IUPAC system of nomenclature of complex compounds

The naming of any organic compound depends on the name of normal parent hydrocarbon from which it has been derived. IUPAC system has framed a set of rules for various types of organic compounds.

(1) Rules for Naming complex aliphatic compounds when no functional group is present (saturated hydrocarbon or paraffins or Alkanes)

(i) Longest chain rule: The first step in naming an organic compound is to select the longest continuous chain of carbon atoms which may or may not be horizontal (straight). This continuous chain is called parent chain or main chain and other carbon chains attached to it are known as side chains (substituents). Examples:



Note:If two different chains of equal length are possible, the chain with maximum number of side chains or alkyl groups is selected.

(ii) Position of the substituent: Number of the carbon atoms in the parent chain as 1, 2, 3,...... etc. starting from the end which gives lower number to the carbon atoms carrying the substituents. For examples,



The number that indicates the position of the substituent or side chain is called locant.

$$\overset{5}{C}H_{3} - \overset{4}{C}H_{2} - \overset{3}{C}H_{2} - \overset{2}{C}H - \overset{1}{C}H_{3} \qquad \overset{1}{C}H_{3} - \overset{2}{C}H_{2} - \overset{3}{C}H - CH - CH_{3} \\ \overset{|}{C}H_{3} \qquad \overset{|}{C}H_{3} - \overset{2}{C}H_{2} - \overset{3}{C}H_{2} - \overset{2}{C}H_{2} - \overset{2}{C}H_{3} \\ \overset{|}{C}H_{2} - \overset{2}{C}H_{2} - \overset{2}{C}H_{3} - \overset{2}{C}H_{3}$$

(iii) Lowest set of locants: When two or more substituents are present, then end of the parent chain which gives the lowest set of the locants is preferred for numbering.

This rule is called lowest set of locants. This means that when two or more different sets of locants are possible, that set of locants which when compared term by term with other sets, each in order of increasing magnitude, has the lowest term at the first point of difference. This rule is used irrespective of the nature of the substituent. For example,

$$H_{3} \stackrel{6}{C} - \stackrel{5}{C} H - \stackrel{4}{C} H_{2} - \stackrel{3}{C} H - \stackrel{2}{C} H - \stackrel{1}{C} H_{3}$$

$$\stackrel{\downarrow}{C} H_{3} \stackrel{\downarrow}{C} H_{3} \stackrel{\downarrow}{C} H_{3} \stackrel{\downarrow}{C} H_{3}$$
Set of locants : 2, 3, 5 (Correct)
$$H_{3} \stackrel{1}{C} - \stackrel{2}{C} H - \stackrel{3}{C} H_{2} - \stackrel{4}{C} H - \stackrel{5}{C} H - \stackrel{6}{C} H_{3}$$

$$\stackrel{\downarrow}{C} H_{3} \stackrel{\downarrow}{C} H_{3} \stackrel{\downarrow}{C} H_{3}$$
Set of locants : 2, 4, 5 (Wrong)

The correct set of locants is 2, 3, 5 and not 2, 4, 5. The first set is lower than the second set because at the first difference 3 is less than 4. (Note that first locant is same in both sets 2; 2 and the first difference is with the second locant 3, 4. We can compare term by term as 2-2, 3-4 (first difference), 5-5. Only first point of difference is considered for preference. Similarly for the compounds,

$$\stackrel{10}{C}H_{3} - \stackrel{9}{C}H_{2} - \stackrel{8}{C}H - \stackrel{7}{C}H - \stackrel{6}{C}H_{2} - \stackrel{5}{C}H_{2} - \stackrel{4}{C}H_{2} - \stackrel{3}{C}H_{2} - \stackrel{2}{C}H - \stackrel{1}{C}H_{3}$$
 Set of locants : 2, 7, 8 (Correct)

$$\stackrel{|}{C}H_{3} \quad \stackrel{|}{C}H_{3} \quad \stackrel{|}{C}H_{3}$$

$$\stackrel{1}{C}H_{3} - \stackrel{2}{C}H_{2} - \stackrel{3}{C}H - \stackrel{4}{C}H - \stackrel{5}{C}H_{2} - \stackrel{6}{C}H_{2} - \stackrel{7}{C}H_{2} - \stackrel{8}{C}H_{2} - \stackrel{9}{C}H - \stackrel{10}{C}H_{3}$$
 Set of locants : 3, 4, 9 (Wrong)

$$\stackrel{|}{C}H_{3} \quad \stackrel{|}{C}H_{3} \quad \stackrel{|}{C}H_{3}$$

First set of locants 2, 7, 8 is lower than second set 3, 4, 9 because at the first point of difference 2 is lower than 3.

Lowest sum rule: It may be noted that earlier, the numbering of the parent chain containing two or more substituents was done in such a way that sum of the locants is the lowest. This rule is called lowest sum rule. For example, the carbon chain of alkanes given below should be numbered as indicated in structures A and not according to structure B.

$$CH_{3} - \overset{3}{\overset{2}{C}}H - \overset{4}{\overset{1}{C}}H - \overset{5}{\overset{1}{C}}H_{2} - \overset{6}{\overset{1}{C}}H_{2} - \overset{7}{\overset{1}{C}}H_{3} - \overset{7}{\overset{1}{C}}H_{2} - \overset{6}{\overset{1}{C}}H_{2} - \overset{7}{\overset{1}{C}}H_{3} - \overset{6}{\overset{1}{C}}H_{2} - \overset{7}{\overset{1}{C}}H_{3} - \overset{6}{\overset{1}{C}}H_{2} - \overset{7}{\overset{1}{C}}H_{2} - \overset{1}{\overset{1}{C}}H_{2} - \overset{1}{\overset$$

(A) Correct Sum of locants =3+4=7 (B) wrong Sum of locants =4+5=9

(A) Correct Sum of locants =2+2+3+4=11 (B) Wrong Sum of locants =2+3+4+4=13

Note:According to latest IUPAC system of nomenclature, the lowest set of locants is preferred even if it violates the lowest sum rule. For example:

$$\overset{10}{C}H_{3} - \overset{9}{C}H_{2} - \overset{8}{C}H - \overset{7}{C}H - \overset{6}{C}H_{2} - \overset{5}{C}H_{2} - \overset{4}{C}H_{2} - \overset{3}{C}H_{2} - \overset{2}{C}H - \overset{1}{C}H_{3} \\ \overset{1}{C}H_{3} \quad \overset{1}{C}H_{3} \\ \text{Structure}^{\text{S}(\text{PAG}) \text{ locants = 2, 7, 8} }$$

$$\stackrel{1}{C}H_{3} - \stackrel{2}{C}H_{2} - \stackrel{3}{C}H - \stackrel{4}{C}H - \stackrel{5}{C}H_{2} - \stackrel{6}{C}H_{2} - \stackrel{7}{C}H_{2} - \stackrel{8}{C}H_{2} - \stackrel{9}{C}H_{2} - \stackrel{10}{C}H_{3}$$

$$\stackrel{|}{C}H_{3} \quad \stackrel{|}{C}H_{3} \quad \stackrel{|}{C}H$$

This compound is numbered as 2, 7, 8 and not as 3, 4, 9 in accordance with latest lowest set of locants rule, even though it violates lowest sum rule.

(iv) Presence of more than one same substituent: If the same substituent or side chain occurs more than once, the prefixes di, tri, tetraetc., are attached to the names of the substituents. For example,

$$\overset{CH_{3}}{\overset{5}{C}H_{3} - \overset{4}{C}H - \overset{3}{C}H_{2} - \overset{2}{C} - \overset{1}{C}H_{3}}_{CH_{3}} \overset{L}{\overset{C}{C}H_{3}}_{2, 2, 4-\text{Trimethylpentane}}$$

(v) Naming different substituents: If two or more different substituents or side chains are present in the molecule, they are named in the alphabetical order along with their appropriate positions.

$$\begin{array}{c} CH_{3} & CH_{3} \\ CH_{2}CH_{3} \\ 5\\CH_{3} - C \\ H_{2} - C \\ - C - C \\ H_{2} - C \\ - C \\ - C \\ H_{3} \\ CH_{3} \\ 0 \\ CH_{3} \\ 3-Ethyl-2, 3-dimethylpe ntane \end{array}$$

(vi) Naming different substituents at equivalent position: In case, there are different alkyl substituents at equivalent positions, then numbering of the parent chain is done in such a way that the alkyl group which comes first in the alphabetical order gets the lower number.

$$\overset{6}{C}H_{3} - \overset{5}{C}H_{2} - \overset{4}{C}H - \overset{3}{C}H_{2} - \overset{2}{C}H_{2} - \overset{1}{C}H_{3} \\ \overset{1}{C}H_{3} - \overset{1}{C}_{2}H_{5} \\ \overset{3-\text{Ethyl-4-methyl hexane}}{} \\ \overset{1}{C}H_{3} - \overset{2}{C}H_{2} - \overset{3}{C} - \overset{4}{C}H_{3} \\ \overset{4}{C}_{2}H_{5} - \overset{6}{C}H_{2} - \overset{6}{C}H_{3} \\ \overset{1}{C}_{2}H_{5} - \overset{6}{C}H_{3} \\ \overset{1}{C}_{2}H_{5} - \overset{6}{C}H_{3} \\ \overset{1}{C}_{2}H_{5} - \overset{6}{C}H_{3} \\ \overset{1}{C}_{3}, 3-\text{Diethyl-4, 4-dimethyl hexane}$$

(vii) Naming the complex substituents (or substituted substituents): If the substituent on the parent chain is complex (i.e. it is branched) it is named as substituted alkyl group by numbering the carbon atom of this group attached to the parent chain as 1. The name of such substituent is given in brackets in order to avoid confusion with the numbering of the parent chain. For example,



5-(1, 2-Dimethylpropyl) nonane

The name of the complex substituent is always written in brackets.

While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of the complete name. It may be remembered that in case of simple substituents, however, the multiplying prefixes are not



considered. The names of simple substituents are first alphabetized and then multiplying prefixes are inserted. For example,

$$\begin{array}{c} CH_2 - CH_3 \\ CH_3 - CH_2 - CH_3 \\ CH_2 - CH_3 \\ CH - CH_3 \\ CH - CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ C-1, 2-Dimethylpropyl)-7-ethyl undecane \end{array}$$

It may be noted that dimethyl propyl (a complex substituent) is alphabetized under d and not under m. Therefore, it is cited before ethyl (e).

