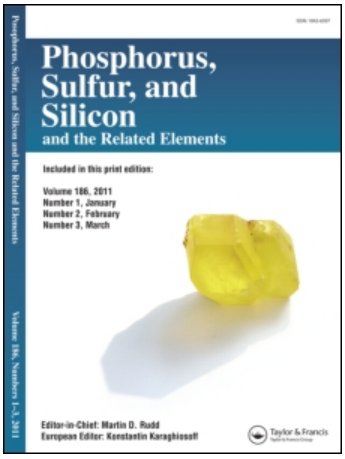

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Inorganic Ring Nomenclature: Past, Present, and Future

Warren H. Powell[a]; Thomas E. Sloan[a]
[a] Chemical Abstracts Service, Columbus, Ohio, U.S.A.

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INORGANIC RING NOMENCLATURE: PAST, PRESENT, AND FUTURE

WARREN H. POWELL and THOMAS E. SLOAN
Chemical Abstracts Service, Columbus, Ohio, U. S. A.

Abstract Increasing numbers and complexity of inorganic ring compounds are being reported. Heretofore, methods for naming organic ring compounds have been adapted for describing most of the inorganic ring compounds involving nonmetals and/or semimetals. However, such methods are either not directly applicable to inorganic rings or are inconsistent with principles important to inorganic chemistry. One of the goals of inorganic nomenclature has been to develop a structural nomenclature based on coordination principles to describe inorganic rings that are more complicated than bis-bridged or chelated metal compounds. Methods now in use and that have been proposed for naming inorganic rings are reviewed and a new proposal based on additive principles is outlined.

INTRODUCTION

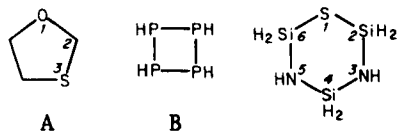
This discussion of ring nomenclature will focus on cyclic systems containing skeletal atoms other than carbon atoms or at the most a low ratio of skeletal carbon atoms to noncarbon atoms. Such "inorganic" rings first became apparent in chemistry during the latter part of the nineteenth and early part of the twentieth centuries, for example, trimetaphosphates (1875)[1], phosphonitrilic halides (1895-7)[2], cyclotrisiloxanes (1905)[3], and borazine (borazole) (1925)[4]. At that time, nomenclature for rings of any kind was not a concern because the limited number of examples and primary investigators did not require such a formalized tool of communication.

As organic ring compounds were synthesized and characterized, an ad hoc ring nomenclature grew steadily, whereas the chemistry of inorganic ring compounds was dormant, or at least not recognized as a chemistry of ring structures. Hence, a nomenclature for inorganic rings separate from that for organic rings did not develop; principles used for naming organic rings were extended and analogies were used where needed. Inorganic rings and ring systems

are still named by the several organic methods, none of which addresses the differences or the unique and important features of inorganic ring compounds over a broad range of structure types.

ORGANIC RING NOMENCLATURE:

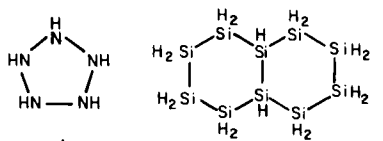
The Hantzsch-Widman system is applicable to heteromonocycles with no more than ten ring skeletal atoms. Originally proposed independently by Hantzsch (1887)[5] and Widman (1888)[6] for naming five- and six-membered heteromonocycles, this system has been extended and refined so that it now includes nineteen elements, most of which are nonmetals[7]. It is based on a defined carbon skeleton; heteroatoms, i.e., noncarbon atoms, are denoted by prefixes attached to a stem that indicates ring size and bonding saturation. For example, the name 1,3-oxathiolane (Fig. 1-A) describes a saturated five-membered ring comprised of an oxygen atom, a sulfur atom, and three carbon atoms. Although designed for organic heteromonocycles, i.e., rings in which the skeletal atom of emphasis is carbon, it can be used to name inorganic rings, for example, tetraphosphetane (Fig. 1-B) and 1,3,5,2,4,6-thiadiazatrisilinane (Fig. 1-C).



A B C

FIGURE 1

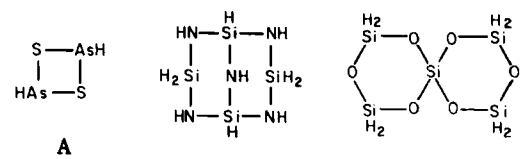
The "cyclo" system used for saturated mono-[8] and polycyclic[9] hydrocarbons, for example, cyclopentane and bicyclo[2.2.2]octane, is used for naming homogeneous inorganic rings by inserting a morpheme for the noncarbon skeletal element[10,11a], for example cyclopentaazane (Fig. 2-A) and bicyclo[4.4.0]decasilane (Fig. 2-B).



A B

FIGURE 2

The "cyclo" system has been adapted for naming inorganic rings consisting of repeating pairs of elements[10,11a] by adding a morpheme to denote the second element of the pair, for example, cyclodiarsathiane (Fig 3-A), bicyclo-[3.3.1]tetrasilazane (Fig. 3-B), and spiro[5.5]pentasiloxane (Fig. 3-C). Since this adaptation is limited to repeating pairs of elements, it is not necessary to cite a numerical prefix for the second morpheme.



A B C

FIGURE 3

Fusion nomenclature[11b-c], the most widely used method for naming polycyclic organic rings, is used for naming saturated polycyclic inorganic rings. Although these names are fully descriptive, they require citation of locants for all the heteroatoms, for example, [1,3,2,4,5]diazatrisilolo[4,5-d]-[1,3,2,4,5]diazatrisilole (Fig. 4).

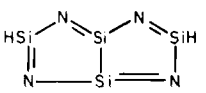
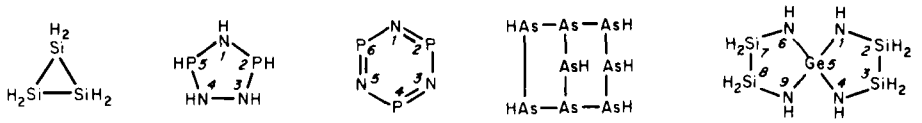


FIGURE 4

Replacement ("a") nomenclature[11d] can be used in the naming of any homogeneous or heterogeneous inorganic ring or ring system. It is based on names for the corresponding hydrocarbon skeleton with the heteroatoms indicated by "a" prefixes. Fig. 5 gives examples along with names generated by other methods described earlier.



A B C D E

FIGURE 5

A. Trisilapropane; Trisilirene (Hantzsch-Widman); Cyclotrisilane ("cyclo" system). B. 1,3,4-Triaza-2,5-diphosphacyclopentane; 1,3,-4,2,5-Triazadiphospholane (Hantzsch-Widman). C. 1,3,5-Triaza-2,4,-6-triphosphabenzene; 1,3,5,2,4,6-Triazatriphosphinine (Hantzsch-Widman); Cyclotriphosphazene (extended "cyclo" system). D. Octa-arsabicyclo[3.2.1]octane; Bicyclo[3.2.1]octaarsane ("cyclo" system). E. 1,4,6,9-Tetraarsa-2,3,7,8-tetrasila-5-germaspiro[4.4]nonane.

Trivial names for inorganic rings, for example, borazine, phosphazene, boroxin, and borthiin, do not occur often for inorganic rings in contrast to organic nomenclature where trivial names are the basis for naming most fused polycyclic rings[11b,d].

All of the above methods are used in CAS index nomenclature for inorganic rings, the preferred method for any particular ring being somewhat a matter of arbitrary choice (Fig. 6)[12].

DEVELOPMENT OF INORGANIC RING NOMENCLATURE

The chemistry of inorganic rings is developing rapidly and the number, variety, and complexity of structures is increasing. Organic methods for naming "inorganic" rings in a manner consistent with principles of inorganic chemistry are limited by a dependence

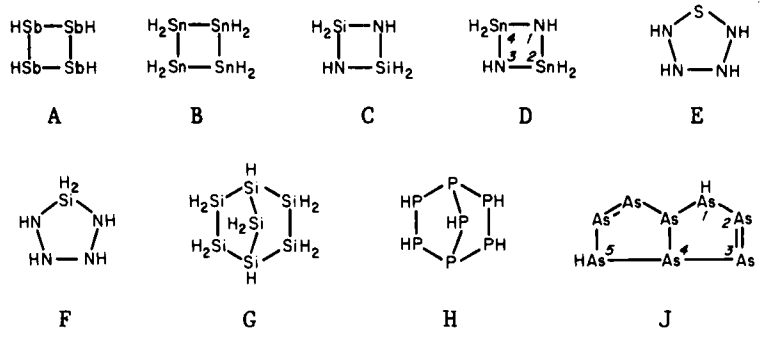


FIGURE 6

A. Tetrastibetane (Hantzsch-Widman). B. Cyclotetrastannane ("cyclo" system). C. Cyclodisilazane (extended "cyclo" system). D. 1,3,2,4-Diazadistannetidine (Hantzsch-Widman). E. Thiatetrazolidine (Hantzsch-Widman). F. Tetraazasilacyclopentane (replacement). G. Bicyclo[2.2.1]heptasilane ("cyclo" system). H. Heptaphosphabicyclo[2.2.1]heptane (replacement). J. 1H,5H-Pentarsolopentarsole (fusion).

on classical bonding representations and valence saturation. Beyond the first eight-membered row of elements in the periodic table the bonding capability of the elements is sufficiently flexible that "organic" methods for describing "unsaturated" structures are not adequate. "Organic" methods often circumvent such inadequacies by using trivial names, such as benzene, pyridine, and naphthalene that imply bonding delocalization or other nonclassical bonding. Even in systematic names, such as Hantzsch-Widman names, it must be assumed that the classically bonded structure described by the name represents several contributing structures.

Other difficulties with "organic" methods include redundancy. In replacement nomenclature, skeletal atoms are cited twice, once as a carbon atom, and then as a hetero atom replacing the carbon atom. Citation of hydro prefixes to indicate hydrogen atoms on skeletal atoms that are subsequently replaced by substituting atoms or groups is redundant. A more serious difficulty is the inability to describe conveniently the presence of a neutral group attached to a skeletal atom. This problem arose some time ago in the development of a nomenclature for polyhedral polyboron compounds and is evident today in metallocycloalkanes, a growing class that is being named by many authors using replacement techniques. In such cases, valence constraints and substitutive (organic) techniques often leads to cumbersome zwitterionic names, for instance, 1,1,3,3-tetramethyl-2,2,4,4-tetrachloro-1,3-diazonia-2,4-diboratacyclobutane (Fig. 7).

The search for a suitable nomenclature for inorganic ring and ring systems began almost thirty years ago. A working group of the IUPAC Commission on Nomenclature of Inorganic Chemistry (CNIC) has been involved since the mid-1960's and several other investigators have made proposals.

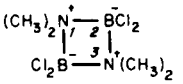
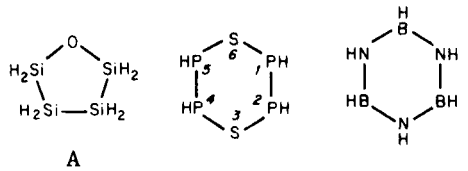


FIGURE 7

One of the first to be concerned with this problem was Ionel Haiduc who published an "extension of the oxa-aza-thia nomenclature" to "inorganic" rings in 1960[13], suggesting names like cyclotriphosphazane and cyclotetrathiazene. Such names are really an extension of the repeating unit nomenclature adopted for the siloxanes, etc.[10].

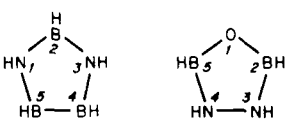
In a review, R. A. Shaw, et al.[14], suggested similar names, such as thiazanes for saturated S-N rings and arsoxanes for saturated As-O rings. Allcock used this "repeating unit" nomenclature in a monograph published in 1967[15], and Haiduc included it in proposals for naming inorganic rings in 1970[16] and 1980[17]. Haiduc's general proposals illustrate an early use of additive methods for inorganic rings. The prefix cyclo was followed by "a" terms for the elements, numerical prefixes and locants being added as needed, for example, cyclooxatetrasilane (Fig. 8-A), cyclo-3,6-dithia-1,2,4,5-tetraphosphane (Fig. 8-B), and cyclo-1,3,5-tribora-2,4-6-triazane (Fig. 8-C) for which cyclotriborazane is an acceptable abbreviated form.



A B C

FIGURE 8

A similar pattern was introduced in the Gmelin Handbuch for boron-nitrogen heterocycles, except that the nitrogen atoms were to be cited before the boron atoms[18], for example, cyclo-1,3-diaza-2,4,5-triboran and cyclo-1-oxa-3,4-diaza-2,5-diboran (Fig. 9).



A B

FIGURE 9

In 1977, Wannagat suggested that a bracketed arabic number be used to indicate the ring size of a monocycle, that the "a" terms be cited and the heteroatoms be numbered according to decreasing atomic number, and that arabic numbers be used to denote the number of each kind of heteroatom, for example, cyclo[6]-(3)aza-(3)borane (Fig. 8-C)[19].

Heal and Bannister applied Haiduc's principles to sulfur-nitrogen rings, for example, cyclo-5,8-diazahexasulfane (Fig. 10)[20].

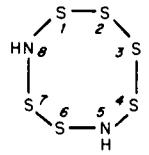
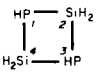
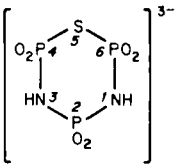


FIGURE 10

Since 1962, CNIC has been concerned with nomenclature for inorganic rings and ring systems. The Commission always included chains in its proposals. At first, hydrocarbon names such as .....pentane were used as the basis of a replacement operation (see Fig. 7). Such names were to indicate only the number of skeletal atoms, including carbon, but it is impossible to avoid the implication of a hydrocarbon that is given by the ending "-ane", because that meaning of this morpheme has been in use since 1892[8]. Later, general terms such as cyclo....hetrane (see Fig. 11) and even



1,3-Diphospha-2,4-disilacyclotetrane
1,3-Diphospha-2,4-disilacyclotetrahetrane
1,3-Diphospha-2,4-disilacyclotetrahetron



2,2,4,4,6,6-Hexaoxo-1,3-dihydrido-1,3-diaza-2,4,6-triphospha-5-thiacyclohexahetrate(3-)

FIGURE 11

[n]cyclane, were suggested. Even though every skeletal atom, including carbon, was indicated by an "a" prefix, an "organic" implication still existed. Further, designation of oxidation states of skeletal atoms and termination of a chain were additional difficulties. Of course, the latter has nothing to do with a nomenclature for rings but, since chains were included in all of the Commission's proposals, it did delay the development of a nomenclature for rings for extended periods. To avoid "organic" implications, terms like ....hetron and ....hetrate (for neutral and anionic compounds, respectively) were suggested, (see Fig. 11), but the use of the organic "a" prefixes retained an implication of fixed valency.

A CNIC PROPOSAL

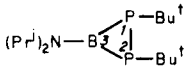
The proposals for naming inorganic rings described above have, in one way or another, relied on one or more organic nomenclature principles. In 1979, CNIC began the development of an additive method for naming inorganic chains and rings based on the well-established and inherently more flexible principles of coordination nomenclature. This work has evolved into a set of recommendations

now at the peer review stage in the IUPAC publication procedure and which we describe briefly here.

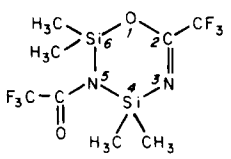
A monocyclic ring is called a "cycle" when neutral; "cyclate" when anionic, and "cyclium" when cationic. The number of skeletal ring atoms is given by a bracketed arabic number, "[n]", preceding the appropriate general term. Thus, a six-membered monocycle is a "[6]cycle", a "[6]cyclate", etc. Each skeletal atom, including all metals and carbon is denoted by a prefix derived from an element name root and is equivalent, in most cases, to substituting "y" for the final "a" of the organic "a" prefix (see Fig. 12). The prefixes are cited from left to right in alphabetical order starting with the prefix that is earliest in alphabetical order, i.e., azy...carby...oxy...sily...[n]cycle. The number of ring atoms of the same element is given by the simple numerical prefixes di-, tri-, tetra-, etc., and all atoms or groups, including hydrogen, attached to the skeletal atoms are described by their ligand names cited as prefixes to the skeletal (unhydrogenated) ring name (see Fig. 13).

Al	aluminy	O	oxy
Cl	chlory	C	carby
S	sulfy	P	phosphy
N	azy	Fe	ferry

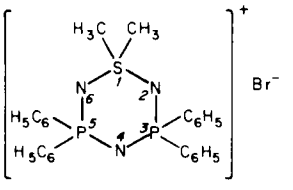
FIGURE 12



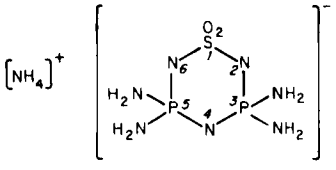
A



B



C



D

A. 1,2-Di-tert-butyl-3-(diisopropylamido)-3-bory-1,2-diphosphy[3]cycle

B. 4,4,6,6-Tetramethyl-5-(trifluoromethyl)-3,5-diazy-2-carby-1-oxy-4,6-disily[6]cycle

C. 1,1-Dimethyl-3,3,5,5-tetraphenyl-2,4,6-triazy-3,5-diphosphy-1-sulfy[6]cyclium bromide

D. Ammonium 3,3,5,5-tetraamido-1,1-dioxo-2,4,6-triazy-3,5-diphosphy-1-sulfy[6]cyclate

FIGURE 13

Numbering of the ring atoms starts with the atom (or one of the atoms) listed first in the element sequence table given in the IUPAC Inorganic Nomenclature Rules (the "Red Book")[21] (see also the seniority list of elements in the IUPAC Organic Nomenclature Rules (the "Blue Book")[11f]. When there is a choice, numbering begins with the atom (or one of the atoms) of preference and proceeds in the direction that gives the lowest number to an atom of equal preference (see Fig. 13-A), or to an atom of next highest preference, i.e., the next atom encountered in the element sequence table, etc.. For example, see Fig. 13-B where the direction is determined by the carbon atom, which is preferred to the silicon atoms, and no decision is attained by considering the nitrogen atoms. Further choices are dependent on the number and then the names of attached ligands.

The current CNIC proposal applies these principles to inorganic chain compounds, but does not include polycyclic inorganic rings. In our opinion, extension of this approach to polycyclic inorganic ring compounds should not present any great difficulties.

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