

PROVISIONAL

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION

COMMISSION ON NOMENCLATURE OF ORGANIC CHEMISTRY*

**THE DESIGNATION OF NON-
STANDARD CLASSICAL VALENCE
BONDING IN ORGANIC
NOMENCLATURE**

Prepared for publication by
W. H. POWELL

Comments on these recommendations are welcome and should be sent within 8 months from January 1982 to the Secretary of the Commission:

Dr. W. H. Powell
Chemical Abstracts Service
2540 Olentangy River Road
P. O. Box 3012
Columbus, Ohio 43210
USA

Comments from the viewpoint of languages other than English are especially encouraged. These may have special significance regarding the publication in various countries of translations of the nomenclature eventually approved by IUPAC.

*Membership of the Commission during the preparation of these recommendations (1975-1981) was as follows:

Titular Members: O. Achmatowicz (Poland), 1979-1983; K. Bláha (Czechoslovakia), 1971-1979, *Vice-Chairman*, 1977-1979; L. C. Cross (UK), 1965-1977; H. Grűnewald (Federal Republic of Germany), 1973-1977; D. Hellwinkel (Federal Republic of Germany), 1979-1983; K. Hirayama (Japan), 1975-1983; S. P. Klesney (USA), *Secretary*, 1968-1979; W. Klyne (UK), 1971-1977; K. L. Loening (USA), 1965-1979; N. Lozac'h (France), 1953-1979, *Chairman*, 1971-1977; A. D. McNaught (UK), 1979-1983; G. P. Moss (UK), 1977-1981, *Vice-Chairman*, 1979-1981; W. H. Powell (USA), *Secretary*, 1979-1983; J. C. Richer (Canada), 1979-1983; J. Rigaudy (France), 1967-1981, *Chairman*, 1977-1981; F. Vögtle (Federal Republic of Germany), 1977-1979.

Associate Members: O. Achmatowicz (Poland), 1977-1979; K. Bláha (Czechoslovakia), 1979-1983; L. C. Cross (UK), 1977-1981; D. Eckroth (USA), 1975-1983; J. H. Fletcher (USA), 1975-1983; E. W. Godly (UK), 1979-1983; S. Hammerum (Denmark), 1977-1979; D. Hellwinkel (Federal Republic of Germany), 1975-1979; S. P. Klesney (USA), 1979-1983; K. L. Loening (USA), 1979-1981; N. Lozac'h (France), 1979-1983; A. D. McNaught (UK), 1977-1979; R. Panico (France), 1979-1981; W. H. Powell (USA), 1975-1979; J. C. Richer (Canada), 1975-1979; F. Vögtle (Federal Republic of Germany), 1972-1977, 1979-1983; O. Weissbach (Federal Republic of Germany), 1979-1983; H. J. Zeigler (Switzerland), 1975-1977.

National Representatives: G. Deak (Hungary), 1979-1981; R. Panico (France), 1978-1979; J. A. Retamar (Argentina), 1980-1981; R. Schoenfeld (Australia), 1980-1981.

ORGANIC CHEMISTRY DIVISION

Commission on Nomenclature of Organic Chemistry

THE DESIGNATION OF NONSTANDARD CLASSICAL VALENCE BONDING IN ORGANIC NOMENCLATURE

PREAMBLE

A general method for naming parent compounds containing heteroatoms (noncarbon atoms) that occur in organic compounds in two or more classical valence bonding 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).

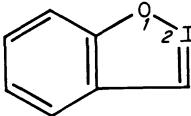
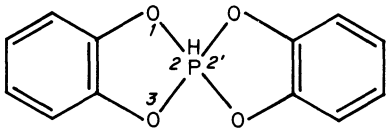
This report describes this general convention in greater detail.

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. 2).

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

Examples:

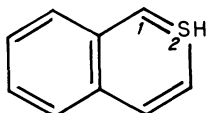
- | | |
|--|---------------------------------------|
| 1. PH_5 | Phosphorane |
| 2. $\text{R-SO}_2\text{-R}$ | Dialkyl sulfone |
| 3. $\text{O}_2\text{I-}$ | Iodyl |
| 4. $\text{F}_3\text{S-}$ | Trifluorothio |
| 5.  | 2,1-Benziodoxole |
| 6.  | 2,2'-Spiro[1,3,2-benzodioxaphosphole] |

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).

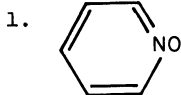
Example:



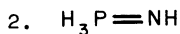
2H-2-Benzothiopyran

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 indicating nonstandard valence of heteroatoms in substituents provided unambiguous locants are available, when needed.

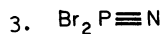
Examples:



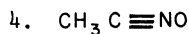
Pyridine 1-oxide



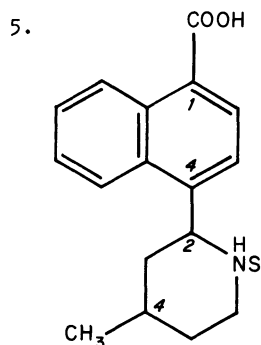
Phosphine imide



Phosponitrile dibromide



Ethanenitrile oxide

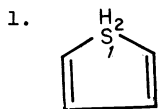


4-(4-Methyl-2-piperidyl)-1-naphthoic acid N-sulfide

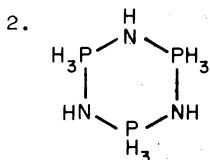
However, for some atoms and groups there are no commonly accepted class terms.

3. The additive prefix "hydro" is used to indicate nonstandard valences of heteroatoms in heterocycles by describing the addition of hydrogen atoms, which may be substituted later, besides those already implied by the name of the heterocycle.

Examples:

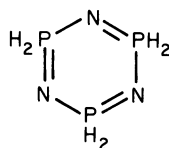
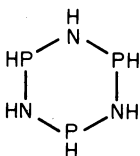


1,1-Dihydrothiophene



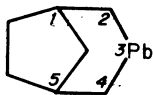
Dodecahydro-s-triazatriphosphorine

This method has disadvantages, particularly when hydro prefixes are treated as detachable, and it can be ambiguous because the practice of omitting locants for hydro prefixes when all double bonds 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 nonstandard valence of heteroatoms in heterocycles by describing the removal of hydrogen atoms implied by the name of the heterocycle.

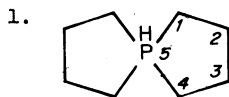
Example:



3,3-Didehydro-3-plumbabicyclo[3.2.1]octane

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

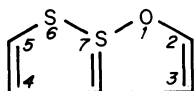
Examples:



5-Phospha(5-p^V)spiro[4.4]nonane

Examples (cont.):

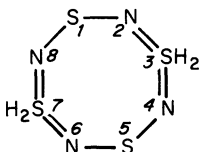
2.



[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 (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-Tetrathia(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 classical valence bonding 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. 3). 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. 4a). However, the fundamental principle of the technique was sound, namely, the specification of the bonding number of a heteroatom, i.e., the number of classical 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 objectionable, it was necessary only to find a suitable replacement for this symbol; a new principle was not needed.

The use of Arabic numbers 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. 4b). These objections were removed in Section D (Ref. 1) by using the Greek letter "λ" in place of the italicized element symbol (see Note a.). A superscript Arabic number is used in place of the Roman numeral and a

Note a. In the first publication of the provisional Section D rules an alternative method using the Greek letter σ was offered (Rule 1.62, Ref. 5). However, the definition of this symbol was not consistent with a fundamental concept in organic nomenclature, i.e., a parent compound (hydride) whose derivatives are derivable directly by substitution of hydrogen atoms attached to its skeletal atoms, and was therefore not included in the revision of Section D (Ref. 1, pp. 323-471).

locant is associated with the resulting symbol to specify 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 Section 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 nonstandard heteroatom 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). 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). Naming of such radical or ionic compounds will be illustrated 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 (lambda), provide a general method for indicating nonstandard, classical valence states of formally neutral, nonradical skeletal atoms in parent hydrides except for cyclic parent hydrides having cumulative double bonds in addition to the maximum number of noncumulative double bonds in the rest of the structure (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 classical valence bonds to adjacent skeletal atoms, if any, and the number of attached hydrogen atoms.

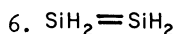
Examples:

1. SH_2	$n = 2$	4. $\text{PH}_4\text{-NH-PH}_4$	N; $n = 3$ P; $n = 5$
2. SnH_2	$n = 2$	5. 	N; $n = 3$ C; $n = 4$
3. $\text{NH}_2\text{-NH}_2$	$n = 3$		

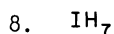
Note a. A symbol, σ^m , where m is the number of σ bonds of the heteroatom, added to the λ^n symbol was suggested in the preliminary publication of the Section D rules (Ref. 5). However, the number of hydrogen atoms attached to the heteroatom would have to be included in this symbolism for a parent hydride, 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, the σ^m 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. These structures will be included in a forthcoming comprehensive treatment of cumulative double bond systems.

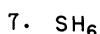
Examples (cont.):



n = 4



n = 7



n = 6

Lm-1.2. A bonding number is standard when it has the value for a neutral atom of the element given in the following table, and nonstandard when its value is either larger or smaller than the value given for the element.

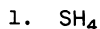
Bonding Number	3	4	3	2	1
	B	C	N	O	F
		Si	P	S	Cl
		Ge	As	Se	Br
		Sn	Sb	Te	I
		Pb	Bi	Po	At

Lm-2.0 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.

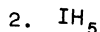
If the locant for an atom with a nonstandard bonding number is used in the name of the normal (standard) parent hydride, the λ^n symbol is cited immediately after this locant. If the locant for such an atom is not expressed in the name, the locant, if necessary, and the λ^n symbol are cited in front 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 in standard valence states. When a further choice is needed, the order of preference for assignment of lowest locants to heteroatoms follows the order of decreasing numerical value of the bonding number, standard or nonstandard.

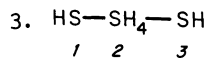
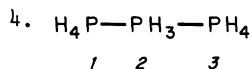
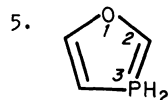
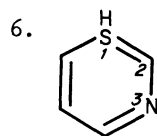
Examples:

 λ^4 -Sulfane

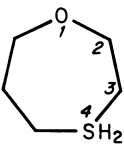
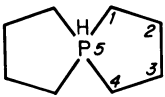
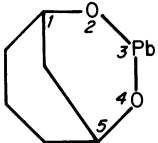
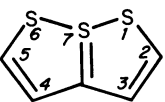
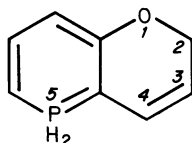
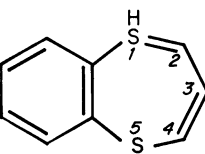
[the name sulfurane has been suggested (Ref. 6)]

 λ^5 -Iodane

[the name periodinane has been suggested (Ref. 7)]

 $2\lambda^6$ -Trisulfane $1\lambda^5, 2\lambda^5, 3\lambda^5$ -Triphosphane
(not Tri- λ^5 -phosphane) $1, 3\lambda^5$ -Oxaphosphole $1\lambda^4, 3$ -Thiazine

Examples (cont.):

7.  1,4λ⁴-Oxathiepane
8.  5λ⁵-Phosphaspiro[4.4]nonane
9.  2,4-Dioxa-3λ²-plumbabicyclo[3.3.1]nonane
10.  7λ⁴-[1,2]Dithiolo[1,5-b][1,2]dithiole
(Note: Nonstandard valence states are indicated only in the complete ring system, not in component rings)
1,6,6aλ⁴-Trithiapentalene
11.  2H-5λ⁵-Phosphorino[3,2-b]pyran
12.  1λ⁴,5-Benzodithiepin
(the λ⁴ sulfur atom is preferred for lowest locants)

Im-3.0 Indicated hydrogen. If a parent ring structure with the maximum number of noncumulative double bonds has 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, then such a ring atom is designated by use of the "indicated hydrogen" convention as described in Rule A-21.6 (Ref. 1).

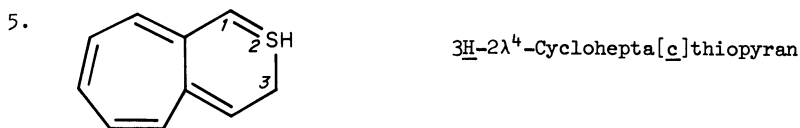
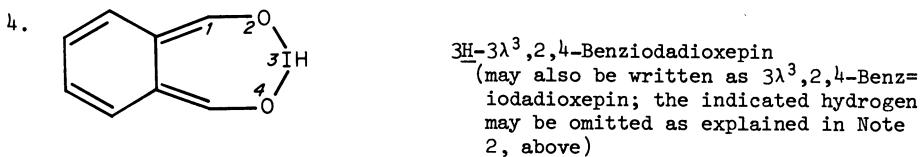
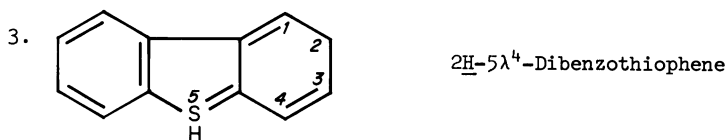
Note 1: Ring atoms with nonstandard bonding numbers are considered as well as those with standard bonding numbers when inserting the maximum numbers of noncumulative double bonds.

Note 2: Designation of indicated hydrogen at nonbridgehead ring positions between two bivalent ring atoms is often omitted.

Examples:

1.  1H-1λ⁴-Thiepin

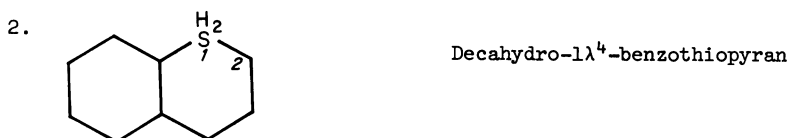
Examples (cont.):



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

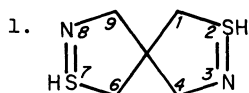
Lm-4.1. Saturation of double bonds in a ring system whose parent name requires the maximum number of noncumulative double bonds is indicated by hydro prefixes, as prescribed by Rules A-23.1 and B-1.2 (Ref. 1).

Examples:

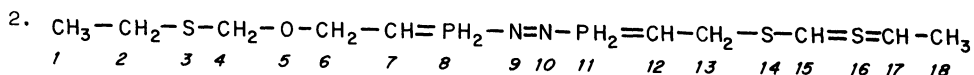


Lm-4.2. The presence of multiple bonds in a parent hydride whose parent name requires saturated skeletal atoms at all positions, is described by subtractive suffixes such as "ene" and "yne" (see Rules A-3, A-11.3, A-31.3, A-41.3 in Ref. 1).

Examples:



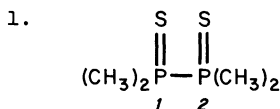
2λ⁴,7λ⁴-Dithia-3,8-diazaspiro[4.4]=
nona-2,7-diene



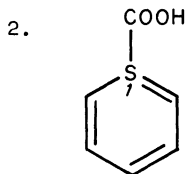
5-Oxa-3,14,16λ⁴-trithia-9,10-diaza=
8λ⁵,11λ⁵-diphosphaoctadeca-7,9,11,=
15,16-pentaene

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 (Subsection C-0.1, Ref. 1).

Examples:



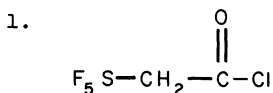
1,1,2,2-Tetramethyl-1,2-dithioxo=
1λ⁵,2λ⁵-diphosphane



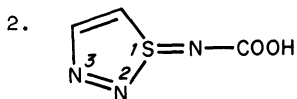
1λ⁴-Thiopyran-1-carboxylic acid

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).

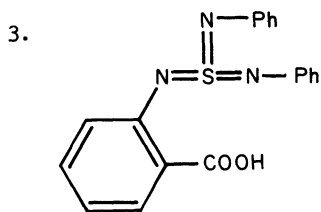
Examples:



(Pentafluoro-λ⁶-sulfonyl)acetyl
chloride



N-(1H-1λ⁴,2,3-Thiadiazol-1-ylidene)=
carbamic acid



N-[Bis(phenylimino)-λ⁶-sulfonylidene]=
anthranilic acid

REFERENCES

1. International Union of Pure and Applied Chemistry, Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F, and H, Pergamon Press, Oxford, 1979.
2. International Union of Pure and Applied Chemistry, Revision of the Extended Hantzsch-Widman System of Nomenclature for Heteromonocycles (Provisional), Pure Appl. Chem. 1979, 51, 1995-2003.
3. A. F. Clifford, J. Chem. Doc. 1965, 5, 91-95; 1970, 10, 180-195.
4. International Union of Pure and Applied Chemistry, Nomenclature of Inorganic Chemistry, 2nd Edition, Butterworths, London, 1979, (a) Rule 0.1, p. 5; (b) Rule 1.31, p. 11.
5. International Union of Pure and Applied Chemistry, Section D (Tentative), IUPAC Information Bulletin Appendices on Tentative Nomenclature, Symbols, Units, and Standards, No. 41, August, 1973.
6. J. C. Martin and R. J. Arhart, J. Am. Chem. Soc. 1971, 93, 2339-2342.
7. R. L. Amey and J. C. Martin, J. Am. Chem. Soc. 1978, 100, 300-301.