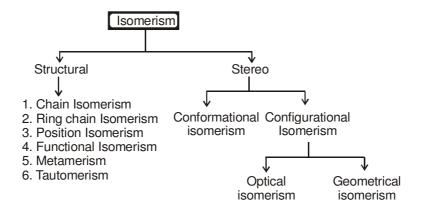
ISOMERISM

Page # 3

ISOMERISM

DEFINATION: Compounds having same molecular formula (M.F.) but differ in thier properties are known as **isomers** and this phenomenon is known as **isomerism.**

CLASSIFICATION:



STRUCTURAL ISOMERISM: Compounds having same M.F. and different in connectivity of atom (Structure is different)

CHAIN ISOMERISM

Compounds having same molecular formula but differing in the length of the principal chain.

e.g.1
$$CH_3 - CH_2 - CH_2 - CH_3$$
 butane (n - butane)

and

$$H_3C-CH-CH_3$$
 2-methylpropane (Isobutane) CH_3

e.g.2
$$CH_3 - CH_2 - CH_2 - COOH$$
 butanoic acid

anc

2-methylpropanoic acid

e.g. Isoheptane

$$\begin{array}{c} \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{CH}_3 \\ | \\ \operatorname{CH}_3 \end{array}$$

* Isooctane (exception of Iso group)

$$\begin{array}{ccc} {\sf CH_3} & {\sf CH_3} \\ | & | \\ {\sf H_3C-C-CH_2-CH-CH_3} \\ | & {\sf CH_3} \end{array}$$

Motion Introduction

Nurturing potential through education

- * Neo group H₃C C –
- * To prepare the neo compound firstly the above group (H_3C-C-) is written. After that required no. of carbon is added in the straight chain. e.g. neopentane

$$\begin{array}{c}\mathsf{CH_3}\\|\\\mathsf{H_3C-C-CH_3}\\|\\\mathsf{CH_3}\end{array}$$

neoheptane

$$CH_3$$

 $CH_3 - C - CH_2 - CH_2 - CH_3$
 CH_3

Alkyl Group:

$$\begin{array}{ccc} C_n H_{2n+2} & \stackrel{-H}{---} & C_n H_{2n+1} \\ \text{Alkane} & \text{Alkyl group} \end{array}$$

$$CH_{4} \xrightarrow{-H} CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{2} - CH_{3} - CH_{3}$$

dark line (-) represents vacant valency where any group can be attached.

(Iso propyl alcohol)

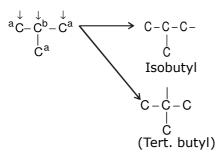
Thus we can conclude that

 $C_3H_7 - \rightarrow \text{Two forms.}$

* C₄H₁₀

$$\downarrow \downarrow \downarrow \downarrow \downarrow \\
C-C-C-C-C \\
a b b a$$

$$C-C-C-C-C \\
n-butyl \\
C-C-C-C \\
| (sec. butyl)$$



- * $C_4H_9 = 4$ forms.
- * C_5H_{12} has it's three forms C-C-C-C-C

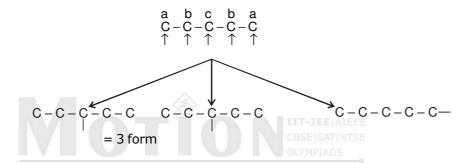
n-pentane

$$\begin{array}{c} C \\ C \\ C \end{array}$$

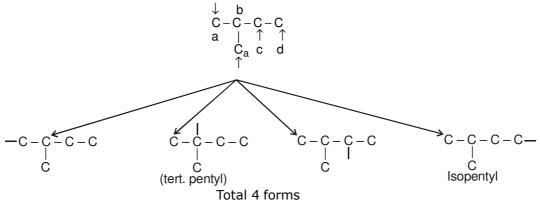
Isopentane

$$\begin{array}{c} C \\ C - C - C \\ C \end{array}$$
 Neopentane

* Consider n-pentane



Nurtur Consider Isopentan rough education



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Consider neopentane

$$\begin{array}{ccc}
 & \rightarrow & C^{a} \\
\downarrow & & | \\
 & \downarrow & C - C - C^{a} \\
 & \downarrow & \uparrow \\
 & \downarrow & C \leftarrow
\end{array}$$

= only one form.

Total forms of $C_5H_{11} - = 8$

Ex.1 Find all the structural isomers of C₆H₁₄

POSITION ISOMERISM

Compound having same molecular formula and same principal chain but differ in position of functional group, multiple bond and substitution group are known as position isomers.

$$C - C - C = C$$

and

$$C - C = C - C$$

1-butene

2-butene

e.g.

and

ISOMERISM

1-chloropropane

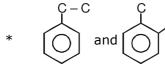
2-chloropropane

e.g.

$$CH_3 - CH_2 - CH_2 - OH$$
 and

1-propanol

2-propanol



VIOTION VIOLEN

The above example can be best understood taking the following example

are chain isomer, not position isomer.

$$C-C-C$$
 and $N_C^3 + C^2 + C^4$ potential through education

In this the last carbon has been placed to IInd position to form chain isomer the same has happier with above example and hence they are chain isomer to each other.

Ex.2 Find the relation between the given compounds

Sol. a, b \longrightarrow chain isomers.

b, $c \longrightarrow position isomers$.

c, $d \longrightarrow$ chain isomers.

d, $e \longrightarrow position isomers$.

* Monochlorination \longrightarrow Replace one H by Cl

Ex.3 How many monochloro derivative will be of C₄H₁₀ (Only structural)

Sol.
$$C_4H_{10} \xrightarrow{CI_2/hv} C_4H_9CI$$

4 forms (product)

Ex.4 An alkane having molecular formula C_5H_{12} can give only one product on monochlorination. Find the IUPAC name of the alkane

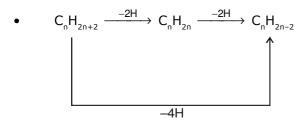
Sol.

(2, 2-dimethyl pentane)

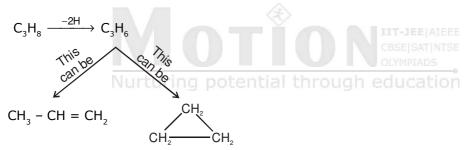
Ex.5 $C_5H_{10} \xrightarrow{\text{Cl}_2}$ Single product (monochlorination)

what is the structure of C_5H_{10} .

Sol. Cyclopentane



e.g.



Page # 8 ISOMERISM

Ex.6 Find the total structural isomer of C_5H_{10} .

Sol. For solving these kinds of problem we should at once draw all possible structure of corresponding alkane and then we should check how many possibilities are there to put double bond.

$$C-C-C-C-C = 2$$

$$\begin{array}{ccc}
\downarrow & \downarrow \\
C - C - C - C &= 3
\end{array}$$

$$C$$
 C $-C$ no double bond can be placed in this compound as valency of C will exceeds from 4 C

Total open chain structural isomers = 5

* To form cyclic structural we should always start with 3 carbon ring.











total structural isomers = 5 + 5 = 10

Ex.7 Find the total structural isomers of C_aH_6 .

Sol. Total unsaturation of $C_4H_6 = 2$

i.e. possibility = one triple bond, or 2 double bond or (one ring + one double bond)

 $\downarrow \downarrow$ C-C-C-C (\downarrow indicate possible position of triple bond)

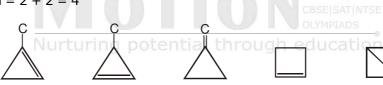
$$C - C - C \rightarrow \{\text{No triple bond}\}\$$

for alkene,

$$C-C=C=C\\C=C-C=C$$

total open chain = 2 + 2 = 4

for cyclic



total structural isomers (cyclic + acyclic) = 9

Ex.8 $C_3H_8 \xrightarrow{mono} ?$ (Only structural in all)

dichlorination →?

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ISOMERISM

Page # 9

Sol. For monochloroderivative,

$$C - C - C - CI$$

$$C - C - C$$

di-chloroderivative

(1)
$$C-C-C < CI$$
 (2) $C-C-C-CI$ (3) $C-C-C-CI$ (4) $C-C-CI$ (7) CI CI

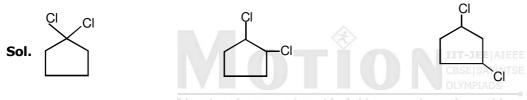
Total dichloroderivative = 4

Trichloroderivative,

* To find di or trichloroderivative

We place two or three chlorine at last carbon and after that rotate one Cl by keeping the other two at the same the place.

Ex.9 Find all the structural dichloroderivative of cyclopentane.



Total structural isomer = 3 Uring potential through education

FUNCTIONAL ISOMERISM

Compound having same molecular formula but different in functional group are known as functional isomers.

Motion (in the plane)
Nurturing potential through education

Page # 10 **ISOMERISM**

$$C_3H_6O$$
 $CH_3 - CH_2$ CHO

$$CH_3 - C - CH_3$$
 $CH_2 = CH - CH_2OH$

$$CH_2 = CH - CH_2OH$$

$$CH_3 - CH - CH_2$$
 OH

- Aldehyde, Ketone, cyclic ethers, cyclic alcohol, unsaturated alcohol etc are functional isomers to each
- Alcohol and ether functional isomers to each other. e.g. CH₃CH₂OH, CH₃OCH₃
- Acids and ester are functional isomers to each other.

O
$$\parallel$$
 eg. $H-C-O-CH_3$ and CH_3COOH

- Cyanide and Isocyanide are functional isomer to each other but HCN and HNC are tautomers to each
- 1°, 2° and 3° amine are functional isomer to each other.

How many primary, secondary and tertiary alcohol are possible for C5H,3O? (Only struc-Ex.10 tural)

Sol. For 1° alcohol (-CH,OH)

$$C_5H_{12}OH \Rightarrow C_4H_9 - CH_2 - OH$$
 (4 form)

OH OH oH for 2° alcohol (–CH–)
$$\rightarrow$$
 C_3H_7 – CH – CH $_3$ (2 form) Replace one C

OH
$$\mid$$
CH $_3$ – CH $_2$ – CH – CH $_2$ CH $_3$ (1 form)

total = 3

for 3° alcohol
$$\begin{pmatrix} OH & OH & OH & OLYMPIADS \\ -C-CH_3-C-CH_2CH_3 = 1 & Table 1 & Table 2 & Table 2 & Table 2 & Table 3 & Table 2 & Table 3 & Table$$

total =
$$4 + 3 + 1 = 8$$

or $C_5H_{13}O \Rightarrow C_5H_{12} - OH$ (8 form)

Ex.11 How many ethers are possible in $C_5H_{12}O$. (Only structural).

Sol.
$$C_4H_9OCH_3 \Rightarrow C_3H_7OC_2H_5$$

(4 form) (2 form)
total = 6

ISOMERISM Page # 11

Ex.12 How many 1°, 2° and 3° amine are possible for $C_5H_{13}N(Only structural)$.

Sol. For 1° amine $(-NH_2)$

 $C_5H_{11} NH_2 \Rightarrow (8 \text{ from}) = 8$

for 2º Amine, (- NH -) C_4H_9 - NH - $CH_3 \Rightarrow 4$ forms

Also, $C_3H_7 - NH - C_2H_5$

(2 form)

total form at $2^{\circ} = 4 + 2 = 6$

for 3º

(2 form)

Also,

 $C_2H_5 - N - C_2H_5$ CH_3 (1 form)

Total form of $3^{\circ} = 2 + 1 = 3$

Total no. of amines = 8 + 6 + 3 = 17

Ex.13 For molecular formula C_4H_9NO , how many amide will be there which will not form H-bond ?(Only structural)

Sol. $R-C-NH_2$ (1° amide) R-C-NH-R' (2° amide) $R-C-N \stackrel{O}{\underset{=::}{|}} (3^\circ \text{ amide})$

for 1º amide

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_3\text{H}_7-\text{C}-\text{NH}_2 \end{array} \text{ (2 form)}$$

for 2° amide, $H-C-N-C_3H_7$ (2 form) $CH_3-C-NH-CH_2CH_3^{-1}$ SATINTSE

total 2º amide = 4

for 3º amide

Page # 12 ISOMERISM

3º amide will not form H-bond hence there will be 2 amides which will not form H-bond.

Ex.14 Find all 1°, 2° and 3° amides for C3H3NO(Only structural)

Sol. For 1º amides

for 2º amide

for 3º amide

$$\begin{array}{c} O \\ \parallel \\ H-C-N \\ \hline CH_3 \end{array} \\ \text{total 3° amide} = 1$$

total amides $(1^0 + 2^0 + 3^0) = 1 + 2 + 1 = 4$

Ex.15 Find the total no. of acid and esters from $C_4H_8O_2$ (Only structural)

Sol. For acid,

$$C_3H_7$$
 – COOH (2 form)

for ester

$$\begin{array}{c|c}
O \\
R_1 - C + O - R_1
\end{array}$$
acid part

$$CH_{3}-C-OC_{2}H_{5}$$

$$CH_{3}COOH+C_{2}H_{5}OH$$

$$CH_{3}COOH+C_{2}H_{5}OH$$

$$CBSE|SAT|NTSE OLYMPIADS$$

$$ONurturing potential through education of the control of the control$$

total esters = 4

$C_2H_5-C-OCH_3$

Ex.16 $C_4H_4O_4$ may be (Only structural)

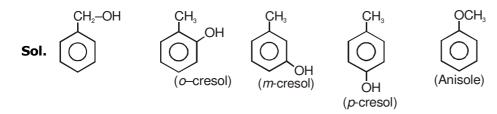
- (i) Saturated dicarboxylic acid
- (iii) Cyclic diester

(ii) Unsaturated dicarboxylic acid (iv) Saturated di aldehyde

- **Sol.** Three unsaturation.
 - (ii) and (iii) is the Ans.

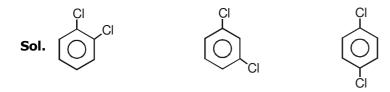
$$\begin{array}{ccccc} & & & & & & & \\ & & & & & & \\ CH-COOH & & and & & & & \\ \parallel & & & & & \\ CH-COOH & & & & & \\ \end{array}$$

Ex.17 How many aromatic isomers will be possible for C,H,O(Only structural)

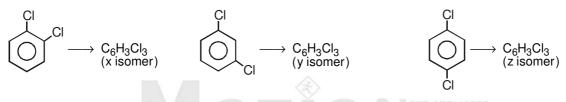


Total = 5

Ex.18 Find the possible dichloroderivative of C₆H₄Cl₂(Only structural)



Ex.19 $C_6H_4Cl_2 \longrightarrow C_6H_3Cl_3$ (Only structural)



find the value of x, y, z

Sol.



There are two possibilities placing Cl in place of H.

Motion Nutruring potential through education

ISOMERISM

There are one possibilities of placing CI, therefore z

$$x = 2, y = 3, z = 1$$

Ex.20 Find the total carbonyl compound (aldehydes and ketones) formed by $C_5H_{10}O$ and also find the relation between carbonyl compounds which have same no. of α -hydrogen. (Only structural)

Sol. For ketones,

$$C_3H_7 - C - CH_3$$

O

$$\parallel$$

 $CH_3 - CH_2 - C - CH_2 - CH_3$

(2 form)

total ketones = 3

for aldehydes

total aldehydes = 4

total carbonyl compounds = 4 + 3 = 7

$$CH_3 - CH_2 - CH_2 - CH_2 - CHC$$

$$(2 \alpha H)$$

$$CH_3 - CH_2 - CH_2 - CH_2 - CHO$$
 (2 α H) $CH_3 - CH_2 - CH - CH_3$ (one α H) CHO

$$\begin{array}{c} \operatorname{CH_3} \\ | \\ \operatorname{CH_3} - \operatorname{C} - \operatorname{CHO} \\ | \\ \operatorname{CH_3} \end{array}$$

ketone,
$$CH_3 - CH_2 - CH_2 - C - CH_3$$
 (5 α H)

$$CH_3 - CH_2 - CH_3$$
 (4 α H)

metamers
$$CH_{30}$$

$$CH_{30}$$

$$CH_{30}$$

$$CH_{3} - CH_{2} - C - CH_{2} - CH_{3}$$
 (4 α H)

Find total acyclic structural isomer of C₆H₁₂(Only structural) Ex.21

$$(1) C-C-C-C-C-C = 3$$

$$(2) C - C - C - C - C = 4$$

Sol. (1)
$$C-C-C-C-C-C=3$$
 (2) $C-C-C-C-C=4$ (3) $C-C-C-C=1$

$$\begin{array}{c|c}
C : C \\
| & | \downarrow \\
\end{array}$$

$$(4) C - C + C - C = 2$$

(4)
$$C - C + C - C = 2$$
 (5) $C - C - C - C = 3$

total = 13 isomers.

Find the total conjugated diene in C_zH_g (Only structural) Ex.22

$$\begin{array}{ccc}
\downarrow & \downarrow \\
C - C - C - C - C & \longrightarrow \text{one possibility}
\end{array}$$

$$C \xrightarrow{\downarrow} C \xrightarrow{\downarrow} C \longrightarrow$$
 one possibility

C $\stackrel{\mbox{\scriptsize C}}{\mid}$ $C-\stackrel{\mbox{\scriptsize C}}{\mid}-C\longrightarrow$ no possibility as placing double bond the valency of C will be more than four.

Ex.23 Find total cumulated diene in C₅H₈. (Only structural)

$$C-C-C-C \longrightarrow C-C=C=C$$

$$\begin{array}{c} C \\ | \\ C - C - C \longrightarrow \text{no form cumulated diene} \\ | \\ C \end{array}$$

total = 3

⇒ Isolated dienes,

$$C-C-C-C \longrightarrow$$
 no form isolated diene C

total = 1

METAMERISM

This type of isomerism is found in those types of compounds which have polyvalent atoms or polyvalent functional group, e.g. ether, 2° amine, ester etc.

Compound having same molecular formula but differ form the nature of alkyl group directly attached with polyvalent atom or polyvalent functional group

$$\left. \begin{array}{c} \mathsf{CH_3O} \; \mathsf{CH_2} \; \mathsf{CH_2CH_3} \\ \mathsf{CH_3CH_2OCH_2CH_3} \end{array} \right\} \; \mathsf{metamers} \\$$

(a)
$$CH_3 - CH_2 - CH - NH - CH_3$$
 (b) $CH_3 - CH_2 - CH_2 - NH - CH_2 - CH_3$

a & b are metamers

Motion

ISOMERISM

TAUTOMERISM

Compound having same molecular formula but different due to ascillation of an atom (usually H⁺) are known as tautomers.

$$\begin{array}{ccc} & & & & & & O \\ & \parallel & & & & & \\ \text{CH}_3 - \text{C} - \text{CH}_3 & & & & & \Theta \\ \text{CH}_2 - \text{C} - \text{CH}_3 & & & & \\ \end{array}$$

as after removal of H+, the anion formed is resonance stabilised.

KETO ENOL TAUTOMERISM

$$CH_{3}-C-CH_{3} \stackrel{OH^{\Theta}}{\longleftarrow} CH_{2}=C-CH_{3}$$

$$keto \qquad enol$$

$$Mechanism: O \qquad O^{\Theta}$$

$$CH_{3}-C-CH_{3} \stackrel{OH^{\Theta}}{\longleftarrow} \Theta CH_{2}-C-CH_{3} \longrightarrow CH_{2}=C-CH_{3}$$

$$OH \qquad \downarrow H_{2}C$$

$$CH_{3}=C CH_{3}+OH^{\Theta}$$

* OH $^{\Theta}$ acts as catalyst.

Base Catalysed Tautomerism:

$$CH_3 - C - CH_3 \xrightarrow{OH^{\Theta}} CH_2 = C - CH_3$$
 $> 99\%$
 $< 1\%$

- * enol is more acidic than keto.
- * After removal of H+ from both form.

$$\begin{array}{c} O \\ || \\ CH_3-C-CH_3 \\ \hline \end{array} \longrightarrow \begin{array}{c} O \\ || \\ CH_2-C-CH_3 \\ \hline \end{array} \\ \begin{array}{c} O \\ || \\ CH_2=C-CH_3 \\ \hline \end{array} \\ \begin{array}{c} O \\ || \\ CH_2=C-CH_3 \\ \hline \end{array} \\ \begin{array}{c} O \\ || \\ CH_2=C-CH_3 \\ \hline \end{array}$$

In I^{st} –ve charge is on C and in II^{nd} –ve charge is on O therefore (ii) is more stable than (i) hence enol form is more acidic than keto form.

Acid Catalysed Tautomerism:

MOTION INT-DEE | ALEEE
COMPANDS
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Ex.24
$$CH_3 - C - CH_2 - CH_3$$
 $OH_3 - C - CH_2 - CH_3$ $OH_3 - C - CH_2 - CH_3$ $OH_4 - CH_2 - CH_3$ $OH_5 - CH_2 - CH_3$ $OH_5 - CH_2 - CH_3$ $OH_5 - CH_3 - CH_3$ $OH_5 - CH_3 - CH_3$ $OH_5 - C$

$$CH_3-C-CH_2-CH_3$$

$$OH^{\Theta}$$

$$OH^{\Theta}$$

$$OH^{\Theta}$$

$$OH^{\Theta}$$

$$OH^{\Theta}$$

$$OH^{\Theta}$$

$$OH_2-C-CH_2-CH_3$$

$$OH_3-C-CH-CH_3$$

$$OH_3-C-CH-CH_3$$

$$OH_3-C-CH-CH_3$$

$$OH_3-C-CH-CH_3$$

$$OH_3-C-CH-CH_3$$

- In case of base catalysed tautomerism the stability of carbanion is the deciding factor.
- * For acid catalysed tautomerism the stability at the product will be the deciding factor.

ISOMERISM

- * Generally keto form is more stable than enol but in some cases the stability of enol form is greater than keto. This is due to
 - (i) Intramolecular H-bonding
- (ii) Aromatic character
- (iii) Extended conjugation
- (iv) Steric factor

e.g.
$$CH_3 - C - CH_2 - C - CH_3$$
 \longrightarrow $CH_3 - C = CH - C - CH_3$ (70 - 80%) (enol)

(Intramolecular H-bond)

- * Due to intramolecular H-bonding formation of 6 member ring takes place which is the cause of stability.
- * This can be also summerised as

*
$$CH_3 - C - CH_2 - C - OC_2H_5$$
 $CH_3 - C - CH - C - OC_2H_5$ (After removal of H+) $CH_3 - C - CH - C - OC_2H_5$ (Cross conjugation)

* Cross conjugation restricts the Resonance.

Ex.27 Compare the enol percent.

(A)
$$CH_3CHO$$
 (B) $CH_3 - C - CH_3$ (C) $CH_3 - C - CH_2 - C - CH_3$ (D) $CH_3 - C - CH_2 - C - H$ (e) $H - C - CH_2 - C - H$ (f) $Ph - C - CH_2 - C - CH_3$ (g) $Ph - C - CH_2 - C - Ph$

ISOMERISM Page # 19

Sol. g > f > e > d > c > b > a

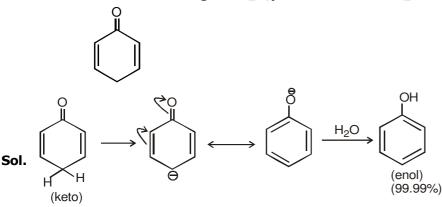
* Incase of a and b

$$CH_2 = CH - OH$$
 (no $\propto H$)

OH
$$CH_2 = C - CH_3 (3 \times H)$$
 more stable = higher %

∴ enol % > keto %

Ex.28 Find the enol form the given compound. | all through education

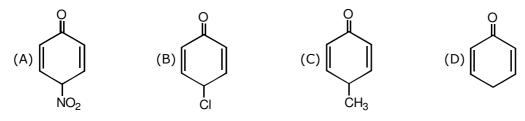


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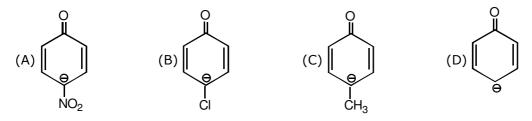
Page # 20 ISOMERISM

Above case is called paratautomerism.
 Here γ-Hydrogen participate in tautomerism.

Ex.29 Compare the enol content



Sol. After removing H⁺ (acidic–H) from the compounds



- Enol percent ∝ stability of carbanion
 a > b > d > c
- * Formation of carbanion is one of step of from keto to enol. Therefore can be calculated as enol percent α stability of carbanion.

Ex.30 Find the enol form of

NITRO AND ACINITRO FORM

$$\begin{array}{c} \text{CH}_{3}\text{NO}_{2} \longrightarrow \overset{\circ}{\text{CH}}_{2} - \overset{\circ}{\text{N}} = \overset{\bullet}{\text{O}} \longleftrightarrow \text{CH}_{2} = \overset{\bullet}{\text{N}} - \overset{\bullet}{\text{O}} \longleftrightarrow \text{CH}_{2} = \overset{\bullet}{\text{N}} - \overset{\bullet}{\text{OH}} \\ \text{O} & \overset{\bullet}{\text{O}} & \overset{\bullet}{\text{O}} \end{array}$$

$$(\text{nitro})$$

* $(CH_3)_3 C - NO_2$ will not show nitro and acinitro form it has no α H w.r.t to NO_2 group.

IMINE AND ENAMINE

$$CH_3 - CH = N - H \Longrightarrow CH_2 - CH = NH$$

$$\downarrow \text{ (imine)}$$
acidic
$$\text{hydrogen}$$

$$CH_2 = CH - NH$$

$$\downarrow H_2O$$

$$CH_3 = CH - NH$$

tautomerism, there must αH w.r.t. (-CH = NH) group.

AMIDE AND IMIDOL

$$\begin{array}{ccc} O & OH \\ \parallel & \parallel \\ R-C-NH_2 & \Longrightarrow & R-C=NH \end{array}$$

NITROSO AND OXIME FORM

$$Ph - CH_2 - N = O \implies Ph - CH = N - OH$$
(nitroso)
(I)
(II)

II > I (stability)

due to extended conjugation in (II)

HYDRAZONE AND AZOFORM

NH, NH, (Hydrazine)

$$C = O + H_2 N - NH_2 \longrightarrow C = N - NH_2$$

$$CH_3 - CH = N - NH_2$$
 $CH_3 - CH_2 - N = NH$ (Azo)

$$CH_3 - CH = N - NH - Ph \implies CH_3 - CH_2N = N - Ph$$

(extended conjugation)

Azo > Hydrazone (stability)

Ex.31 Compare enol percent.

Sol. As we know C - D > C - H (Bond strength)

- \Rightarrow C D will not break easily.
- \Rightarrow Compound will have less tendency to come into in enol form as C D bond breaking is one of the step for conversion of keto into end.
- \Rightarrow enol percent will be less.
- \Rightarrow (i) > (ii) > (iii)

(enol content)

ISOMERISM

DEUTERIUM EXCHANGE REACTION

(Deuterium Exchange Tautomerism)

$$CH_{3} - C - CH_{3} \xrightarrow{D_{3}O^{+}} CH_{3} - C - CH_{3} \xrightarrow{-H^{+}} CH_{2} = C - CH_{3} \longrightarrow CH_{2}D - C - CH_{3} \xrightarrow{D^{+}} CH_{2} = C - CH_{3} \longrightarrow CH_{2}D - C - CH_{3} \xrightarrow{D^{+}} CH_{2} = C - CH_{3} \longrightarrow CH_{2}D - C - CH_{3} \xrightarrow{D^{+}} CH_{2} = C - CH_{3} \xrightarrow{D^{+$$

* To get the product directory replace all α -hydrogen w.r.t. carbonyl group by D(Deuterium)

RING-CHAIN ISOMERISM

If one isomer has open chain structure and the other has cyclic structure then isomers are known as ring-chain isomers and isomerism between them is known as ring-chain isomerism.

For examples:

(i) Alkene and cycloalkane, (C_nH_{2n})

$$CH_3 - CH = CH_2$$
 $CH_2 - CH_2$

(ii) Alkyne and cycloalkene, (C_nH_{2n-2})

$$C_4H_6$$
: $CH_3 - CH_2 - C \equiv CH$ $CH - CH_2$ III-JEE ALEEE CH - CH₂ CH - C

(iii) Alkenols and cyclic ethers, $(C_n H_{2n} O)_{tential through education}$

$$C_3H_6O$$
: $CH_2 = CH - CH_2OH$ $CH_2 - CH_2$ $CH_2 - CH_2$ $CH_2 - CH_2$

Note: Ring-chain isomers are always functional isomers.

GEOMETRICAL ISOMERISM

Definition:

Isomers which possess the same molecular and structural formula but differ in the arrangement of atoms or groups in space due to restricted rotation are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

ISOMERISM

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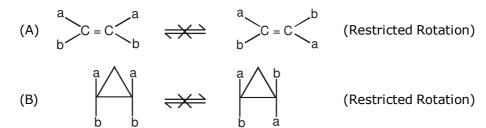
CONDITIONS OF GEOMETRICAL ISOMERISM

(I) Geometrical isomerism arises due to the presence of a double bond or a ring structure

(i.e.
$$C = C$$
, $C = N - C - N = N - Or ring structure)$

Due to the rigidity of double bond or the ring structure to rotate at the room temperature the molecules exist in two or more orientations. This rigidity to rotation is described as restricted rotation / hindered rotation / no rotation.

e.g.



(II) Different groups should be attached at each doubly bonded atom. For example

$$a$$
 $C = C$ a and a $C = C$ a are identical but not geometrical isomers.

On the other hand, following types of compounds can exist as geometrical isomers:

Examples of Geometrical isomers:

(I) Along C = C bond

$$CH_3$$
 $C = C$ H CH_3 CH

(II) Along C = N - bond

$$CH_3$$
 C_2H_5
 $C = N$
 CH_3
 C_2H_5
 $C = N$
 CH_3
 C_2H_5
 $C = N$

Page # 24 ISOMERISM

(III) Along -N = N - bond

$$CH_3$$
 $N = N$

and

and

$$N = N$$

(IV) Along σ bond of cycloalkane



and



CH, CH

and



CH₃

and



Me Me

and



(V) Along $\supset C = C \subset \text{in ring structures}$:

Usually in cycloalkenes double bond has its configuration. Their trans isomers do not exist due to large angle strain. But if the ring is large enough a trans stereoisomer is also possible. The smallest trans cycloalkene that is stable enough to be isolated & stored is trans-cyclooctene.



trans-cyclohexene highly unstable (non existant)



trans-cyclooctene less stable than cis (isolable at – 90°C)

Configurational nomenclature in geometrical Isomerism

IIT-JEE AIEEE

		TAT SEE MICE		
Configuration	Criterla	Remarks BSE SAT NTSE		
cis / trans	Similarity of groups	If the two similar groups are on same side of restricted bond the configuration is cis otherwise trans.		
E/Z	Seniority of groups	If the two senior groups are on same side of restricted bond the configuration is Z (Z = zusammen = together) otherwise E (E = entgegen = opposite).		

Sequence rules: (Cahn - Ingold - Prelog sequence rules)

For deciding the seniority of groups following rules are applied:

Rue I: The group with the first atom having higher atomic number is senior. According to this rule the seniority of atom is:

I > Br > Cl > S > F > O > N > C > H

Rule II: The higher mass isotope is senior.

Thus (A) - T > - D > - H.

(B) $-C^{14}H_3 > -C^{12}H_3$



ISOMERISM Page # 25

Rule III: If the first atom of group is identical then second atom is observed for seniority.

e.g. (A)
$$-CH_2CI > -CH_2OH > -CH_2NH_2 > -CH_2CH_3 > -CH_3$$

(B)
$$-C-CI > -C-C$$

OH NH_2

Rule IV : Groups containing double or triple bonds are assigned seniority as if both atoms were duplicated or triplicated that

> C = Y as if it were
$$(Y) (C)$$

 $(Y) (C)$
 $(Y) (C)$
 $(Y) (C)$
 $(Y) (C)$
 $(Y) (C)$

e.g. for deciding seniority among – C = CH, – $CH = CH_2$, their hypothetical equivalents are compared.

$$\begin{array}{c|cccc} C & C & C & C \\ | & | & | & \\ -C - C - C - H & > & -C - C - H \\ | & | & | & \\ C & C & H & C \\ (for - C \equiv C - H) & (for - CH = CH_2) \end{array}$$

Rule V: Bond pair is senior to lone pair.

Number of Geometrical Isomers:

Number of geometrical isomers can be found by calculating the number of stereocentres in the compound. (stereocentre is defined as an atom or bond bearing groups of such nature that an interchange of any two group will produce a stereoisomer).

Nature of compound	No. of G.I. (n = no. of stereocentres)	Example	No. of Isomers	Isomers
(I) Compound with dissimilar ends	2 ⁿ	$CH_3 - CH = CH - CH = CH - C_2H_5$	4	I : (cis, cis) II : (trans, trans) III : (cis, trans) IV : (trans, cis)
(II) Compound with similar ends with even stereocentres	$2^{n-1} + 2^{\frac{n}{2}-1}$	CH ₃ -CH = CH-CH = CH-CH ₃ turing potential through e	CBSE SAT DLYM3IAD: ducat	I : (cis, cis) II : (trans, trans) III : (cis, trans) ≅ (trans, cis)
(III) Compound with similar ends with odd stereocentre	$2^{n-1} + 2^{\frac{n-1}{2}}$	$CH_3 - CH = CH - CH = CH - CH = CH - CH_3$	6	I: (cis, cis, cis) II: (cis, cis, trans) ≅ (trans, cis, cis) III: (cis, trans, trans) ≅ (trans, trans, cis) IV: (trans, trans, trans) V: (cis, trans, cis) VI: (trans, cis, trans)

MOTION COSSISATIONS
Nurturing potential through education

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Physical Properties of Geometrical Isomers:

Physical properties	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Remarks	
Dipole moment	l > II	cis-isomer has resultant of dipoles while in trans isomer dipole moments cancel out	
Boiling point	l > II	Molecules having higher dipole moment have higher boiling point due to larger intermoleculer force of attraction	
Solubility (in H ₂ O)	l > II	More polar molecules are more soluble in H ₂ O	
Melting point	II > I	More symmetric isomers have higher melting points due to better packing in crystalline lattice & trans isomers are more symmetric than cis.	
Stability	II > I	The molecule having more vander waal strain are less stable. In cis isomer the bulky groups are closer they have larger vander waals strain.	

Table

Physical properties	H_3C H $C = C$ H H $C = C$ H	■ IIT-JEE AIEEE
Dipole moment	turing potential through	CBSE SAT NTSE OLYMPIADS
Boiling point	I > II	
Solubility (in H ₂ O)	l > II	
Melting point	l > II	
Stability	l > II	

ISOMERISM Page # 27

Unsolved problem: Find the number of geometrical isomers in

(A)
$$CH_3 - CH = C - CH = CH - CH = N - OH$$

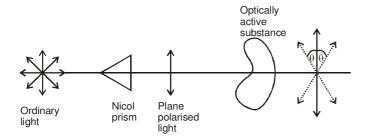
 CH_3

(B)
$$CH = CH - CH_3$$

$$CH_3$$

Unsolved problem : Compare the physical properties (μ , b.p., m.p., solubility & stability) in the geometrical isomers of CH₃ – CH = CH – CN.

OPTICAL ISOMERISM



If rotation of light

If rotation of light

is clock wise

is anticlock wise \downarrow \downarrow dextro rotatory substance

laevo rotatory

(J-form)

If there is no rotation of light then substance is called optically inactive.

CHIRAL CARBON

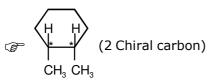
If all the four valencies of carbon are satisfied by four different atom or four different group atom then carbon is known as chiral carbon.

e.g.

$$\begin{array}{c}
H \\
C \\
C \\
HO
\end{array}$$
Chiral Carbon
Chiral Chiral Carbon
Chiral Chi

Motion In Secial Effective Constitution of Con

*CH(OH)COOH | Tartaric Acid *CH(OH)COOH



P Chiral carbon ढूढँने के लिए पहले point of doubt check करना चाहिए

For optically active isomer the object and its mirror image must be non superimposible.

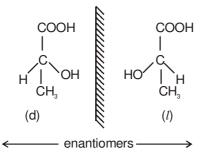
F If image and object are superimposible then they are not optically isomer to each other.

To check, superimposible either of object or mirror image is rotated 180° along the mirror. After that mirror image is checked for superimposible.

After 180° rotation, mirror image and object are identical. (mirror image of meso compound will be indentical)

F If the compound have only one chiral carbon then it will be certainly optically active.

Mirrorimage



Object and its nonsuperimposible mirror image are called enantiomer to each other

Object

ISOMERISM Page # 29

32. A and B are enantiomer to each other. If specific rotation of A is $+20^{\circ}$ and rotation of mix of A and B is -10° then find the percentage of A and B in the mixture?

Sol. Let x mol A

(1-x) mol of B

total rotational of $A = x \times 20$

total rotational of B = (1 - x)(-20)

Total rotation of the mixture = -10

$$x \times 20 + (1 - x)(-20) = -10$$

$$20 \times -20 + 20 \times = -10$$

$$40 \text{ x} = 10 \Rightarrow \text{ x} = \frac{10}{40} = 0.25$$

$$\Rightarrow$$
 % A = 25%

FISHER PROJECTION

By fisher projection three dimensional structure is converted into 2D.

33. Write the Fisher projection of CH₂CH(OH)COOH

Maximum carbon must be in vertical line.

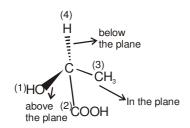
Place higher priority carbon containing functional group on top of vertical line.

34. Write Fisher projection of

- **Sol.** (i) Place higher priority carbon containing functional group on top of vertical line.
 - (ii) Arrange other group according to its clock wise or anticlock wise position w.r.t. group on the top.

ISOMERISM

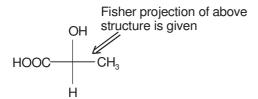
WEDGE DASH STRUCTURE



केवल Fourth priority order को Cross कर सकते हैं, during checking of clock or anticlockwise.

To draw Fisher projection of such structure

- (1) Dotted group is placed below
- (2) The group attached by dark line is placed on the top.
- (3) Remaining group are placed according to their clock wise or anticlock wise position w.r.t. group in dark line.



35. Draw the fisher projection of

Sol. H Br CH3O Br CH3O Br CH3O Br

If fourth valency is not given then we assume it to be hydrogen

R AND S FORM

$$\bigcap$$
 R \rightarrow Rectus \rightarrow Right \rightarrow Clock wise.

$$\bigcap \hspace{0.1in} S \to Sinister \hspace{0.5in} \to Left \to Anticlock wise.$$

ISOMERISM

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PRIORITY ORDER

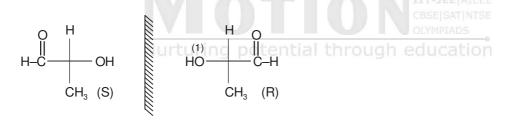
Higher the atomic number of the element, greater will be its priority.

e.g.

 \bigcirc In case of double bond (=) or triple (\equiv) bond

(4)
$$(4) H \xrightarrow{(3)} CH_2OH$$
 $O H^{(4)}$ $(4) H \xrightarrow{(2)} CHO$ $H \xrightarrow{(3)} CH_3$ $(4) CH_3$

 $1 \rightarrow 2 \rightarrow 3$ If clock wise \Rightarrow R $1 \rightarrow 2 \rightarrow 3$ If Anti clock wise \Rightarrow S



 \Rightarrow Mirror image of R is S

If lowest priority element is in horizontal then exact order is obtained by reversing the form (i.e. it comes R then exact form will be S and vice versa)

e.g.

Page # 32 ISOMERISM

$$HO \xrightarrow{(3)} H^{(2)} H^{(4)}$$

⇒ It comes as R but will be S form,

If lowest priority order element is in dotted then

 $1 \rightarrow 2 \rightarrow 3$ If clock wise $\Rightarrow R$

and if $1 \rightarrow 2 \rightarrow 3$ If Anti clock wise $\Rightarrow S$

If lowest priority element is not in dotted then we bring it in dotted by doing even number of inter changes (2,4 or 6) as by even no. of inter change, the configuration does not change.

After odd number of change the configuration changes (If R then goes into S and vice versa).

For Example:

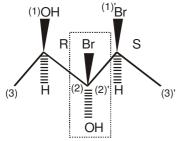
Ex.36 Draw the Fisher projection of

Sol.

All the carbons are placed in vertical

Group attached to the chiral carbons are placed on any side. After that they are adjusted whether they are R or S form w.r.t chiral carbons.

Ex.37 Draw the Fisher projection of the following.



Wedge Dash formula

Sol.



Fisher projection

RACEMIC MIXTURE

It is an equimolar mixture of R and S or d and l. Racemic mixture is optically inactive

A compound is optically active due to

- (1) Absence of plane of symmetry (POS)
- (2) Absence of centre of symmetry (COS)

MOTION COSSISATIVES
Nurturing potential through education

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(meso form)

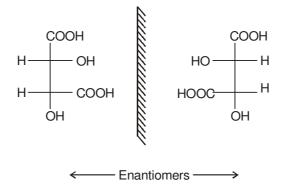
POS is an imaginary plane where if we place a mirror, mirror image will exactly overlap the other half.

For meso form, there must be at least two identical chiral carbon.

Identical carbon \Rightarrow Chiral carbons having identical group attached.

If compound has POS then it will be certainly optically inactive and will be called meso form.

After finding two identical carbons. We assign them as R or S. If first part is R and other is S then they will rotate the light in opposite direction but to equal extent the compound will be optically inactive (meso form)



If a compound have 'n' different chiral carbon then total no. of optically active isomers = 2^n No. of meso form = 0

e.g.

no. of different chiral carbon = 4 total optical isomer = $2^n = 2^4 = 16$

There will be no meso as the compound does not have identical chiral carbon.



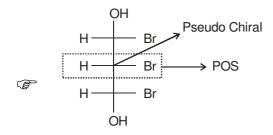
- (i) If n is even optical isomer (a) = 2^{n-1} mesoform (m) = $2^{n/2-1}$ total optical isomer = a + m
- (ii) If n is odd

$$a = 2^{n-1} - 2^{\frac{n-1}{2}}$$

$$m = 2^{\frac{n-1}{2}}$$

Total optical isomer = $2^{n-1} - 2^{\frac{n-1}{2}} + 2^{\frac{n-1}{2}}$

$$= 2^{n-1}$$



When there is odd no. of identical carbon atom (i.e. symmetrical) then this compound will certainly contain pseudo chiral w.r.t. to which compound be symmetrical (i.e. POS)

Other meso compound of the above compound will form by changing the place Br and H around Pseudo Chiral carbon.

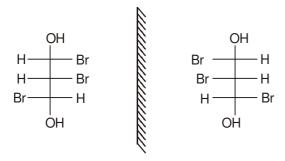


Total
$$meso = 2$$

optical =
$$2^{n-1} - 2^{\frac{n-1}{2}}$$

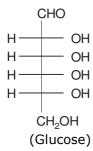
= $2^{3-1} - 2^{\frac{3-1}{2}}$
= $2^2 - 2$
= $4 - 2 = 2$





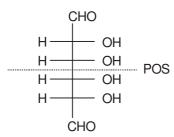
← Enantiomers →





Total no. of different chiral carbon = 4 Total optical isomer = 2^4 = 16





Total no. of even chiral = 4

$$a = 2^{n-1} = 2^{4-1} = 2^3 = 8$$

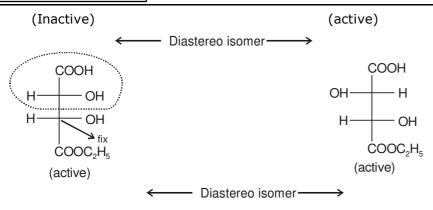
$$m = 2^{\frac{n}{2}-1} = 2^{\frac{4}{2}-1} = 2^{2-1} = 2^1 = 2$$

Total isomer = 8 + 2 = 10 uring potential through education

DIASTEREO ISOMERS

For single chiral centre, there is no diastereoisomer. The stereoisomer which are not related as object and mirror image. They may be optically active or optically inactive.

ISOMERISM Page # 37

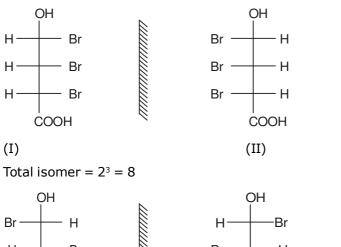


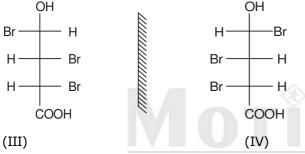
Fix one chiral carbon

After one inter change

If
$$(R, R) \rightarrow (R, S)$$

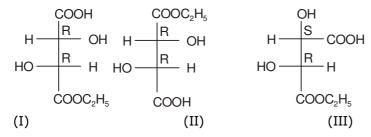
For compound having 3 chiral carbon to get diastereoisomer, fix two chiral carbon and one interchange with left carbon or fix one chiral carbon and inter change with other two,





(I) and (III), I and (IV), (II) and (III), (II) and (IV) are diastereoisomers.

Ex.38



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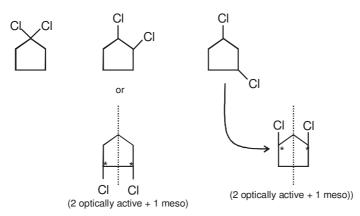
$$\begin{array}{c|c} O & OH \\ \parallel & \parallel R \\ HO & - \parallel S \\ HO & H \\ \end{array}$$

What are the relation among the above compounds?

Sol. I and II are identical III and IV are identical

Ex.39 Find total isomers obtained by dichlorination of cyctopentane?

Sol.



Total isomers = 3 + 3 + 1 = 7

Optically active isomers = 6

Ex.40 Find the total isomers obtained by trichlorination of propane.

Sol.

Total isomers = 6 optically isomers = 2

Ex.41 Find total isomers obtained by dichlorination of n-butane

Sol. C-

$$C-C-C-C < CI$$

$$\begin{array}{cccc} C-C-C-C & & & \\ & & & \\ CI & & CI \end{array} \tag{1}$$

$$C - \overset{*}{C} + \overset{*}{C} - C$$

 $\begin{vmatrix} & & \\ & &$

Total isomers = 10 (6 optically active + 1 meso + 3 structural)

Ex.42 How many stereoisomers of 1,2,3-cyclohexantriol

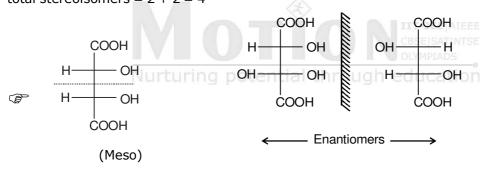
Sol.

No. of Chiral carbon = 3 (identical) symmetrical)

$$a = 2^{n-1} - 2^{\frac{n-1}{2}} = 2^{3-1} - 2^{\frac{3-1}{2}} = 4-2$$

$$m = 2^{\frac{n-1}{2}} = 2^{\frac{3-1}{2}} = 2$$

total stereoisomers = 2 + 2 = 4



Mesoform is optically inactive due to internal compensation and racemic mixture is optically inactive due to external compensation.

Ex.43 A and B are enantiomer of each other. Specific rotation of A is 20 °. Rotation of mixture of A and $B = -5^{\circ}$ what is the percentage of racemic part?

Sol. x mol A, 1-x mol B

MOTION COSESATIVES

Nurturing potential through education

Page # 40 ISOMERISM

$$x \times 20 + (1-x)(-20) = -5$$

 $20 \times -20 + 20 \times = -5$

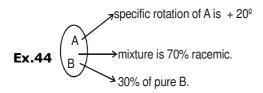
$$40 x = 15 \Rightarrow x = \frac{3}{8} = 0.375$$

moles of A = $\frac{3}{8}$

moles of B = $1 - \frac{3}{8} = \frac{5}{8}$

 $\frac{3}{8}$ moles of A and $\frac{3}{8}$ moles of B will form racemic mixture.

Enantiomer excess or optical purity $=\frac{5}{8}-\frac{3}{8}=\frac{2}{8}=\frac{1}{4}$



What is rotation of mixture?

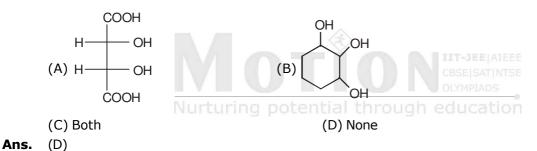
Sol. Rotation will be due to B only,

$$= 0.3 \times (-20^{\circ})$$

= -6°

© Chiral compound → optically active compound

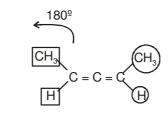
Ex.45 Which of the following compound is Chiral (Optically active)?



ALLENE SYSTEM

(non-planer) (optically inactive)

$$CH_3$$
 $C = C = C$ H Allene system



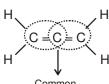
They are non superimposible.mirror image

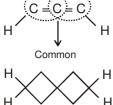
Enantiomers
$$C = C = C = C$$
 CH_3
 $C = C = C = C$
 CH_3

(Optically active)

(Inactive)

SPIRO COMPOUNDS





If no. of rings are even \Rightarrow optically active

If no. of rings are odd \Rightarrow Inactive

(Optically active)

Motion

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$$H \longrightarrow H$$
 $CH_3 \longrightarrow CH_2$

(Optically Inactive)

CH₃
$$\Rightarrow$$

This is the even no of double bond case.

(Optically active)

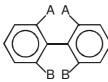
For optical activity, the carbons at extreme position must have different group attached.

$$\begin{array}{c} H \\ C = C = C = C \end{array}$$

⇒ Planer compound

Always have POS .. Optically inactive

BIPHENYLS

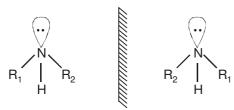


If biphenyl contain bulky group at its ortho position (only) then due to repulsion the planarity of compound disappears and its mirror image is non superimposible.

In the biphenyls none of the two ring must have symmetry.



In 2º Amines.



Optically inactive due to formation of racemic mixture.

 \bigcirc Order of flipping in amines $1^{\circ} > 2^{\circ} > 3^{\circ}$

D-Form:- For compound having one chiral carbon

- (a) If OH is right side \rightarrow D
- (b) If OH is left side $\rightarrow L$

D-form

(**Note** \rightarrow All the carbon must be in vertical having highest O. N. Carbon on the top)

CONVERSION OF FISHER PROJECTION IN SAWHORSE STRUCTURE

L-form

- सबसे पहले, First Chiral Carbon को As it is लिख लेते है। फिर अगर दोनों Vertical वाले group, same side में हैं, तो दूसरे chiral carbon के, Respect में बाकी दोनों group जैसे लगे हैं वैसे ही लगा देगे जैसे उपर वाले example में दूसरे chiral में , Left में H और Right मे OH हैं तो उसे वैसे ही Place कर देगे।
- और दोनों Vertical में situated group को opposite में place करेगे तो दूसरे वाले Chiral से attached बाकी दोनों group का side reverse कर देगे i.e. left वाले group को Right में और Right वाले group को left में place कर देगें।

 The above Fisher projection can also written in Saw Horse form as follows

CONVERSION OF NEWMANN PROJECTION IN TO SAWHORSE PROJECTION

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(OH और OH opposite करके इसलिए लिखे गये हैं क्योंकि Newmann projection में COOH ओर COOH opposite में हैं।

Above example में दोनें COOH, same side में हे। इसलिए second chiral carbon में के respect में लगे group का place बदला नहीं जायेगा।

If all the identical groups are same side or in exactly opposite direction to each other in Newmann projection then compound will be meso.

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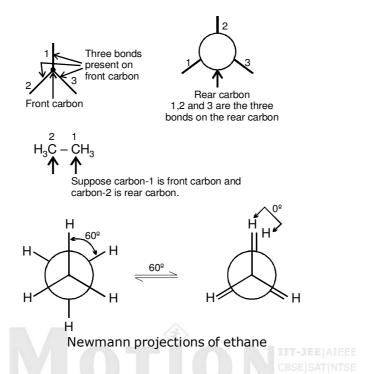
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CONFORMATIONAL ISOMERS

Conformational Isomerism in Alkanes

Different spatial arrangements of the atoms that result from **restricted** rotation about a single bond are called conformations. Different conformations are also called conformational isomers or **conformers**.

When an ethane molecule rotates about its carbon-carbon single bond, two extreme conformations can result: the **staggered conformation** and the **eclipsed conformation**. An infinite number of conformations between these two extreme conformation is also possible. There are several ways to represent on paper the three dimensional confermation that, occur as a result of rotation about a single bond. **Wedge-and-dash** structures, **Sawhorse** projections and **Newmann** projections are all commonly used methods. But here we will use only Newmann projections. In a Newmann projection you will look down the length of a particular carbon-carbon single bond. The carbon that is in the front, is represented by the point at which three bonds intersect and the carbon that is in the back is represented by a circle. The three lines emanating from each of the carbons represent the carbon's other three bonds.



Staggered conformations: A conformation with a 60° dihedral angle is known as staggered conformation. **Eclipsed conformation:** A conformation with a 0° dihedral angle is known as eclipsed conformation.

The electrons in a carbon-hydrogen bond will repel the electrons in another carbon-hydrogen bond if the bonds get too close to each other. The staggered conformation, therefore, is the most stable conformation because the carbon-hydrogen bond are as far away from each other as possible. The eclipsed conformation is the least stable conformation, because in no other conformation are the carbon-hydrogen bond closer to one another. In staggered conformation the distance between the hydrogen nuclei is 2.55 Å. but, they are only 2.29 Å apart in the eclipsed conformation. The rotational barrier in ethane is 2.9 Kcal/mole. This rotational barrier can be described in terms of the change in potential energy of the molecule as a function of the change in dihedral angle. The extra energy of the eclipsed conformation is called **torsional strain**. Torsional strain is the name given to the repulsion felt by bonding electrons of one substituent as they pass close the bonding electrons of another substituent. The energy barrier between staggered and eclipsed conformation in ethane molecule is 2.9 Kcal/mole (12 kJ/mole). This barrier is more than RT (\approx 0.6 Kcal/mole) at room temperature (energy for free rotation) and less than 16-20 Kcal/mole (energy barrier for frozen rotation). Hence the rotation

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about carbon-carbon single bond is neither completely free nor frozen but only restricted.

Note: (i) For free rotation energy barrier is 0.6 Kcal/mole.

- (ii) For restricted rotation energy barrier is in between > 0.06 and < 16 Kcal/mole.
- (iii) For frozen rotation energy barrier is \geq 16 Kcal/mole.

Similarly propane has also two conformations.

$$CH_{3} \xrightarrow{-2} C \xrightarrow{-1} C - H$$

$$H \qquad H$$

Staggered Eclipsed In this case, out of six substituents on two C's (carbon -1 and carbon-2) five, are hydrogens and one is CH_3 group.

Butane has three carbon-carbon single bonds and the molecule can rotate about each of them

If rotation will be about C - 2 and C -3 bond then conformation will be symmetrical.

For conformational analysis treat butane as the derivative of ethane. Out of six substituents four are hydrogens and two are methyl groups Different conformations of butane are obtained by rotation.

Butane has three staggered conformers (I, III and V).

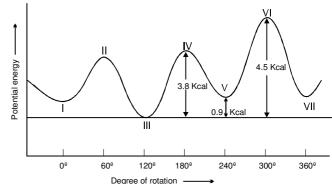
Conformer -(III), in which the two methyl groups are as far apart as possible, is more stable than the other two staggered conformers (I and V). The most stable of the staggered conformers is called the **anti conformer** (in anti conformation the angle between two methyl groups is 180°) and the other two staggered conformers are called gauche conformers. (anti in Greek for "opposite of' gauche in French for " left"). In gauche conformation the angle between two methyl groups is 60° .

In the anti conformer, the largest substituents (CH_3 and CH_3) are opposite to each other; in the gauche conformer, they are adjacent. Two gauche conformers have the same energy but each is 0.9 Kcal/mole less stable than the anti conformer.

Anti and gauche conformers do not have the same energy because of the steric strain. **Steric strain** or **steric hindrance** is the strain put on a molecule when atoms or groups are large in size and due to this they are too close to each other, which causes repulsion between the electrons of atoms or groups. There is more steric strain in the gauche conformer than in the anti because the two methyl groups are closer together in the gauche conformer. Steric strain in gauche conformer is called gauche interaction.

The eclipsed conformer in which the two methyl groups are closest to each other (VI) is less stable than the other eclipsed conformers (II and IV). All these eclipsed conformers have both torsional and steric strain. Torsional strain is due to bond-bond repulsion and steric strain is due to the closeness of the eclipsing groups.

In general steric strain in the molecule is directly proportional to the size of the eclipsing groups. Eclipsed conformer (VI) is called the fully eclipsed conformer (angle between two methyl groups is zero) whereas (II) and (IV) are called eclipsed conformers. The energy diagram for rotation about the C-2–C-3 bond of butane is shown in the **Fig.**



Thus the relative stabilities of the six conformers of n-butane in decreasing order is as follows:

Thus molecules with carbon-carbon single bonds have many interconvertible conformers. Conformers cannot be separated because they rapidly interconvert.

(VI)

Although anti conformation is more stable than the gauch conformation but in some cases gauch conformation is more stable than the anti because of the intramolecular hydrogen bonding which is geometrically possible only in the gauch conformation.

In ethylenechlorohydrin also gauch conformation is more stable than the anti conformation due to the dipole-dipole attraction between OH and Cl which is geometrically possible only in the gauch conformation.



Dipole -dipole attraction between OH and CI (more stable)

Ex.46 Write Gauch conformation of the compound CH,CI - CH,CI?

Sol. Gauch conformation of the given compound is:

(i) Mole fraction of anti and gauch form: Mole fraction of stable conformers (i. e., mole fraction of anti and gauch can be calculated if dipole moment of anti and gauch form is known.

$$\mu ob = \mu(anti) \times x_a + \mu(gauch) \times x_g$$

where

 $x_a = mole fraction of anti form and$

 $x_b = mole fraction of gauch form.$

Suppose

$$\mu ob = 1.00$$

$$\mu g = 5.55$$

Then x_a can be calculated as follows:

$$\mu ob = \mu_a \times x_a + \mu g \times x_g$$

$$1 = 0 \times x_a + 5.55 x_a$$

.

$$x_g = \frac{1}{5.55} = 0.18$$

Sum of mole fraction of $x_a + x_g = 1$

$$x_a = 1 - x_g = 1 - 0.18 = 0.82$$

(ii) relative amounts of anti and gauch conformers up heducation

The anti conformer of n-butane is more stable than the gauch may about 900 Kcal/mole (i.e., 0.9 Kcal/mole). This is energy barrier between anti and gauch.

Thus

gauch
$$\rightleftharpoons$$
 anti, $\Delta H = -900$ cal/mole.

Suppose at room temp ΔG is negligible.

So

$$\Delta G = - RT \ln K_{ec}$$

$$K_{eq} = \frac{[anti]}{[gauch]}$$

and

In
$$K_{eq} = \frac{-\Delta G}{BT} = \frac{-900 \text{ cal/mole}}{1.99 \text{ cal/mole} \text{K} \times 298 \text{K}} = 1.52$$



The ratio of K_{eq} is $4.57 \approx 4.6$, which means that about 82% mole $\left(\frac{4.6 \times 100}{5.6}\right)$ of the molecule are in the anti conformation and 18% in the gauch conformation at any one time.

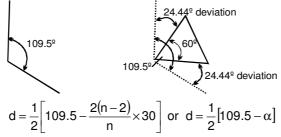
STABILITY OF CYCLOALKANES

Compounds with three and four membered rings are not as stable as compounds with give or six membered rings.

The German chemist Baeyer was the first to suggest that the instability of these small ring compounds was due to angle strain. This theory is known as Baeyer-Strain theory.

Baeyer strain theory was based upon the assumption that when an open chain organic compound having the normal bond angle 109.5° is converted into a cyclic compound, a definite distortion of this normal angle takes place leading to the development of a strain in the molecule.

Baeyer assumed that cyclic rings are planar. Assuming that the rings are planar, the amount of strain in various cycloalkanes can be expressed in terms of angle of deviation (d).

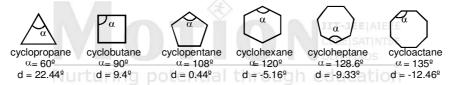


where n = number of carbon-carbon bonds in cycloalkane ring $\alpha = inner$ bond angle in the cycloalkane ring.

Angle strain
$$\propto d \propto \frac{1}{\text{inner angle}}$$

Stability
$$\propto \frac{1}{d} \propto \text{inner angle } (\alpha)$$

Now let us take the case of three to eight membered cyclic compounds.



The positive and negative values of (d) indicate whether the inner angle is less than or more than the normal tetrahedral value.

Baeyer thus predicted that a five membered ring compound would be the most stable. He predicted that six membered ring compounds would be less stable and as cyclic compound became larger than five membered ring they would become less and less stable.

Contrary to what Baeyer predicted, however, cyclohexane is more stable than cyclopentane. Furthermore, cyclic compounds do not become less and less stable as the number of side increase. Thus Baeyer strain theory is applicable only to **cyclopropane**, **cyclobutane and cyclopentane**.

The mistake that Baeyer made was to assume that all cyclic compounds are planar. In real sense only cyclopropane is planar and other cycloalkanes are not planar. Cyclic compounds **twist** and **bend** in



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order to achieve a final structure that minimises the three different kinds of strain that can destabilise a cyclic compound.

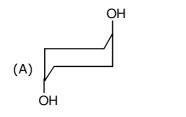
- 1. **Angle strain** is the strain that results when the bond angle is different from desired tetrahedral bond angle of 109.5°.
- 2. **Torsional strain** is caused by repulsion of the bonding electrons of one substituent with bonding electrons a nearby substituent.
- 3. **Steric strain** is caused by atoms or groups of atoms approaching each other too closely.

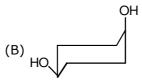
Ex.47 According baeyer-strain theory which compound has minimum angle strain?

- (A) n-butane
- (B) cyclopentane
- (C) cyclopropane
- (D) cyclohexane

Sol. (B)

Ex.48 Which form of trans 1,4-cyclohexane diol is most stable?



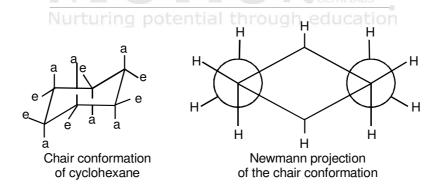


$$(D) \bigvee_{\mathsf{OH}}^{\mathsf{OH}}$$

Sol. (C)

CONFORMATION OF CYCLOHEXANE

Despite Baeyer's prediction that give-membered cyclic compound would be the most stable, the six membered cyclic compound is the most stable. Six membered cyclic compound are most stable because they can exist in a conformation that is almost completely free of strain. This conformation is called the **chair conformation.** In a chair conformation of cyclohexane all bond angles are 111° which is very close to the 109.5° and all the adjacent carbon-hydrogen bonds are staggered.



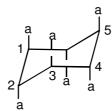
- ⇒ Each carbon in chair conformation has an axial bond and an equatorial bond.
- ⇒ Axial bonds are perpendicular to the plane of the ring and equatorial bonds are in the plane of the ring.



 \Rightarrow If axial bond on carbon-1 is above the plane of the ring then axial bond on carbon-2 will be below the plane of the ring. Thus

C-1, C-3 and C-5 axial bonds are above

C-1, C-4 and C-6 axial bonds are below

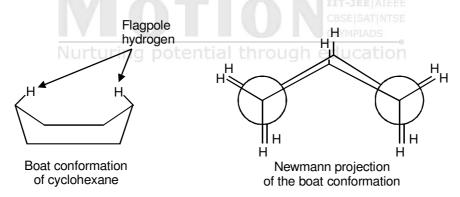


- \Rightarrow Thus C -1 axial and C 2 axial are trans to each other. Similarly C 1 and C 5 axials are cis to each other.
- \Rightarrow It axial bond on carbon I will be above the plane then equatorial bond on this carbon will be below the plane.

- (i) Thus C 1 equatorial and C -2 equatorial will be cis
- (ii) C 1 axial and C-2 equatorial will be cis
- \Rightarrow As a result of rotation about carbon-carbon single bonds cyclohexane rapidly intercoverts between two stable chair conformations. This interconversion is known as ring-flip. When the two chair forms interconvert, axial bonds become equatorial and equatorial bonds become axial.



⇒ Cyclohexane can also exist in a boat conformation. Like the chair conformation, the boat conformation is free of angle strain. However, the conformation is less stable than the chair conformation by 11 Kcal/mole. Boat conformation is less stable because some of the carbon-hydrogen bonds in boat conformation are eclipsed.



The boat conformation is further destabilised by the close proximity of the flagpole hydrogens. These hydrogens are 1.8 $\mathring{\text{A}}$ apart but the van der Waal's radii is 2.4 $\mathring{\text{A}}$. The flagpole hydrogens are also known as trans nuclear hydrogens.

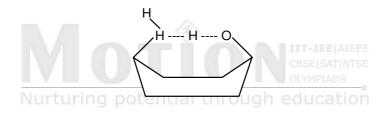
When one hydrogen of cyclohexane is placed by a larger atom or group, crowding occurs. The most

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sever crowding is among atoms held by the three axial bonds on the same side of the molecule; the resulting respulsive interaction is called 1,3-diaxial interaction. This causes steric strain in the molecule. Thus, monosubstituted cyclohexane will assume chair conformation in which the substituent occupies an equatorial position. Similarly in disubstituted cyclohexanes the chair conformation containing both the substituents in equatorial positions will be the preferred conformation. In general, the conformation with bulkier substituent in an equatorial position will be the preferred conformation. For examples:

cis 1,3-cyclohexanediol has shown to have diaxial rather than the diequatorial orientation. This is because of the stabilisation orientation. This is because of the stabilisation of the diaxial form by intramolecular hydrogen bonding which is not possible in the diequatoroial form.

The preferred conformation of the cyclohexane ring is the chair form, but when intromolecular hydrogen bonding is possible between groups in 1 and 4 positions the molecule assumes a boat conformation rather than the chair conformation in which this hydrogen bonding is not possible.



SOME IMPORTANT TERMINOLOGY

Asymmetric carbon: The carbon which is attached with four different groups of atoms is called asymmetric carbon.

Asymmetric molecule: If all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.

Achiral molecule: A molecule that is superimposable on its mirror image. Achiral molecules lack handedness and are incapable of existing as a pair of enantiomers.

Axial bond: The six bonds of a cyclohexane ring (below) that are perpendicular to the general plane of the ring, and that alternate up and down around the ring.

Boat conformation : A conformation of cyclohexane that resembles a boat and that has eclipsed bonds along its two sides.

Chair conformation : The all-staggered conformation of cyclohexane that has no angle strain or torsional strain and is therefore, the lowest energy conformation.

Chiral molecule: A molecule that is not superimposable on its mirror image. Chiral molecules have handedness and are capable of existing as a pair of enantiomers.

Chirality: The property of having handeness.

Configuration: The particular arrangement of atoms (or groups) in space that is characteristic of a given stereoisomer.

Conformatoin: A particular temporary orientation of a molecule that results from rotations about its single bonds.

Conformational analysis: An analysis of the energy changes that a molecule undergoes as its groups undergo rotation (sometimes only partial) about the single bonds that join them.

Conformer: A particular staggered conformation of a molecule.

Connectivity: The sequence, or order, in which the atoms of a molecule are attached to each other.

Diastereomers: Stereoisomers that are not mirror images of each other.

Dextrorotatory: Those substances which rotate the plane of polarisation of light towards right are called dextrorotatory. Currently, dextro and laevo rotations are represented by algebraic signs of (+) and (-) respectively.

Eclipsed conformation: A temporary orientation of groups around two atoms joined by a single bond such that the groups directly oppose each other.

Enantiomers: Stereoisomers that are mirror images of each other. enantiomers rotate the plane of polarised light to the same extent but in opposite direction.

Equatorial bond: The six bonds of a cyclohexane ring that lie generally around the "equator" of the molecule.

Levorotatory: A compound that rotates planepolarized light in a counterclockwise direction.

Meso compound: An optically inactive compound whose molecules are achiral even though they contain tetrahedral atoms with four different attached groups. A meso-compound is optically inactive due to internal compensation.

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Optically active substances: Those substances which rotate the plane of polarisation of plane-polarised light when it is passed through their solution are called optically active substances. This phenomenon is called optical activity.

Plane of symmetry: An imaginary plane that bisects a molecule in a way such that the two halves of the

molecule are mirror images of each other. Any molecule with a plane of symmetry will be achiral.

Plane-polarized light: Ordinary light in which the oscillations of the electrical field occur only in one plane. It is obtained by passing a monochromatic light (light of single wavelength) through a Nicol prism.

Polarimeter: A device used for measuring optical activity.

(R-S) System: A method for designating the configuration of tetrahedral stereogenic centres.

Racemic form (racemate or racemic mixture): An equimolar mixture of enantiomers. A racemic mixture is optically inactive due to external compensation.

Racemisation: The process of conversion of an enantiomer into racemic mixture is known as an racemisation.

Retention: If in an optically active molecule that relative configuration of the atoms groups around a chiral centre remains the same before and after the reaction, the reaction is said to proceed with retention of configuration.

Relative configuration: The relationship between the configuration of two chiral molecules. Molecules are said to have the same relative configuration when similar or identical groups in each occupy the same position in space. The configuration of molecules can be related to each other through reactions of known stereochemistry, for example through reactions that cause no bonds to a stereogenic center to be broken.

Resolution: The process by which the enantiomers of a recemic form are separated.

Ring flip: The change in a cyclohexane ring (resulting from partial bond rotations) that converts one ring conformation to another. A chair-chair ring flip converts any equatorial substitutent to an axial substituent and vice verse.

Ring strain: The increased potential energy of the cyclic form of a molecule (usually measured by heats of combustion) When compared to its acyclic form.

Specific rotation : Specific rotation is defined as the number of degrees of rotation observed when the concentration of optically active substance is 1 g cm⁻³ and length of polarimeter tube is 1 decimetre (dm) for D-line of sodium vapour lamp at 25°C.

Stereogenic center: An atom bearing group of such nature that an interchange of any two groups will produce a stereoisomer.

Steric hindrance : An effect on relative reaction rates caused when the spatial arrangement of atoms or groups at or near the reacting site hinders or retards a reaction.

Torsional strain: The strain associated with an eclipsed conformation of a molecule; it is caused by repulsions between the aligned electron pairs of the eclipsed bonds.

