)



(D)



Sol. **A**



Sucrose

(dextrorotatory)

Hydrolysis of sucrose brings about a change in the sign of rotation from dextro(+) to laevo(–) and the product named as invert sugar.

SECTION 2 (Maximum Marks: 12)

- This section contains **THREE (03)** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +4 **ONLY** if (all) the correct option(s) is(are) chosen;
  Partial Marks : +3 If all the four options are correct but **ONLY** three options are chosen;
  Partial Marks : +2 If three or more options are correct but **ONLY** two options are chosen, both of which are correct;
  Partial Marks : +1 If two or more options are correct but **ONLY** one option is chosen and it is a correct option;
  Zero Marks : 0 If unanswered;
- *Negative Marks :* −2 In all other cases. · For example, in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answers, then
  choosing ONLY (A), (B) and (D) will get +4 marks;
  choosing ONLY (A) and (B) will get +2 marks;
  choosing ONLY (A) and (D) will get +2marks;
  choosing ONLY (B) and (D) will get +2 marks;
  choosing ONLY (A) will get +1 mark;
  choosing ONLY (B) will get +1 mark;
  choosing ONLY (D) will get +1 mark;
  choosing no option(s) (i.e. the question is unanswered) will get 0 marks and
  choosing any other option(s) will get −2 marks.

Q.5 The complex(es), which can exhibit the type of isomerism shown by $[Pt(NH_3)_2Br_2]$, is(are)
[en = $H_2NCH_2CH_2NH_2$]
(A) $[Pt(en)(SCN)_2]$ (B) $[Zn(NH_3)_2Cl_2]$
(C) $[Pt(NH_3)_2Cl_4]$ (D) $[Cr(en)_2(H_2O)(SO_4)]^+$

Sol. **C, D**

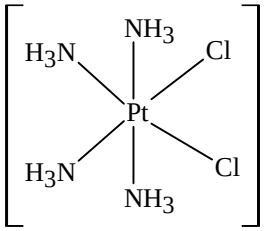
$\left[Pt(NH_3)_2Br_2\right]$ is a square planar complex.

The given compound can show geometrical isomerism (cis-trans form)

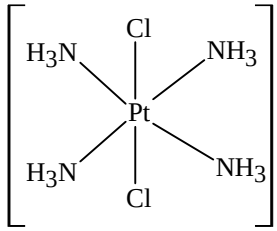
Option (A) : $\left[Pt(en)(SCN)_2\right]$ cannot show geometrical isomerism.

Option (B) : $\left[Zn(NH_3)_2Cl_2\right]$ is a tetrahedral complex, cannot show geometrical isomerism.

Option (C) : $\left[Pt(NH_3)_2Cl_4\right]$ is a octahedral complex, can show geometrical isomerism.

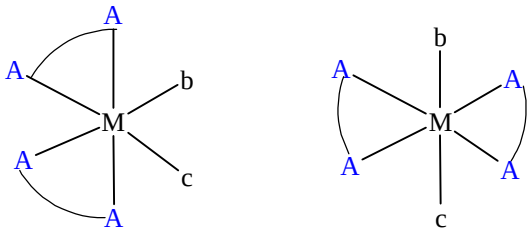


cis – form



trans – form

Option (D) : $\left[Cr(en)_2(H_2O)(SO_4)\right]^+$ is octahedral complex and is of type $\left[M(AA)_2bc\right]$, can show geometrical isomerism.



Q.6 Atoms of metals x, y, and z form face-centred cubic (fcc) unit cell of edge length L_x, body-centred cubic (bcc) unit cell of edge length L_y, and simple cubic unit cell of edge length L_z, respectively.

If $r_z = \frac{\sqrt{3}}{2} r_y$; $r_y = \frac{8}{\sqrt{3}} r_x$; $M_z = \frac{3}{2} M_y$ and $M_Z = 3M_x$,

then the correct statement(s) is(are)

[Given: M_x, M_y, and M_z are molar masses of metals x, y, and z, respectively.
r_x, r_y, and r_z are atomic radii of metals x, y, and z, respectively.]

(A) Packing efficiency of unit cell of x > Packing efficiency of unit cell of y > Packing efficiency of unit cell of z

(B) $L_y > L_z$

(C) $L_x > L_y$

(D) Density of x > Density of y

Sol. **A, B, D**

For metal 'x'

Fcc: Edge length , $a_1 = L_x$

For metal 'y'

Bcc: Edge length , $a_2 = L_y$

For metal 'z'

Bcc: Edge length , $a_3 = L_z$

$$r_z = \frac{\sqrt{3}}{2} r_y, r_y = \frac{8}{\sqrt{3}} r_x, M_z = \frac{3}{2} M_y \text{ and } M_Z = 3M_x$$

For option (A)

(i) For FCC (Z = 4) metal 'x', $4r_x = \sqrt{2}L_x$

$$\text{P.E} = \frac{Z \times \frac{4}{3}\pi(r_x)^3}{a_1^3} = \frac{4 \times \frac{4}{3}\pi(r_x)^3}{(L_x)^3} = \frac{4 \times \frac{4}{3}\pi(r_x)^3}{\left(\frac{4}{\sqrt{2}} r_x\right)^3} = 0.24\pi$$

(ii) For BCC (Z = 2) metal 'y', $4r_y = \sqrt{3}L_y$

$$\text{P.E} = \frac{Z \times \frac{4}{3}\pi(r_y)^3}{a_2^3} = \frac{2 \times \frac{4}{3}\pi(r_y)^3}{(L_y)^3} = \frac{2 \times \frac{4}{3}\pi(r_y)^3}{\left(\frac{4}{\sqrt{3}} r_y\right)^3} = 0.22\pi$$

(iii) For SC (Z = 1) metal 'z', $2r_z = L_z$

$$\text{P.E} = \frac{Z \times \frac{4}{3}\pi(r_z)^3}{a_3^3} = \frac{1 \times \frac{4}{3}\pi(r_z)^3}{(L_z)^3} = \frac{1 \times \frac{4}{3}\pi(r_z)^3}{(2r_z)^3} = \frac{\pi}{6} = 0.17\pi$$

$$(\text{P.E})_{FCC} > (\text{P.E})_{BCC} > (\text{P.E})_{SC}$$

For option (B)

$$4r_y = \sqrt{3}L_y \qquad 2r_z = L_z$$

$$L_y = \frac{4r_y}{\sqrt{3}}$$

$$\frac{L_y}{L_z} = \frac{4r_y}{\sqrt{3}\times 2r_z} = \frac{2r_y}{\sqrt{3}r_z} = \frac{2r_y}{\sqrt{3}.\frac{\sqrt{3}}{2}r_y} = \frac{4}{3}$$

So, $L_y > L_z$

For option (C)

$$4r_x = \sqrt{2}L_x \text{ , } 4r_y = \sqrt{3}L_y$$

$$L_x = \frac{4r_x}{\sqrt{2}},\ L_y = \frac{4r_y}{\sqrt{3}}$$

$$\frac{L_x}{L_y} = \frac{\sqrt{3}r_x}{\sqrt{2}\times 8/\sqrt{3}r_x} = \frac{3}{8\sqrt{2}}$$

So, $L_x < L_y$ **incorrect**

For option (D)

$$d_x = \frac{4\times M_x}{\left(\frac{4r_x}{\sqrt{2}}\right)^3 \times N_A}$$

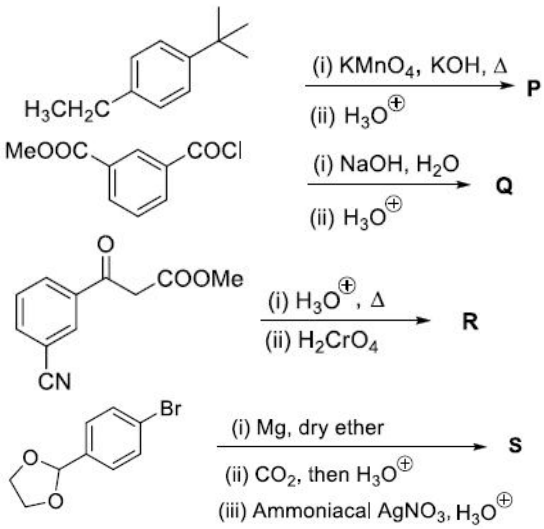
$$d_y = \frac{2\times M_y}{\left(\frac{4r_y}{\sqrt{3}}\right)^3 \times N_A}$$

$$r_y = \frac{8}{\sqrt{3}}r_x,\ \frac{M_x}{M_y} = \frac{1}{2}$$

$$\frac{d_x}{d_y} = \frac{512}{2\sqrt{2}} = \frac{256}{\sqrt{2}}$$

So $d_x > d_y$ (correct)

Q.7 In the following reactions, **P**, **Q**, **R**, and **S** are the major products.



The correct statement(s) about **P**, **Q**, **R**, and **S** is(are)

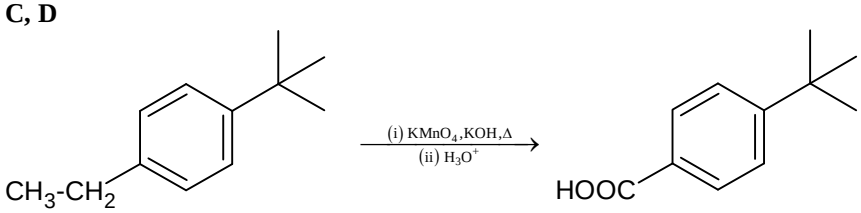
(A) **P** and **Q** are monomers of polymers dacron and glyptal, respectively.

(B) **P**, **Q**, and **R** are dicarboxylic acids.

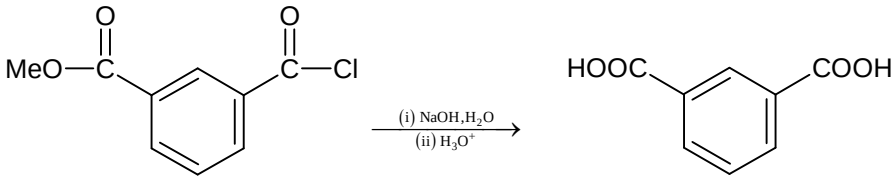
(C) Compounds **Q** and **R** are the same.

(D) **R** does **not** undergo aldol condensation and **S** does **not** undergo Cannizzaro reaction.

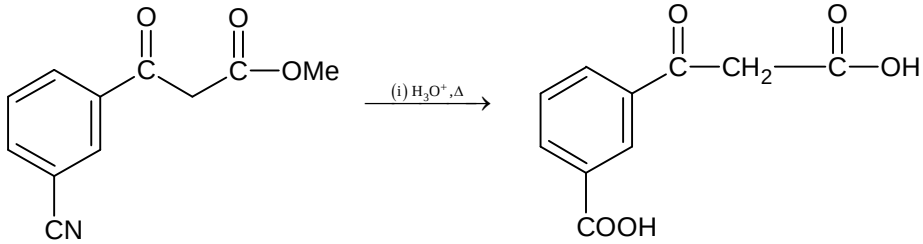
Sol. **C, D**

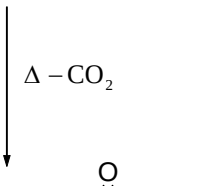


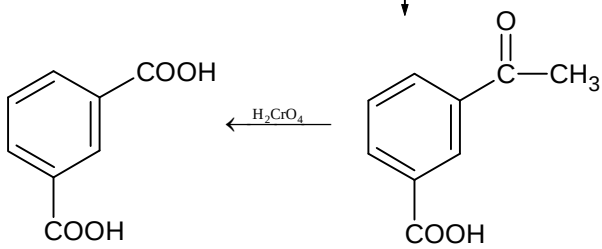
(P)



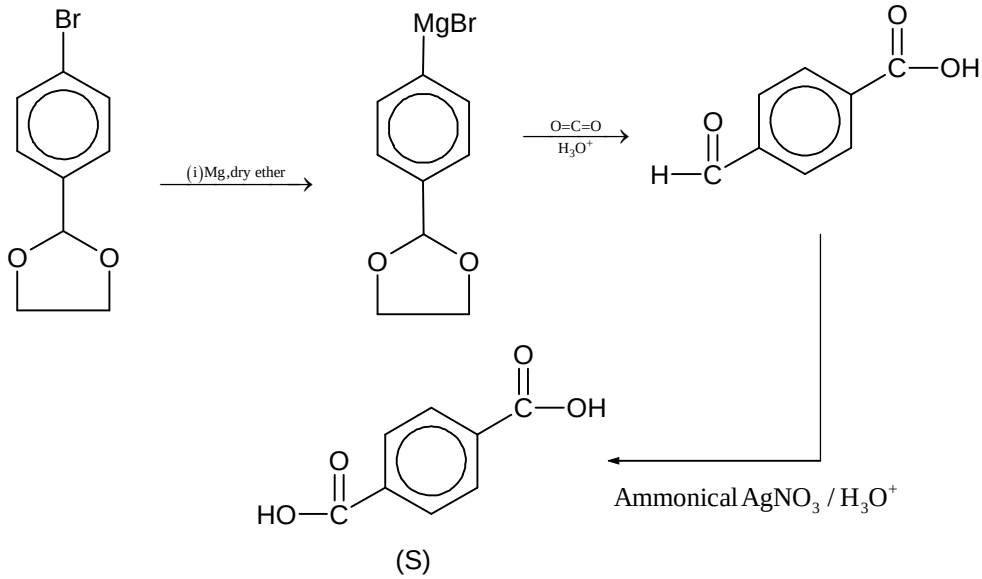
(Q)







(R)



(S)

SECTION 3 (Maximum Marks: 24)

- This section contains **SIX (06)** questions.
- The answer to each question is a **NON-NEGATIVE INTEGER**.
- For each question, enter the correct integer corresponding to the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +4 If **ONLY** the correct integer is entered;
  Zero Marks : 0 In all other cases.

*Q.8 H_2S (5 moles) reacts completely with acidified aqueous potassium permanganate solution. In this reaction, the number of moles of water produced is **x**, and the number of moles of electrons involved is **y**. The value of (**x** + **y**) is ____.

Sol. **18**

$$\left(8H^+ + MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O\right)\times 2$$

$$\left(H_2S \longrightarrow S + 2H^+ + 2e^-\right)\times 5$$

$$2MnO_4^- + 16H^+ + 5H_2S \longrightarrow 2Mn^{2+} + 5S + 10H^+ + 8H_2O$$

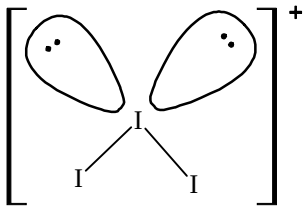
$$2MnO_4^- + 6H^+ + 5H_2S \longrightarrow 2Mn^{2+} + 5S + 8H_2O$$

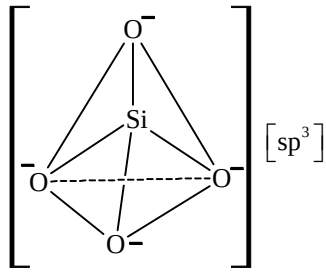
x = 8

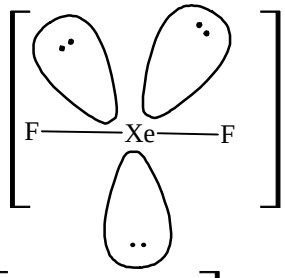
y = 10

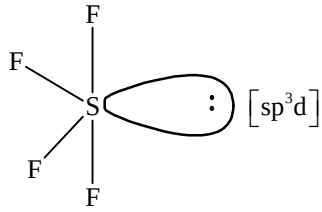
Q.9 Among $[I_3]^+$, $[SiO_4]^{4-}$, SO_2Cl_2, XeF_2, SF_4, ClF_3, $Ni(CO)_4$, XeO_2F_2, $[PtCl_4]^{2-}$, XeF_4, and $SOCl_2$, the total number of species having sp^3 hybridised central atom is _____.

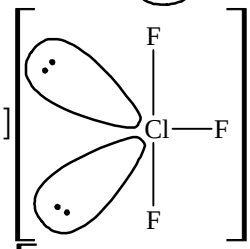
Sol. **5**

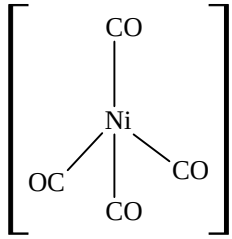
I_3^+  $[sp^3]$

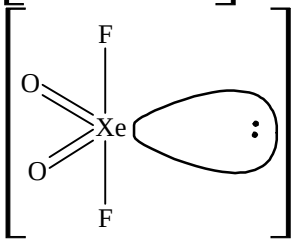
$[SiO_4]^{4-}$  $[sp^3]$

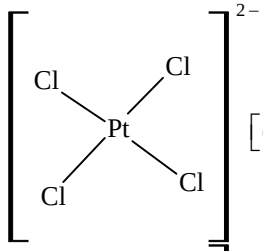
$[XeF_2]$  $[sp^3d]$

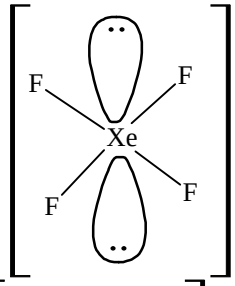
$[SF_4]$  $[sp^3d]$

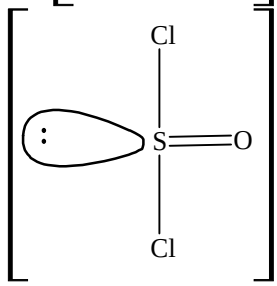
$[ClF_3]$  $[sp^3d]$

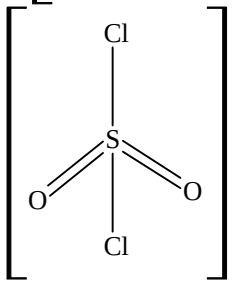
$[Ni(CO)_4]$  $[sp^3]$

$[XeO_2F_2]$  $[sp^3d]$

$[PtCl_4]^{2-}$  $[dsp^2]$

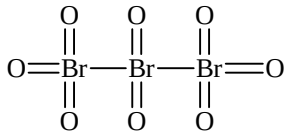
$[XeF_4]$  $[sp^3d^2]$

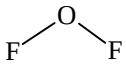
$[SOCl_2]$  $[sp^3]$

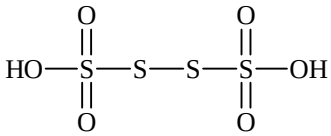
$[SO_2Cl_2]$  $[sp^3]$

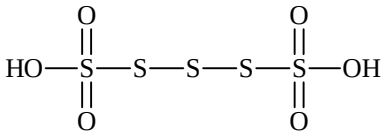
*Q.10 Consider the following molecules: Br_3O_8, F_2O, $H_2S_4O_6$, $H_2S_5O_6$, and C_3O_2.
Count the number of atoms existing in their zero oxidation state in each molecule.
Their sum is____.

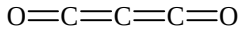
Sol. **06**

(i) 

(ii) 

(iii) 

(iv) 

(v) 

Total number of atoms having zero oxidation state = **6.**

*Q.11 For He^+, a transition takes place from the orbit of radius 105.8 pm to the orbit of radius 26.45 pm. The wavelength (in nm) of the emitted photon during the transition is ___.
[Use:
Bohr radius, a = 52.9 pm
Rydberg constant, $R_H = 2.2\times10^{-18}$ J
Planck's constant, h = 6.6×10^{-34} J s
Speed of light, c = 3×10^8 m s^{-1}]

Sol. **30**

$$r_n = \frac{52.9\times n^2}{Z}\text{pm}$$

$$105.8 = \frac{52.9\times n_1^2}{2} \qquad \therefore n_1^2 = 4,\ n_1 = 2$$

$$26.45 = \frac{52.9\times n_2^2}{2} \qquad \therefore n_2 = 1$$

$$\frac{1}{\lambda} = 109677\times 4\times\frac{3}{4}$$

$$\lambda = \frac{4}{109677\times 4\times 3}\text{cm}$$

$$= \frac{10^7}{109677\times 3} = \frac{10^7}{329031}\text{nm}$$

λ = 30.3 nm ≈ 30 nm

Q.12 50 mL of 0.2 molal urea solution (density = 1.012 g mL^{-1} at 300 K) is mixed with 250 mL of a solution containing 0.06 g of urea. Both the solutions were prepared in the same solvent. The osmotic pressure (in Torr) of the resulting solution at 300 K is ___.
[Use: Molar mass of urea = 60 g mol^{-1}; gas constant, R = 62 L Torr K^{-1} mol^{-1} ;
Assume, $\Delta_{mix}H = 0$, $\Delta_{mix}V = 0$]

Sol. **682**

0.2 molal means 0.2 moles in 1000 g of solvent.

Volume = $\frac{M}{d}$

Mass of solution = 1012 g

Volume = $\frac{1012\text{g}}{1.012\text{ g ml}^{-1}}$

V = 1000.00 ml

1000.00 ml $\longrightarrow$ 0.2 moles

50 ml of solution $= \frac{0.2}{1000} \times 50$ moles

n_{urea} = 0.01 moles

In 2nd solution:

$n_{urea} = \frac{0.06}{60} = 0.001$

Final molarity (M) = $\frac{n_1 + n_2}{V_1 + V_2} = \frac{0.01 + 0.001}{\frac{(50+250)}{1000}}$

$M = \frac{11}{300}$

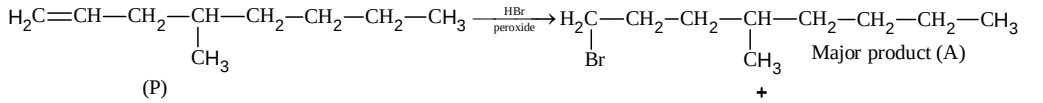
$\pi = CRT$

$= \frac{11}{300} \times 62 \times 300$

= 682 torr

Q.13 The reaction of 4-methyloct-1-ene (**P**, 2.52 g) with HBr in the presence of $(C_6H_5CO)_2O_2$ gives two isomeric bromides in a 9 : 1 ratio, with a combined yield of 50%. Of these, the entire amount of the primary alkyl bromide was reacted with an appropriate amount of diethylamine followed by treatment with aq. K_2CO_3 to give a non-ionic product **S** in 100% yield.
The mass (in mg) of **S** obtained is ___.
[Use molar mass (in g mol^{-1}): H = 1, C = 12, N = 14, Br = 80]

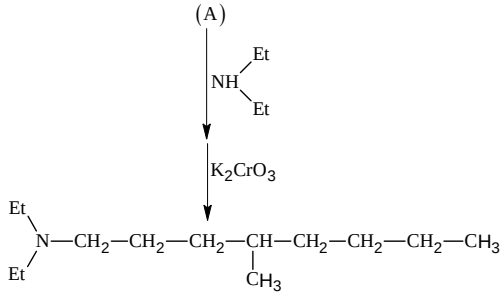
Sol. **1791**



(P)

Moles of P $= \frac{2.52}{126} = 0.02$ mole

Moles of A $= 0.02 \times \frac{9}{10} \times \frac{50}{100} = 0.009$ mole



$\Rightarrow 0.009 \times 199 = 1.791$ g

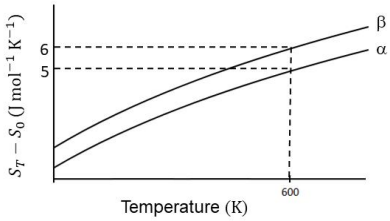
= 1791 mg

SECTION 4 (Maximum Marks: 12)

- This section contains **TWO (02)** paragraphs.
- Based on each paragraph, there are **TWO (02)** questions.
- The answer to each question is a **NUMERICAL VALUE.**
- For each question, enter the correct numerical value of the answer using the mouse and the onscreen virtual numeric keypad in the place designated to enter the answer.
- If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +3 If ONLY the correct numerical value is entered in the designated place;
  Zero Marks : 0 In all other cases.

"PARAGRAPH I"

The entropy versus temperature plot for phases α and β at 1 bar pressure is given.
S_T and S_0 are entropies of the phases at temperatures T and 0 K, respectively.



The transition temperature for α to β phase change is 600 K and $C_{p,\beta} - C_{p,\alpha}$ = 1 J mol^{-1} K^{-1}. Assume ($C_{p,\beta} - C_{p,\alpha}$) is independent of temperature in the range of 200 to 700 K. $C_{p,\alpha}$ and $C_{p,\beta}$ are heat capacities of α and β phases, respectively.

*Q.14 The value of entropy change, $S_\beta - S_\alpha$ (in J mol^{-1} K^{-1}), at 300 K is ___.
[Use: ln2 = 0.69
Given: $S_\beta - S_\alpha$ = 0 at 0 K]

Sol. **0.31**

$$S = S_0 + \int C_p \frac{dT}{T}$$

$$S_\alpha = S_0 + \int (C_p)_\alpha \frac{dT}{T}$$

$$S_\beta = S_0 + \int (C_p)_\beta \frac{dT}{T}$$

$$S_\beta - S_\alpha = \left[(C_p)_\beta - (C_p)_\alpha\right] \int \frac{dT}{T}$$

Given $C_{P_\beta} - C_{P_\alpha} = 1$

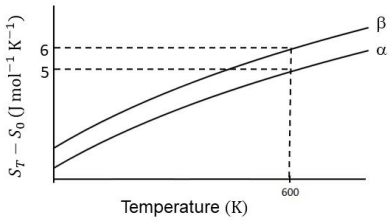
$S_\beta - S_\alpha = \ln T + C$ at any temperature T.

$$(S_\beta - S_\alpha)_{T_2} - (S_\beta - S_\alpha)_{T_1} = \ln T_2 - \ln T_1$$

T_2 = 600 K, T_1 = 300 K, from the graph $S_\beta - S_\alpha$ at 600°C = 1
$(1) - (S_\beta - S_\alpha)_{300} = \ln 600 - \ln 300$
$1 - (S_\beta - S_\alpha)_{300} = \ln 2 = 0.69$
$\Rightarrow (S_\beta - S_\alpha)_{300} = 1 - 0.69$
= 0.31

"PARAGRAPH I"

The entropy versus temperature plot for phases α and β at 1 bar pressure is given.
S_T and S_0 are entropies of the phases at temperatures T and 0 K, respectively.



The transition temperature for α to β phase change is 600 K and $C_{p,\beta} - C_{p,\alpha}$ = 1 J mol^{-1} K^{-1}. Assume ($C_{p,\beta} - C_{p,\alpha}$) is independent of temperature in the range of 200 to 700 K. $C_{p,\alpha}$ and $C_{p,\beta}$ are heat capacities of α and β phases, respectively.

*Q.15 The value of enthalpy change, $H_\beta - H_\alpha$ (in J mol^{-1}), at 300 K is ___.

Sol. 300

Transition : $\alpha \rightleftharpoons \beta$; $\Delta G = 0$

So, $\Delta H = T\Delta S$

$\Delta H_{600} = 600 \times 1 \quad \because \Delta S = 1$

$= 600$ J mol^{-1}

From Krichoff's law

$$\Delta C_p = \frac{\Delta H_{600} - \Delta H_{300}}{600 - 300}$$

$$1 = \frac{600 - \Delta H_{300}}{300}$$

$\Delta H_{300} = 300$ J mol^{-1}

"PARAGRAPH II"

A trinitro compound, 1,3,5-tris-(4-nitrophenyl)benzene, on complete reaction with an excess of Sn/HCl gives a major product, which on treatment with an excess of $NaNO_2$/HCl at 0°C provides **P** as the product. **P**, upon treatment with excess of H_2O at room temperature, gives the product **Q**. Bromination of **Q** in aqueous medium furnishes the product **R**. The compound **P** upon treatment with an excess of phenol under basic conditions gives the product **S**.

The molar mass difference between compounds **Q** and **R** is 474 g mol^{-1} and between compounds **P** and **S** is 172.5 g mol^{-1}.

Q.16 The number of heteroatoms present in one molecule of **R** is _____ .
[Use: Molar mass (in g mol–1): H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5
Atoms other than C and H are considered as heteroatoms]

Sol. 9

"PARAGRAPH II"

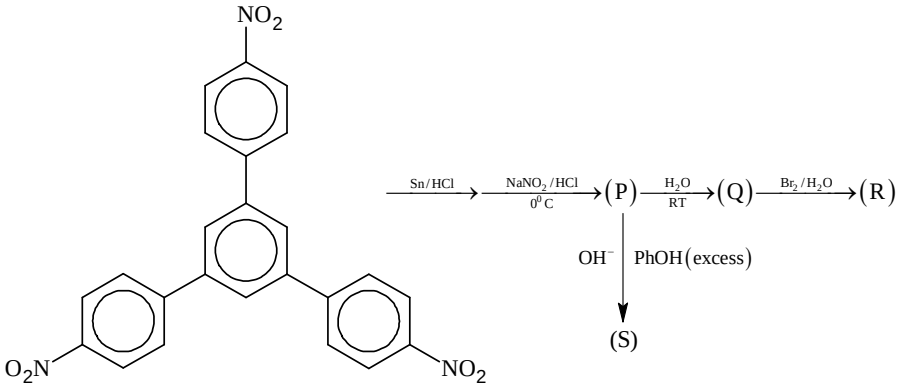
A trinitro compound, 1,3,5-tris-(4-nitrophenyl)benzene, on complete reaction with an excess of Sn/HCl gives a major product, which on treatment with an excess of $NaNO_2$/HCl at 0^oC provides **P** as the product. **P**, upon treatment with excess of H_2O at room temperature, gives the product **Q**. Bromination of **Q** in aqueous medium furnishes the product **R**. The compound **P** upon treatment with an excess of phenol under basic conditions gives the product **S**.

The molar mass difference between compounds **Q** and **R** is 474 g mol^{-1} and between compounds **P** and **S** is 172.5 g mol^{-1}.

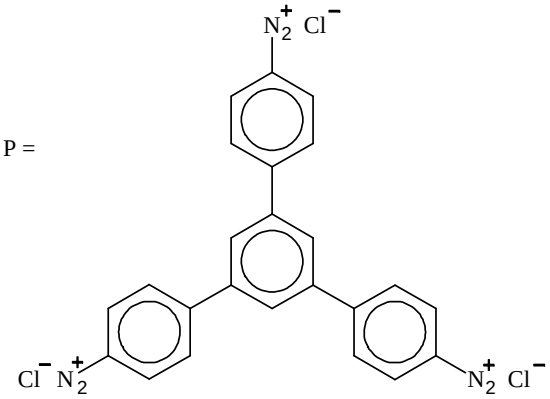
Q.17 The total number of carbon atoms and heteroatoms present in one molecule of **S** is _____ .
[Use: Molar mass (in g mol^{-1}): H = 1, C = 12, N = 14, O = 16, Br = 80, Cl = 35.5
Atoms other than C and H are considered as heteroatoms]

Sol. 51

Solution for the Q. No. 16 & 17.



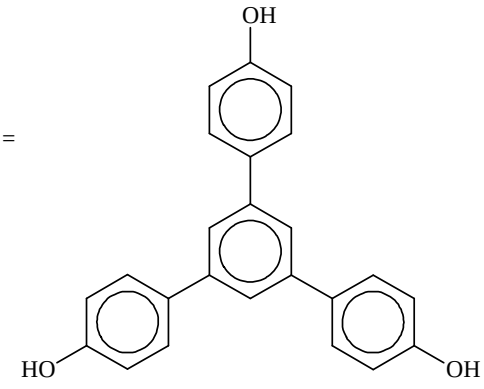
P =



$(C_{24}H_{15}N_6Cl_3)$

493.5 g mol^{-1}

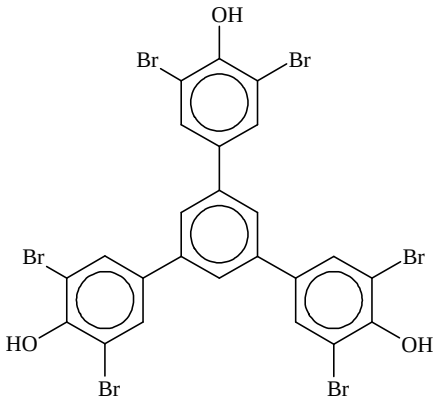
Q =



$(C_{24}H_{18}O_3)$

354 g mol^{-1}

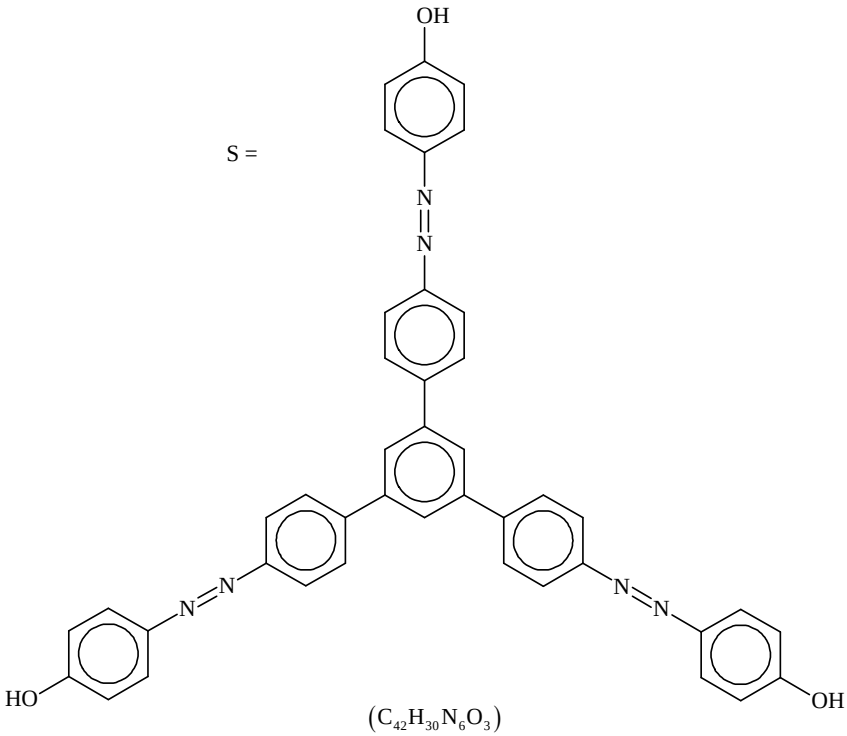
R =



$(C_{24}H_{12}Br_6O_3)$

828 g mol^{-1}

S =



$(C_{42}H_{30}N_6O_3)$

666 g mol^{-1}