ORGANIC NOMENCLATURE

Introduction

Confusion can arise in organic chemistry because of the variety of names that have been applied to compounds; common names, trade names and systematic names are prevalent. For example, a compound of formula, C_6H_6O has variously been known as phenol, carbolic acid, phenic acid, phenyl hydroxide, hydroxybenzene, phenylic acid and oxobenzene!

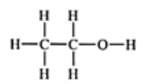
To help eliminate the proliferation of many names for a compound, a systematic IUPAC naming system has been derived to uniquely name the several million organic different compounds based on considerations of their structure.

This hand-out will address the naming of simple organic compounds and is by no means complete, for instance the compound, hexahydroazepinium-1-spiro-1'-imidazolidine-3'-spiro-1''-piperidinium dibromide may be regarded as being too complicated for this course!

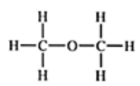
In general compounds are classified and named by consideration of:
- a) the number and types of atoms that are present,
- b) the bond types in the molecule, and
- c) the geometry of the molecule.

Formulae

Prior to setting out the rules for naming compounds it is pertinent to review some aspects of formulae. The molecular formula of a compound gives no explicit information about the structure of the compound. The formula C_2H_6O makes no mention as to how the various atoms are arranged, indeed two different compounds share this formula but have different structures and vastly different properties.



ethanol



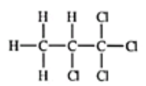
dimethyl ether

By writing their formulae in a structural form we can differentiate between these two compounds.

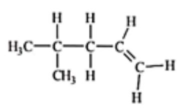
ethanol	CH_3-CH_2-OH	or	CH_3CH_2OH	or	C_2H_5OH
dimethyl ether	CH_3-O-CH_3	or	CH_3OCH_3		

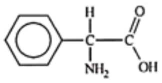
In writing these formulae the atoms after a carbon indicate the elements or groups, attached to that carbon. It must be remembered that all C atoms in organic compounds must be involved in four bonds.

$CH_3CHClCCl_3$

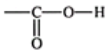


$CH_3CH(CH_3)CH_2CH{=}CH_2$



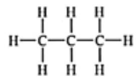
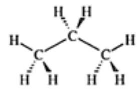
$C_6H_5CH(NH_2)COOH$ 

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

1 Introduction

Chemical nomenclature is at least as old as the pseudoscience of alchemy, which was able to recognise a limited number of reproducible materials. These were assigned names that often conveyed something of the nature of the material (vitriol, oil of vitriol, butter of lead, aqua fortis . . .). As chemistry became a real science, and principles of the modern atomic theory and chemical combination and constitution were developed, such names no longer sufficed and the possibility of developing systematic nomenclatures was recognised. The names of Guyton de Morveau, Lavoisier, Berthollet, Fourcroy and Berzelius are among those notable for early contributions. The growth of organic chemistry in the nineteenth century was associated with the development of more systematic nomenclatures, and chemists such as Liebig, Dumas and Werner are associated with these innovations.

The systematisation of organic chemistry in the nineteenth century led to the early recognition that a systematic and internationally acceptable system of organic nomenclature was necessary. In 1892, the leading organic chemists of the day gathered in Geneva to establish just such a system. The Geneva Convention that they drew up was only partly successful. However, it was the forerunner of the current activities of the International Union of Pure and Applied Chemistry (IUPAC) and its Commission on Nomenclature of Organic Chemistry (CNOC), which has the remit to study all aspects of the nomenclature of organic substances, to recommend the most desirable practices, systematising trivial (i.e. non-systematic) methods, and to propose desirable practices to meet specific problems. The Commission on the Nomenclature of Inorganic Chemistry (CNIC) was established rather later, because of the later systematisation of this branch of the subject, and it now fulfils functions similar to those of CNOC but in inorganic chemistry. In areas of joint interest, such as organometallic chemistry, CNIC and CNOC collaborate. The recommendations outlined here are derived from those of these IUPAC Commissions, and of the Commission on Macromolecular Nomenclature (COMN) and of the International Union of Biochemistry and Molecular Biology (IUBMB).

The systematic naming of substances and presentation of formulae involve the construction of names and formulae from units that are manipulated in accordance with defined procedures in order to provide information on composition and structure. There are a number of accepted systems for this, of which the principal ones will be discussed below. Whatever the pattern of nomenclature, names and formulae are constructed from units that fall into the following classes:

- Element names, element name roots, element symbols.
- Parent hydride names.
- Numerical prefixes (placed before a name, but joined to it by a hyphen), infixes (inserted into a name, usually between hyphens) and suffixes (placed after a name).
- Locants, which may be letters or numerals, and may be prefixes, infixes or suffixes.
- Prefixes indicating atoms or groups — either substituents or ligands.
- Suffixes in the form of a set of letters or characters indicating charge.
- Suffixes in the form of a set of letters indicating characteristic groups.
- Infixes in the form of a set of letters or characters, with various uses.

Table 2.1 Names, symbols and atomic numbers of the atoms (elements).

Name	Symbol	Atomic number	Name	Symbol	Atomic number
Actinium	Ac	89	Mercury[6]	Hg	80
Aluminium	Al	13	Molybdenum	Mo	42
Americium	Am	95	Neodymium	Nd	60
Antimony[1]	Sb	51	Neon	Ne	10
Argon	Ar	18	Neptunium	Np	93
Arsenic	As	33	Nickel	Ni	28
Astatine	At	85	Niobium	Nb	41
Barium	Ba	56	Nitrogen[7]	N	7
Berkelium	Bk	97	Nobelium	No	102
Beryllium	Be	4	Osmium	Os	76
Bismuth	Bi	83	Oxygen	O	8
Bohrium	Bh	107	Palladium	Pd	46
Boron	B	5	Phosphorus	P	15
Bromine	Br	35	Platinum	Pt	78
Cadmium	Cd	48	Plutonium	Pu	94
Caesium	Cs	55	Polonium	Po	84
Calcium	Ca	20	Potassium[8]	K	19
Californium	Cf	98	Praseodymium	Pr	59
Carbon	C	6	Promethium	Pm	61
Cerium	Ce	58	Protactinium	Pa	91
Chlorine	Cl	17	Radium	Ra	88
Chromium	Cr	24	Radon	Rn	86
Cobalt	Co	27	Rhenium	Re	75
Copper[2]	Cu	29	Rhodium	Rh	45
Curium	Cm	96	Rubidium	Rb	37
Dubnium	Db	105	Ruthenium	Ru	44
Dysprosium	Dy	66	Rutherfordium	Rf	104
Einsteinium	Es	99	Samarium	Sm	62
Erbium	Er	68	Scandium	Sc	21
Europium	Eu	63	Seaborgium	Sg	106
Fermium	Fm	100	Selenium	Se	34
Fluorine	F	9	Silicon	Si	14
Francium	Fr	87	Silver[9]	Ag	47
Gadolinium	Gd	64	Sodium[10]	Na	11
Gallium	Ga	31	Strontium	Sr	38
Germanium	Ge	32	Sulfur[11]	S	16
Gold[3]	Au	79	Tantalum	Ta	73
Hafnium	Hf	72	Technetium	Tc	43
Hassium	Hs	108	Tellurium	Te	52
Helium	He	2	Terbium	Tb	65
Holmium	Ho	67	Thallium	Tl	81
Hydrogen[4]	H	1	Thorium	Th	90
Indium	In	49	Thulium	Tm	69
Iodine	I	53	Tin[12]	Sn	50
Iridium	Ir	77	Titanium	Ti	22
Iron[5]	Fe	26	Tungsten[13]	W	74
Krypton	Kr	36	Ununbiium	Uub	112
Lanthanum	La	57	Ununhexium	Uuh	116
Lawrencium	Lr	103	Ununnilium	Uun	110
Lead	Pb	82	Ununoctium	Uuo	118
Lithium	Li	3	Ununpentium	Uup	115
Lutetium	Lu	71	Ununquadium	Uuq	114
Magnesium	Mg	12	Ununseptium	Uus	117
Manganese	Mn	25	Ununtriium	Uut	113
Meitnerium	Mt	109	Unununium	Uuu	111
Mendelevium	Md	101	Uranium	U	92

Continued.

2 Definitions

An element (or an elementary substance) is matter, the atoms of which are alike in having the same positive charge on the nucleus (or atomic number).

In certain languages, a clear distinction is made between the terms 'element' and 'elementary substance'. In English, it is not customary to make such nice distinctions, and the word 'atom' is sometimes also used interchangeably with element or elementary substance. Particular care should be exercised in the use and comprehension of these terms.

An atom is the smallest unit quantity of an element that is capable of existence, whether alone or in chemical combination with other atoms of the same or other elements.

The elements are given names, of which some have origins deep in the past and others are relatively modern. The names are trivial. The symbols consist of one, two or three roman letters, often but not always related to the name in English.

Examples

1. Hydrogen	H
2. Argon	Ar
3. Potassium	K
4. Sodium	Na
5. Chlorine	Cl
6. Ununquadium	Uuq

For a longer list, see Table 2.1. For the heavier elements as yet unnamed or unsynthesised, the three-letter symbols, such as Uuq, and their associated names are provisional. They are provided for temporary use until such time as a consensus is reached in the chemical community that these elements have indeed been synthesised, and a trivial name and symbol have been assigned after the prescribed IUPAC procedures have taken place.

When the elements are suitably arranged in order of their atomic numbers, a Periodic Table is generated. There are many variants, and an IUPAC version is shown in Table 2.2.

An atomic symbol can have up to four modifiers to convey further information. This is shown for a hypothetical atomic symbol X:

$${}^{\mathrm{D}}_{\mathrm{C}}\mathrm{X}^{\mathrm{A}}_{\mathrm{B}}$$

Modifier A indicates a charge number, which may be positive or negative (when element X is more properly called an ion). In the absence of modifier A, the charge is assumed to be zero. Alternatively or additionally, it can indicate the number of unpaired electrons, in which case the modifier is a combination of an arabic numeral and a dot. The number 'one' is not represented.

Table 2.2 IUPAC Periodic Table of the Elements.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	*n*
1 **H**																	2 **He**	1
3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**	2
11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**	3
19 **K**	20 **Ca**	21 **Se**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**	4
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**	5
55 **Cs**	56 **Ba**	57–71 **La–Lu**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**	6
87 **Fr**	88 **Ra**	89–103 **Ac–Lr**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Uun**	111 **Uuu**	112 **Uub**	113 **Uut**	114 **Uuq**	115 **Uup**	116 **Uuh**	117 **Uus**	118 **Uuo**	7
	57 **La**	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**			6
	89 **Ac**	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**			7

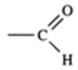
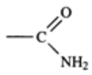
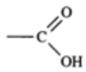
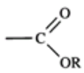
- Additive prefixes: a set of letters or characters indicating the formal addition of particular atoms or groups to a parent molecule.
- Subtractive suffixes and/or prefixes: a set of letters or characters indicating the absence of particular atoms or groups from a parent molecule.
- Descriptors (structural, geometric, stereochemical, etc.).
- Punctuation marks.

The uses of all these will be exemplified in the discussion below.

The material discussed here is based primarily on *A Guide to IUPAC Nomenclature of Organic Chemistry, Recommendations 1993*, issued by CNOC, on the *Nomenclature of Inorganic Chemistry, Recommendations 1990* (the Red Book), issued by CNIC, on the *Compendium of Macromolecular Chemistry* (the Purple Book), issued in 1991 by COMN, and on *Biochemical Nomenclature and Related Documents*, 2nd Edition 1992 (the White Book), issued by IUBMB.

In many cases, it will be noted that more than one name is suggested for a particular compound. Often a preferred name will be designated, but as there are several systematic or semi-systematic nomenclature systems it may not be possible, or even advisable, to recommend a unique name. In addition, many non-systematic (trivial) names are still in general use. Although it is hoped that these will gradually disappear from the literature, many are still retained for present use, although often in restricted circumstances. These restrictions are described in the text. The user of nomenclature should adopt the name most suitable for the purpose in hand.

Table 3.2 Some important compound classes and functional groups.

Class	Functional group	General constitution*	
Alkanes	None	C_nH_{2n+2}	
Alkenes	C=C	$R_2C{=}CR_2$	(R or Ar or H)
Alkynes	C≡C	RC≡CR	(R or Ar or H)
Alcohols	-OH	R-OH	
Aldehydes		R-CHO	(R or Ar)
Amides		$R\text{-}CONH_2$	(R or Ar)
Amines	$-NH_2$, -NHR, $-NR_2$	$R\text{-}NH_2$ R-NH-R $R\text{-}NR_2$	(R or Ar)
Carboxylic acids		R-COOH	(R or Ar)
Ethers	-O-	R-O-R	(R or Ar)
Esters		R-COOR	(R or Ar)
Halogeno compounds	-F, -Cl, -Br, -I	R-F, R-Cl R-Br, R-I	(R or Ar)
Ketones	>C=O	R-CO-R	(R or Ar)
Nitriles	-CN	R-CN	(R or Ar)

* In this table, and in common organic usage, Ar represents an aromatic group rather than the element of atomic number 18, and R represents an aliphatic group.

Examples

8. $[IrHCl_2(C_5H_5N)(NH_3)]$
9. $K_3[Fe(CN)_6]$
10. $[Ru(NH_3)_5(N_2)]Cl_2$
11. $K_2[Cr(CN)_2O_2(O_2)(NH_3)]$
12. $[Cu\{OC(NH_2)_2\}_2Cl_2]$
13. $[ICl_4]^-$

It is often a matter of choice whether a species is regarded as a coordination entity or not. Thus, sulfate may be regarded as a complex of S^{VI} with four O^{2-} ligands. It would then be represented as $[SO_4]^{2-}$, but it is not considered generally necessary to use square brackets here. The position with regard to $[ICl_4]^-$ is not so clear-cut: $[ICl_4]^-$, $(ICl_4)^-$ and ICl_4^- would all be acceptable, depending upon the precise circumstances of use.

For certain species it is not possible to define a central atom. Thus, for chain species, such as thiocyanate, the symbols are cited in the order in which they appear in the chain.

Examples

14. -SCN
15. HOCN
16. $(O_3POSO_3)^-$
17. -NCS
18. HCNO

Addition compounds are represented by the formulae of the individual constituent species, with suitable multipliers that define the appropriate molecular ratios of the constituent species, and separated by centre dots. In general, the first symbols determine the order of citation.

Examples

19. $3CdSO_4 \cdot 8H_2O$
20. $8H_2S \cdot 46H_2O$
21. $BF_3 \cdot 2H_2O$

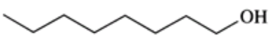
These suggestions are advisory and should be used where there are no overriding reasons why they should not be. For example, PCl_3O is a correct presentation but, because the group P=O persists in whole families of compounds, the presentation $POCl_3$ may be more useful in certain contexts. There is no objection to this.

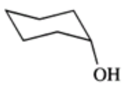
The concept of a group is especially important in organic chemistry. A functional group represents a set of atoms that is closely linked with chemical reactivity and defined classes of substances. For instance, the functional group hydroxyl, -OH, is characteristic of the classes alcohol, phenol and enol. Alcohols are often represented by the general formula R-OH, in which R- represents a hydrocarbon group typical of aliphatic and alicyclic substances.

A functional group is a set of atoms that occurs in a wide range of compounds and confers upon them a common kind of reactivity (see Table 3.2). Phenols are generally represented by Ar-OH, in which Ar- represents an aromatic skeleton, composed of benzene rings or substituted benzene rings. Enols are molecules in which the -OH group is linked to an atom that is also engaged in a double bond.

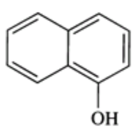
Examples

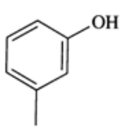
Typical alcohols

22. 

23. 

Typical phenols

24. 

25. 

26.