Organic Chemistry

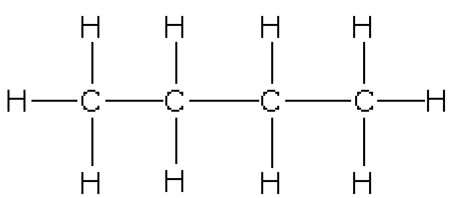
To understand life as we know it, we must first understand a little bit of organic chemistry. Organic molecules contain both carbon and hydrogen. Though many organic chemicals also contain other elements, it is the carbon-hydrogen bond that defines them as organic. Organic chemistry defines life. Just as there are millions of different types of living organisms on this planet, there are millions of different organic molecules, each with different chemical and physical properties. There are organic chemicals that make up your hair, your skin, your fingernails, and so on. The diversity of organic chemicals is due to the versatility of the carbon atom. Why is carbon such a special element? Let's look at its chemistry in a little more detail.

Versatile Nature of Carbon

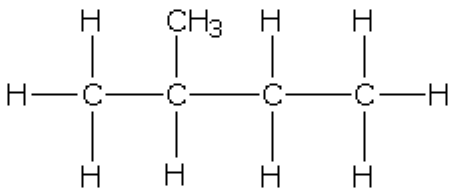
Catenation

The property of self-linking with atoms of the same element is termed Catenation. Carbon has a unique property of linking itself to other carbon atoms to give open chain or/and cyclic structures. Catenation is favored by atoms where atom to atom covalent bond is quite strong.

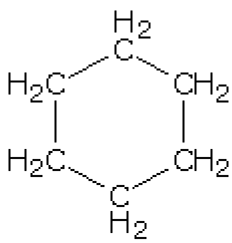
In carbon, C-C bond energy is very high (347.3 kJ mol^{-1}) causing catenation. Further, the carbon atom due to its tetravalency, can be bonded to two, three or four carbon atoms by forming single and multiple bonds. Therefore, chains of carbon atoms may be linear, branched or cyclic. For example,



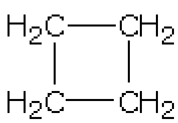
(linear chain)



(branched chain)



(Cyclic)



(Cyclic)

Catenation is responsible for the existence of a large number of organic compounds.

Strength of Bonds with Other Elements

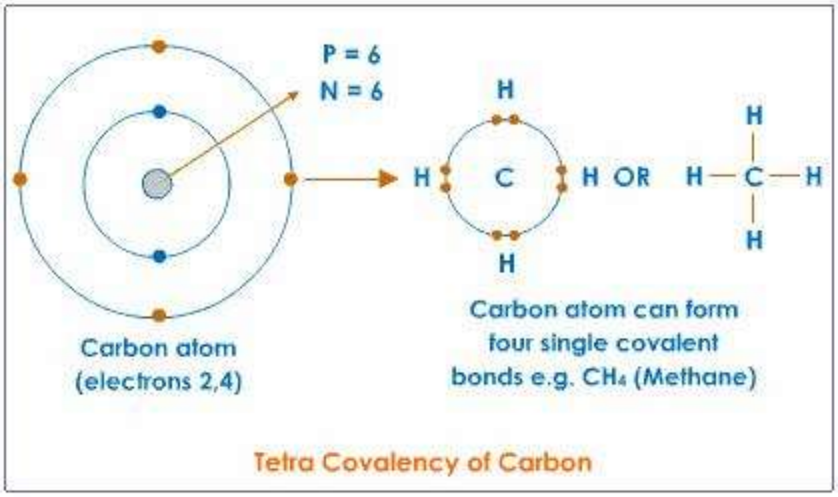
The C-C and C-H bonds in organic compounds are very strong. During chemical reactions, these bonds generally do not break easily. However other atoms or groups such as Cl, OH, etc., attached to the carbon atom may get replaced easily. For example, aqueous KOH reacts with haloalkanes to give the corresponding alcohol

$$\underset{\text{chloroethane}}{CH_3—CH_2—Cl} + KOH_{(aq)} \longrightarrow \underset{\text{ethanol}}{CH_3—CH_2—OH} + KCl$$

All these features make carbon to form a more variety of compounds

Tetravalent Nature

Due to its tetravalent nature carbon always form covalent bonds by sharing electrons with one, two, three or four carbon atoms or atoms of other elements or groups of atoms as discussed earlier.



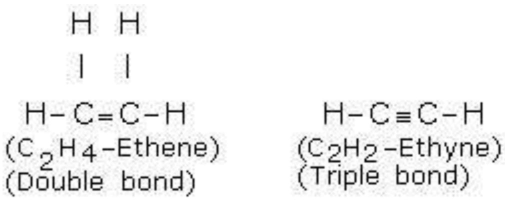
The tetra covalency of carbon atom allows it to combine easily with other carbon atoms to form a stable chain like structure i.e., exhibiting the property of catenation. Catenation usually occurs because the atom-to-atom covalent bond is quite strong. The chains having different chain lengths and structures and combines with different elements it leads to the formation of a large number of compounds. Two unique features of carbon stand out due to this. They are:

Formation of Strong C-C Covalent Bonds

The single bond formed between the carbon atoms is strong. This results in the formation of stable compounds. Carbon atom can also form stable bonds with other atoms like H, Cl, Br, O, etc.

Formation of C-C Multiple Bonds

Due to its small size the carbon atom can also form multiple bonds i.e., double and triple bonds with not only carbon but with atoms of other elements like oxygen, nitrogen, etc. The formation of these multiple bonds gives rise to a variety in the carbon compounds.



Homologous Series

Many organic compounds in the different functional groups have similar chemical properties but their physical properties change throughout a homologous series.

A series of compounds in which each member differs from the next member by a $-CH_2$ Group is called a homologous series, and the members of the series are called homologues.

The study of a homologous series is very important in organic chemistry.

Example:

1. Alkanes (saturated hydrocarbons) form a homologous series.

The general formula for this series is C_nH_{2n+2}

The first ten members of this series are:

Methane CH_4

Ethane C_2H_6

Propane C_3H_8

Butane C_4H_{10}

Pentane C_5H_{12}

Hexane C_6H_{14}

Heptane C_7H_{16}

Octane C_8H_{18}

Nonane C_9H_{20}

Decane $C_{10}H_{22}$

2. Homology as applied to the functional group of alcohols.

Methanol CH_3-OH

Ethanol CH_3-CH_2-OH

Propanol CH_3-CH_2-CH_2-OH

Butanol CH_3-CH_2-CH_2-CH_2-OH

Pentanol CH_3-CH_2-CH_2-CH_2-CH_2-OH

Properties of Compounds within the same Homologous Series:

Two types of properties of substances (of all types, incl. elements, mixtures and compounds) are described within the subject of chemistry. They are the chemical properties of the substance and the physical properties of the substance.

1. Chemical Properties

Organic compounds that are part of the same homologous series generally have similar chemical properties as each other, due to the presence of the same functional group in the molecules of all compounds in the series.

Even though members of the same homologous series generally have similar chemical properties there may still be trends through the group (e.g. as reactivity and rates of reaction vary with parameters such as molecular weights).

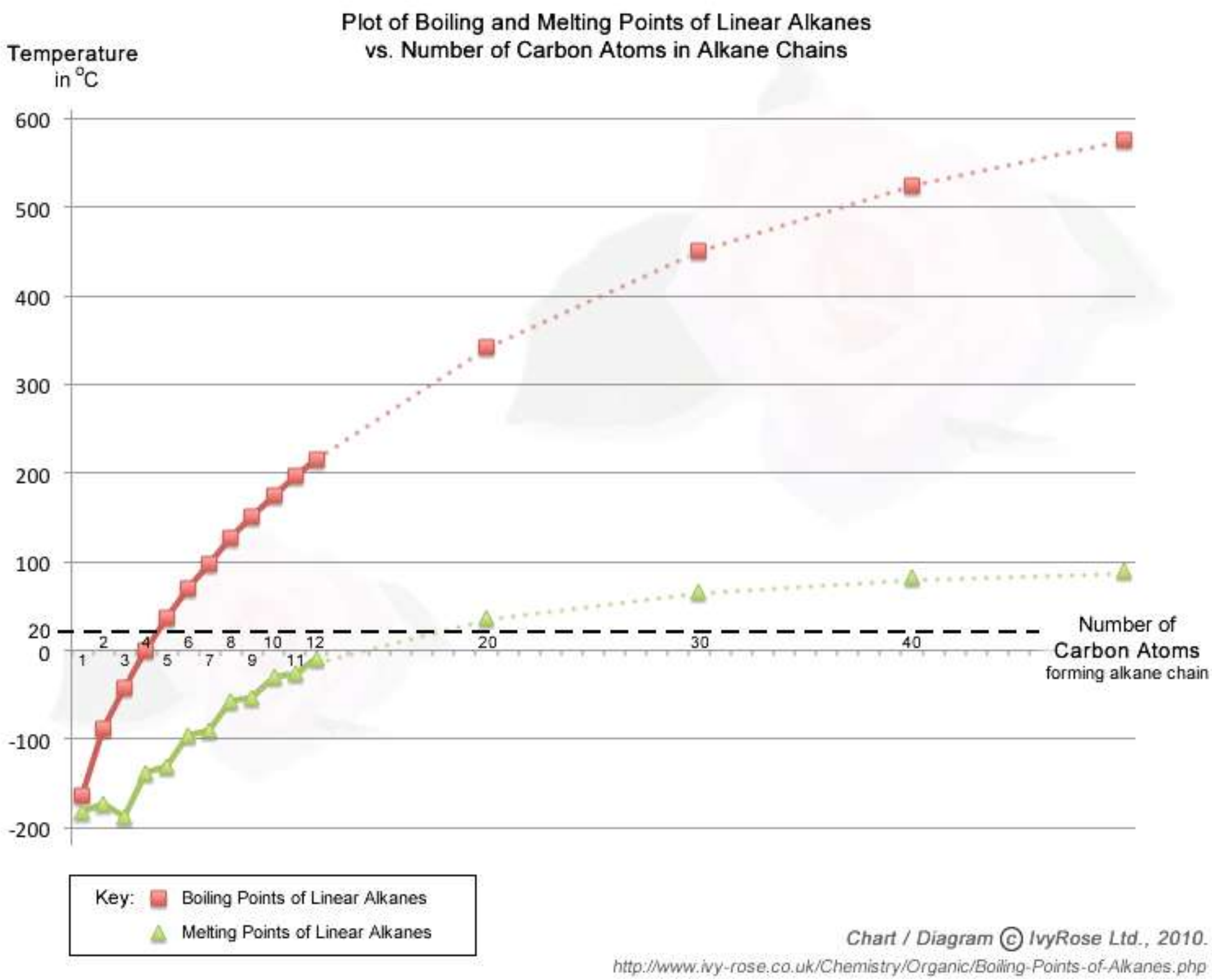
2. Physical Properties

Physical properties of organic compounds that are part of the same homologous series follow trends through the series.

The physical properties of any particular member of a homologous series depends on its size, or (therefore) it's position within the homologous series.

A common example of trends within homologous series is that of the boiling points of the members of the series.

See, for example, boiling points of alkanes.



As mentioned above, the trends in physical properties of compounds within a homologous series are primarily due to the progression of sizes and therefore weights of the molecules that form the homologous series. Using the example of the boiling points of alkanes, ethane having a higher boiling point than methane is explained by molecules of ethane (C_2H_6) having more Van der Waals forces (intermolecular forces) with neighbouring molecules than is true for methane (CH_4) due to the greater number of atoms forming molecules of ethane, compared with methane.

Characteristic features of a homologous series:

1. All the homologues of a given series can be represented by a general formula.

2. There is a common difference of - CH_2 - between the molecular formulae of any two consecutive

homologues in each and every series.

3. The chemical properties of homologues are almost similar.

4. Homologues show a gradation (regular change) in their physical properties.

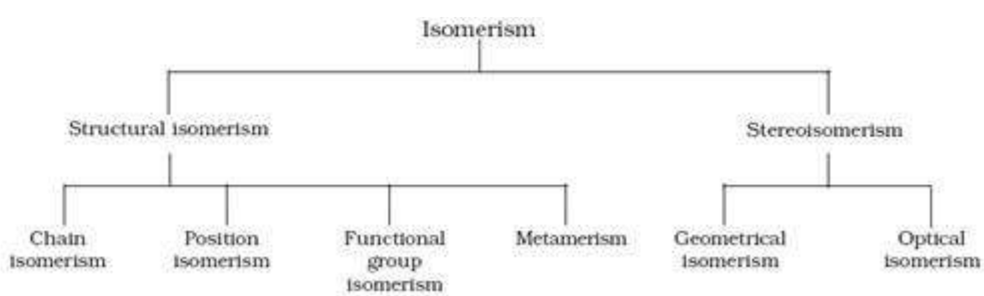
5. Homologues have the same common methods of preparation.

6. If you are aware of the chemistry of one or two members of a homologous series, you can easily predict the chemistry of all the other members of the same series. Therefore, the study of organic chemistry is much simplified by the concept of homology.

Isomerism

Isomerism: There are some compounds which have the same molecular formula but different physical and chemical properties. They are called as isomers and this phenomenon is called isomerism.

Types of isomerism: Two types, Structural and Stereoisomerism.

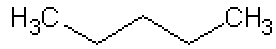
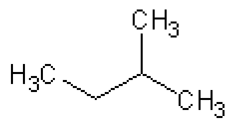
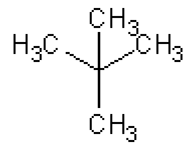


Structural Isomerism

Compounds having the same molecular formula but different structures are structural isomers.

The various types of structural isomerism are:

- **Chain isomerism**: Similar molecular formula but different carbon skeletons.
  e.g. Pentane(C_5H_{12})has three isomers

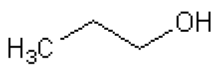
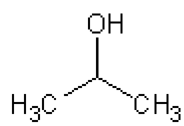
  

Pentane | 2-Methylbutane (Isopentane) | 2,2-Dimethylpentane (Neopentane)

Find the no. of chain isomers in Butane (C_4H_{10}) and Hexane (C_6H_{14}).

- **Position Isomerism**: Same structure of carbon chains but differ only in the positions of functional group or the multiple bond.

  e.g.

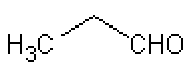
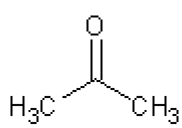
   

  Propan-1-ol Propan-2-ol

  Find the position isomer of But-2-ene, 2-Pentanone, o-Xylene

- **Functional Isomerism**: Same molecular formula but different functional groups.

  e.g. C_3H_6O represents an aldehyde and a ketone as shown

  Propanal Propanone

Find the Functional isomers of Ethanol, Propanoic acid, 1.3-Butadiene, Nitroethane, Propanamine, Ethanenitrile, Benzyl alcohol

Stereoisomerism

Isomers which have the same structures but differ in the relative arrangements of atoms or groups in space are called stereoisomers. These are of three types

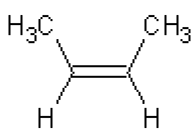
(b) Geometrical Isomerism

(c) Optical Isomerism

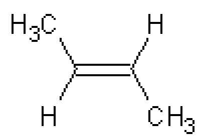
Geometrical Isomerism

The compounds containing a double bond have two types of bonds, σ-bond and π-bond. π-bond forms because of the lateral overlap of p-orbitals. So rotation about double bond is difficult as it will break the π-bond (which requires high energy). So the groups attached to the Carbon get fixed. These types of stereoisomers which have the same structural formula but differ in the spatial arrangement of atoms around the double bond are called geometrical isomers. The isomer in which the two similar atoms/groups lie on the same side of the double bond is called the cis-isomer while that isomer in which the two similar atoms/groups lie on the opposite side of the double bond is called the trans-isomer.

e.g.



cis-But-2-ene



trans-But-2-ene

Compounds of type abC=Cab, abC=Cad and abC=Cde exhibit geometrical isomerism.

Nomenclature

Nomenclature has five parts:

Word root	denotes the number of carbon atoms present in the principal chain of the compound. C_1-meth C_2-eth C_3-prop C_4-but These are the special names for first four carbons. Others follow Greek numbering
1^0 prefix	is used to differentiate between cyclic and acyclic compounds
2^0 prefix	In IUPAC some functional groups are not considered as functional groups but are treated as substituents. To denote these we use secondary prefixes. Example:

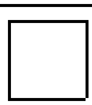
	Flouro: -F, Chloro:-Cl, $-NO2$: nitro
1^0 suffix	always added to the word root to indicate whether carbon chain is saturated or unsaturated.
2^0 suffix	added to indicate a particular functional group present in the principal chain. Ex: alcohols, acids acid derivatives etc

<u>**NAME = 2^o prefix + 1^o prefix+ word root +1^o suffix + 2^o suffix**</u>

Some points to be noted:

- an extra 'a' is added to word root if primary suffix begins with a consonant.
- while adding the secondary suffix to primary the terminal 'e' of the primary suffix is dropped if secondary begins with a vowel else it's retained.

Examples

	Word root	*Primary suffix*	*Secondary suffix*	*IUPAC name*
CH_3-CH_2-OH	eth	ane	ol	ethanol
CH_2=CH-CO-CH_3	but	ene	one	butenone
	Primary prefix	*Word root*	*Primary suffix*	*IUPAC name*
	cyclo	but	ane	cyclobutane

There are at least three systems in use for naming alkanes. However, the IUPAC system of nomenclature is used almost universally. According to this system, the first four members of the alkane series have special names related to their history. Thereafter, the alkanes are named after the number of carbon atoms it contained in the continuous open chain. The names of all alkanes end with the suffix '-ane'.

Names of some typical n-alkanes

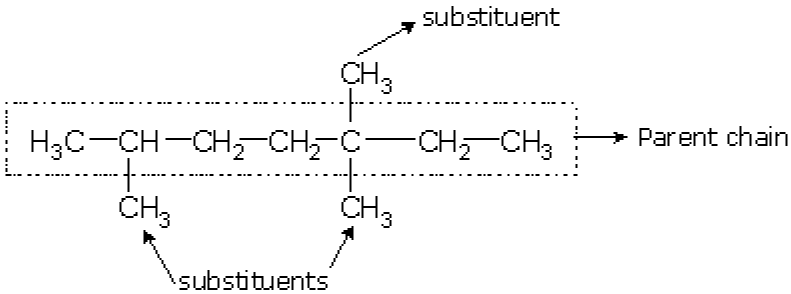
Number of 'C' atoms	Word root	IUPAC name	Structure	Molecular formula
1	Meth	Methane	CH_4	CH_4
2	Eth	Ethane	$CH_3—CH_3$	C_2H_6
3	Prop	Propane	$CH_3—CH_2—CH_3$	C_3H_8
4	But	Butane	$CH_3—(CH_2)_2—CH_3$	C_4H_{10}
5	Pent	Pentane	$CH_3—(CH_2)_3—CH_3$	C_5H_{12}
6	Hex	Hexane	$CH_3—(CH_2)_4—CH_3$	C_6H_{14}
7	Hept	Heptane	$CH_3—(CH_2)_5—CH_3$	C_7H_{16}
8	Oct	Octane	$CH_3—(CH_2)_6—CH_3$	C_8H_{18}
9	Non	Nonane	$CH_3—(CH_2)_7—CH_3$	C_9H_{20}
10	Dec	Decane	$CH_3—(CH_2)_8—CH_3$	$C_{10}H_{22}$
11	Undec	Undecane	$CH_3—(CH_2)_9—CH_3$	$C_{11}H_{24}$
12	Dodec	Dodecane	$CH_3—(CH_2)_{10}—CH_3$	$C_{12}H_{26}$
13	Tridec	Tridecane	$CH_3—(CH_2)_{11}—CH_3$	$C_{13}H_{28}$
14	Tetradec	Tetradecane	$CH_3—(CH_2)_{12}—CH_3$	$C_{14}H_{30}$
15	Pentadec	Pentadecane	$CH_3—(CH_2)_{13}—CH_3$	$C_{15}H_{32}$
16	Hexadec	Hexadecane	$CH_3—(CH_2)_{14}—CH_3$	$C_{16}H_{34}$
20	Icos	Icosane	$CH_3—(CH_2)_{18}—CH_3$	$C_{20}H_{42}$
30	Triacont	Triacontane	$CH_3—(CH_2)_{28}—CH_3$	$C_{30}H_{62}$

The branched-chain alkanes are named as the derivatives of the parent alkane, which is identified by the number of carbon atoms in the continuous, straight chain of carbon atoms. The IUPAC rules for naming alkanes are:

Rules For Naming Straight and Branched Chain Alkanes

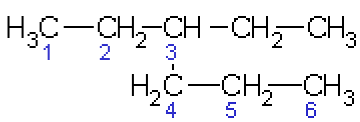
Rule 1

Long chain rule

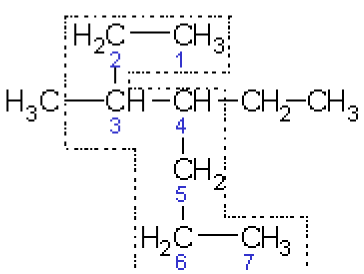


Select the longest continuous chain of carbon atoms in the molecule of the given compound. This longest chain is regarded as the parent chain. The number of carbon atoms in the parent chain determines the word root. Carbon atoms, which are not included in the parent chain are identified as substituents or branched chains.

The longest chain may or may not be straight, but it must be continuous. The selection of the longest continuous chain in molecules is illustrated below:



Longest chain consisting of six carbon atoms

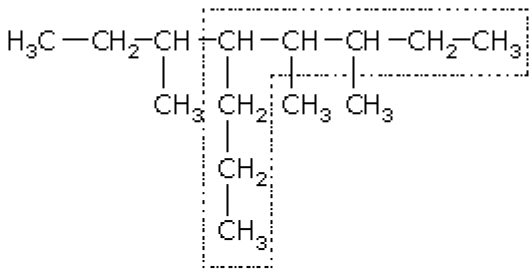


Longest chain consisting of seven carbon atoms

Rule 2

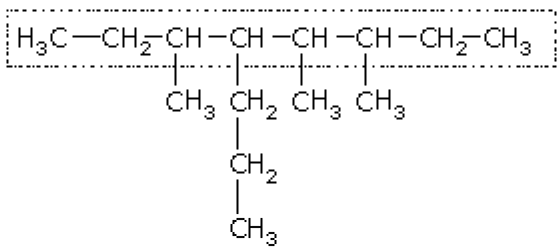
Larger number of side-chains rule

If two different chains of equal lengths (equal number of C atoms) are possible, then select the chain which has larger number of side-chains i.e., select the more-branched chain. For example, in the following molecule, there could be two continuous chains of eight carbon each. The correct choice is the chain as shown because it has more side-chains.



Not correct

(Longest chain but only 3-substituents)



Correct

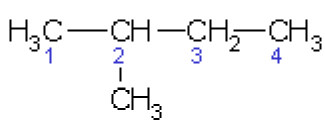
(Longest chain with 4-substituents)

Rule 3

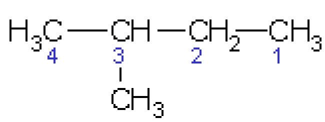
Lowest number rule

When only one side chain is present:

The carbon atoms in the selected parent chain are numbered as 1, 2, 3… from one end to the other. The numbering is done in such a way that the carbon atom carrying the side-chain is given the lowest possible number. For example,



Correct (1)



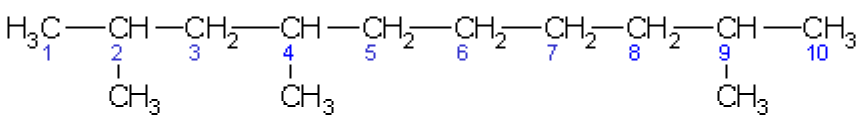
wrong (2)

The numbering in formula 1 is correct because the carbon at which the substituent is present gets a lower number.

The number indicating the position of the substituent or side chain on the main chain is called its position number or locant.

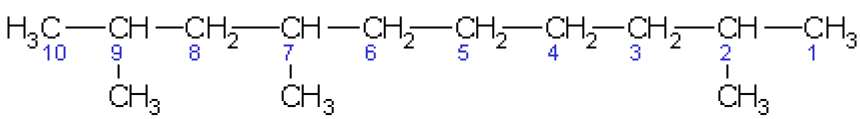
When more than one side chains are present:

- If more than one side-chains containing the same number of carbon atoms are present, then the numbering is done so that the sum of the numbers given to the carbon atoms (i.e., sum of the locants) is the lowest. This is called the lowest sum rule. For example, the numbering of chain as done in I is correct because the sum of the locants in this chain is lower than that in II.



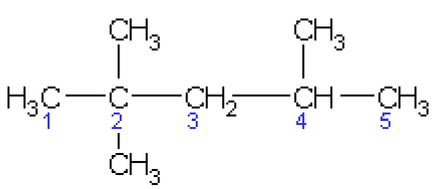
(I) Correct

Sum of the locants = 2 + 4 + 9 = 15

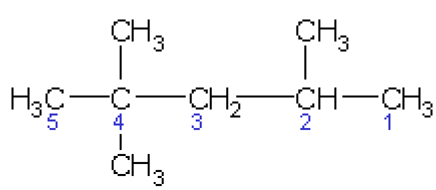


(II) Wrong

Sum of the locants = 2 + 7+ 9 = 18



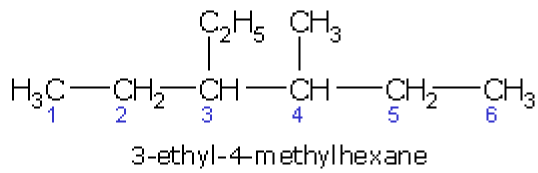
(I) Correct



(II) Wrong

Sum of the locants =2 + 2 + 4 = 8 Sum of the locants = 2 + 4 + 4= 10

- If the side chains containing different number of C atoms are at equal distance from the two ends of the chain, then numbering of the chain is done in such a way that the alkyl group which comes first in alphabetic order gets the lower position. For example, if ethyl and methyl groups are present at equivalent positions, then carbon bearing ethyl group should get the lower number.



Naming the Side Chains (or substituents)

- Each side chain is named on the basis of number of carbon atoms it contains. For example, the side chain containing one carbon atom (- CH_3) is called methyl, that containing two carbon atom (-C_2H_5) is called ethyl and so on.
- If the same substituent or side chain occurs more than once in the molecule, the name of the substituent or side chain is prefixed with a suitable prefix: di for two, tri for three. For example, if methyl group occurs twice on the chain then the substituent is designated as dimethyl.
- Names of the side chains are arranged alphabetically. The prefixes such as, di-tri- etc., are not considered while arranging the names of the side-chains alphabetically. For example, if a molecule contains one ethyl (-C_2H_5) and one methyl (-CH_3) group then while naming, the ethyl is written first followed by methyl i.e., as ethyl-methyl.
- The position of each substituent (or side chain) is indicated by the serial number of the carbon atom (in the chain) to which it is attached. The position number is written before the name of the side chain (or substituent) and separated from it with a hyphen. For example, if a methyl group occurs at carbon atom number 2 in the chain, then it is designated as 2-methyl.
- If in a molecule, one methyl group occurs at carbon number 2 and an ethyl group at carbon number 4, then the side chains are written as 4-ethyl-2-methyl.
- If in a molecule, two methyl groups occur at carbon number 3 and one ethyl group at carbon number 5, then the side chains are described as 5-ethyl-3,3-dimethyl.