CHAPTER

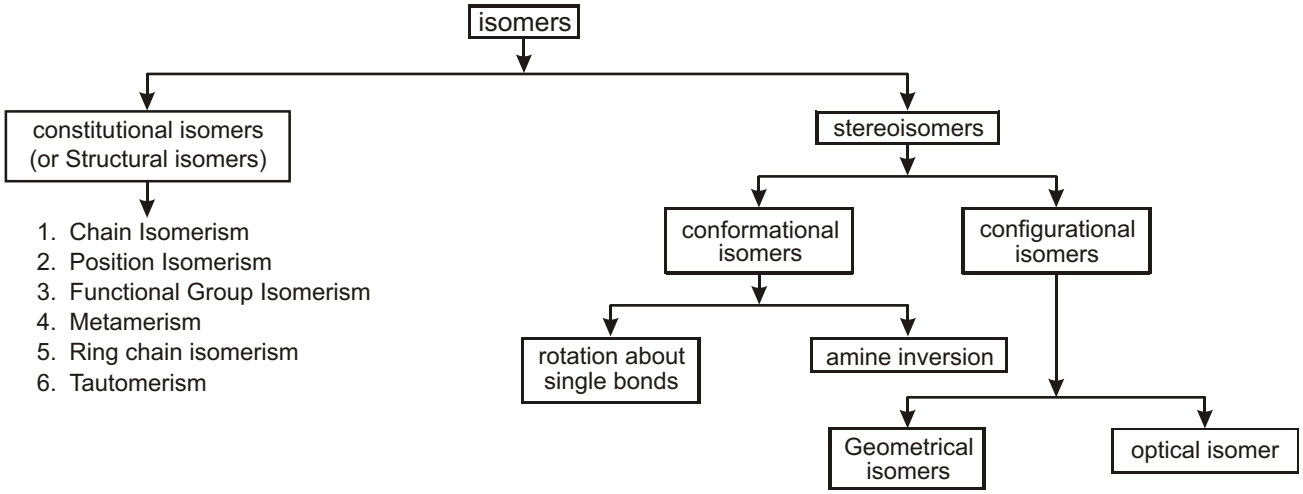
22

Isomerism

Different compounds that have the same molecular formula are called isomers (Greek : isos, equal; meros = part).

They contain the same numbers of the same kinds of atoms, but the atoms are attached to one another in different ways. Isomers are different compounds because they have different molecular structures.

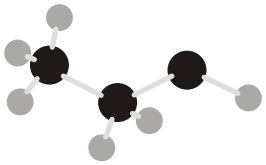
CLASSIFICATION OF ISOMERISM



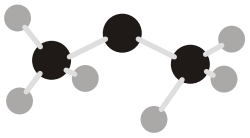
Analysis of dimethyl ether shows that it contains carbon, hydrogen, and oxygen in the same proportion as ethyl alcohol, 2C : 6H : 1O. It has the same molecular weight as ethyl alcohol, 46. We conclude that it has the same molecular formula C_2H_6O.

The compound dimethyl ether is a gas with a boiling point of –24°C. It is clearly a different substance from ethyl alcohol, differing not only in its physical properties but also in its chemical properties. It does not react at all with sodium metal.

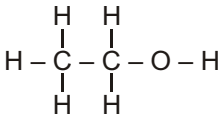
The compound ethyl alcohol is a liquid boiling at 78ºC. It contains carbon, hydrogen, and oxyen in the proportions 2C : 6 H : 1O. It has a molecular weight of 46. The molecular formula of ethyl alcohol must therefore be C_2H_6O. Ethyl alcohol is a quite reactive compound. For example, if a piece of sodium metal is dropped into a test tube containing ethyl alcohol, there is a vigorous bubbling and the sodium metal is consumed; hydrogen gas is evolved and there is left behind a compound of formula C_2H_5ONa. Ethyl alcohol reacts with hydriodic acid to form water and a compound of formula C_2H_5I.



Ethyl alcohol

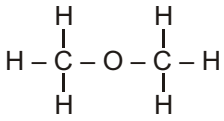


Dimethyl ether



I

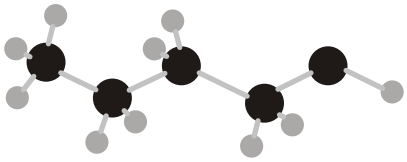
Ethyl alcohol



II

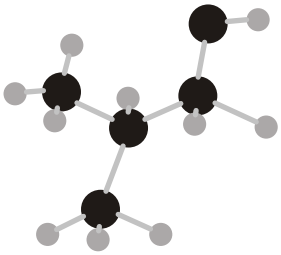
Dimethyl ether

e.g. n-butyl alcohol and isobutyl alcohol (same molecular formula $C_4H_{10}O$) are isomers :



n-butyl alcohol

$CH_3CH_2CH_2CH_2OH$



isobutyl alcohol

$CH_3—CH(CH_3)—CH_2—OH$

Broadly speaking, isomerism is of two types :

(i) Structural isomerism

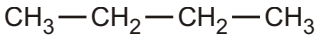
(ii) Stereoisomerism

Structural isomerism : Structural isomers possess the same molecular formula but different connectivity of atoms. The term constitutional isomerism is a more modern term for structural isomerism.It arises because of the difference in the sequence of covalently bonded atoms in the molecule without reference to space.

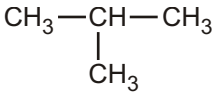
It is further classified into following types.

Chain Isomerism : The different arrangement of carbon atoms give rise to chain isomerism. Chain isomers possess different lengths of carbon chains (straight or branched). Such isomerism is shown by each and every family of organic compounds.

(i) Butane : C_4H_{10}



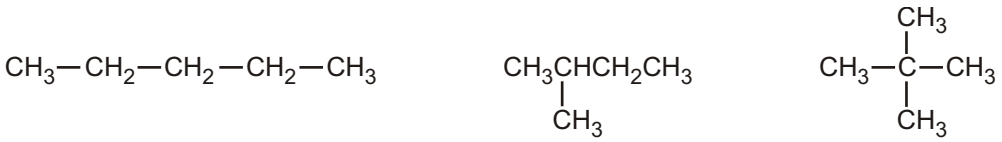
n-butane



iso butane

n-butane has the chain of four carbon while isobutane has three. Hence they are chain isomers.

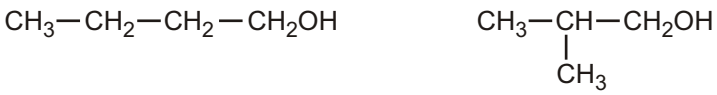
(ii) Pentane : C_5H_{12}



n-Pentane isopentane Neopentane

n-Pentane, isopentane and neopentane possesss the chain of five, four and three carbons, respectively. hence they are chain isomers.

(iii) Butyl alcohol : C_4H_9OH



n-Butyl alcohol isobutyl alcohol

Position Isomerism : Position isomerism is shown by the compounds in which there is difference in the position of attachment of functional group, multiple bond or substituent along the same chain length of carbon atoms. Its characterestics are :

(i) The same molecular formula

(ii) The same length of carbon chain

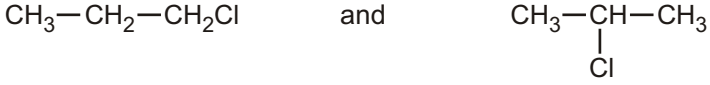
(iii) The same functional group.

e.g.,

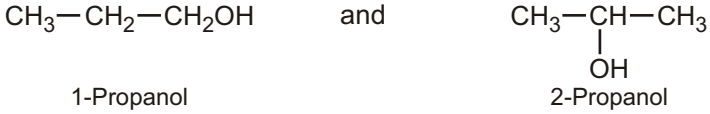
(i) Molecular formula : C_3H_7X (X = halogen, NH_2OH or OR)

(i) (ii)

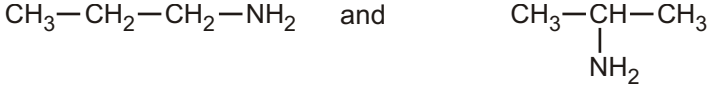
In these structure three carbon atoms form a chain, and X is joined at the end in (i), while at the middle carbon in (ii). Let us look at the following examples along with type of isomerism shown by them.

(a)  : Position isomers

1-Chloropropane 2-Chloropropane

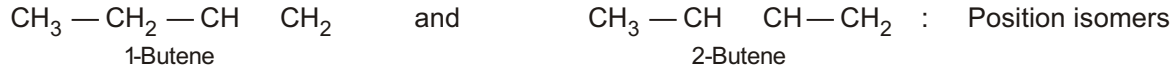
(b)  : Position isomers

1-Propanol 2-Propanol

(c)  : Position isomers

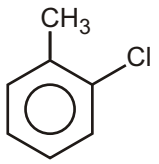
n-Propylamine Isopropylamine

(ii) Similarly, Molecular formula : C_4H_8

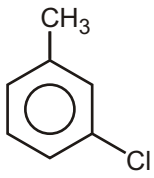
 : Position isomers

1-Butene 2-Butene

In the disubstituted benzene derivatives position isomerism also exists because of the relative position occupied by the substituents on the benzene ring. Thus, Chlorotoluene, $C_6H_4(CH_3)Cl$ exists in three isomeric forms–ortho, meta and para.



O-Chorotoluene



m-Chlorotoluene

p-Chlorotoluene

❑ **NOTE : Carboxylic acid, nitrile, aldehyde will not show positional isomerism**

Functional Group Isomerism :

These isomers possess same molecular formula but different functional groups. Such compounds are called functional group isomers.

(i) Molecular formula : C_2H_6O

$CH_3 - CH_2 - OH$ (Ethyl alcohol (Alcohol)) and $CH_3 - O - CH_3$ (Dimethyl ether (Ether)) : Functional isomers

(ii) Molecular formula : C_3H_6O

$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$ (Aldehyde (Alcohol)) and $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (Propanone (Ketone)) : Functional isomers

(iii) Molecular formula : $C_3H_6O_2$

CH_3-CH_2-COOH (Propanoic acid (Acid)) and $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$ (Methyl acetate (Ester)) : Functional isomers

(iv) Molecular formula : CH_3NO_2

$CH_3-\overset{\overset{O}{\|}}{N}\rightarrow O$ (Nitromethane) and $CH_3-O-N=O$ (Methyl nitrite) : Functional isomers

(v) Molecular formula : C_2H_5NO

$CH_3-CH=N-OH$ (Ethyl oxime) and $CH_3\overset{\overset{O}{\|}}{C}-NH_2$ (Ethanamide) : Functional isomers

Metamerism :

(1) This type of Isomerism is due to unequal distribution of substituents on either side of the functional group.

(2) Members belong to the same homologous series

***e.g.,*:** (i) Diethyl ether and methyl propyl ether

$CH_3CH_2OCH_2CH_3$ Diethyl ether

$CH_3OCH_2CH_2CH_3$ Methyl propyl ether

(ii) Diethyl amine and methyl propylamine

$CH_3CH_2 - NH - CH_2CH_3$ Diethyl amine

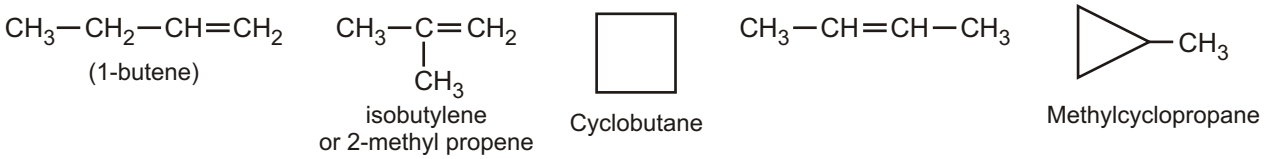
$CH_3CH_2CH_2 - NH - CH_3$ Methyl propyl amine

Ring chain isomerism :

Such isomerism arises because of the difference of carbon–chain or ring.

For example :

(i) Molecular formula : C_4H_6



each of 1-butene and 2-butene is the chain isomer of 2-methylpropene while cyclobutane is the ring chain isomer of each of 1-butene, 2-butene and iso-butylene. Several; similar examples may be cited. Alkanes in no case exhibit ring-chain isomerism.

EXERCISE

SINGLE CHOICE QUESTIONS

1. How many distinct terminal alkynes exist with a molecular formula of C_5H_8?

(A) 1 (B) 2 (C) 3 (D) 4

(E) 5

2. How many distinct terminal alkynes exist with a molecular formula of C_6H_{10}?

(A) 1 (B) 2 (C) 3 (D) 4

(E) 5

3. Which of the following statements are correct?

(1) A pair of position isomers differs only in the position of the functional group(s).

(2) A pair of structural isomers has the same relative molecular mass.

(3) A pair of functional group isomers belongs to different homologous series.

(A) (1) and (2) only (B) (1) and (3) only

(C) (2) and (3) only (D) (1), (2) and (3)

4. Butanoic acid can be reduced to a primary alcohol. Which of the following compounds is the position isomer of the primary alcohol?

(A) $CH_3COCH_2CH_3$ (B) $CH_3CH_2CH_2CH_2OH$

(C) $CH_3CH_2CH_2CHO$ (D) $CH_2CH_2C(OH)HCH_3$

5. How many structural isomers does C_4H_8 have ?

(A) 3 (B) 4 (C) 5 (D) 6

6. Which of the following compounds are structural isomers of C_5H_{10}?

(1) 2-methylbut-2-ene (2) 3-methylbut-1-ene (3) Pent-1-ene

(A) (1) and (2) only (B) (1) and (3) only

(C) (2) and (3) only (D) (1), (2) and (3)

7. How many structural isomers does $C_3H_6Cl_2$ have?

(A) 2 (B) 3 (C) 4 (D) 5

8. Which of the following compounds are the structural isomers of $C_5H_{10}O$?

(1) 2-methylbutanal (2) Propyl ethanoate (3) Pentanal

(A) (1) and (2) only (B) (1) and (3) only

(C) (2) and (3) only (D) (1), (2) and (3)

9. How many different dibromophenols are possible?

(A) 8 (B) 7 (C) 6 (D) 5

(E) 4

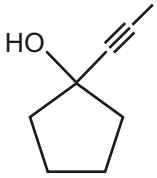
10. How many alcohols are possible for the molecular formula $C_5H_{12}O$ (consider only structural isomers) :

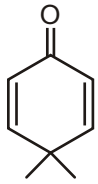
(A) 6 (B) 7 (C) 8 (D) 9

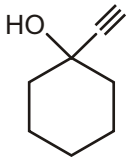
11. How many different structural isomers of molecular formula C_7H_{16} are possible, which contains five membered Parent Chain?

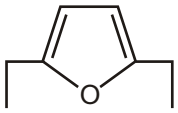
(A) 4 (B) 5 (C) 6 (D) 7

12. Among the following compounds, which is not a structural isomers of others?

(A) 

(B) 

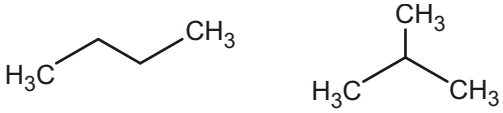
(C) 

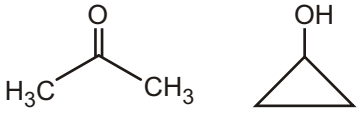
(D) 

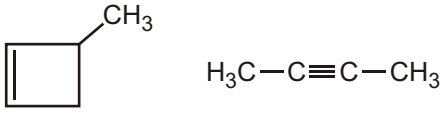
13. Number of structural isomer of C_6H_{14}?

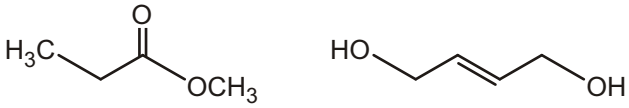
(A) 4 (B) 5 (C) 6 (D) 7

14. Which of the following pairs of molecules are NOT structural isomers?

(A) 

(B) 

(C) 

(D) 

15. How many structurally different alkynes are formed having molecular formula C_5H_8.

(A) 2 (B) 3 (C) 4 (D) 5

16. How many possible structural isomers for $C_5H_{11}Cl$

(A) 6 (B) 7 (C) 8 (D) 9

17. What are the number of structural isomers possible in 1-butene and 1,3-butadiene one H is replaced by D.

(A) 2, 0 (B) 4, 2 (C) 2, 4 (D) 4, 4

18. Position isomers of 1-bromo-1-chloro cyclohexane are :

(A) 6 (B) 5 (C) 4 (D) 3

19. The number of strutural isomers of C_8H_{18} is '*a*' and the number of structural isomers of C_7H_{16} is '*b*.' What is the sum of *a* *b*?

(A) 15 (B) 24 (C) 27 (D) 20

20. Number of structural isomers of C_3H_6O are :

(A) 5 (B) 7 (C) 9 (D) 10

21. Number of structural isomers of $C_4H_8Br_2$ are :

(A) 7 (B) 8 (C) 9 (D) 10

22. Number of structural isomers of C_4H_7Cl are :

(A) 5 (B) 7 (C) 8 (D) 12

23. Number of structural isomers of C_3H_8O are :

(A) 2 (B) 3 (C) 5 (D) 6

24. Two isomeric forms of a saturated hydrocarbon :

(A) have the same structure (B) have different compositions of elements

(C) have the same molecular formula (D) All of these are correct

25. Number of structural isomers of C_4H_9Br are :

(A) 4 (B) 5 (C) 6 (D) 7

26. Number of structural isomers of C_4H_6 are :

(A) 4 (B) 5 (C) 6 (D) 9

27. Number of 6 membered aromatic compounds with molecular formula $C_2H_2N_4$ are :

(A) 3 (B) 4 (C) 5 (D) 6

28. Number of cyclic isomers of C_6H_{12} are :

(A) 11 (B) 12 (C) 13 (D) 14

29. Number of structural isomers of C_3H_6O are :

(A) 8 (B) 9 (C) 5 (D) 6

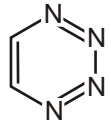
30. Number of isomers of C_5H_{10} are :

(A) 10 (B) 11 (C) 9 (D) 8

31. Number of non-cyclic isomers of C_4H_8O are :

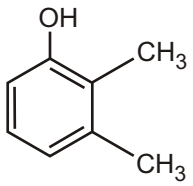
(A) 6 (B) 7 (C) 8 (D) 15

32. Number of positional isomers of given compound with 6 membered aromatic ring are :



(A) 3 (B) 4 (C) 5 (D) 6

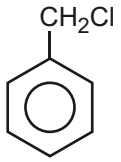
33. Number of positional isomers of given compound with 6 membered aromatic ring are :



(Xylenol)

(A) 3 (B) 4 (C) 5 (D) 6

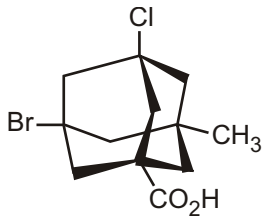
34. Number of positional isomers of given compound with 6 membered aromatic ring are :



(A) 3 (B) 4 (C) 5 (D) 6

SUBJECTIVE TYPE QUESTIONS

1. How many stereoisomers are theoretically possible for the following adamantane derivative?



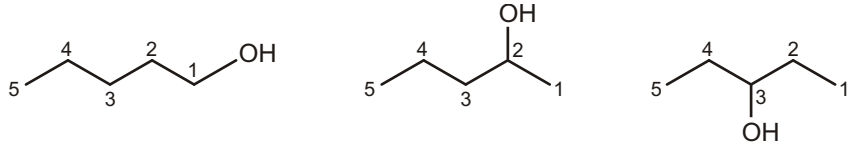
Answers

Single Choice Questions

1. (B)	**2.** (C)	**3.** (C)	**4.** (D)	**5.** (C)	**6.** (D)	**7.** (C)	**8.** (D)
9. (C)	**10.** (C)	**11.** (B)	**12.** (B)	**13.** (B)	**14.** (C)	**15.** (B)	**16.** (C)
17. (B)	**18.** (D)	**19.** (C)	**20.** (C)	**21.** (B)	**22.** (D)	**23.** (B)	**24.** (C)
25. (A)	**26.** (D)	**27.** (A)	**28.** (B)	**29.** (B)	**30.** (A)	**31.** (C)	**32.** (A)
33. (D)	**34.** (B)						

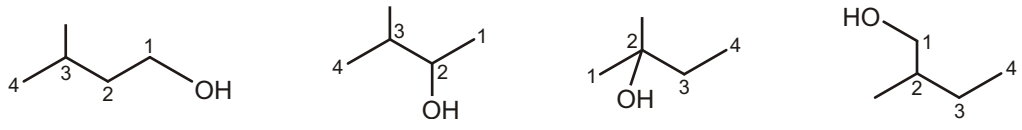
10. $C_5H_{12}O$ D.B.E. value = 0 that means, saturated alcohol is been made.

Taking parent chain to be 5 membered :



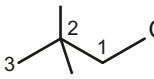
Above three are structurally different (means have different IUPAC names)

Taking parent chain to be 4 membered :



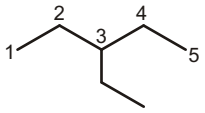
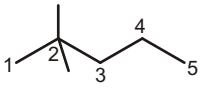
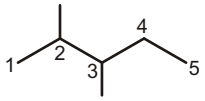
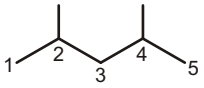
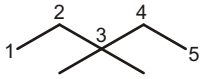
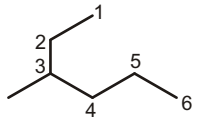
Above four are also structually different.

Now, taking parent chain to be 3 membered :

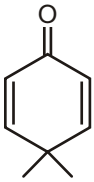


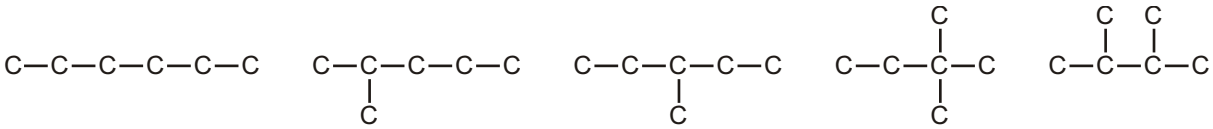
Only 1 possible alcohol

Thus, total 8 alcohols are possible for molecular formula $C_5H_{12}O$.

11. 





(Six carbon parent chain)

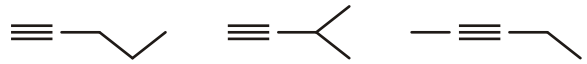
Thus, 5 structures are possible.

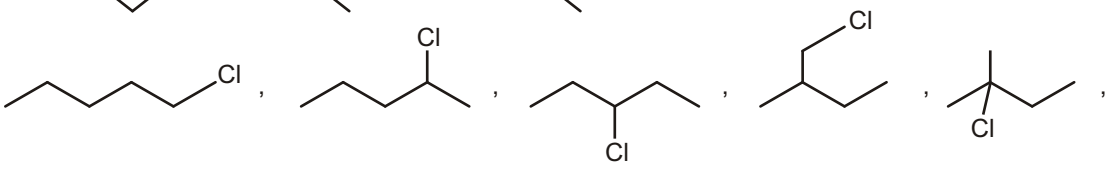
12. 
have D.B.E. value = 4, rest all have DBE value = 3

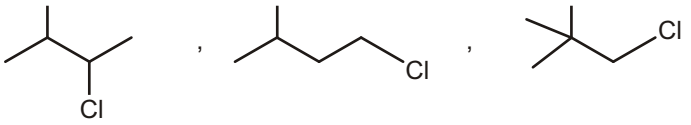
13. 

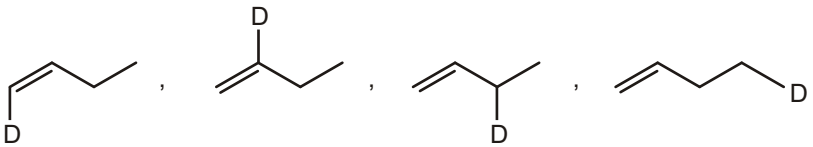
Total structural isomers = 5

14. In (C) number of carbons are not same.

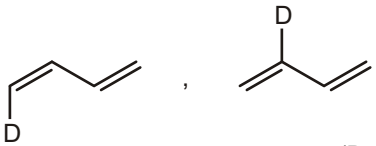
15. 
3 alkynes

16. 



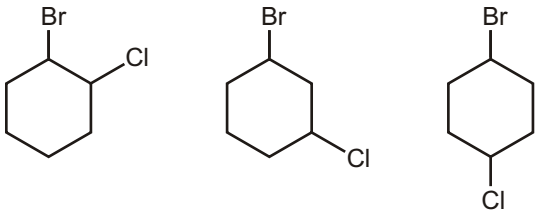
17. 

(1-Butene)



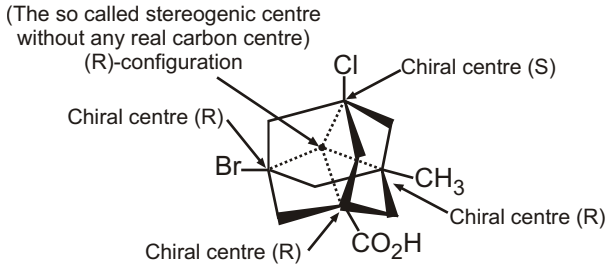
(Buta-1, 3-diene)

18.



Subjective Type Questions

1. Although four asymmetric carbon atoms are present in this compound, it exists in the form of only two stereoisomers (enantiomers) rather than the sixteen predicted by the 2^n rule. There is, in fact, only one stereogenic centre, shown by the black dot at the centre of the molecule (in the following diagram), and the configuration shown here is (R). The asymmetric carbon atoms are not stereogenic centres, because any two substituents on any of these bridgehead carbons cannot be exchanged without destroying the constitutional integrity of this rigid, highly bridged molecule. The configurations of the asymmetric bridgehead carbon units in this structure are (R), (S), (R) and (R) respectively, for the Br, Cl, CO_2H and CH_3 substituents. Its enantiomer would, of course, have the opposite configurations.



❑❑❑