1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 2)
Module Name/Title	Organic Chemistry – Some Basic Principles and Techniques: Part 2
Module Id	kech_21202
Pre-requisites	Knowledge about functional groups and classification of organic compounds
Objectives	After going through this lesson, the learners will be able to: • Learn about nomenclature for various organic compounds. • Write IUPAC nomenclature for aliphatic and aromatic organic compounds. • Differentiate between structural isomerism and stereoisomerism. • Explain different types of structural isomerism possible for organic compounds.
keywords	IUPAC nomenclature of organic compounds, nomenclature of benzene compounds, Structural isomerism and stereoisomerism

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1. Introduction

In this module you will learn about the International Union of Pure and Applied Chemistry (IUPAC) nomenclature of organic compounds. According to IUPAC, there are certain set of rules for the systematic naming of the organic compounds. IUPAC names are written in such a way that they are correlated with the structure and learner can easily deduce the structure from the name.

You will also learn about isomerism in organic compounds in this module. Two types of isomerism are possible in organic compounds and that are; 1) structural isomerism and 2) stereoisomerism. However, there are many subtypes for structural isomerism and stereoisomerism.

2. Nomenclature of Organic Compounds

There are millions of compounds in organic chemistry. In order to clearly identify every compound, a systematic method of naming has been established and is known as the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature. According to IUPAC nomenclature, the names are written in in such a way that they are correlated with the structure and reader can easily deduce the structure from the name. International Union of Pure and Applied Chemistry (IUPAC) have given a set of rules for the systematic naming of the organic compounds.

2.1 Trivial or Common Names

The names of organic compounds were either based on their origin or certain properties, before the IUPAC system of nomenclature was developed. For example, citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is formica. These names are traditional and are considered as trivial or common names. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases important, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 1.

Table 1 Common and trivial names of some organic compounds

Compound	**Common name**
CH_4	Methane
$H_3CCH_2CH_2CH_3$	n-Butane
$(H_3C)_2CHCH_3$	Isobutane
$(H_3C)_4C$	Neopentane
$H_3CCH_2CH_2OH$	n-propylalcohol
HCHO	Formaldehyde
$(H_3C)CO$	Acetone
$CHCl_3$	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$C_6H_5OCH_3$	Anisole

$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
$CH_3OCH_2CH_3$	Ethyl methyl ether

2.2 The IUPAC System of Nomenclature

For systematic naming of an organic compound, usually, we have to first identify the parent hydrocarbon and then the functional group(s) attached to it. For example: longest possible hydrocarbon chain is known as parent chain, there can be branching of small chains of carbon atoms to the parent chain and functional groups are also written as branches (Figure 1).

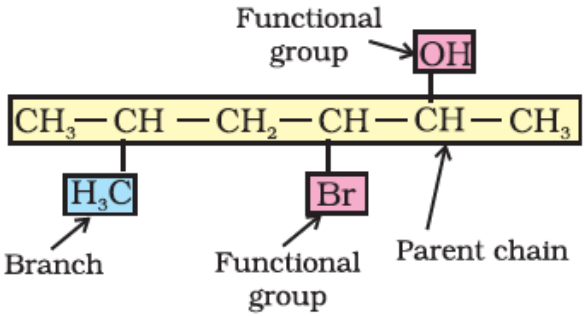


Figure 1

Then further prefixes and suffixes are used and the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. If a hydrocarbon contains only carbon-carbon single bonds, it is termed as saturated. The IUPAC name for a homologous series of saturated hydrocarbon is alkane. Saturated hydrocarbons were earlier named as Paraffin (Latin: little affinity). However, if a hydrocarbon contains at least one carbon-carbon double or triple bond that are termed as unsaturated hydrocarbons.

2.2.1 IUPAC Nomenclature of Alkanes

(i) Straight chain hydrocarbons

The names of straight chain hydrocarbons are based on their chain structure and end with suffix ‘-ane’ and carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10}, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 2. The

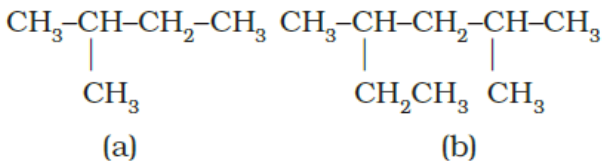
alkanes in table 2 differ from each other by merely the number of -CH_2 groups in the chain. They are homologues of alkane series.

Table 2 IUPAC names of some unbranched saturated hydrocarbons

Names	**Molecular Formula**	**Names**	**Molecular Formula**
Methane	CH_4	Heptane	C_7H_{16}
Ethane	C_2H_6	Octane	C_8H_{18}
Propane	C_3H_8	Nonane	C_9H_{20}
Butane	C_4H_{10}	Decane	$C_{10}H_{22}$
Pentane	C_5H_{12}	Isocane	$C_{20}H_{42}$
Hexane	C_6H_{14}	Triacontane	$C_{30}H_{62}$

(ii) Branched chain hydrocarbons

The compound containing small chains of carbon atoms are attached at one or more carbon atoms of the parent chain are called branched chain hydrocarbons. These small carbon chains (branches) are called alkyl groups. For example:



(a) (b)

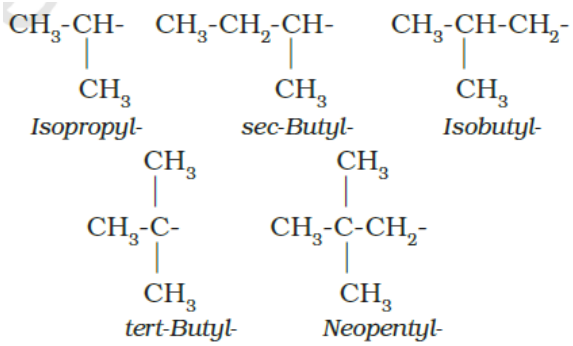
To write the name of these compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH_4 becomes -CH_3 and is called methyl group. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding alkane. Some alkyl groups are listed in Table 3.

Table 3 Some alkyl groups

Name of alkane	**Molecular Formula**	**Name of alkyl**	**Molecular Formula**
Methane	CH_4	Methyl	-CH_3
Ethane	C_2H_6	Ethyl	-CH_2CH_3
Propane	C_3H_8	Propyl	-$CH_2CH_2CH_3$
Butane	C_4H_{10}	Butyl	-$CH_2CH_2CH_2CH_3$

Decane	$C_{10}H_{22}$	Decyl	$-CH_2(CH_2)_8CH_3$

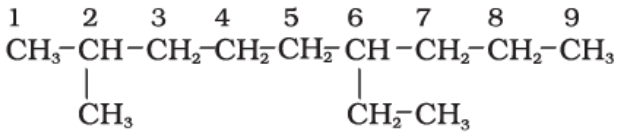
For some alkyl groups abbreviations are used. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can also have branches. For example, propyl and butyl groups can have branched structures as shown below.



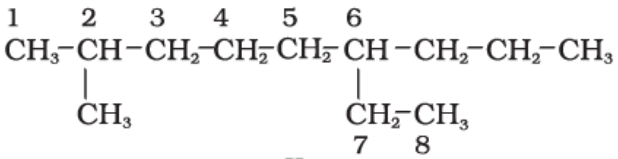
Specific trivial names are assigned to the common branched groups. Such as the propyl groups can either be n-propyl group or isopropyl group. The branched butyl groups are called sec-butyl, isobutyl and tert-butyl group. We also encounter the structural unit, $-H_2CC(CH_3)_3$, which is called neopentyl group.

Nomenclature of branched chain alkanes: If there are more than one branched chain alkanes, the rules for naming them are given below.

1. First of all, we have to identify the parent chain means the longest carbon chain in the molecule. For example: In compound (I) given below, there are nine carbons in the longest chain and it is considered as the parent or root chain, however, the selection of parent chain for the same compound as shown in (II) is incorrect because it has only eight carbons.

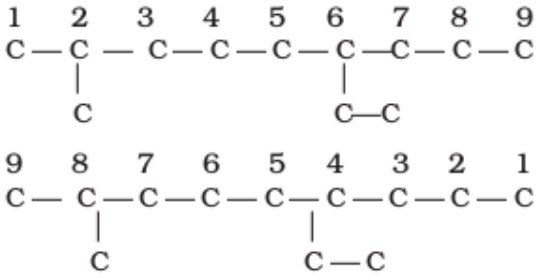


I



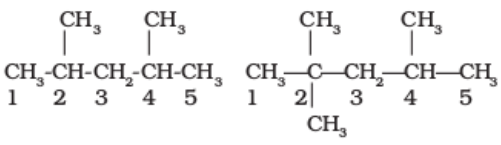
II

2. The parent chain carbon atoms are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching is there due to the substitution of alkyl group in place of hydrogen atoms. The numbering of parent chain carbon is done in such a way so that the branched carbon atoms get the lowest possible numbers. Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached).

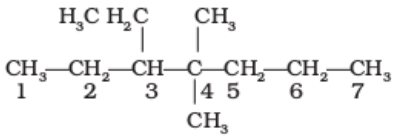


3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present then they should be listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2-methylnonane. The other name 2-methyl-6-ethylnonane is incorrect. [Note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane.

4. If there are two or more identical substituent groups then the numbers are separated by commas. The names of identical substituents should not be repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:

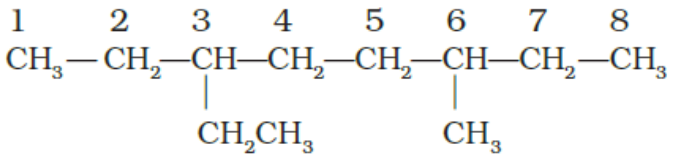


2,4-Dimethylpentane *2,2,4-Trimethylpentane*

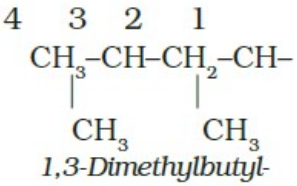


3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical order. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane.



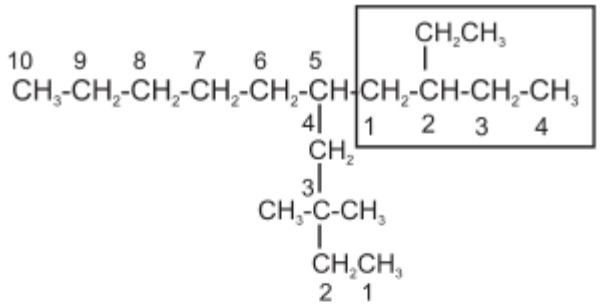
6. The branched alkyl groups can be named by following the above mentioned procedures. However, the carbon atom of the branch that attaches to the root alkane is numbered 1 as exemplified below.



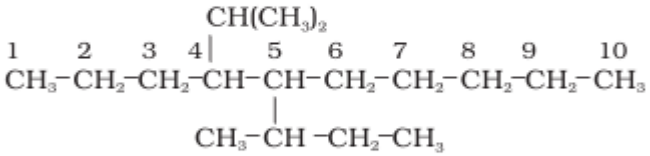
1,3-Dimethylbutyl-

The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name. The use of iso and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multisubstituted compounds, the following rules may also be remembered:

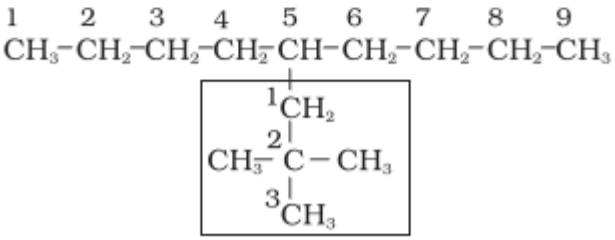
- If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
- After selection of the chain, numbering is to be done from the end closer to the substituent.



5-(2-Ethylbutyl)-3,3-dimethyldecane
[and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]



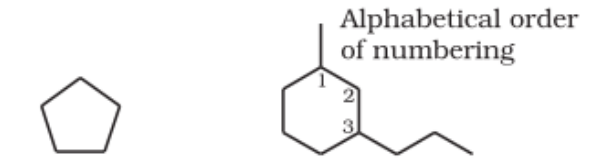
5-sec-Butyl-4-isopropyldecane

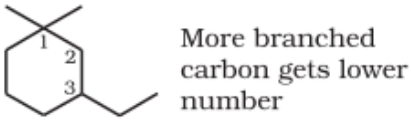


5-(2,2-Dimethylpropyl)nonane

2.2.2 IUPAC Nomenclature of Cyclic Compounds

The naming of saturated monocyclic compound is done by prefixing ‘cyclo’ to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.

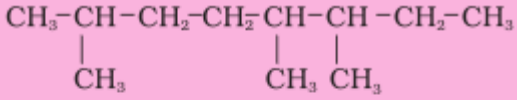




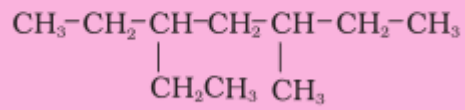
3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane)

Problem 1

Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

(a) 

2,5,6- Trimethyloctane
[and not 3,4,7-Trimethyloctane]

(b) 

3-Ethyl-5-methylheptane
[and not 5-Ethyl-3-methylheptane]

Solution

(a) Lowest locant number, 2, 5, 6 is lower than 3, 5, 7

(b) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order.

2.2.3 IUPAC Nomenclature of Organic Compounds having Functional Group(s)

As we are already aware, a functional group is an atom or a group of atoms bonded together in a unique manner. Functional group is usually the site of chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$ — all having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematization of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in **table 4**.

Table 4 Some functional groups and classes of organic compound

Class of compounds	**Functional group structure**	**IUPAC group prefix**	**IUPAC group suffix**	**Example**
Alkanes	-	-	-ane	Butane $-CH_3CH_2CH_2CH_3$
Alkenes	$>C=C<$	-	-ene	But-1-ene

				$CH_2=CH_2CH_2CH_3$
Alkynes	-C≡C-	-	-yne	But-1-yne $CH≡CH_2CH_2CH_3$
Arenes	-	-	-	Benzene
Halides	-X, X= F, Cl, Br, I	Halo-	-	1-Bromobutane $CH_3CH_2CH_2CH_2Br$
Alcohols	-OH	Hydroxyl-	-ol	Butan-2-ol $CH_3CH_2CHOHCH_3$
Aldehydes	-CHO	Formyl, or oxo	-al	Butanal $CH_3CH_2CH_2CHO$
Ketones	$^{>}C=O$	Oxo	-one	Butan-2-one $CH_3CH_2COCH_3$
Nitriles	-C≡N	Cyano	Nitrile	Pentanenitrile $CH_3CH_2CH_2CH_2CN$
Ethers	-R-O-R-	Alkoxy-	-	Ethoxyethane $CH_3CH_2OCH_2CH_2$
Carboxylic acids	-COOH	Carboxy	-oic acid	Butanoic acid $CH_3CH_2CH_2COOH$
Carboxylate ions	$-COO^-$	-	-oate	Sodium butanoate $CH_3CH_2CH_2COO^-Na^+$
Esters	-COOR	Alkoxycarbonyl	-oate	Methyl propanoate $CH_3CH_2COOCH_3$
Acyl halides	-COX (X= F, Cl, Br, I)	halocarbonyl	-oyl halide	Butanoyl chloride $CH_3CH_2CH_2COCl$
Amines	$-NH_2$, $^{>}NH$, $^{>}N-$	Amino	-amine	Butan-2-amine $CH_3CHNH_2CH_2CH_3$
Amides	$-CONH_2-$ -CONHR, $-CONR_2-$	Carbomyl	-amide	Butanamide $CH_3CH_2CH_2CONH_2$
Nitro compounds	$-NO_2$	Nitro	-	1-Nitrobutane $CH_3CH_2CH_2CH_2NO_2$
Sulphonic acids	$-SO_3H$	Sulpho	Sulphonic acid	Methylsulphonic acid CH_3SO_3H

For the naming organic molecule with functional group, first of all, the functional group is identified which determines the choice of appropriate suffix. The parent chain of carbon atoms

containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain. By using the suffix as given in table 4, the name of the compound is assigned. In the case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. The order of decreasing priority for some functional groups is:

-COOH, $–SO_3H$, -COOR (R=alkyl group), COCl, $-CONH_2$, -CN,-HC=O, >C=O, -OH, $-NH_2$, >C=C<, -C≡C- .

The –R, $C_6H_5^-$, halogens (F, Cl, Br, I), $–NO_2$, alkoxy (–OR) etc. are always prefix substituents. Thus, a compound containing both an alcohol and a keto group is named as hydroxyalkanone as the keto group is preferred to the hydroxyl group. For example, $HOCH_2(CH_2)_3CH_2COCH_3$ will be named as 7-hydroxyheptan-2-one and not as 2-oxoheptan-7-ol.

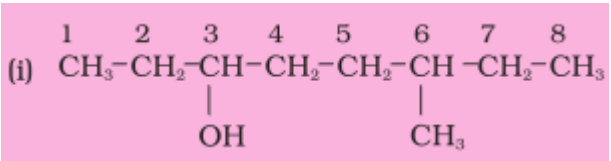
Similarly, $BrCH_2CH=CH_2$ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

If more than one functional group of the same type are present, their number is indicated by adding di, tri, etc. before the class suffix. In such cases the full name of the parent alkane is written before the class suffix. For example $CH_2(OH)CH_2(OH)$ is named as ethane–1,2–diol. However, the ending – ne of the parent alkane is dropped in the case of compounds having more than one double or triple bond; for example, $CH_2=CH-CH=CH_2$ is named as buta–1,3–diene.

Problem 2

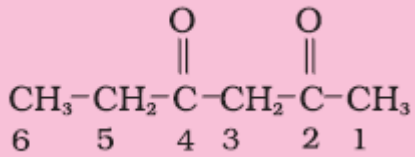
Write the IUPAC names of the following compounds i-iv from their given structures.

Solution

(i) 

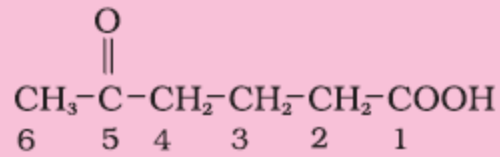
- The functional group present is an alcohol (OH). Hence the suffix is ‘-ol’.
- The longest chain containing -OH has eight carbon atoms. Hence the corresponding saturated hydrocarbon is octane.
- The -OH is on carbon atom 3. In addition, a methyl group is attached at 6th carbon.

Hence, the systematic name of this compound is 6-Methyloctan-3-ol.

(ii) 

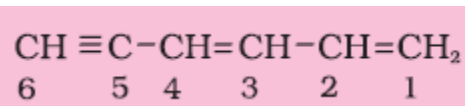
Solution

The functional group present is ketone (>C=O), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione.

(iii) 

Solution

Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. Numbering of the chain starts from carbon of – COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as 5-Oxohexanoic acid.

(iv) 

Solution

The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of compound, therefore, is Hexa-1,3-dien-5-yne.

Problem 3

Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3- Nitrocyclohexene,
(iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxyheptanal.

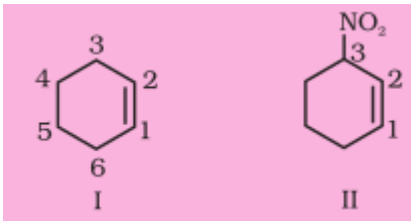
Solution

i. ‘hexane’ indicates the presence of 6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is $CH_3CH_2CH_2CH_2CH(Cl)CH_3$.

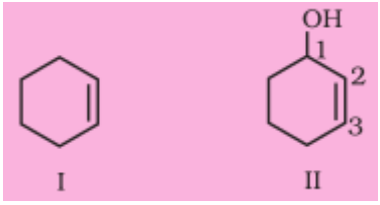
ii. ‘pent’ indicates that parent hydrocarbon contains 5 carbon atoms in the chain. ‘en’ and ‘ol’ correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is $CH_2=CHCH_2CH(OH)CH_3$.

iii. Six membered ring containing a carbon-carbon double bond is implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3.

Thus, complete structural formula of the compound is (II). Double bond is suffixed functional group whereas NO_2 is prefixed functional group therefore double bond gets preference over –NO_2 group:



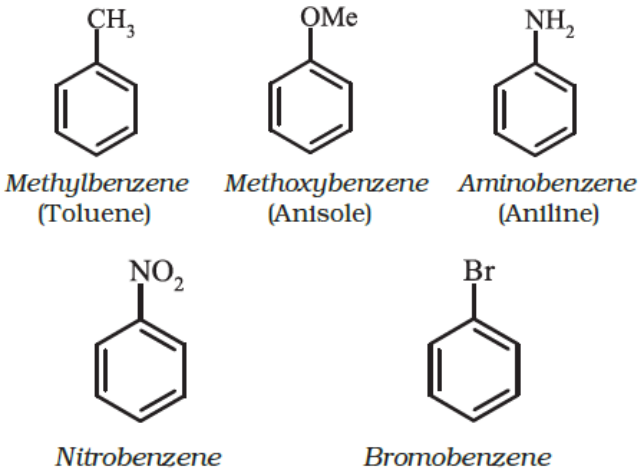
(iv) ‘1-ol’ means that a -OH group is present at C-1. OH is suffixed functional group and gets preference over C=C bond. Thus the structure is as shown in (II):



(v) ‘heptanal’ indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The ‘6-hydroxy’ indicates that -OH group is present at carbon 6. Thus, the structural formula of the compound is: **$CH_3CH(OH)CH_2CH_2CH_2CH_2CHO$**. Carbon atom of –CHO group is included while numbering the carbon chain.

2.2.4 IUPAC Nomenclature of Substituted Benzene Compounds

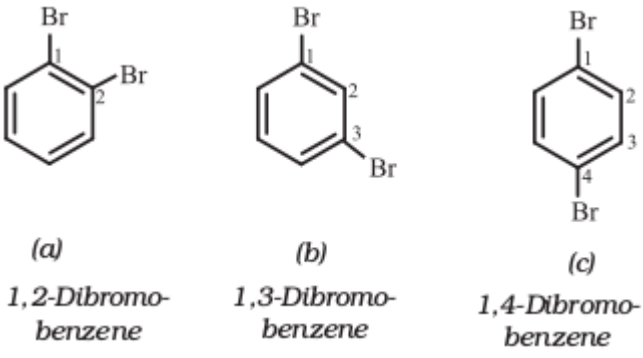
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.



Methylbenzene (Toluene) | *Methoxybenzene* (Anisole) | *Aminobenzene* (Aniline)

Nitrobenzene | *Bromobenzene*

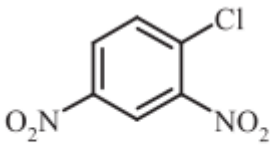
If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible. For example, the compound (b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene.



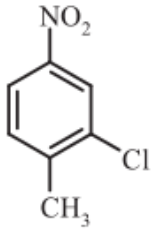
(a) *1,2-Dibromo-benzene* | *(b)* *1,3-Dibromo-benzene* | *(c)* *1,4-Dibromo-benzene*

For substituted benzene compounds, trivial system of nomenclature is commonly used. In the trivial system of nomenclature, the relative positions 1, 2; 1,3 and 1,4 are indicated by prefixes ortho (o), meta (m) and para (p), respectively. Thus, 1,3-dibromobenzene (b) is named as m-dibromobenzene (meta is abbreviated as m-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c), are named as ortho (or just o-) and para (or just p-)-dibromobenzene, respectively.

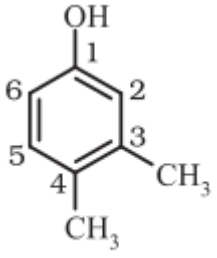
For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound. Substituent of the base compound is assigned number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below.



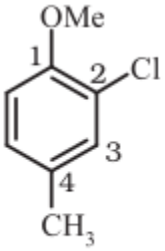
1-Chloro-2,4-dinitrobenzene
(not 4-chloro,1,3-dinitrobenzene)



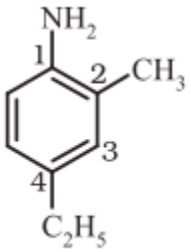
2-Chloro-1-methyl-4-nitrobenzene
(not 4-methyl-5-chloro-nitrobenzene)



3,4-Dimethylphenol



2-Chloro-4-methylanisole



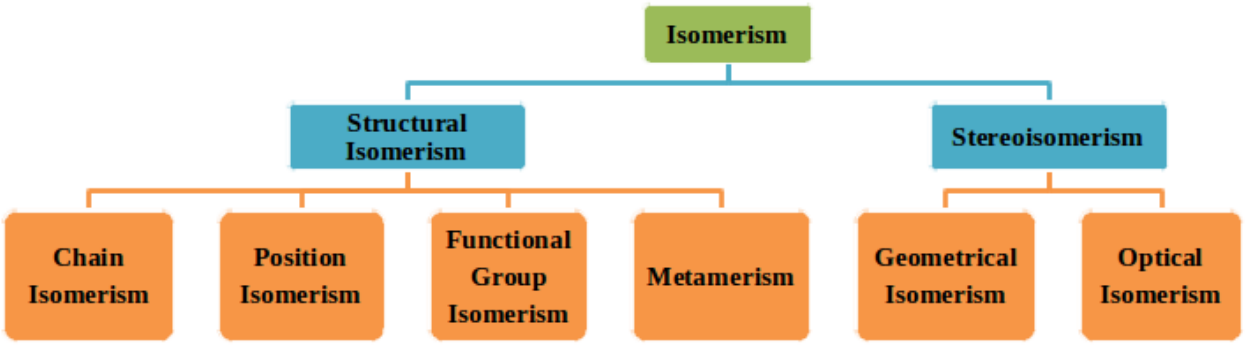
4-Ethyl-2-methylaniline

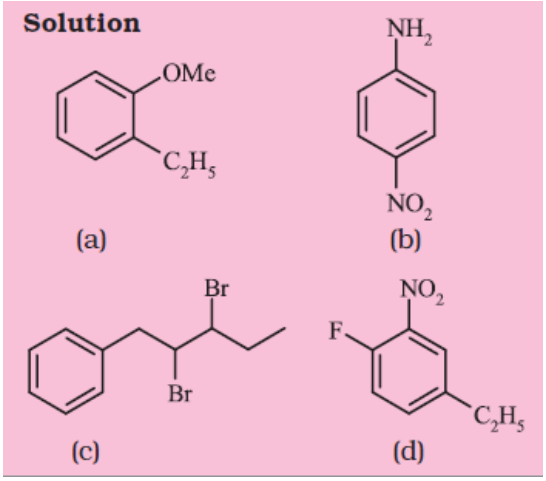
When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is phenyl (C_6H_5-, also abbreviated as Ph).

Problem 4

Write the structural formula of:

(a) o-Ethylanisole, (b) p-Nitroaniline, (c) 2,3 - Dibromo -1 - phenylpentane, (d) 4-Ethyl-1-fluoro-2-nitrobenzene.





3. Isomerism

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism.

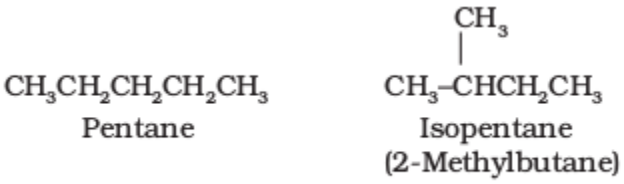
3.1 Structural Isomerism

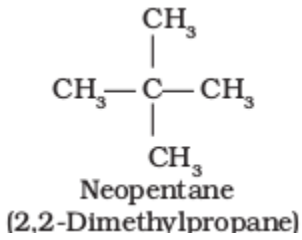
Compounds having the same molecular formula but different structures are classified as structural isomers. These isomers are differing in the manner of connectivity of atoms. These are also called constitutional isomers. They have the same parts, but those parts are attached to each

other differently. Some typical examples of different types of structural isomerism are given below:

3.1.1 Chain isomerism

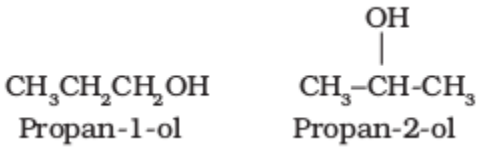
When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:





3.1.2 Position isomerism

When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:



3.1.3 Functional Group Isomerism

Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone:

3.1.4 Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$).

3.2 Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as geometrical and optical isomerism.

4. Summary

- International Union of Pure and Applied Chemistry (IUPAC) have given a set of rules for the systematic naming of the organic compounds.
- According to IUPAC nomenclature, the names are written in in such a way that they are correlated with the structure and reader can easily deduce the structure from the name.
- There are two types of isomerism possible for organic compounds and they are; 1) structural isomerism and 2) stereoisomerism. However, there are many subtypes for structural isomerism and stereoisomerism.
- There are four types of structural isomerism: 1) Chain isomerism, 2) Position isomerism, 3) Functional group isomerism and 4) Metamerism.
- Stereoisomerism can be of two types: 1) Geometrical isomerism, 2) Optical isomerism