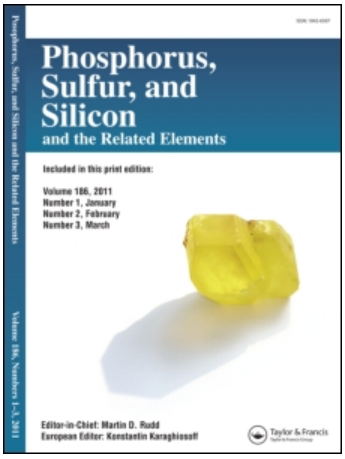

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THE NOMENCLATURE OF SULPHUR-NITROGEN HETEROCYCLES

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THE NOMENCLATURE OF SULPHUR-NITROGEN HETEROCYCLES†

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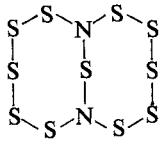
The inadequacy of the present IUPAC Rules and the relative merits of the binary, coordination, thiazene and thiazyl types of nomenclature are discussed. Some recommendations are made for trivial and systematic names. A reformed systematic nomenclature should be of the additive type.

1 INTRODUCTION

Compounds **1** and **2** are listed in the Indexes to "Chemical Abstracts" under the names 1,7-diaza-2,3,4,5,6,8,9,10,11,12,13-undecathiabicyclo[5.5.1]-tridecane[1] and 1,3,5-trifluoro-1H,3H,5H-1,3,5,2,4,6-trithiatriazine 1,3,5-trioxide.[2]



1 $S_{11}N_2$

2 $(NSOF)_3$

These Index names must very seldom have been written down; and in speaking, who would prefer them to (respectively) $S_{11}N_2$ and sulphanuric fluoride? We have all discovered that some systematic names are totally unsuitable for verbal communication. We then turn to a trivial or shortened systematic name—whichever is more easily spoken and understood. Otherwise we resort to formulae or some type of numeric or alphanumeric designation.

The other use of chemical names is, of course, information classification and retrieval; such names must be systematic, unambiguous and in one-to-one correspondence with structural formulae. But here again, names, in the usual sense of the term, are not essential. A number of other ways of codifying molecular structures have been devised and some are in use.[3] For organic compounds it is a practicable, if complicated, task to invent either a systematic nomenclature or a coding system. For inorganic heterocycles it is in principle more difficult because of the variable oxidation states of some of the atoms concerned. [Also a more serious problem arises in that some inorganic rings (especially S–N rings) do not lend themselves to simple bond descriptions]. Consequently several types of nomenclature have been used in the literature or could be proposed. $[S_5N_5]^+$ for example, could be described by four systems, as illustrated below:

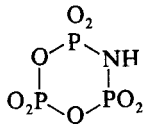
System	Name	Source
"Thiazyl"	(1) Pentathiazyl (cation)	*Chem. Abs.* Index[7] (current) and most journals
	(2) Cyclopentathiazyl	*J. Chem. Soc.*[5]
"Coordination"	(3) *Cyclo*-penta-μ-thioxo-pentanitrogen(1+)	*Chem. Abs.* Index[6]
"Binary"	(4) Pentasulfur penta-nitrogen(1+)	
"Thiazene"	(5) Cyclopentathiazenium	
	(6) 1,3,5,7,9-Pentathia-2,4,6,8,10-penta-azacyclodecahetra-nenium	*J. Chem. Soc.*[7]
	(7) Cyclo-1,3,5,7,9-penta-thia-2,4,6,8,10-pentazenium	Recommendations of this paper (see 6 ii below)

† Based on a lecture for the Second Reunion of the First International Symposium on the Chemistry of Inorganic Heteroatom Ring Systems, Madrid, June 1977.

Let us next look at "approved" international nomenclature for S–N ring systems as it now exists.

2 IUPAC NOMENCLATURE

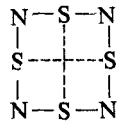
The "Red Book"[8] in its latest (1970) edition, scarcely recognizes the existence of inorganic heterocycles, discussing just a few examples under the heading "Iso and Heteropolyanions".† The most relevant recommendation in this section is for the prefix "cyclo". On page 28, however, there is an unfortunate example (**3**) of the use of "μ" (bridging) to denote one component of a simple ring. The naming recommended in this chapter for cages simply shows composition, not structure. Table III on page 103 recommends the italicization of "cyclo", in conflict with organic practice, on the doubtful grounds that it is a "modifier" in inorganic chemistry but changes the molecular formula in organic.



3

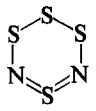
μ-imido-*cyclo*-triphosphate(3–)

Ring compounds containing only sulphur and nitrogen can be named as binary compounds under the IUPAC Inorganic Nomenclature Rules. Since no case of isomerism is known among these compounds, this method has the virtue of giving short, unambiguous, speakable names. Unfortunately, however, the order in which sulphur and nitrogen are to be named under Rule 2.161 is in conflict with the usual current practice and with chemical common sense. Most chemists call compound **4**



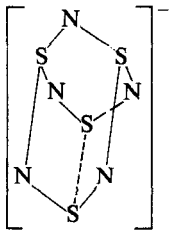
4

S_4N_4



5

S_4N_2



6

$S_4N_5^-$

† The IUPAC has subsequently considered boron heterocycles and cages, and has ruled in favour of organic nomenclatural principles for them.[9]

tetrasulphur tetranitride, not tetranitrogen tetrasulphide as the rule would require, and **5** is tetrasulphur dinitride. The cage structure **6** is similarly named the tetrasulphur pentanitride anion.[10] Even *Chemical Abstracts* used the index term "sulphur nitrides" until 1972, though "nitrogen sulphides" has now been adopted. The sequence of elements in Rule 2.161

Rn Xe Kr B Si C Sb As P N H Te Se S At I Br Cl O F

appears to be a compromise based on the standard sequence of elements given in Table IV of Ref. 8, with hydrogen added and oxygen moved. It corresponds roughly but not exactly to the order of electronegativities; nitrogen is badly out of place with regard to its electronegativity. The widely-accepted practice of putting the more electronegative elements second in a binary name, as in "tetrasulphur tetranitride", can consequently be at variance with Rule 2.161, though it is endorsed by implication in Rule 2.22.

The IUPAC has nothing to say about the naming of cyclic S–N ions, S–N rings with exocyclic groups, or S–N fused rings and cages.

Obviously the Commission on Inorganic Nomenclature of IUPAC has given little thought to S–N heterocycles or to inorganic heterocycles in general. In this connection it is interesting to note that a list of examples on p. 17 of Ref. 8 includes a compound "N_2S_5" the existence of which was disproved in 1951.

3 RING INDEX-CHEMICAL ABSTRACTS NOMENCLATURE

Lacking guidance from the IUPAC's Inorganic Nomenclature Commission, the compilers of the Indexes to "Chemical Abstracts" have resorted to the IUPAC's system of organic nomenclature[11] for the naming of inorganic heterocycles. They are so named in the "Ring Index" and its three supplements, and in the "Index of Ring Systems" to be found after the Formula Index in all recent "Chemical Abstracts". A monocyclic inorganic ring of more than ten members is named as if derived by replacement from a monocyclic hydrocarbon; the "replacing" hetero atoms are named by means of prefixes ("thia", "aza" etc). Monocyclic rings of ten members or less have their size shown by a suffix ("ole", "epine" etc). Polycyclic rings are named by the von Baeyer system or by fusion nomenclature. The resulting names, though unambiguous, tend to

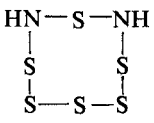
be cumbersome even when the structures are simple, (as in our first example of this paper) because of the need to name and number all ring atoms. Parts of such names are really redundant: if all the atoms in a ring are listed, it should not also be necessary to show the ring size. Here are examples of the Ring Index system: names a–d and formulae **6**, **7**, and **8**:

a) Monocyclic ring with more than ten ring members: Undecathiaazacyclododecane.

b) Monocyclic ring with ten or fewer ring members; 1,3,5,2,4,6-Trithiatriazine.

c) Polycyclic von Baeyer ring system: 2,4,6,8,9-Pentaaza-1,3,5,7-tetraarsabicyclo [3.3.1] nonane.

d) Polycyclic fused-ring system: Hexaphosphorinohexaphosphorin

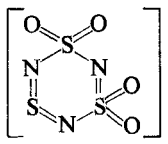


7

1,2,3,4,5,7,6,8-hexathiadiazocine.

8

1,3,2,4-dithiadiazete



9

1,3,5,2,4,6-trithia(5-S^{IV})triazine 1,1,3,3-tetroxide ion (1–).[4]

These names are for compounds with known structures and with organic hydrocarbon analogues (e.g. derivable in principle by replacing CH_2 by S or CH by N). For S–N structures unknown or not obviously related to organic analogues, the Chemical Abstracts Service uses binary nomenclature, or the "thiazyl" nomenclature introduced by Demarçay in 1881[12] and popular with chemists working in this field ever since; for example, $S_3N_2Cl_2$ is "thiodithiazyl dichloride". "Thiazyl" names are adequate for rings containing equal numbers of S and N atoms (e.g. $[S_5N_5]^+$) but become clumsy for less symmetrical structures, such as $S_3N_2Cl_2$ just mentioned, and may in future become ambiguous in the event of isomeric rings being discovered (e.g. of the trithiadithazyl cation, $[S_5N_2]^{2+}$, which may well be preparable).

Ring Index-Chemical Abstracts names for S–N heterocycles may be criticized on the following grounds. They are often long-winded and hard to read. They are hard to devise, because several different principles of nomenclature have to be used in different circumstances.[13] And they sometimes seem to imply a relationship to carbon compounds which is wholly unreal (e.g., S_4N_4 as a derivative of cyclooctane[14]).

4. THE PROBLEM

The amount of structural information needing to be encoded in the name of an inorganic heterocycle depends, of course, on the use to which the name will be put and on how much the user can be expected to know about the particular area of chemistry. At one end of the scale, we have the fully structural, systematic names required for indexing in the "Abstracts", which must suffice, with the help of a few rules, to enable the user to write a structural formula. At the other end, there are trivial names; in the S–N field, these usually express composition but give no more structural information than is required for identification, e.g. tetrasulphur dinitride, hexasulphur 1,3-diimide; most names frequently used in speech and writing by S–N chemists fall into this category. In between are semi-systematic shortened names, lacking some structural information but unambiguous in their context.

In principle, of course, relatively long names are bound to be needed for full systematic descriptions of structure. What we ask of a fully systematic name, however, is that it not be *needlessly* long and that it be easily read. In these respects our examples I and II seem less than ideal. An ideal systematic name, too, would lend itself to shortening without total reorganization.

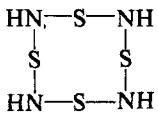
One problem with S–N heterocycles is that S–N bonds often cannot be categorized as "single", "double" or "triple", their true orders being fractional. So a systematic nomenclature which required the location of multiple bonds to be specified would be artificial and almost unworkable. This problem arises occasionally with organic compounds too, but at least the connectivities of atoms in organic molecules are usually known, which is not always the case with S–N compounds (Section 7 below).

5 HOW DO PRACTISING CHEMISTS ACTUALLY NAME S–N HETEROCYCLICS?

In trying to solve a problem from on high it is always instructive to see what chemists do when regularly confronted with it on the ground. We

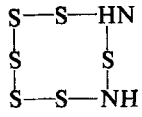
suspect that most chemists who work with, and publish on, S–N heterocyclics regard the Ring Index and IUPAC recommendations as a form of editorial persecution necessary when writing up for posterity but not something to be used very day. What could be more arbitrary than treating compound **1** as a derivative of bicyclo-tridecane?† In the past three complementary systems have grown up among practising chemists, which provide speakable names and so have deservedly survived. Here are their main features:

(i) Simply binary names such as "tetrasulphur dinitride" (formula **5**) and "undecasulphur dinitride" (formula **1**) are used for binary compounds. Becke-Goehring's school and many later workers have used the simple designation "sulphur imides" for "saturated" rings such as **10** and **11**, and by analogy **12** is a sulphuryl (or better, sulphonyl) imide.



10

tetrasulphur tetraimide



11

1,3-hexasulphur diimide

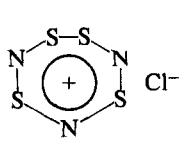
$-(SO_2NH-)_6$

12

hexasulphuryl hexaimide *or* hexasulphimide

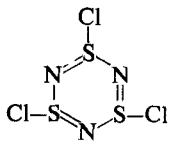
These are essentially binary names again and are still much used.

(ii) The second system, based on "thiazyl" for the SN fragment, has been used for nearly 100 years for rings not covered by the binary-type nomenclature,



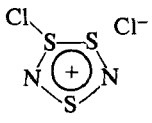
13

thiotrithiazyl chloride



14

trithiazyl trichloride



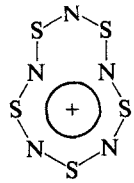
15

chlorothiodithiazyl chloride

† Cf. also Ref. 14.

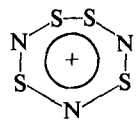
as, in examples **13** and **14**. This is still widely used but it does not easily describe the less symmetrical rings like **15**. It has been used for non-cyclic as well as for cyclic compounds.[15]

In practice its use in inorganic heterocyclic chemistry is restricted to "unsaturated" rings, i.e., rings containing bicoordinate nitrogen. "Thiazyl" is not listed as an approved term by the IUPAC, which, strangely, gives "thionitrosyl".[8] Recently the "thiazyl" nomenclature has been modified by adopting the term "thiazenium"[7] for cations; see formulae **16** and **17**.



16

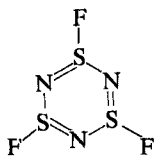
pentathiazyl *or* [cyclo]pentathiazenium



17

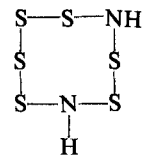
[cyclo]thiotrithiazenium

(iii) Probably the man who has had to think hardest about the nomenclature of inorganic heterocycles in recent times is Ionel Haiduc. The system used in his superb book[16] (the most comprehensive yet published on inorganic heterocycles) deserves study. It has no revolutionary features but simply adopts good points from other systems. He uses the prefix "cyclo" to denote a ring of any size and rejects the awkward ring-size suffixes of the Ring Index, e.g. -ocine for an 8-membered ring. Locant numbers are used mainly where necessary—for rings with irregular sequences of atoms, or regular rings with irregular substituents. The suffix "ane" means saturated and "ene" unsaturated. Here are two examples of Haiduc nomenclature:



18

trifluoro-cyclotrithiazene



19

cyclo-1,4-diaza-2,3,5,6,7,8-hexasulphane

The virtues of the Haiduc scheme include the following:

(a) Names of rings are devised on an *additive*

principle, not a *replacement* principle.† Replacement names, in this field, often have little relationship to chemical facts and threaten us with confusion in the future. Wannagat, too, supports the additive principle.[17]

(b) Names of ligands on ring atoms are likewise additive and not substitutive. We prefer this to the use (as in *Chemical Abstracts*) of prefixes such as "1H, 3H, 5H" in the names of compounds containing no hydrogen (example **2** in this paper).

(c) Haiduc names can readily be shortened by the omission of redundant locant numbers. An example: S_4N_2, **5**, has the full Haiduc name cyclo-5-thia-4,6-diazene-1,2,3-trisulphane, but its shortened name, cyclothiadiazene-trisulphane is fairly convenient and defines the structure completely. We also like Haiduc's shortened names for rings with regularly alternating atoms, such as cyclotetrathiazene for S_4N_4.

6 POSSIBLE REFORMS

Any reform of S–N heterocyclic nomenclature should, of course, form part of a general reform of inorganic ring nomenclature. Reform is certainly needed but it is not urgent, and we hope that IUPAC's Inorganic Nomenclature Commission will consider the whole issue very carefully from the most fundamental standpoint before reaching any decisions. In the meantime, we think the situation could be improved by adopting the following recommendation. The editors of learned journals should accept two levels of nomenclature, trivial and systematic.

(i) *Trivial names*: these should include binary-type names such as tetrasulphur dinitride, hexasulphur di-imide, tetrathionylimide, ammonium trisulphimide, trithiazyl trichloride, sulphanuric fluoride (not sulphanuryl), tetrathiazyl(2+) and tetrasulphur pentanitride(1–). Locant numbers (where required) should precede the atoms concerned e.g. pentasulphur 2,4,6-triimide.

(ii) *Systematic names*: editors should be prepared to accept systematic names complying with the rules in Haiduc's book, and we would like to see trivial names mildly discouraged in favour of shortened systematic Haiduc names. Such a policy would result in briefer, clearer names.

If it were decided internationally to go over to a new system based on the main Haiduc principles, a number of problems would need to be faced. Although we would not expect any great difficulty in solving these, we confine ourselves here to drawing attention to them without trying to offer definite solutions. The problems include:

(i) The order of naming elements in a ring: we find Haiduc's system confusing and would instead recomment Wannagat's proposal[17] to name them in order of decreasing atomic number, or use of the IUPAC standard sequence (Ref. 8 p. 104).

(ii) How to show unsaturation: in most cases the termination "ane" (saturated) and "ene" (unsaturated) would suffice, but rings are now being discovered which contain both saturated and unsaturated segments. Perhaps there is no need to solve this problem at all. If the ring atoms are listed, and their ligands, if any, also listed, both with appropriate locant numbers, the structural formula can be written down. Then anyone who wants to put double bonds into it can easily do so in appropriate places.

(iii) How to name fused rings and spiro structures, few of which were known when Haiduc's book was published.

(iv) Terminations for ions: "enium" and "enate" are established for positive and negative ions respectively, but the former creates some risk of confusion with the "onium" and "inium" terminations used traditionally for ions formed by adding protons or carbonium ions. It would, however, suffice to end the name with, e.g., "ane" or "ene", and add the ion charge in parentheses, e.g. cyclotetrathiazene(2+) for $[S_4N_4]^{2+}$.

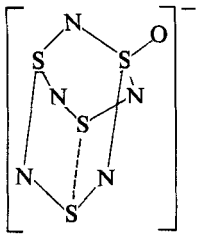
Whatever is done about these points, we again emphasize our conviction that a reformed nomenclature should be of the additive type, as regards both ring components and exocyclic groups, not of the substitutive or replacement type.

7 THE FUTURE

This all seems fairly straightforward. But many of us who work with inorganic heterocycles, and especially with S–N heterocycles, can now see that

† Our attention has been drawn to the risk that an additive name such as cyclo-1,4-diazahexasulphane (S_6N_2 ring) might be taken for a replacement name and so thought to mean an S_4N_2 ring. Haiduc's numbering system (Rule (b) on page 14 of his Volume 1) would tend to prevent this particular ambiguity, for under this rule the compound XIX should be called cyclo-5,8-diazahexasulphane. Unfortunately, the numbering of formula **19** above, which comes from Haiduc's Vol. 2, does not obey his own rule in Vol. 1!

we are sailing towards an iceberg, only the tip of which is visible, but on which we may well get wrecked before long. The problem is that *we do not always know where the bonds are.* Are there, for example, S–S bonds in S_4N_4, $[S_4N_5]^-$ and $[S_4N_5O]^-$? The consensus of opinion says "yes" but that they are of order less than 1. Should we, then, use ring or cage nomenclature for S_4N_4 etc? Are the sulphur atoms in S_4N_4 simply bicoordinate ring members or are they bridgeheads? Quite often, too, the formal bond orders in sulphur-nitrogen rings and cages do not fall clearly into "single" or "double" categories so that sulphur formal covalencies are in doubt. Compound **20** is a good example[18] of both problems.



20

tetrasulphur pentanitrogen oxide (1–)

It is hard to imagine the upheavals in inorganic nomenclature that may eventually result from the full realization of this problem in S–N and other areas of covalent inorganic chemistry. But there are a few things we can do to prepare ourselves. Let us adopt a few simple rules, retain some flexibility and be prepared to consider cage structures afresh when structural patterns become clearer.

ACKNOWLEDGEMENT

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