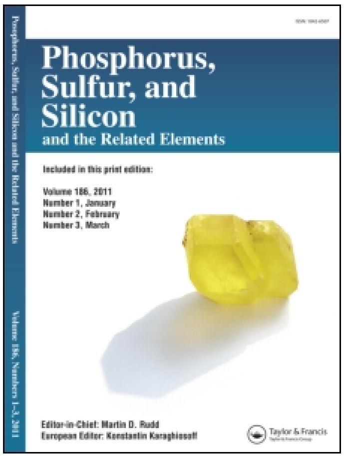

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A GRAPH-BASED CLASSIFICATION AND ENUMERATION OF INORGANIC HOMO- AND HETEROCYCLES

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Abstract A systematization based upon the graph theory is presented and the skeletal isomerism of inorganic heterocycles is discussed.

INTRODUCTION

The work presented here suggests a rational classification of inorganic ring systems, needed for the systematization of the increasing amount of literature in the field, with possible use in computer handling of this information.

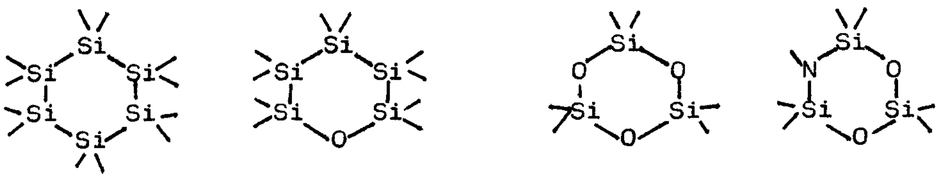
An earlier proposed classification of inorganic ring systems recognized the following types :[1,2]

(a) homocycles

(b) heterocycles formed by insertion of a heteroatom into a parent homocyclic system

(c) heterocycles formed by regular alternation of two different elements, or "repeating unit heterocycles" (called "pseudoheterocycles")

(d) mixed type heterocycles , in which the regular alternation was disturbed :



(a) (b) (c) (d)

This classification can be translated into the language of graph theory, with the following advantages :

(a) all known rings can be systematized within the frame of certain possible types

(b) new inorganic heterocycles can be predicted

(c) composition- and structure-based criteria for systematization can be established

(d) the application of the general concepts of nodal nomenclature[3-5] to the nomenclature of inorganic heterocycles is facilitated.

DEFINITIONS

A cyclic structure can be described in terms of its graph.[6] A cyclic graph is a closed arrangement of connected points, called nodes. All six-membered rings derive from the same graph, the hexagon. By replacing the nodes with atom symbols, the abstract graph becomes a chemical graph , which in fact represents the ring skeleton.

In inorganic heterocycles the most frequent structures are formed by alternation of electropositive elements (e.g. boron, silicon, germanium, tin, phosphorus, arsenic, antimony or a metal) with an electronegative element (oxygen, nitrogen).[7,8] The borderline between the two types is carbon (with an electronegativity $x_C = 2.5$). Donor-acceptor and charge alternation [9] are also stabilizing factors and are usually associated with the electronegativity.

The electropositive elements ($x < 2.5$) will be called here basis elements of a ring structure ; the electronegative elements are regarded as heteroatoms.[10] Thus, all silicon-containing rings have a common basis element, silicon ; particular heterocycles are then defined by the nature of the heteroatoms.

(a) In terms of graph theory an inorganic heterocycle can be described by a graph containing two types of nodes: basis nodes and hetero nodes. The basis nodes define the ring : the ring sites occupied by the less electronegative elements ($x < 2.5$) i.e. boron, silicon, germanium, phosphorus, arsenic, antimony, etc., are defined as basis nodes ; the sites occupied by electronegative elements ($x > 2.5$) are described as hetero nodes.

(b) A cyclic graph may consist of only basis nodes (homocycle) or it may contain both basis nodes and hetero nodes to form heterocycles .

(c) Both basis nodes and hetero nodes can be separated (alternating) or can be connected in fragments of catenated identical nodes (atoms).

In agreement with the definitions discussed above, the inorganic rings can be systematized according to: a) ring size, and b) the nature and number of basis nodes.

ENUMERATION OF THE CYCLIC GRAPHS

All possible cyclic graphs, from three- to eight-membered, consisting of basis nodes and hetero nodes, are illustrated in Figs. 1-3 . A basis node is represented by a full (black) circle and a hetero node by an open circle. Cyclic graphs consisting of only hetero nodes are included, but are not numbered separately, as they cannot be in fact distinguished from graphs made up of only basis nodes.

The cyclic graphs illustrated reveal the possible existence of many isomeric graphs, i.e. skeletal isomers in heterocycles. The number of isomeric graphs increases with the ring size and varies symmetrically with the number of heteroatoms, as shown in Table 1.

Table 1 The number of skeletal isomeric graphs

Ring size	Number of hetero nodes 0[a]	1	2	3	4	5	6	7	8[a]	Total number of rings (graphs)
8	1	1	4	5	8	5	4	1	(1)	29
7	1	1	3	4	4	3	1	(1)		17
6	1	1	3	3	3	1	(1)			12
5	1	1	2	2	1	(1)				7
4	1	1	2	1	(1)					5
3	1	1	1	(1)						3
									Total	73

[a] Homocycles

Many inorganic rings corresponding to the graphs No.1 to 73 are known [1,2], but cannot be shown here because of space restrictions.

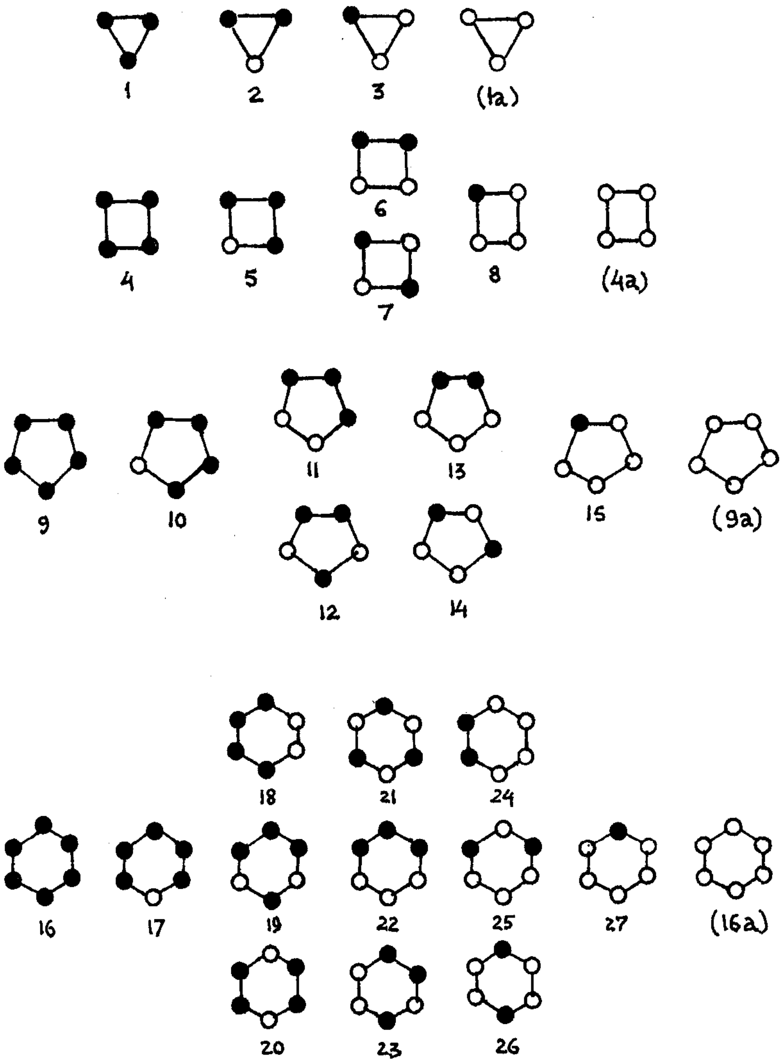


Fig.1. Three-membered , four-membered, five-membered and six-membered cyclic graphs.

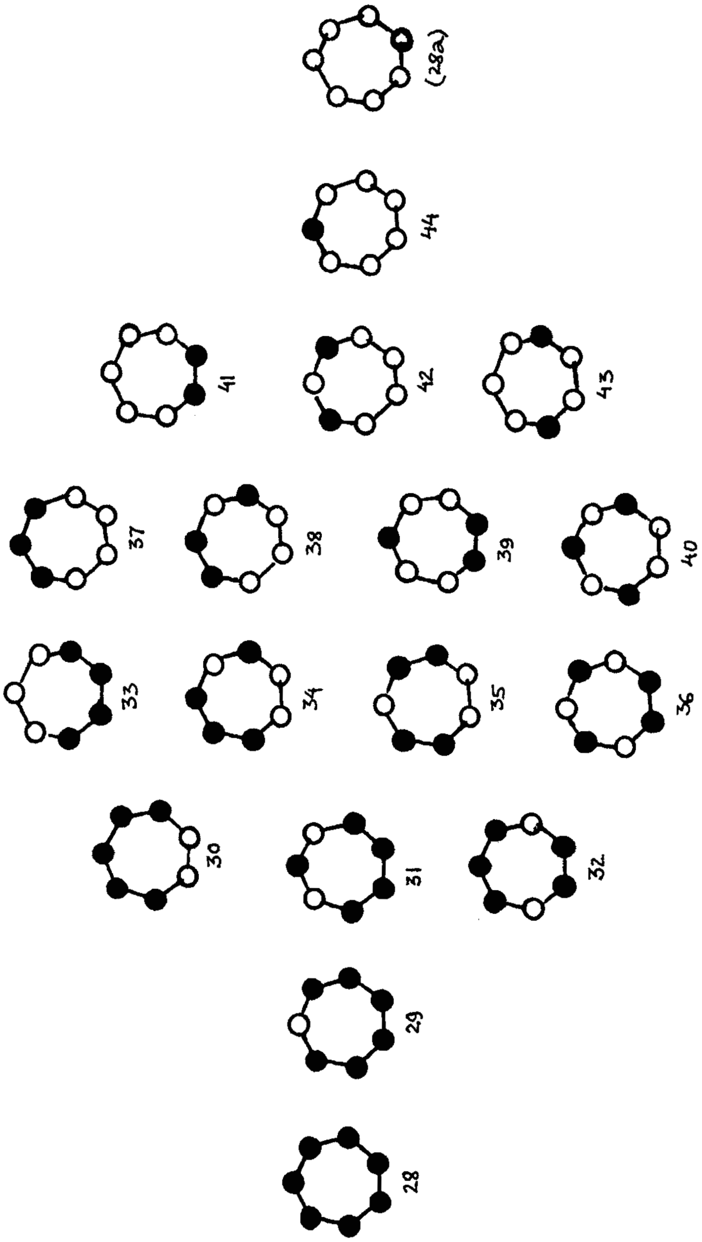


Fig.2. Seven-membered cyclic graphs.

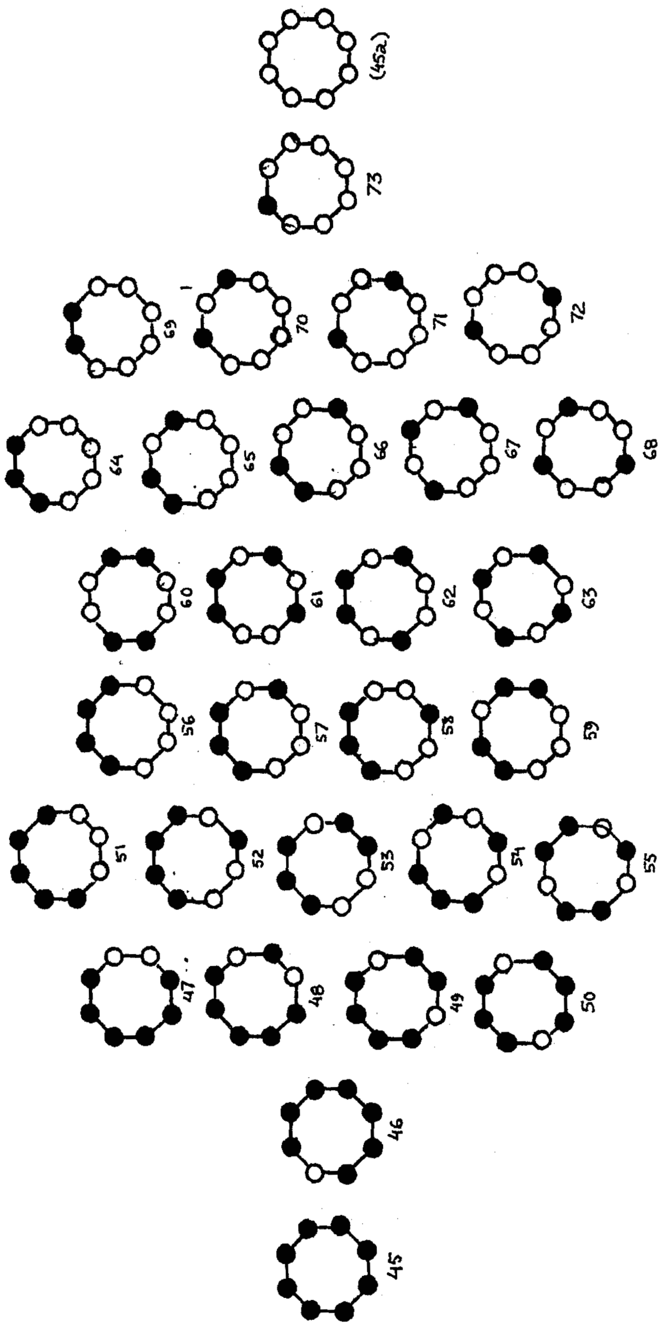
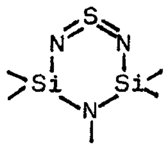
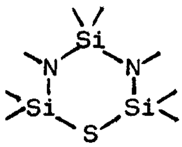


Fig.3. Eight-membered cyclic graphs

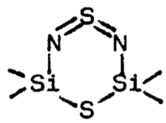
It should be noted that sulfur, having an electronegativity $x_S = 2.5$ like carbon (and to some extent selenium, with $x_{Se} = 2.4$) may play a double role in inorganic heterocycles: it can occupy basis nodal positions (usually as S^{IV} or S^{VI}) in rings with more electronegative partners, or can occupy hetero nodes (as S^{II}) in rings with a more electropositive partner which occupies the basis nodes. In some rings sulfur can occupy both basis and hetero nodes.



sulfur(IV) in basis node



sulfur(II) in hetero node

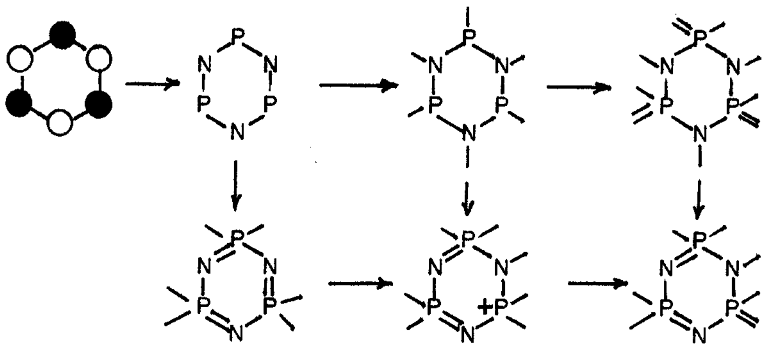


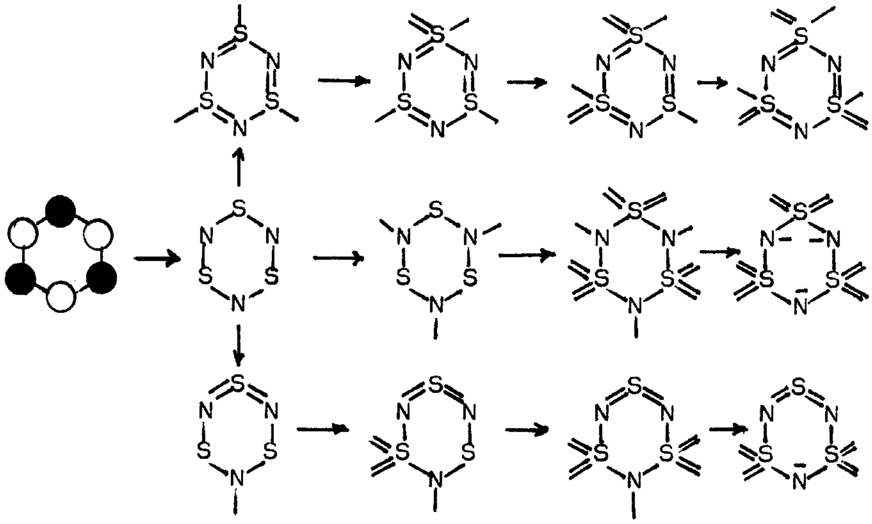
sulfur in both basis node (S^{IV}) and hetero node (S^{II})

Larger rings can be discussed in a similar manner, but the number of possible graphs, including many skeletal isomers, increases dramatically with the ring size, while the number of actually known inorganic heterocycles (macrocycles) sharply decreases. The few known examples are either homocycles (cyclopolysilanes, cyclopolysulfanes) or alternating types (cyclosiloxanes, cyclophosphazenes).[1,2]

DERIVING ACTUAL RINGS FROM A CYCLIC GRAPH

From the abstract cyclic graphs shown in Fig.1-3, actual inorganic ring systems can be deduced in several steps. The first step is to writte the chemical graph, by introducing the element symbols. The chemical graph, as defined above, shows only the composition of the ring (ring skeleton) with no information about the valence (connectivity) of the elements, number of bonds, oxidation states, etc. To obtain the actual ring the next step is therefore to add further exocyclic single and double bonds and endocyclic double bonds and/or charges (when appropriate) in agreement with the oxidation (valence)state of the elements involved. Two examples are illustrated, for the P_3N_3 and S_3N_3 rings.



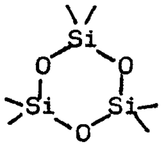


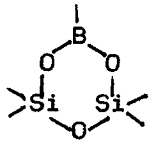
All these rings derive from the same abstract graph No. 21 ; only selected examples were given, and many more P_3N_3 and S_3N_3 ring systems are possible.

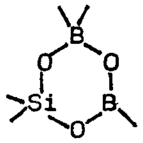
ISOTYPICAL REPLACEMENT. TRANSITION SERIES OF MIXED RINGS

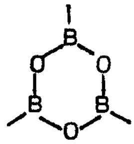
The 73 cyclic graphs shown in Figs. 1-3 represent all possible inorganic ring types made up of only two elements. Further compositional and structural variations are obtained by partially replacing either the electropositive element (in basis nodal sites) or the electronegative hetero atom (in hetero nodal sites), or both, with elements of the same type (similar electronegativity and donor-acceptor properties.

The isotypical replacement can be illustrated for the Si_3O_3 ring (graph No.21). Silicon can be partially replaced by boron, leading to mixed heterocycles with two different basis noded and identical hetero nodes, forming a transition series between Si_3O_3 and B_3O_3 rings :







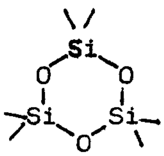


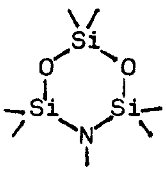
Si_3O_3 — ring with a single basis node (atom)

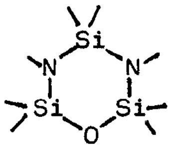
Si_3BO_3, SiB_2O_3 — rings with two basis nodes (atoms)

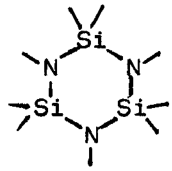
B_3O_3 — ring with single basis node

Similarly, hetero atoms can be replaced. Thus, in Si_3O_3 oxygen can be partially replaced by another electronegative hetero atom, to form a series of mixed heterocycles with identical basis nodes but different hetero nodes:









ring with a single hetero node

rings with two hetero nodes (atoms)

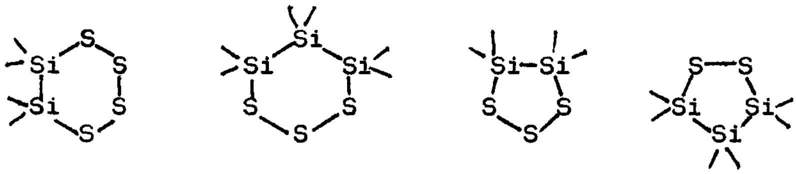
ring with a single hetero node

Partial replacement of both basis nodes and hetero nodes leads to heterocycles containing four different elements in the same ring, with pairs of skeletal isomers. Thus, the six-membered rings corresponding to graph No.21, can be obtained with combinations of boron-silicon-oxygen-nitrogen. This treatment reduces the ternary and quaternary ring compositions to binary patterns, by allowing for only two types of nodes, which is convenient from a pragmatical point of view, since includes an extremely large number of inorganic heterocycles into a limited number of types and underscores the relationships between various rings.

FURTHER COMMENTS

The discussion presented above illustrates two sources of skeletal isomerism in inorganic heterocycles : the existenc of isomeric graphs and the heteronodal replacement, which leads to isomers generated from the same graph.

The graph-based classification predicts new heterocycles. Thus, for example rings containing fragments of catenated identical atoms are rare :



and many more could be envisaged.

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