Isomerism (Structural / Constitutional)

Def^n: Compounds which possess the same molecular formula but differ in bonding arrangements of atoms (or) groups within the molecule are structural isomers & the phenomenon is known as structural isomerism.

They are classified as

1. Chain or nuclear isomerism
2. Position isomerism.
3. Functional isomerism.
4. Metamerism.
5. Ring chain isomerism.

1. Chain isomers: If compounds have same mf but differ in carbon chain / skeleton then they are related as chain isomers.

Example: a) n butane vs Isobutane

b) C-C-C-C-C ; C-C(C)-C-C ; C-C(C)(C)-C

npentane Isopentane neopentane.

c) $H_3C-CH_2-CH_2-CO_2H$; $H_3C-CH(CO_2H)-CH_3$

butanoic acid 2-methyl propanoic acid.

d) $H_3C^5-CH_2^4-CH_2^3-CH_2^2-CN^1$ / $-C(=O)^{1'}-OH$ / $-C(Cl)^{1'}$ / $-CH=O^{1'}$ / $-C(=O)^1-NH_2$

If numbering is started with carbon containing group

vs

$CH_3-CH_2-CH_2-CH_2$

$-CN^1$ / $-C(=O)^{1'}-OH$ / $-C(=O)^1-Cl$ / $-CH=O^{1'}$ / $-C(=O)^1-NH_2$

& if its position is changed, then they are called chain isomers.

=> Minimum carbon required for alkane to show chain isomerism = 4., for alkene it is also 4 but for alkyne it is 5.

e.g C-C-C=C vs C-C(C)=C are chain isomers.

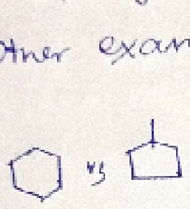
a) 1-butene 2 methyl 1 propene

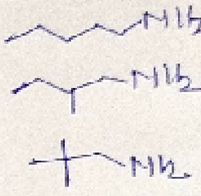
b) C-C-C-C≡C C-C(C)-C≡C are chain isomers.

1-pentyne 3 methyl 1 butyne

: Other examples:

a)

i)  (chain isomers)

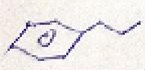
ii)  chain isomers.

- The most branched alkane hydrocarbon with given m.formula i) C_4H_{10} : Isobutane

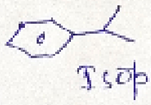
=> Sometimes if there is any change in side chain, then they are also called chain isomers.

ii) C_5H_{12} : Neopentane

iii) C_6H_{16} : Neohexane.



n-propyl benzene



Isopropyl benzene.

: Position Isomers:

If the isomers differ in the attachments of the functional group(or) substituents to the main carbon chain, then they are called position isomers.

: example:

a) $CH_3-CH_2-C\equiv CH$ Butyne-1-yne

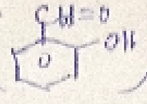
$CH_3-C\equiv C-CH_3$ Butyne-2-yne

(b) 1-chlorobutane vs 2-chlorobutane

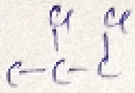
(c) Hexan-1-ol. vs Hexan-3-ol.

d) Catechol ; Resorcinol ; Quinol.

e) Phthalic Acid ; Isophthalic Acid ; Terephthalic Acid

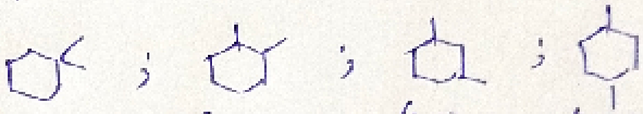
f) Salicyladehyde  vs p-hydroxy benzaldehyde

=> vicinal dihalide & geminal dihalide are example of positional isomers.

e.g  vs 

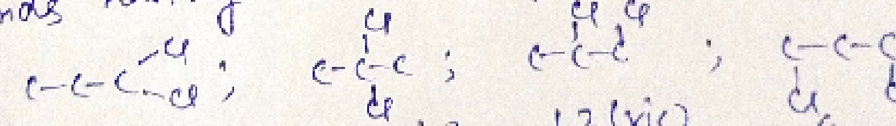
1,1 dichloro propane 1,2-dichloropropane

=> o, m-p - isomers are related as positional isomers.

Q. How many positional isomers possible for dimethyl cyclohexane.  Ans: 4.

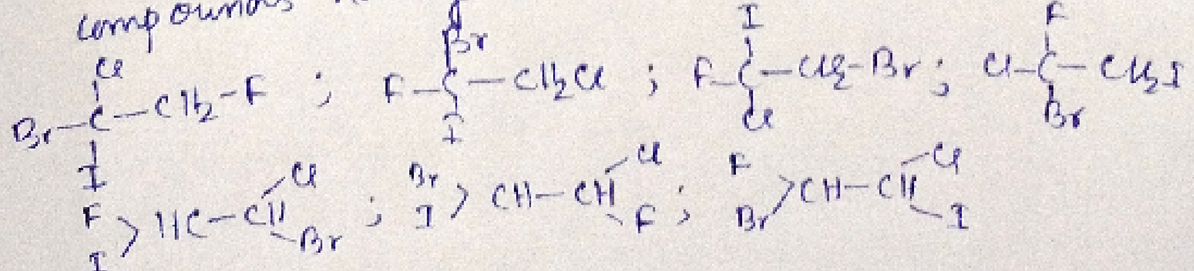
(1,1) (1,2) (1,3) (1,4)

Q. How many positional isomers possible for compounds having molecular formula $C_3H_6Cl_2$?

Ans: 4. 

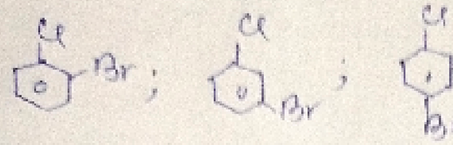
1,1 (gem) 2,2 (gem) 1,2 (vic) (1,3)

Q. How many positional isomers possible for compounds having molecular formula $C_2FClBrIH_2$

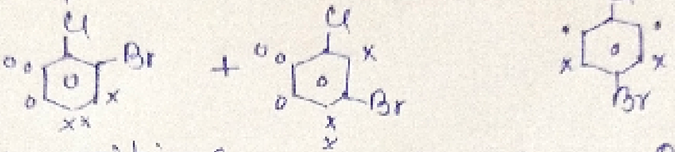


Ans: 7. All are positional isomers.

Q. How many benzenoid structure possible which are related as positional isomers with m.f C_6H_3ClBr

Ans:  (3)

Q. How many benzenoid structure possible which are related as positional isomers with m.f C_6H_3ClBrI.



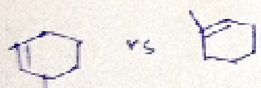
2 different positions where I can occupy.

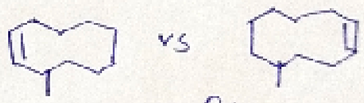
4 different positions where I can occupy.

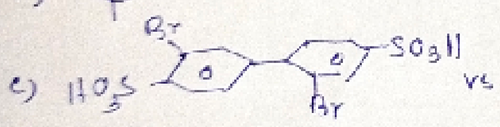
2 different positions.

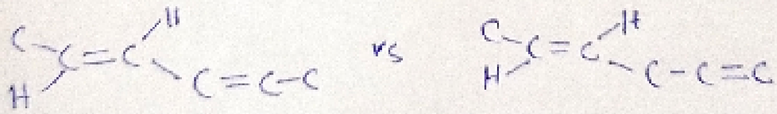
So total number of positional isomers = 4+4+2 = 10.

Other examples of position isomers.

a) 

b) 

c) 

d) 

: Functional isomers:

Compounds with same molecular formula but have different functional groups are related as functional isomers.

$CH_3-\underset{OH}{CH}-CH_3$ vs $CH_3-O-CH_2-CH_3$

2-propanol (Alcohol) Methoxy ethane (ether)

b) $CH_3-CH_2-CH_2-C(=O)-OH$ vs $CH_3-CH_2-C(=O)-O-CH_3$

butanoic acid (Carboxylic acid) — Methyl propanoate (ester)

c) $CH_3-CH_2-CH_2-CH=O$ (Aldehyde) — All same m.f but differ in functional grp

$CH_2=CH-CH_2-CH_2-OH$ (enol) ⇒ Alkenol.

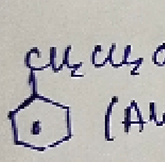
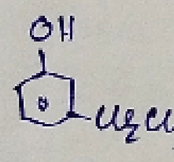
$CH_3-C(=O)-CH_2-CH_3$ (ketone)

$CH_2=CH-CH_2-O-CH_3$ (alkoxy alkene)

d) $CH_3-CH_2-CH_2-NH_2$ (1° Amine) — All have same molecular formula but differ in functional grp. So related as functional isomers.

$H_3C-NH-CH_2-CH_3$ (2° amine)

$H_3C-N(CH_3)-CH_3$ (3° amine)

e)  (Alcoholic -OH) vs  (Phenolic -OH).

f) $CH_3-CH_2-C\equiv N$ (cyanide) vs $CH_3CH_2-N^+\equiv C^-$ (Isocyanide)

g) $CH_3CH_2-N^+(=O)-O^-$ (nitroalkane) vs $CH_3-CH_2-O-N=O$ (alkyl nitrite)

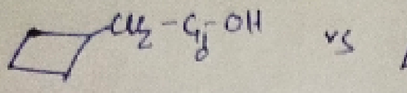
h) $CH_3-O-C\equiv N$ (methyl cyanate) vs $CH_3-N=C=O$ (methyl isocyanate)

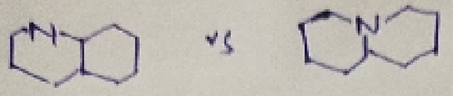
i) $CH_3-CH=N-OH$ (Aldoxime) vs $CH_3-C(=O)-NH_2$ amide.

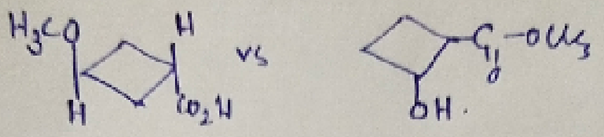
j) CH_3-CH_2-SH (Thiol) vs CH_3-S-CH_3 (Thioether)

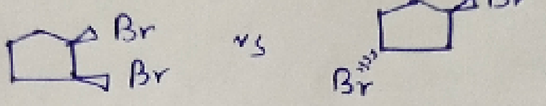
k) $CH_3-C\equiv C-CH_3$ (But-2-yne) vs $CH_2=CH-CH=CH_2$ (1,3 butadiene)

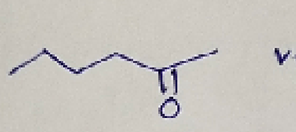
Q. What is the relationship between compounds?

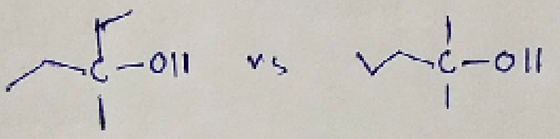
a)  Ans: functional

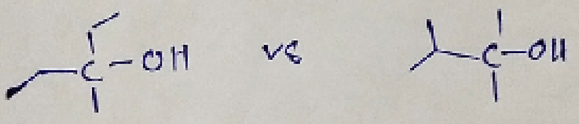
b)  Ans: functional

c)  Ans: functional

d)  Ans: Positional

e)  Ans: Chain.

f)  Ans: Positional

g)  Ans: Chain.

: Metamers: Compounds with same m.f but have different distribution of alkyl groups along divalent functional groups are called metamers. So monovalent functional groups like $-OH$, $-X$ (halide); $-CN$; $-CO_2H$; $-CH=O$ $-C(=O)-Cl$ containing compounds can not show metamerism. Example of bivalent functional grps like

$-O-$	: ether	$-C(=O)-$	: ketone
$-S-$	: Thioether	$-C(=O)-O-$	: Ester
$-NH-$	: 2° amine.	$-C(=O)-O-C(=O)-$	: Acid anhydride

metamerism is possible.

Examples are : i) $CH_3-O-CH_2-CH_2-CH_3$; $CH_3-CH_2-O-CH_2-CH_3$

(methyl propyl ether) & (diethyl ether)

ii) $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$ vs $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

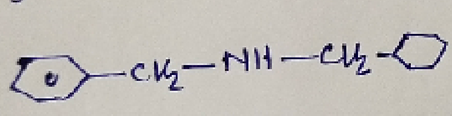
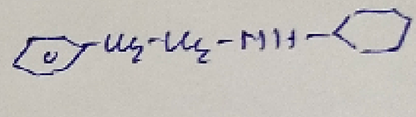
(propyl propanoate) ethyl butanoate.

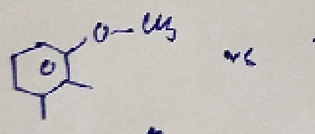
iii) $H_3C-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ vs $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

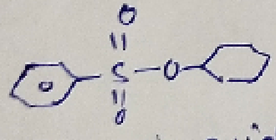
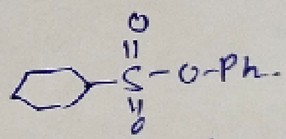
2-pentanone 3 pentanone

↳ they are related as metamer / positional isomer.

iv) $CH_3-S-CH_2-CH_2-CH_3$ $CH_3-S-CH(CH_3)-CH_3$

v)  vs 

vi) 

vii)  vs 

[sulphonic acid ester : Bivalent functional grp].

: Ring chain Isomers:

If one isomeric compound has openchain str & another has ring structure then they are related as Ring chain structure. Examples are

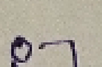
a) $CH_3-CH_2-CH=CH_2$ vs 

but-1-ene cyclobutane.

b) $H_3C-CH_2-C\equiv C-CH_3$ 

Pent-2-yne Cyclopentene.

(e)  (oxirane) vs $CH_2=CH-OH$ (vinyl alcohol)

d)  (oxitane) vs $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (acetone).

Q. The ring chain functional isomers of compounds but-2-ene are Ans:  ; 

Q. Ring chain isomers have different functional grp, but ring chain isomers have one π & R one open chain structure respectively.

Q. Total number of isomeric compound with str. m.f $C_4H_{10}O$. Ans: C_4H_9-OH Ans: 4.
Butyl (4 types).

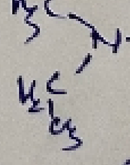
Q. Total number of structural isomeric compound with m.f $C_5H_{12}O$. Ans: $C_5H_{11}-OH$ Ans: 8
Pentyl (8 types)

Q. Total number of structural isomeric compound with m.f $C_4H_{11}N$. Ans: a) $C_4H_9-NH_2$ 4 no. of
Butyl (4 types) 1° amine.

b) $H_3C-NH-CH_2-CH_2-CH_3$

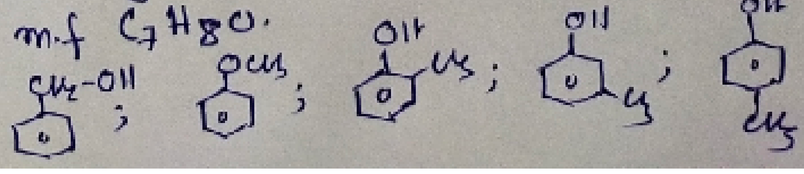
c) $H_3C-NH-CH(CH_3)_2$ 3. no. of 2° amine

d) $H_3C-CH_2-NH-CH_2-CH_3$

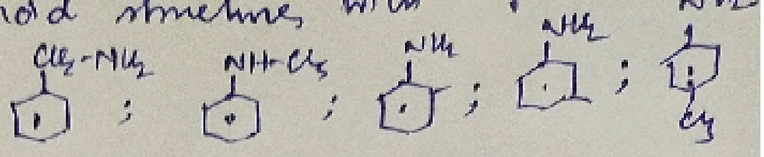
e)  1. no. of 3° amine.

Total = (4 + 3 + 1) = 8 no. of structural isomer.

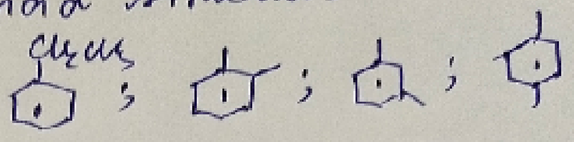
Q. Total number of benzonoid str. possible with m.f C_7H_8O.

Ans: (5). ⇒ 

Q. Total number of benzenoid structures with m.f. C_7H_9N. Ans: 5 =>



Q. Total number of benzenoid structures with m.f $C_8H_{10}O$. Ans: 4 =>



Q. Total numbers of structural isomeric compounds possible with m.f $C_5H_{13}N$.

Pentyl $-NH_2$ => 8 no. of 1° amine.

(8) H_3C-NH-Butyl (4 types)

H_3C-H_2C-NH-Propyl (2 types).

H_2C-NH 6 no. of 2° amine.

$H_3C-N(CH_3)-$Propyl (2 types)

$H_3C-N(CH_2-CH_3)-CH_2-CH_3$

3 no. of 3° amine

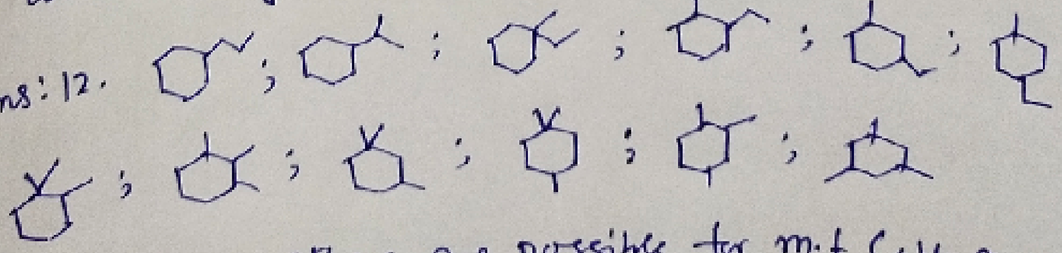
Total no. of amines present = (8+6+3) = 17.

Q. Find out number of acyclic hydrocarbon with molecular formula C_4H_4.

Ans: (2). $CH_2=C=C=CH_2$; $HC\equiv C-CH=CH_2$.

Q. Total number of structural isomers of m.f C_9H_{18} containing cyclohexane ring.

Ans: 12.



Q. How many ethers are possible for m.f $C_4H_{10}O$.

$H_3C-O-CH_2-CH_2-CH_3$; $CH_3-O-CH(CH_3)-CH_3$; $CH_3-CH_2-O-CH_2-CH_3$

Ans: 3.

Q. How many acids & ester are possible for compounds with molecular formula $C_4H_8O_2$

a) (2 types) Propyl $-CO_2H$ — 2 Acids & 4 esters are possible. 2 acids are related as chain isomers.

b) $H_3C-H_2C-\overset{O}{\overset{\|}{C}}-O-CH_3$

c) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$. — All 4 esters are related as metamers.

d) $H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$.

e) $H-\overset{O}{\overset{\|}{C}}-O-CH(CH_3)_2$

Q. How many structural isomeric diens with molecular formula C_5H_8 are possible ?

Ans: 6. $H_2C=C=CH-CH_2-CH_3$ } $CH_3-HC=C=CH-CH_3$ } All are cumulated diene

$H_2C=C=\underset{CH_3}{C}-CH_3$

$H_2C=CH-CH=CH-CH_3$ } All are example of conjugated diene.

$H_2C=CH-\underset{CH_3}{C}=CH_2$.

$H_2C=CH-CH_2-CH=CH_2$ } Isolated diene.

Q. Find out the number of all structurally isomeric alkyne with m.f C_6H_{10}.

Ans: 7. $H-C\equiv C-$ Butyl (4 times)

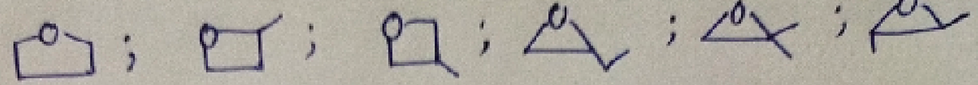
all are example of terminal alkyne

$H_3C-C\equiv C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ } all are example of non-terminal or internal alkyne.

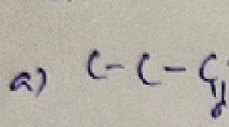
$H_3C-C\equiv C-\underset{CH_3}{CH}-CH_3$

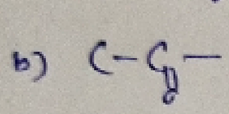
$H_3C-CH_2-C\equiv C-CH_2-CH_3$

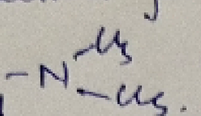
Q. How many structurally isomeric cyclic ether possible with molecular formula C_4H_8O.

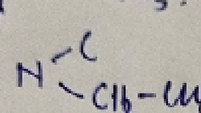
Ans: 6. 

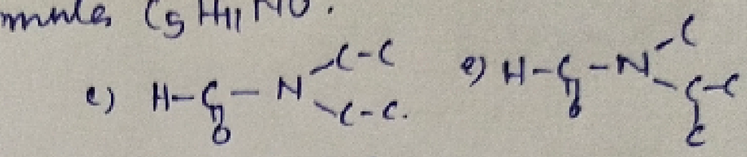
Q. How many 3° amides (structural isomers) possible with molecular formula $C_5H_{11}NO$.

a) 

b) 

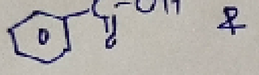
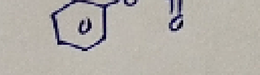
c) 

d) 

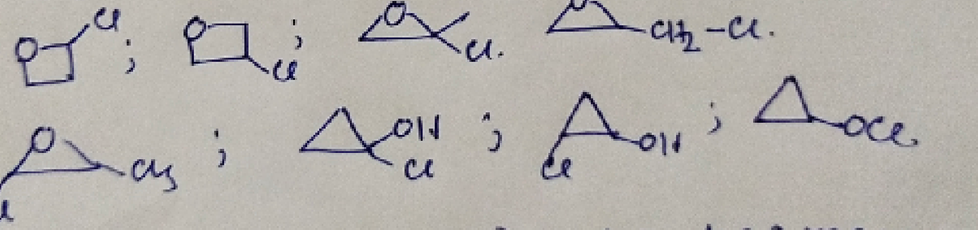
e) 

Ans: 5.

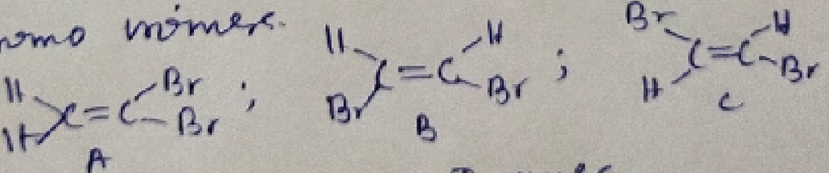
Q. How many benzonoid structures possible for $C_7H_8O_2$

Ans: 2.  &  Related as functional isomers

Q. Find the number of total isomeric structural cyclic compounds possible with m.f C_3H_5ClO.

Ans: 8 

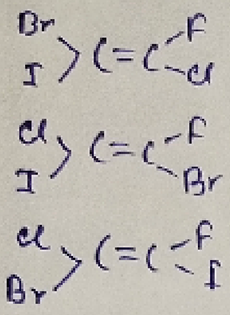
Q. An alkene (m.wt: 186) has how many dibromo isomers.

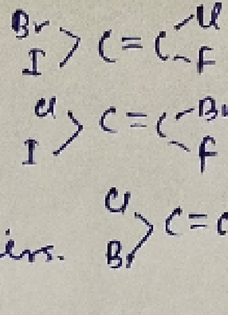


A B C

Ans: 3. A, B: Positional Isomers
A, C: Positional Isomers.
B, C: Stereoisomers (Geometrical isomers)

Q. $C_2FClBrI$ have how many structures possible.

Ans:  X, Y, Z are related as Positional isomers.



X, X' ; Y, Y' ; Z, Z' are related as geometrical isomers.

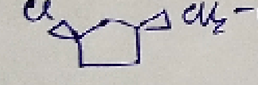
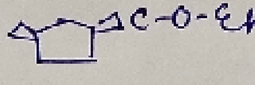
Q. $CH_3-CH_2-NH-CH=O$ & $CH_3-\underset{NH_2}{CH}-CH=O$: functional Isomers.

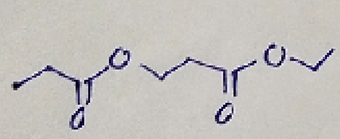
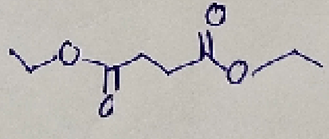
a)

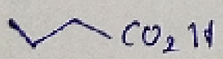
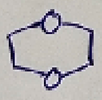
b) $H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ & $H_3C-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$: functional Isomers.

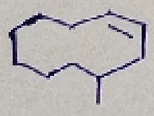
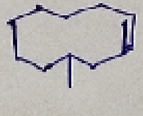
c) 1°, 2°, 3° amines are related as functional isomers but 1°, 2°, 3° alcohols are not related as functional isomers.

d) Ethyl benzene & o-xylene : Chain isomers.

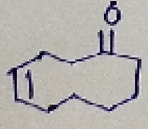
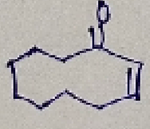
e)   : Metamers.

f)  vs  : metamers.

g)  vs  : Ring chain isomers.

h)  vs  : Identical.

i)  vs  : Homologue.

j)  vs.  : Position isomers.

Molecular formula	No. of Str. isomers
$C_4H_{10}O$	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{20}$	75

C_3H_6	2
C_4H_8	6
C_5H_{10}	9
C_3H_4	2
C_4H_6	6

Monohalide.

C_3H_7X : 2

C_4H_9X : 4

Dihalide.

$C_2H_4X_2$: 2.

$C_3H_6X_2$: 4.

$C_4H_8X_2$: 9.

$C_5H_{10}X_2$: 21.

Alcohol & Ether

C_2H_6O : 1 alcohol + 1 ether.

C_3H_8O : 2 alcohols + 1 ether.

$C_4H_{10}O$: 4 alcohols + 3 ether.

$C_5H_{12}O$: 8 alcohols + 6 ether.

Aldehyde & ketone:

C_3H_6O : 1 aldehyde + 1 ketone.

C_4H_8O : 2 aldehyde + 1 ketone.

$C_5H_{10}O$: 4 aldehyde + 3 ketones.

Acid & Ester:

$C_2H_4O_2$: One acid & 1 ester.

$C_3H_6O_2$: One acid & 2 esters.

$C_4H_8O_2$: 2 acids & 4 esters.

$C_5H_{10}O_2$: 4 acids & 9 esters.

Aliphatic Amine:

C_2H_7N : 1 no. of 1° amine & 1 no. of 2° amine

C_3H_9N : 2 no 1° amine, 1 & 1 no. of 2° & 3° amin

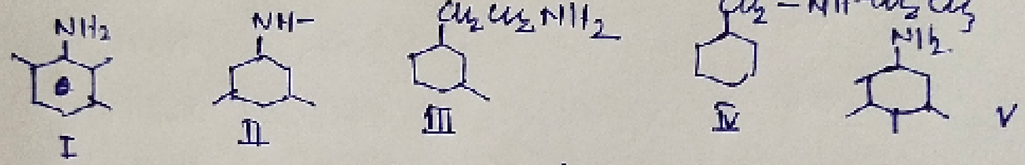
Q. Isomers of $C_{10}H_{14}$ (only aromatic) are

a) 22. b) 23 c) 20 d) 18.

Q. Minimum carbon number for positional isomers for alkane: 5; alkene: 4; alkyne: 4.

Q. The molecular formula of diphenyl methane is $PhCH_2-Ph$. How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom.

a) 6. b) 4. c) 8. d) 7.

Q. 

I II III IV V

Which of the following statements are correct.

a) II & IV are related as metamers.

b) I & II are related as functional isomers.

c) I, III are related as chain isomers.

d) I, V are related as positional isomers.

Q. Which of the following pair is related as constitutional isomers.?

a)  ; Hexa-1,3,5-triene.

b) $CH_2=CH-CH_2-CH_3$. ; 

c) $CH_2(Cl)-CH(Cl)-CH_2CH=O$; $CHCl_2-CH=CH-CH_2OH$

d) $CH_3OCH_2CH_3$. CH_3COCH_3

Q. The correct order of hydrogenation order is

(p) 1,3-pentadiene (r) 2,3-dimethyl-1,3 butadiene

(q) 1,3-butadiene (s) Propadiene

a) p > q > r > s b) s > q > p > r.

c) q > s > p > r. d) s > q > p > r.