The hydrogen nomenclature can also be adapted to yield satisfactory names for derivatives obtained in formal fashion by replacing a coordinated oxo group from the acid. A small selection is given below.

Examples

18. H_2SO_3S	hydrogen trioxothiosulfate(2–)
19. HSO_3Cl	hydrogen chlorotrioxosulfate
20. SO_2Cl_2	dichlorodioxosulfur
21. $H[PF_6]$	hydrogen hexafluorophosphate(1–)
22. $SO_2(OCH_3)_2$	dimethoxodioxosulfur
23. $HOSO_2NH_2$	hydrogen amidotrioxosulfate
24. $PO(OCH_3)_3$	oxotrimethoxophosphorus
25. $SO_2(NH_2)_2$	diamidodioxosulfur

These names may not be the only ones used for these compounds, but they are systematic and easily comprehensible.

4.5 SUBSTITUTIVE NOMENCLATURE

4.5.1 Introduction

Substitutive nomenclature was developed using the concepts that governed the development of organic chemistry. However, in nomenclature the term substitution is used in a very restricted sense: only hydrogen atoms can be exchanged with other atoms or groups of atoms. Thus a parent hydride must always be the starting point of a substitution operation. For instance, the two molecules CH_3-Cl and CH_3-OH are always derived from the parent hydride CH_3-H. When atoms other than hydrogen are exchanged, the operation is instead called 'replacement' and the resulting nomenclature called 'replacement nomenclature.'

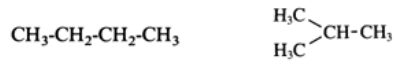
A substitutive name consists of the name of a parent hydride to which prefixes and suffixes are attached as necessary following the general pattern:

prefixes/name of parent hydride/suffixes

A given organic molecule is generally composed of a carbon skeleton and functional groups. A name matches a structure when the name of the parent hydride corresponds to the skeleton, while prefixes and suffixes represent the functional groups and other structural characteristics, such as geometry.

4.5.2 Alkanes and the basic approach to substitutive names

4.5.2.1 *General.* Alkanes are acyclic hydrocarbons of general formula C_nH_{2n+2}. The carbon atoms are arranged in chains that are either branched or unbranched. Chains are called continuous or unbranched when they are composed of -CH_2- groups with two terminal -CH_3 groups. They are branched when they contain more than two terminal -CH_3 groups. In this case, at least one carbon atom must be joined by single bonds to at least three other carbon atoms.



an unbranched alkane a branched alkane

4.5.2.2 *Unbranched alkanes.* Unbranched alkanes are also called normal alkanes. The names of the first four members of the homologous series of unbranched or normal alkanes, C_nH_{2n+2}, are retained names. They were coined more than 100 years ago, officially recognised by the Geneva Conference in 1892, and have been used ever since. There are no alternative names for them.

Examples

1. methane CH_4
2. ethane $CH_3\text{-}CH_3$
3. propane $CH_3\text{-}CH_2\text{-}CH_3$
4. butane $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$

However, higher members of the series are named systematically by combining the ending -ane, characteristic of the first four members and implying complete saturation, with a multiplicative prefix of the series penta-, hexa-, etc. of Table 4.2, which indicates the number of carbon atoms constituting the chain. The letter 'a', which ends the name of the multiplicative prefix, is elided.

Example

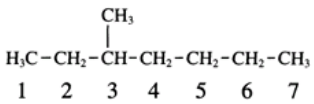
5. pent(a) + ane = pentane $CH_3\text{-}[CH_2]_3\text{-}CH_3$

The names of unbranched alkanes are of the utmost importance because these alkanes are the parent hydrides used to name all aliphatic molecules, i.e. molecules having a carbon-chain skeleton.

4.5.2.3 *Branched alkanes.* Branched-chain alkanes can be considered to be constituted of a principal chain and side-chains. They are named by using a precise set of operations:

1 Selection of the principal chain, which will serve as the parent hydride.
2 Identification and naming of side-chains, which will be treated as prefixes.
3 Determination of the position of side-chains on the principal chain and selection of locants using the rule of lowest locants.
4 Selection of the appropriate multiplicative prefixes.
5 Construction of the full name.

The following example illustrates the step-by-step construction of the name of the branched alkane shown below.



The construction of the name begins by selecting the longest chain, which has seven carbon atoms. The disallowed alternatives have four or six. The parent

hydride is therefore heptane, and there is one carbon atom in a side-group. This is, of course, a methyl group. Putting these together leads to the partial name methylheptane. Multiplicative prefixes are not needed in the present example, as the prefix 'mono' is never used in a substitutive name; finally, the locant '3' is added immediately in front of the part of the name it qualifies: methyl. Locants are separated from other parts of names by hyphens. The full name is 3-methylheptane.

The following three trivial names are still used, but only for the unsubstituted hydrocarbons. Derivatives are named using systematic procedures. These particular names are referred to as retained names.

Examples

1. $(CH_3)_2CH\text{-}CH_3$ isobutane
2. $(CH_3)_2CH\text{-}CH_2\text{-}CH_3$ isopentane
3. $(CH_3)_4C$ neopentane

The general characteristics of substitutive nomenclature are now presented in more detail.

4.5.2.4 *Names of alkyl groups.* Unbranched alkyl groups are monovalent groups created by the subtraction of a hydrogen atom from a terminal $-CH_3$ of the unbranched alkane considered to be the parent hydride. They are named by replacing the ending -ane in the name of the parent hydride by -yl. The carbon atom with the free valence always receives the smallest locant, namely '1'. These alkyl groups are called normal or unbranched.

Examples

1. methyl $-CH_3$
2. ethyl $-CH_2\text{-}CH_3$
3. propyl $-CH_2\text{-}CH_2\text{-}CH_3$
4. decyl $-CH_2\text{-}[CH_2]_8\text{-}CH_3$

Branched alkyl groups are named by prefixing the names of the side-chains to that of the longest unbranched alkyl group.

Example

5. $\overset{5}{CH_3}\text{-}\overset{4}{CH_2}\text{-}\overset{3}{CH}(CH_3)\text{-}\overset{2}{CH_2}\text{-}\overset{1}{CH_2}\text{-}$ 3-methylpentyl

The following names are still used, but only for the unsubstituted groups. These particular names are also referred to as retained names. If there are substituents within these groups, systematic procedures must be followed.

Examples

6. $(CH_3)_2CH\text{-}$ isopropyl
7. $(CH_3)_2CH\text{-}CH_2\text{-}$ isobutyl
8. $CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}$ *sec*-butyl
9. $(CH_3)_3C\text{-}$ *tert*-butyl

10. $(CH_3)_2CH\text{-}CH_2\text{-}CH_2-$ isopentyl
11. $CH_3\text{-}CH_2\text{-}C(CH_3)_2-$ *tert*-pentyl
12. $(CH_3)_3C\text{-}CH_2-$ neopentyl

The groups attached to the principal chain are called substituents, and these may be simple or complex. Simple substituents are formed directly from parent hydrides; when a simple substituent is itself substituted, it becomes complex as a consequence. Normal alkyl groups are simple substituents; branched alkyl groups are complex substituents. However, as exceptions the names isopropyl, isobutyl, *sec*-butyl, *tert*-butyl, isopentyl, *tert*-pentyl and neopentyl are taken to refer to simple substituents.

4.5.2.5 *Multiplicative prefixes.* Multiplicative prefixes (Table 4.2) are used when more than one substituent of a given kind is present in a compound or group. The name of the substituent is cited as a prefix, and two sets of multiplicative prefixes are used, depending on whether the substituent is simple or complex.

Basic multiplicative prefixes di-, tri-, tetra-, etc. are used with the names of simple substituents and retained names. Different or modified prefixes are used with complex substituents: bis-, tris-, tetrakis-; from tetrakis- onwards the ending -kis is attached to the basic multiplicative prefix, giving pentakis-, hexakis-, etc. (compare the use in coordination nomenclature).

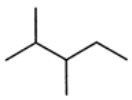
Examples
1. 3,3-dimethylpentane
2. 5,5-bis(1,2-dimethylpropyl)nonane
3. 4,4-diisopropylheptane or 4,4-bis(1-methylethyl)heptane

In general, chemists like to use retained names. The shorter an approved name, the better.

4.5.2.6 *Lowest locants.* Locants are used to indicate the position of substituents in a compound or group. An almost invariable rule is that locants are selected so that the set used has the lowest possible values. Lowest locants are determined by comparing alternative sets of locants. When compared term-by-term with other locant sets, each in order of increasing magnitude, a set of lowest locants has the lowest term at the first point of difference; for example, 2,3,6,8 is lower than 3,4,6,8 or 2,4,5,7.

Examples

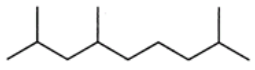
1.



1 2 3 4 5
5 4 3 2 1

2,3-dimethylpentane
(the set 2,3 is *lower* than 3,4)

2.



1 2 3 4 5 6 7 8 9
9 8 7 6 5 4 3 2 1

2,4,8-trimethylnonane
(the set 2,4,8 is *lower* than 2,6,8)

4.5.2.7 *Alphabetical order for citation of detachable prefixes.* Prefixes are used to name substituents, as discussed above. Such prefixes are called detachable prefixes. There is a further class of prefix described as non-detachable. An example is cyclo-, as in cyclohexyl, which is different in stoichiometry from the unmodified hexyl. Non-detachable prefixes are used to modify permanently the name of a parent hydride and thus to create a new parent hydride (see also section 4.5.3.4, p. 78).

When constructing a name, detachable prefixes are cited in front of the name of the parent hydride in alphabetical order. The names are alphabetised by considering the first letter of each name: 'm' in methyl, 'b' in butyl, 'd' in 1,2-dimethylpropyl. In retained names, the first non-italicised letter is considered: 'i' in isobutyl, 'n' in neopentyl, but 'b' in *tert*-butyl.

The assembly of the components to construct a full name starts by attaching the names of the detachable prefixes in alphabetical order to the name of the parent hydride. Then, and only then, necessary multiplicative prefixes are introduced, without changing the alphabetical order obtained previously. Finally, locants are inserted.

Examples

1. 4-**e**thyl-2-**m**ethylhexane
2. 4-**e**thyl-2,2-di**m**ethylhexane
3. 6,6-bis(1,2-**d**imethylpropyl)-3,4-di**m**ethylundecane

In some names with more than one detachable prefix, a set of locants can be attributed in more than one way, as with the locants 3 and 5 in the following example. In such a case, the lowest locant is allocated to the substituent cited first.

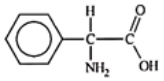
Example

4. 3-**e**thyl-5-**m**ethylheptane

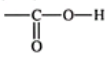
As a consequence, the general pattern of substitutive names becomes:

detachable prefixes	non-detachable prefixes	name of parent hydride	suffixes

4.5.2.8 *Criteria for the selection of the principal chain.* It is necessary to lay down rules for the selection of the parent hydride where its identity is not self-evident. The criteria for the selection of the principal chain are listed in Appendix 1. They are very general, as they deal with saturated and unsaturated molecules, and include the use of prefixes and suffixes to characterise all kinds of substituent. In the case of alkanes, neither criterion (a) (there is no principal characteristic group) nor criterion (b) (there is no unsaturation) is relevant. The third criterion (c) is applicable: the principal chain must be the longest. The next relevant criterion (h) is applied when criterion (c) does not permit a definitive choice to be made. According to criterion (h), the principal chain will then be the most substituted amongst all those of equal length that are considered.

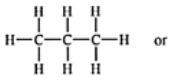
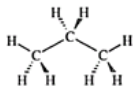
$C_6H_5CH(NH_2)COOH$ 

Note: C_6H_5 invariably refers to a benzene ring (minus a hydrogen atom).



COOH or CO_2H invariably refers to an acid group

In these examples the bond angles in many instances are drawn as right angles and the molecules appear planar. It should be emphasized that we are drawing 2-dimensional representations of 3-dimensional molecules and that the actual bond angles are rarely of 90 degrees. Configurational structures are sometimes used if the absolute geometry is of importance.

propane: C_3H_8 or $CH_3CH_2CH_3$ or  or 

where dashed lines represent bonds behind the plane of the page and solid lines are are bonds coming out from the page. All other lines are in the plane of the page and all bond angles are 109°.

Nomenclature

As indicated previously, compounds are classified in terms of their structure and are named accordingly. The simplest classification is that of the hydrocarbons, compounds of carbon and hydrogen. Hydrocarbons are further identified as being aliphatic or aromatic (nothing to do with smell).

The aliphatics may be alkanes, alkenes or alkynes; aromatic hydrocarbons contain one or more benzene rings.

It is important that students get a good grasp of the convention used in naming the simplest class, the alkanes, as the naming of other classes is an extension of alkane nomenclature.

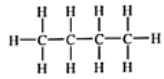
Alkanes

- contain only C, H
- are *saturated*, i.e. contain only single bonds
- straight chain (*normal*) alkanes are named according to the number of C atoms present.
- normal alkanes form a series, a homologous series of formula C_nH_{2n+2} where n is an integer.

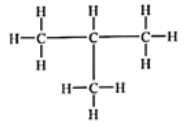
Number of Carbon atoms (n)	Name
1	methane
2	ethane
3	propane
4	butane
5	pentane
6	hexane
7	heptane
8	octane
9	nonane
10	decane

- these names should be memorized

- hence butane, C_4H_{10}, has the structure

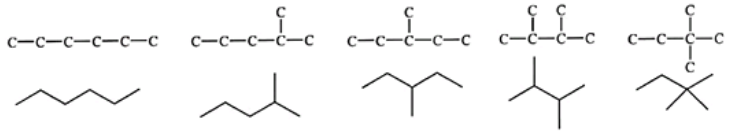


- complications set in when branching occurs. The compound below also has the formula C_4H_{10}



- compounds of the same formula are called isomers
- structural isomers have the same formula but different groupings branch from the main carbon chain.

The following few structures show only the carbon atoms, this is an unacceptible method of drawing structures and marks will be lost in exams or quizes if this format is used. It is only shown here to simplify the structures so that you can clearly see the differences. The preferred method of drawing structures (line format) is shown below.
Structural isomers of C_6H_{14} (hexane)



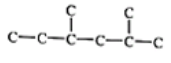
- each of these compounds needs to be identified by having a unique name, they can't be all be called hexane!
- hexane is applied to the normal (straight chain) structure, thereafter the following rules apply:

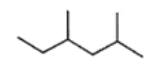
1) Name the longest continuous carbon chain in the molecule as the parent name.
2) Identify the side groups attached to this chain and place them before the parent name in alphabetical order. In general, a side group can be regarded as an alkane that is deficient in a hydrogen atom,

alkane ⟶ alkyl group CH_4 (methane) ⟶ CH_3- (methyl) C_2H_6 (ethane) ⟶ CH_3CH_2- or C_2H_5- (ethyl)

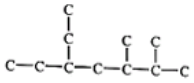
A table of common side groups appears at the end of this section on naming alkanes.

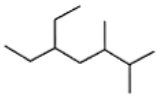
3) If several groups of the same kind are attached to the main chain, list the groups only once using the appropriate numerical prefix di, tri, tetra, penta, hexa, hepta, octa, nona, deca etc. to indicate how many times that side group appears.
4) Assign a number to each of the side groups to indicate where the group is attached to the main chain. Start the numbering of the main chain from whichever end of the main chain will give the lowest set of numbers. The lowest set of numbers is selected on the basis of **the lowest number at the first point of difference.**



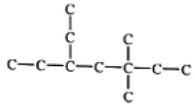


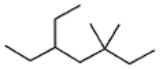
2,4-dimethylhexane





5-ethyl-2,3-dimethylheptane





5-ethyl-3,3-dimethylheptane
(not 3-ethyl-5,5-dimethylheptane)

5) You may wish to attach the following names to the C_6H_{14} isomers mentioned previously: 2,2-dimethylbutane; 3-methylpentane; 2,3-dimethylbutane; 2-methylpentane; hexane.
a) hyphens **must** separate numbers and letters
b) commas **must** separate numbers
c) the di, tri, tetra etc. are not included in the alphabetizing process.
d) n, s, and t are not included in the alphabetizing process, but iso is (see next paragraph).
e) the prefix 'cyclo' is used for cyclic alkanes.

cyclobutane

ethylcyclopentane

cyclohexane
(not benzene)

Common Side Groups

CH_3- methyl

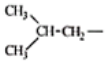
CH_3CH_2- ethyl

$CH_3CH_2CH_2-$ propyl (n-propyl)

$CH_3CH_2CH_2CH_2-$ butyl (n-butyl)

$CH_3-CH(CH_3)-$ isopropyl

$CH_3CH_2-CH(CH_3)-$ s-butyl (sec-butyl)



isobutyl

phenyl

t-butyl
(tert-butyl

In identifying the longest chain in a molecule, and hence the parent name, do not be deceived by the 2-dimensional representation of the molecule. For instance, 2,5-dimethylheptane could have be drawn in the following ways (and several more).