

IR-7 Additive Nomenclature (Draft March 2004)

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IR-7.1 INTRODUCTION

IR-7.1.1 **General**

Additive nomenclature was originally developed for Werner-type coordination compounds, which were regarded as composed of a central atom (or atoms) surrounded by added groups known as ligands, but many other types of compound may also be conveniently given additive names. Such names are constructed by placing the names of the ligands (sometimes modified) as prefixes to the name(s) of the central atom(s).

This Chapter deals with the general characteristics of additive nomenclature and provides examples of additive names for simple mononuclear and polynuclear compounds. Chain and ring compounds are then treated using additive principles supplemented by further conventions. Additive names for inorganic acids are discussed in Chapter IR-8. Additive nomenclature as applied to metal coordination compounds is described in further detail in Chapter IR-9. Additive names for a large number of simple compounds are given in Table IX*.

* Tables numbered with a Roman numeral are collected together at the end of this book.

Note that in some cases, compounds named additively may alternatively and equally systematically be named substitutively (Chapter IR-6). It is important to note, however, that additive names for parent hydrides cannot be used as parent names in substitutive nomenclature.

IR-7.1.2 **Choosing a central atom or atoms, or a chain or ring structure**

Making a choice of central atom or atoms is a key step in the process of naming a compound using additive nomenclature. If there is/are (a) metal atom(s) in the compound, it/they should be chosen as the central atom(s). Such atom(s) should also be relatively central in the structure and, where possible, should be chosen to make use of molecular symmetry (thereby shortening the name).

For some compounds, a choice of central atom or atoms will remain. If a choice has to be made between atoms in order to select one as the central atom, the atom that occurs latest when following the arrow in Table VI should be chosen as the central atom (except that oxygen is regarded as between chlorine and fluorine in this context).

If there is more than one central atom in a structure according to the above criteria then the compound can be named as a binuclear or polynuclear compound.

As an alternative to the procedure above, a group of atoms forming a chain or ring substructure within a compound may be chosen in order to give the compound an additive name using the 'chains and rings' nomenclature outlined in Section IR-7.4.

IR-7.1.3 **Representing ligands in additive names**

Additive names are constructed by placing (sometimes modified) ligand names as prefixes to the name of the central atom.

For anionic ligands, the anion endings 'ide', 'ate' and 'ite' (*cf.* Section IR-5.3.3) are changed to 'ido', 'ato' and 'ito', respectively, when generating the prefix for the central atom, except in a few special cases, most notably water (prefix 'aqua'), ammonia (prefix 'ammine'), carbon monoxide (prefix 'carbonyl'), and nitrogen monoxide (prefix 'nitrosyl').

In principle, it is a matter of convention whether a ligand is considered to be anionic, neutral or cationic. The default is to consider ligands as anionic, so that OH, for example, receives the prefix 'hydroxido', Cl the prefix 'chlorido', SO₄ the prefix 'sulfato', *etc.* Some ligands are

conventionally regarded as neutral, (*e.g.* amines and phosphanes, ligands derived from hydrocarbons by removal of a hydrogen atom, such as methyl, benzyl, *etc.*).

Appropriate prefixes to represent many simple ligands within names are given in Table IX. For further details, see Section IR-9.2.2.3.

IR-7.1.4 Ions and radicals

Anionic species take the ending 'ate' in additive nomenclature, whereas no distinguishing termination is used for cationic or neutral species. Additive names of ions end with the charge number (see Section IR-5.4.2.2). In additive names of radicals, the radical character of the compound is indicated by a radical dot, •, added in parentheses and centred, after the name of the compound. Polyradicals are indicated by the appropriate numerical prefix to the dot. For example, a diradical is indicated by '(2•_').

IR-7.2 MONONUCLEAR COMPOUNDS

Names of mononuclear compounds, *i.e.* of species with a single central atom, are formed by citing the appropriate prefixes for the ligands alphabetically before the name of the central atom. Ligands occurring more than once are collected in the name by means of multiplicative prefixes (Table IV), *i.e.* 'di', 'tri', 'tetra', *etc.*, for simple ligands such as chlorido, benzyl, aqua, ammine and hydroxido, and 'bis', 'tris', 'tetrakis', *etc.*, for more complex ligands *e.g.* 2,3,4,5,6-pentachlorobenzyl and triphenylphosphane. The latter prefixes are also used to avoid any ambiguity which might attend the use of 'di', 'tri', *etc.* Multiplicative prefixes which are not inherent parts of the ligand name do not affect the alphabetical ordering.

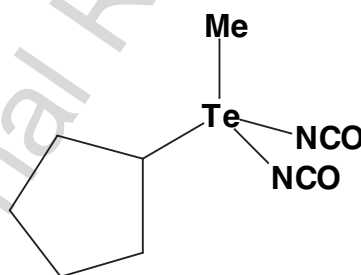
Prefixes representing ligands can be separated using enclosing marks (see also, Section IR-9.2.2.3), and this should be done for all but the simplest ligands, including organic ligands. In some cases the use of enclosing marks is essential in order to avoid ambiguity, as in Examples 10 and 11 below.

In several of the examples below, substitutive names (see Chapter IR-6) are also given. In some cases, however, there is no parent hydride available for the construction of a substitutive name (see Examples 9 and 11). Note also that formulae given below in square brackets are coordination compound-type formulae with the central atom listed first.

Examples:

- | | | |
|----|---------------------|---|
| 1. | Si(OH) ₄ | tetrahydroxidosilicon (additive),
or silanetetrol (substitutive) |
| 2. | B(OMe) ₃ | trimethoxyboron or |

- tris(methanolato)boron (both additive),
or trimethoxyborane (substitutive)
3. $\text{FCIO} = [\text{ClFO}]$ fluoridooxidochlorine (additive),
or fluoro- λ^3 -chloranone (substitutive)
4. $\text{ClOCl} = [\text{OCl}_2]$ dichloridooxygen (additive),
or dichlorooxidane (substitutive)
5. $[\text{Ga}\{\text{OS}(\text{O})\text{Me}\}_3]$ tris(methanesulfinato)gallium (additive),
or tris(methanesulfinyloxy)gallane (substitutive)
6. $\text{MeP}(\text{H})\text{SiH}_3$ trihydrido(methylphosphanido)silicon (additive),
 $= [\text{SiH}_3\{\text{P}(\text{H})\text{Me}\}]$ or methyl(silyl)phosphane (substitutive)
7. $\text{NH}^2\bullet$ hydridonitrogen(2 \bullet) (additive),
or azanylidene (substitutive)
8. $\text{HOCO}\bullet$ hydroxidooxidocarbon(\bullet) (additive),
or hydroxyoxomethyl (substitutive)
9. $\text{FArH} = [\text{ArFH}]$ fluoridohydridoargon (additive)
10. $[\text{HgMePh}]$ methyl(phenyl)mercury
11. $[\text{Hg}(\text{CHCl}_2)\text{Ph}]$ (dichloromethyl)phenylmercury (additive)
12. $[\text{Te}(\text{C}_5\text{H}_9)\text{Me}(\text{NCO})_2]$



bis(cyanato-*N*)cyclopentyl(methyl)tellurium (additive),
or cyclopentyl[bis(isocyanato)](methyl)- λ^4 -tellane
(substitutive)

13. $[\text{Al}(\text{POCl}_3)_6]^{3+}$ hexakis(trichloridooxidophosphorus)aluminium(3+)
14. $[\text{Al}(\text{OH}_2)_6]^{3+}$ hexaaquaaluminium(3+)
15. $[\text{H}(\text{py})_2]^+$ bis(pyridine)hydrogen(1+)
16. $[\text{H}(\text{OH}_2)_2]^+$ diaquahydrogen(1+)
17. $[\text{BH}_2(\text{py})_2]^+$ dihydridobis(pyridine)boron(1+) (additive),
or bis[pyridine](*N-B*)]boranylium (substitutive)
18. $[\text{PFO}_3]^{2-}$ fluoridotrioxidophosphate(2 $-$)
19. $[\text{Sb}(\text{OH})_6]^-$ hexahydroxidoantimonate(1 $-$) (additive),
or hexahydroxy- λ^3 -stibanuide (substitutive)

20.	$[\text{HF}_2]^-$	difluoridohydrogenate(1 ⁻)
21.	$[\text{BH}_2\text{Cl}_2]^-$	dichloridodihydridoborate(1 ⁻) (additive), or dichloroboranuide (substitutive)
22.	$\text{OCO}^{\bullet-}$	dioxidocarbonate(\bullet 1 ⁻)
23.	$\text{NO}^{(2\bullet)-}$	oxidonitrate($2\bullet$ 1 ⁻)
24.	$\text{PO}_3^{\bullet 2-}$	trioxidophosphate(\bullet 2 ⁻)
25.	$[\text{ICl}_2]^+$	dichloridoiodine(1+) (additive), or dichloroiodanium (substitutive)
26.	BH_4^-	tetrahydridoborate(1 ⁻) (additive), or boranuide (substitutive)
27.	CH_5^-	pentahydridocarbonate(1 ⁻) (additive), or methanuide (substitutive)
28.	PH_6^-	hexahydridophosphate(1 ⁻) (additive), or λ^5 -phosphanuide (substitutive)
29.	$[\text{PF}_6]^-$	hexafluoridophosphate(1 ⁻) (additive), or hexafluoro- λ^5 -phosphanuide (substitutive)

IR-7.3 POLYNUCLEAR COMPOUNDS

IR-7.3.1 Symmetrical dinuclear compounds

In symmetrical dinuclear compounds each of the central atoms is of the same type and they are identically ligated. Two general additive methods of naming are available. Again, in some cases substitutive names are also easily constructed, as exemplified below.

(i) The ligands are represented in the usual way and the multiplicative affix 'di' is added immediately before the name of the central atom. The name of the central element is modified to the 'ate' form if the compound is an anion. A bond between the two central atoms is indicated by adding to the name the italicized symbols for those two atoms, separated by an 'em' dash and enclosed in parentheses.

Examples:

1.	$[\text{Et}_3\text{PbPbEt}_3]$	hexaethyldilead(<i>Pb—Pb</i>) (additive), or 1,1,1,2,2,2-hexaethyldiplumbane (substitutive)
2.	$\text{HSSH}^{\bullet-}$	dihydridodisulfate(<i>S—S</i>)(\bullet 1 ⁻) (additive), or disulfanuidyl (substitutive)
3.	NCCN	dinitridodicarbon(<i>C—C</i>)
4.	$\text{NCCN}^{\bullet-}$	dinitridodicarbonate(<i>C—C</i>)(\bullet 1 ⁻)

5. (NC)SS(CN) bis(nitridocarbonato)disulfur(*S—S*), or dicyanidodisulfur(*S—S*)
6. (NC)SS(CN)^{•-} bis(nitridocarbonato)disulfate(*S—S*)(^{•1-}), or dicyanidodisulfate(*S—S*)(^{•1-})

(ii) Alternatively, the name is formed by starting with 'bis' and then citing the name of the half-molecule in parentheses. Thus, Examples 1-6 become:

Examples:

7. [Et₃PbPbEt₃] bis(triethyllead)(*Pb—Pb*)
8. HSSH^{•-} bis(hydridosulfate)(*S—S*)(^{•1-}) (additive)
9. NCCN bis(nitridocarbon)(*C—C*)
10. NCCN^{•-} bis(nitridocarbonate)(*C—C*)(^{•1-})
11. (NC)SS(CN) bis{(nitridocarbonato)sulfur}(*S—S*), or bis(cyanidosulfur) (*S—S*)
12. (NC)SS(CN)^{•-} bis{(nitridocarbonato)sulfate}(*S—S*) (^{•1-}), or bis(cyanidosulfate)(*S—S*)(^{•1-})

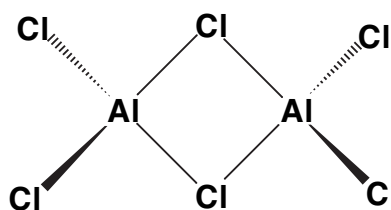
Note that the last five compounds may also easily be named as chain compounds, as shown in Section IR-7.4.

Note also that the names in Examples 11 and 12 differ from those given in Ref. 1. The present names are chosen because the sulfur atoms are more obviously the central atoms.

Yet another possibility is to view the compounds as bridged dinuclear species. Bridging ligands are indicated by the Greek letter μ , placed before the ligand name and separated from it by a hyphen. The whole term, *e.g.* ' μ -chlorido', is separated from the rest of the name by hyphens. If the bridging ligand occurs more than once, multiplicative prefixes are employed (see also Sections IR-9.1.2.10 and IR-9.2.5.2).

Examples:

13. ClOCl μ -oxido-dichlorine
- 14.



di- μ -chlorido-tetrachloridodialuminium,
or di- μ -chlorido-bis(dichloridoaluminium)

15. [NCSSCN] μ -disulfanediido-bis(nitridocarbon)
16. [NCSSCN]^{•-}
 μ -disulfanediido-bis(nitridocarbonate)([•]1-)

Note that the names given in Ref. 1 for the species in Examples 6, 12 and 16 were constructed in a format not used in the present recommendations and thus differ from the names given here.

IR-7.3.2 Non-symmetrical dinuclear compounds

There are two types of non-symmetrical dinuclear compounds: (i) those with identical central atoms differently ligated, and (ii) those with different central atoms. In both cases names are formed by means of the procedure described in Section IR-9.2.5.5, which also deals with bridging groups.

Priority is assigned to the central atoms as follows. For cases of type (i) the central atom carrying the greater number of alphabetically preferred ligands is numbered 1. For cases of type (ii) the number 1 is assigned to the higher priority central element of Table VI, whatever the ligand distribution.

In both types of compound, names are constructed in the usual way, by first citing the prefixes representing the ligands, in alphabetical order. Each prefix representing a ligand is followed by a hyphen, the number assigned to the central atom to which the ligand is attached, the Greek letter κ (kappa) (see Section IR-9.2.4.2) with a right superscript denoting the number of such ligands bound to the central atom (the number 1 being omitted for a single ligand), and the italic capital element symbol for the ligating atom by which the ligand is attached to the central atom. This describes the ligands and their mode of attachment. The κ construction can be omitted in very simple cases (see Examples 1 and 2 below).

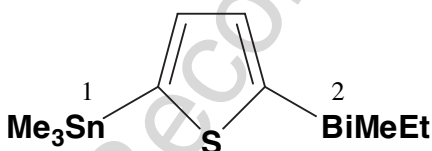
The central atoms are listed after the ligands. The multiplicative prefix 'di' is used where the central atoms are the same element. Otherwise, the order of the central atoms is obtained using Table VI (except that in this context oxygen is regarded by custom as being placed between chlorine and fluorine). The order of the central atoms reflects the numbering employed with the κ symbols. The ending 'ate' is added if the dinuclear compound is an anion, and a radical dot may be added for radicals. In the case of two different central atoms,

the two names are cited in alphabetical order inside parentheses and 'ate' is added outside the parentheses.

Examples:

1. ClClO oxido-1 κ O-dichlorine($\text{Cl}-\text{Cl}$),
or simply oxidodichlorine
2. ClOO^\bullet chlorido-1 κ Cl-dioxygen($\text{O}-\text{O}$)(\bullet),
or simply chloridodioxygen(\bullet)
3. ClClF^+ fluorido-1 κ F-dichlorine($\text{Cl}-\text{Cl}$)(1+),
or simply fluoridodichlorine(1+)
4. $[\text{O}_3\text{POSO}_3]^{2-}$
 μ -oxido-hexaoxido-1 κ^3 O,2 κ^3 O-(phosphorussulfur)ate(2-),
or simply μ -oxido-hexaoxido(phosphorussulfur)ate(2-)

5.



ethyl-2 κ C-tetramethyl-1 κ^3 C,2 κ C- μ -thiophene-2,5-diyl-tinbismuth

6.

$[\text{Cl}(\text{HPhN})_2\text{GeGeCl}_3]$
tetrachlorido-1 κ^3 Cl,2 κ Cl-bis(phenylamido-2 κ N)-digermanium($\text{Ge}-\text{Ge}$)

7.

LiPbPh_3 triphenyl-2 κ^3 C-lithiumlead($\text{Li}-\text{Pb}$)

Where the precise positions of ligation are unknown, or are known to be mixed, the situation is met appropriately by use of names in the style of Section IR-7.3.1.

Examples:

8. $[\text{Pb}_2(\text{CH}_2\text{Ph})_2\text{F}_4]$ dibenzyltetrafluoridodilead
9. $[\text{Ge}_2(\text{CH}_2\text{Ph})\text{Cl}_3(\text{NPh})_2]$
(benzyl)trichloridobis(phenylamido)digermanium

IR-7.3.3 Oligonuclear compounds

In simple cases, the principles of the preceding sections may be generalised for the naming of oligonuclear compounds. Again, there are compounds which are also easily named by substitutive nomenclature because of the availability of obvious parent hydrides.

Examples:

1. HO_3^\bullet hydrido-1 κH -trioxygen(\bullet), or simply hydridotrioxygen(\bullet)
2. $\text{HON}_3^{\bullet-}$ hydroxido-1 κO -trinitrate(2 $N-N$)($\bullet 1-$)
3. $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$
octachloridotrisilicon(2 $Si-Si$) (additive), or
octachlorotrisilane (substitutive)
4. $\text{FMe}_2\text{SiSiMe}_2\text{SiMe}_3$
1 κF -fluoridoheptamethyltrisilicon(2 $Si-Si$) (additive), or
1-fluoro-1,1,2,2,3,3,3-heptamethyltrisilane (substitutive)

(An alternative additive name for the compound in Example 3, based on the longest chain in the molecule, can also be constructed by the method described in Section IR-7.4.3).

For heterooligonuclear systems, more conventions are needed to identify and name the collection of central atoms, and to number the central atoms so as to provide locants for the ligands.

Example:

5. $\text{Me}_3\text{SiSeSiMe}_3$
 μ -selenidobis(trimethylsilicon) (additive), or
hexamethyl-1 $\kappa^3 C, 3\kappa^3 C$ -2-selenium-1,3-disilicon(2 $Si-Se$) (additive),
or 1,1,1,3,3,3-hexamethyldisilaselene (substitutive)

Note that in the last example one can choose to name the compound as dinuclear or trinuclear. The complexities deriving from the structural variations which may occur due to homonuclear and heteronuclear central atom clusters and bridging groups are dealt with in more detail in Sections IR-9.2.5.6 to IR-9.2.5.8.

IR-7.4 INORGANIC CHAINS AND RINGS

IR-7.4.1 General

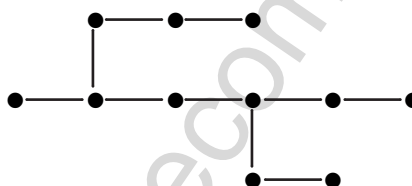
Inorganic chain and ring compounds can be named² according to a particular system of additive nomenclature which does not require prior knowledge about the nature of bonds between atoms. The method can be applied to all chain and ring compounds but its use is

principally intended for species mainly composed of atoms other than carbon. While small compounds can more conveniently be named by using several alternative methods, the advantage of this nomenclature system lies in the simple way in which complicated structures can be derived from the name and *vice versa*.

A neutral chain compound is called 'catena' preceded by a multiplicative prefix, 'di', 'tri', *etc.*, to indicate the number of branches in the molecule. Likewise, cyclic compounds are called 'cycle' preceded by the appropriate multiplicative prefix. A mixed chain and ring compound is named as 'catenacycle'. In the case of cationic and anionic species the names are modified by the suffixes 'ium' and 'ate', respectively. Radical species may be further specified using the radical dot (Section IR-7.1.4).

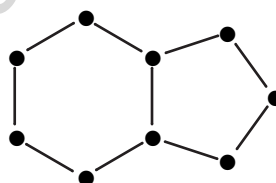
Examples:

1.



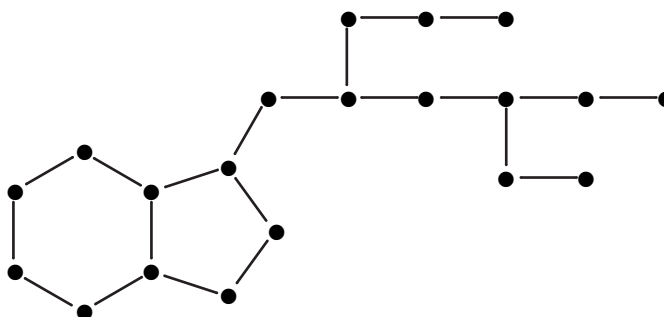
tricatena

2.



dicycle

3.



tricatenadicycle

The connectivity in the molecular framework is indicated by a nodal descriptor, which is placed in square brackets immediately before the terms 'catena', 'cycle' or 'catenacycle'. The atoms are numbered according to the general nodal nomenclature regardless of their chemical identity. Only in the case of ambiguity is the chemical nature of the atoms taken into consideration.

The first part of the descriptor indicates the number of atoms in the main chain. The arabic numerals after the full stop indicate the lengths of the branches cited in priority order. A superscript locant for each branch denotes the atom in the part of the molecule already numbered to which the branch is attached. A zero in the descriptor indicates a ring and is followed by an arabic numeral indicating the number of atoms in the main ring. The numbering begins from one of the bridgeheads and proceeds in the direction to give the lowest possible locant for the other bridgehead. The construction of the descriptor for assemblies consisting of several modules is treated in detail in Ref. 2.

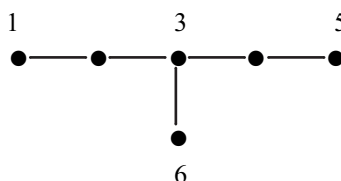
Examples:

1.



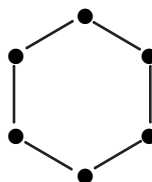
descriptor: [7]

2.



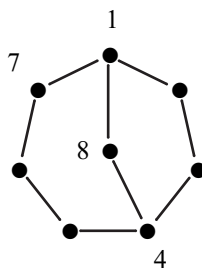
descriptor: [5.1³]

3.



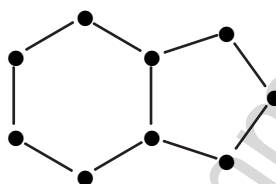
descriptor: [06]

4.



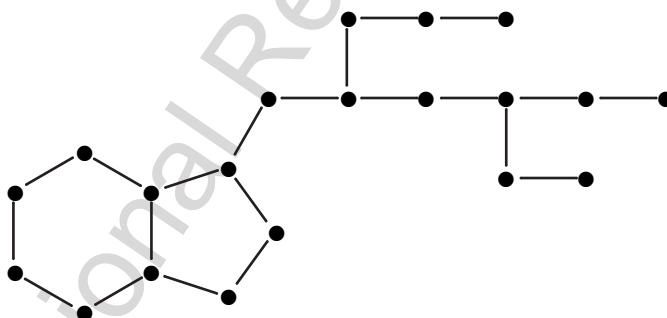
descriptor: [07.1^{1,4}]

5.



descriptor: [09.0^{1,5}]

6.



descriptor: [(09.0^{1,5})₂:20(8.2³1⁵)]

IR-7.4.3 Name construction

The atoms forming the nodal skeleton are listed in alphabetical order complete with their locants and are named using 'y' terms, examples of which are given in Table IR-7.1; a full list is given in Table X.

Table IR-7.1. Some 'y' terms for naming elements in the nodal framework

H	hydrony	C	carby	N	azy	O	oxy
B	bory	Si	sily	P	phosphy	S	sulfy

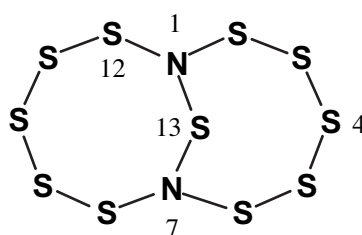
Ge	germy	As	arsy	Se	seleny
Sn	stanny	Sb	stiby	Te	tellury

Atoms and groups of atoms which are not a part of the nodal framework are named as ligands and are cited in alphabetical order, together with their locants, before the cited sequence of the atoms constituting the nodal framework.

The first six examples below were also named in Section IR-7.3.1. These simple molecules would be better named by other nomenclature systems, but they illustrate the name construction. The power of additive ring and chain nomenclature lies in the straightforward way in which structures of complicated branched-chain and polycyclic molecules can be arrived at from the name and *vice versa*. It should be evident that a systematic name of a complicated molecule will be necessarily long.

Examples:

1. $\text{Cl}_3\text{SiSiCl}_2\text{SiCl}_3$ 2,2,3,3,4,4-hexachlorido-1,5-dichloro-2,3,4-trisilyl-[5]catena
2. $\text{HSSH}^{\bullet-}$ 1,4-dihydrony-2,3-disulfy[4]catenate($\bullet 1-$)
3. NCCN 1,4-diazy-2,3-dicarby[4]catena
4. $\text{NCCN}^{\bullet-}$ 1,4-diazy-2,3-dicarby[4]catenate($\bullet 1-$)
5. NCSSCN 1,6-diazy-2,5-dicarby-3,4-disulfy[6]catena
6. $\text{NCSSCN}^{\bullet-}$ 1,6-diazy-2,5-dicarby-3,4-disulfy[6]catenate($\bullet 1-$)
- 7.

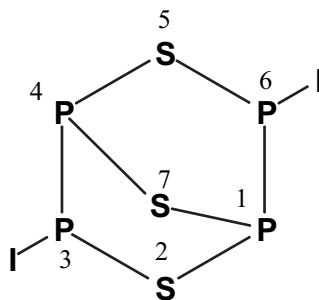


1,7-diazyundecasylyl-[012.1^{1,7}]dicycle

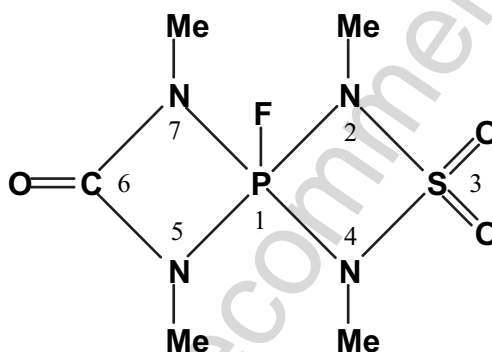
Since this compound contains only nitrogen and sulfur, it is not necessary to indicate the locants of all sulfur atoms. Only the locants of the two nitrogen atoms are needed.

Examples:

- 8.

3,6-diiodido-1,3,4,6-tetraphospho-2,5,7-trisulfo-[06.1^{1,4}]dicycle

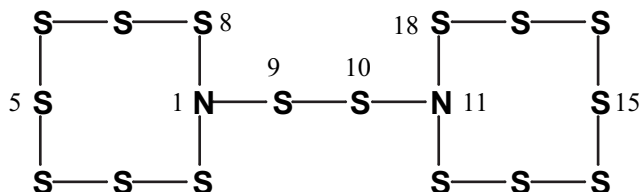
9.

1-fluorido-2,4,5,7-tetramethyl-3,3,6-trioxido-2,4,5,7-tetraazy-6-carby-1-phospho-3-sulfo-[04.3^{1,1}]dicycle

Compounds containing both cyclic and acyclic parts are named as *assemblies*, which are composed of *modules*. The descriptors of individual modules are connected by a colon. The locants on either side of the two colons indicate the points of attachment between the modules. (For naming assemblies, see Ref. 2).

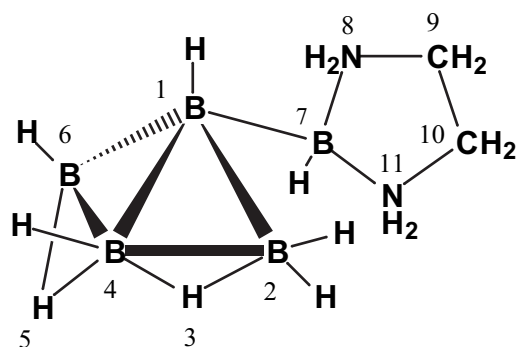
Examples:

10.



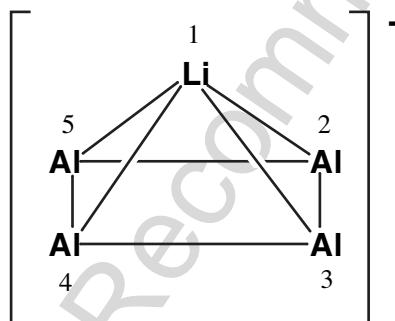
1,11-diazyhexadecasulfo-[(08)1:9(2)10:11(08)]catenadicycle

11.



1,2,2,4,6,7,8,8,9,9,10,10,11,11-tetradecahydrido-8,11-diazy-1,2,4,6,7-pentaboro-9,10-dicarby-3,5-dihydrony-[(06.0¹,4⁰2,4⁰4,6)1:7(05)]pentacycle

12. [LiAl₄]⁻



tetraalumino-1-lithy-[05.0¹,3⁰1,4⁰2,5]tetracyclate(1-)

IR-7.5

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