

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION

COMMISSION ON NOMENCLATURE OF ORGANIC CHEMISTRY*

**TREATMENT OF VARIABLE
VALENCE IN ORGANIC NOMENCLATURE
(LAMBDA CONVENTION)†**

(Recommendations 1983)

Prepared for publication by

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†Title as provisional recommendations: The Designation of Nonstandard Classical Valence Bonding in Organic Nomenclature.

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ORGANIC CHEMISTRY DIVISION

Commission on Nomenclature of Organic Chemistry

NOMENCLATURE OF ORGANIC CHEMISTRY

TREATMENT OF VARIABLE VALENCE IN ORGANIC NOMENCLATURE (λ -CONVENTION)

Recommendations 1983

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PREAMBLE

A general method for naming organic parent compounds containing skeletal atoms that occur in two or more valence states has been developed. This method is consistent with the fundamental principles of substitutive nomenclature and is directly applicable to naming organic derivatives of the inorganic hydrides. Its main principles were introduced briefly in Section D of the IUPAC Organic Nomenclature Rules, as revised for publication in combination with Sections A, B, C, E, F, and H (see Bonding number under Subsection D-0.3 and Rule D-1.62, Ref. 1), and the general convention was described in greater detail in 1982 as provisional recommendations (Ref. 2).

INTRODUCTION

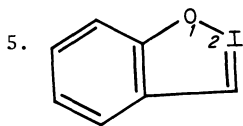
The basic principles of organic nomenclature depend on the classical concepts of constant valence and definite bond order. Therefore, in order to include compounds containing heteroatoms capable of exhibiting two or more valence states within the scope of organic nomenclature, it is necessary to define a standard valence for such heteroatoms. Defined standard valences, related to the Group number in the Periodic Table, for up to thirty heteroatoms are given in Rules B-1.1, D-1.61 (Ref. 1), and RB-1.1 (Ref. 3).

Nonstandard valence states of heteroatoms, i.e., valence states other than those defined in the rules, are often implied by: (a) semisystematic or trivial names of simple parent compounds; (b) class names; (c) names for groups; or (d) names of ring systems, where the nonstandard valence is unambiguous because of specific structure requirements of the system.

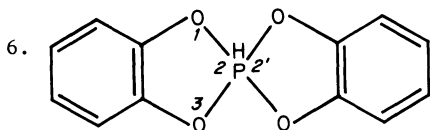
Examples:

- | | |
|-----------------------------|-----------------|
| 1. PH_5 | phosphorane |
| 2. $\text{R-SO}_2\text{-R}$ | dialkyl sulfone |
| 3. $\text{O}_2\text{I—}$ | iodyl |
| 4. $\text{F}_3\text{S—}$ | trifluorothio |

Examples (cont.):



2,1-benziodoxole

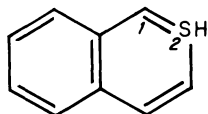
2,2'-spirobi[1,3,2-benzodioxaphos=
phole]

Although this method is quite useful for simple compounds, common groups, and ring systems with specific structural constraints, it is limited by the large number of names that must be remembered and the lack of systematization apparent in the creation of names for different compounds and groups.

A number of techniques have been used in organic nomenclature to indicate the presence of heteroatoms in nonstandard valence states. Most of these are useful in one way or another, but each has limitations as a general method, or has been considered to be unsuitable for one reason or another.

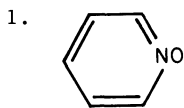
1. An "indicated hydrogen" assigned to a normally bivalent heteroatom of a ring system clearly indicates a higher valence state. However, this technique is not entirely consistent with the "indicated hydrogen principle" as defined by Rule A-21.6 (Ref. 1).

Example:

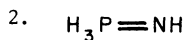
2H-2-benzothiopyran

2. Additive class terms, such as oxide, imide, and bromide, are very useful for indicating nonstandard valence of heteroatoms in parent compounds and can be used for nonstandard valence of heteroatoms in substituents provided unambiguous locants are available, when needed.

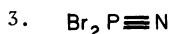
Examples:



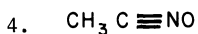
pyridine 1-oxide



phosphine imide

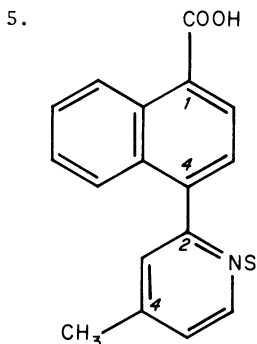


phosphonitrile dibromide



ethanenitrile oxide

Examples (cont.):

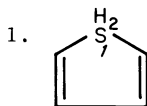


4-(4-methyl-2-pyridyl)-1-naphthoic acid N-sulfide

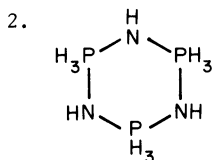
However, for some atoms and groups there are no commonly accepted class terms.

3. The additive prefix "hydro" indicates nonstandard valences of heteroatoms in heterocycles by describing the addition of hydrogen atoms, which may be later substituted just as those already implied by the name of the heterocycle.

Examples:

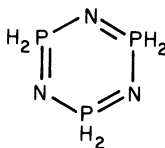
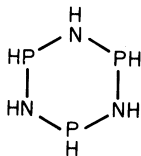


1,1-dihydrothiophene



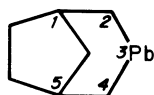
dodecahydro-s-triazatriphosphorine

This method has disadvantages, particularly when hydro prefixes are treated as detachable, and the method can be ambiguous because the practice of omitting locants for hydro prefixes when all double bonds of a ring or ring system are fully saturated is common. For example, the name hexahydro-s-triazatriphosphorine could refer to either of the following structures.



4. The subtractive prefix "dehydro" is used occasionally to indicate non-standard valence of heteroatoms in heterocycles by describing the removal of hydrogen atoms implied by the name of the heterocycle.

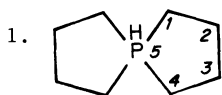
Example:



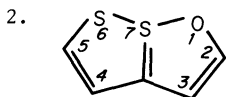
3,3-didehydro-3-plumbabicyclo=[3.2.1]octane

5. A Roman numeral cited as a superscript to an italicized element symbol, and usually associated with a locant, has been used quite extensively for indicating nonstandard valence of heteroatoms in ring systems, but rarely in acyclic structures.

Examples:



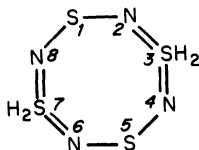
5-phospha(5-P^V)spiro[4.4]nonane



[1,2]dithiolo[1,5-b][1,2]oxathiole-7-S^{IV}

6. A combination of indicated hydrogen (see item 1, above) with the superscript Roman numeral symbolism (see item 5, above) has been used to describe nonstandard valence of heteroatoms in ring systems, especially where unusual structural features, such as cumulative double bonds, are found.

Example:



3H, 3H, 7H, 7H-1,3,5,7,2,4,6,8-tetra-thia(3,7-S^{VI})tetrazocine

Two of the techniques above (items 2 and 3) are codified briefly, as Rules D-1.54 and D-1.53, respectively, in the IUPAC Organic Nomenclature Rules (Ref. 1) and a third (item 4) can be considered to be an extension of Rule C-41.2 (Ref. 1). However, these techniques were not designed to cover the general case of nonstandard valence states in organic nomenclature and therefore the method described by the following rules should be preferred.

DISCUSSION

The need for a general method for indicating nonstandard valence of heteroatoms has been recognized and suggestions have been offered to deal with it. For example, the use of different endings (suffixes) added to the name of a parent hydride, indicating the number of nonbonding electron pairs in the valence shell of heteroatoms, has been proposed (Ref. 4). Although apparently sound in principle, this technique did not appear to be consistent with fundamental principles of organic nomenclature, and therefore was not assimilated into general usage.

Perhaps the most general technique used for designating nonstandard valence of heteroatoms described above (item 5) was not included as such in Section D of the Organic Rules (Ref. 1) mainly because of its use of the Roman numeral. This symbol is used extensively in inorganic nomenclature to denote oxidation number (Ref. 5a). However, the fundamental principle of the technique was sound, namely, the specification of the bonding number of a heteroatom, i.e., the number of valence bonds connecting a formally neutral nonstandard heteroatom to other skeletal atoms and to the hydrogen atoms associated with it in a parent hydride. Therefore, since it was the Roman numeral as a symbol that was unacceptable, it was necessary only to find a suitable replacement for this symbol; a new principle was not needed.

The use of arabic numerals as superscripts to italicized element symbols was suggested, but not well received because italicized element symbols with numerical superscripts are used quite often as locants in nomenclature and because this superscript position on an element symbol is used to indicate an ionic charge (Ref. 5b). These objections were removed in Section D (Ref. 1) by using the Greek letter "lambda" in place of the italicized element symbol

(see Note a) and a superscript arabic numeral is used in place of the Roman numeral. A locant associated with the resulting symbol specified the position of the nonstandard heteroatom in the structure. This system, which has become known as the " λ " convention, is completely compatible with the principles of organic nomenclature. Substituents are expressed in the usual way by appropriate prefixes or suffixes and the numbering practices established in Sections A, B, and C (Ref. 1) are followed. The "indicated hydrogen" principle, as defined by Rule A-21.6 (Ref. 1), is used, when necessary, to distinguish among isomeric ring systems containing the maximum number of noncumulative double bonds by specifying the position of one or more hydrogen atoms.

Structures containing formal cumulative double bonds at a skeletal atom in a nonstandard valence state have been difficult to describe by principles of organic nomenclature, especially in ring systems where the concept of maximum number of noncumulative double bonds is crucial to the interpretation of the name. As noted above, a combination of the superscript Roman numeral method and the unusual use of "indicated hydrogen" has been used for such structures. The " λ " convention alone also is inadequate in these cases. Therefore, the symbol δ^c , where c is the number of double bonds in the skeletal structure terminating at the heteroatom, added to the λ^n symbol, was introduced in the provisional Section D Rules (see Note a) (Ref. 1, D-0.3, pp. 324-325, and D-1.62, pp. 334-335, especially example 3). However, structures of this type are part of the general subject of cumulative double bonds, now under study by the Commission, and will be included in a later report.

The formation of a radical or ionic center at a skeletal atom in a nonstandard valence state by the addition or removal of a hydrogen atom or ion is described by a suffix ("yl", "ium", "ylium", "ide") added to the name of the neutral parent hydride in the usual manner as prescribed in Subsection C-0.8 (Ref. 1). Derivation of such names for radical or ionic compounds will be described in a future report.


RECOMMENDATIONS

The extension of substitutive nomenclature to compounds containing heteroatoms of variable valence requires a method for distinguishing between the various valence states of each atom. These recommendations, designated by Lm (λ), provide a general method for indicating nonstandard valence states of formally neutral skeletal atoms in parent hydrides (but see Note b).

Lm-1.0. Terminology

Lm-1.1. The bonding number, " n ", of a skeletal atom in a parent hydride is the sum of the total number of valence bonds to adjacent skeletal atoms, if any, and the number of attached hydrogen atoms. The relevance of these recommendations to naming radicals and ions is not considered in this report.

Examples:

1. SH ₂	$n = 2$	5. 	N; $n = 3$ C; $n = 4$
2. SnH ₂	$n = 2$	6. SiH ₂ =SiH ₂	$n = 4$
3. NH ₂ -NH ₂	$n = 3$	7. SH ₆	$n = 6$
4. PH ₄ -NH-PH ₄	N; $n = 3$ P; $n = 5$	8. IH ₇	$n = 7$

Note a. In the first publication of the provisional Section D rules the symbol σ^m , where m is the number of σ bonds terminating at the heteroatom was suggested either as an alternative to or in conjunction with the λ^n symbol (Rule 1.62) (Ref. 6). However, the number of hydrogen atoms attached to the heteroatom would have to be included in this symbolism for a parent hydride, which is not consistent with the basic principles of substitutive nomenclature. In organic nomenclature, implied (or expressed) valence requirements of a skeletal atom in a parent hydride are satisfied with hydrogen atoms after other structural requirements are met. Hence, this symbolism was not included in the revision of the Section D rules for the 1979 edition of the IUPAC Organic Rules (Ref. 1).

Note b. Cyclic parent hydrides having cumulative double bonds in addition to the maximum number of noncumulative double bonds in the rest of the structure will be included in a forthcoming comprehensive treatment of cumulative double bond systems.

Lm-1.2. The bonding number of a neutral atom in a parent hydride is standard when it has the value given in the following table of elements that occur more or less frequently in organic compounds. It is nonstandard when its value is either larger or smaller.

Bonding number	3	4	3	2	1
	B	C	N	O	F
		Si	P	S	Cl
		Ge	As	Se	Br
		Sn	Sb	Te	I
		Pb	Bi	Po	At

Lm-2.0. Designation of Nonstandard Bonding Numbers. A nonstandard bonding number of a neutral skeletal atom in a parent hydride is indicated by the symbol λ^n , where n is the bonding number as defined in Lm-1.1.

If the locant for an atom with a nonstandard bonding number is used in the name of the normal (standard) parent hydride, the λ^n symbol is cited immediately after this locant. If the locant for such an atom is not expressed in the name, the locant, if necessary, and the λ^n symbol are cited in front of the name of the parent hydride, but after any indicated hydrogen (see Lm-3.0).

Numbering of parent hydrides with heteroatoms in nonstandard valence states follows the rules of Sections B and C of the IUPAC Organic Nomenclature Rules (Ref. 1) for numbering heteroatoms as far as possible. When a choice is needed between the same skeletal atom in different valence states, the one in a nonstandard valence state is preferred for assignment of the lower locant. If a further choice is needed between the same skeletal atom in two or more nonstandard valence states, preference for lower locant is given in order of the decreasing numerical value of the bonding number, i.e., λ^6 is preferred to λ^4 .

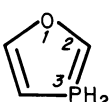
Examples:

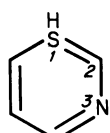
- SH_4

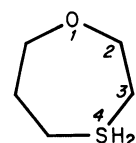
λ^4 -Sulfane
[the name sulfurane has been suggested (Ref. 7)]
- IH_5

λ^5 -Iodane
[the name periodinane has been suggested (Ref. 8)]
- $\text{HS}-\text{SH}_4-\text{SH}$
 $\quad \quad \quad 1 \quad 2 \quad 3$

$2\lambda^6$ -Trisulfane
- $\text{H}_4\text{P}-\text{PH}_3-\text{PH}_4$
 $\quad \quad \quad 1 \quad 2 \quad 3$

$1\lambda^5, 2\lambda^5, 3\lambda^5$ -Triphosphane
(not Tri- λ^5 -phosphane; see Note a)
- 

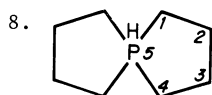
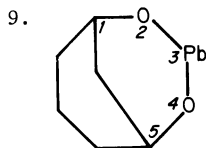
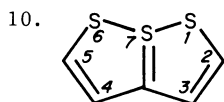
$1, 3\lambda^5$ -Oxaphosphole
- 

$1\lambda^4, 3$ -Thiazine
- 

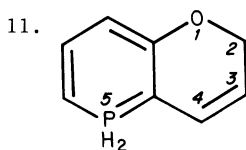
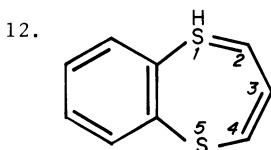
$1, 4\lambda^4$ -Oxathiepane

Note a. An abbreviated form (λ^5)₃-triphosphane (in speech tri- λ^5 -triphosphane is perhaps better) is permissible.

Examples (cont.):

5λ⁵-Phospha[4.4]nonane2,4-Dioxa-3λ²-plumbabicyclo[3.3.1]=
nonane7λ⁴-[1,2]Dithio[1,5-b][1,2]=
dithiolen
1,6,6aλ⁴-Trithiapentalene

Note: Nonstandard valence states in fused ring systems are indicated only in the complete ring system, not in component rings.

2H-5λ⁵-phosphinino[3,2-b]pyran1λ⁴,5-Benzodithiepin (the λ⁴ sulfur
atom is preferred for lowest
locants)

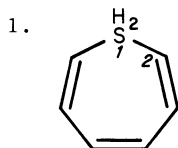
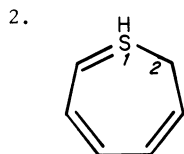
Lm-3.0. Indicated Hydrogen.

Lm-3.1. When the maximum number of noncumulative double bonds is assigned to a parent ring structure, account must be taken of the modified valence of ring atoms with nonstandard bonding numbers.

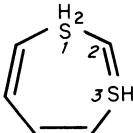
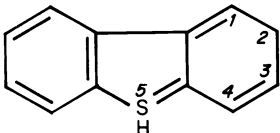
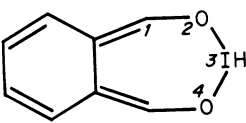
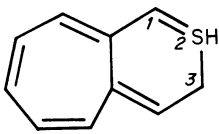
Lm-3.2. After the maximum number of noncumulative double bonds has been assigned according to Rule Lm-3.1, any ring atom with a bonding number of three or higher connected to adjacent ring atoms by single bonds only, and carrying one or more hydrogen atoms, is designated by the "indicated hydrogen" symbolism as described in Rule A-21.6 (Ref. 1). If the preceding rules leave a choice, such ring atoms are preferred for low locants.

Note: Designation of indicated hydrogen at nonbridgehead ring positions between two bivalent ring atoms is often omitted.

Examples:

1H-1λ⁴-Thiepine2H-1λ⁴-Thiepine

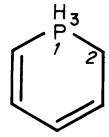
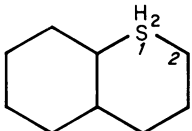
Examples (cont.):

3.  $1\text{H}-1\lambda^4,3\lambda^4$ -Dithiepine (the $-\text{SH}_2-$
 λ^4 -sulfur atom is preferred for
low numbering)
4.  $2\text{H}-5\lambda^4$ -Dibenzothiophene
5.  $3\text{H}-3\lambda^3,2,4$ -Benziodioxepin
6.  $3\text{H}-2\lambda^4$ -Cyclohepta[c]thiopyran (not
 $2\text{H}-3\lambda^4$ -cyclohepta[c]thiopyran)

Lm-4.0. Derivatives of parent hydrides with skeletal atoms in nonstandard valence states are named according to the established rules of organic nomenclature (Ref. 1) as exemplified below.

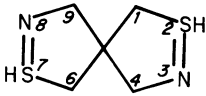
Lm-4.1. Saturation of double bonds in a ring system whose parent name requires the maximum number of noncumulative double bonds is indicated by hydro prefixes, as prescribed by Rules A-23.1 and B-1.2 (Ref. 1).

Examples:

1.  $1,2$ -Dihydro- $1\lambda^5$ -phosphinine
2.  Decahydro- $1\lambda^4$ -benzothiopyran

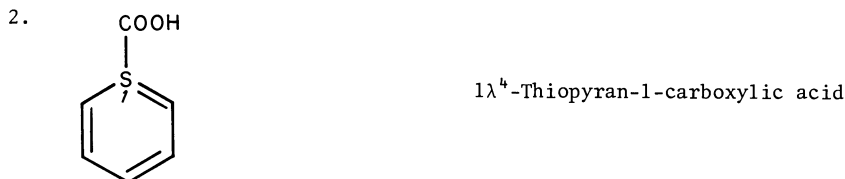
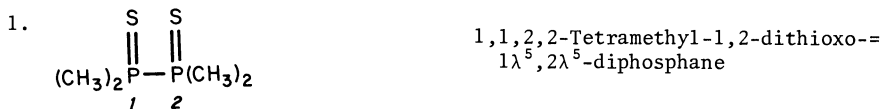
Lm-4.2. The presence of multiple bonds in a parent hydride whose parent name requires saturated skeletal atoms at all positions, is described by subtractive suffixes such as "ene" and "yne" (see Rules A-3, A-11.3, A-31.2, A-41.3 in Ref. 1).

Examples:

1.  $2\lambda^4,7\lambda^4$ -Dithia-3,8-diazaspiro[4.4]=
nona-2,7-diene
2. $\text{CH}_3-\text{CH}_2-\text{S}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}=\text{PH}_2-\text{N}=\text{N}-\text{PH}_2=\text{CH}-\text{CH}_2-\text{S}-\text{CH}=\text{S}=\text{CH}-\text{CH}_3$
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
- 5 -Oxa-3,14,16 λ^4 -trithia-9,10-diaza=
 $8\lambda^5,11\lambda^5$ -diphosphaoctadeca-7,9,=
11,15,16-pentaene

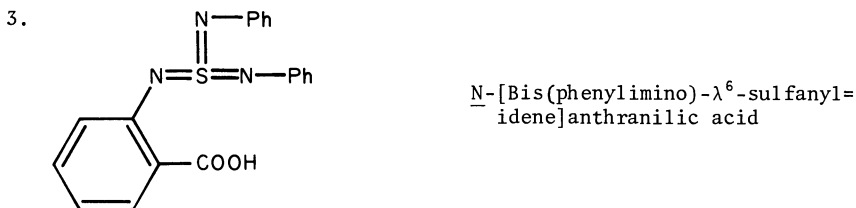
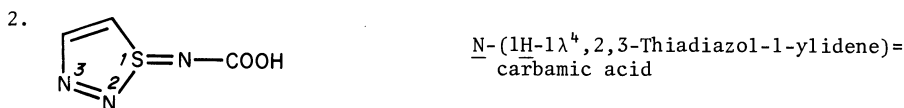
Lm-4.3. Derivatives formed by substitution of hydrogen atoms of the parent hydride are named by means of prefixes and/or suffixes in the established manner (Rule C-0.1, Ref. 1).

Examples:



Lm-4.4. Prefixes for describing substituents derived from parent hydrides having heteroatoms in nonstandard valence states are formed in the usual manner by using endings such as "yl", "ylidene", "diyl", etc. (Ref. 1).

Examples:



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