Preparation and Reactions of Sulfur-Nitrogen Ring Systems*

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Two routes for the preparation of (CH₃)₂SnS₂N₂ are given, which are kinetically controlled reactions. The molecule (CH₃)₂SnS₂N₂ was characterized by X-ray analysis. It is an interesting starting material for the preparation of S₂N₂CO and S₂N₂O. The latter reacts with iminosulfur oxides and isocyanates under the formation of S₂N₂SO₂F and S₂N₂SO₂CF₃. The structure of S₂N₂SO₂F was established by X-ray analysis. The bonding properties are discussed.

The cleavage of thin-nitrogen derivatives with S₂N₂Cl₂ yields also five membered sulfur-nitrogen rings. The structure and properties of P₃N₃F₃S₄N₂ and C₅N₅F₃S₄N₂ are reported. Six, eight and ten membered rings are formed by the reactions of

\[(CH₃)₂Sn-N=S-N-Sn(CH₃)\]

with FSO₂-N=S=O, these are S₂N₂O₂ and S₅N₅”S₅N₅O₄”, respectively. The cation S₅N₅” is a planar molecule, while the oxygen containing species are puckered. In S₅N₅O₄ the oxygens are attached to one sulfur atom, which has a tetrahedral configuration.

The structure of the silicon containing cyclic and bicyclic rings (CH₃)₂Si(SN₅)₂Si(CH₃)₂ and CH₃Si(NSN)₃SiCH₃ were determined.

Although tetrasulfur tetranitride was prepared 140 years ago, little is known about other kinetically controlled reactions in this field. The preferred method for preparing S₄N₄ is the reaction of sulfur chlorides having a composition “SCl₃” with ammonia. SCl₃ is not known and therefore SCl₂ is treated in carbon tetrachloride solution with chlorine.

\[4 \text{SCl}_2 + 16 \text{NH}_3 \rightarrow S_4 \text{N}_4 + 12 \text{NH}_4\text{Cl}\]

Recently we used tin substituted amines instead of ammonia because the N-H (391 kJ mol⁻¹) bond energy is significantly greater than the tin-nitrogen bond energy \((\text{e.g. in } (\text{CH₃})₂\text{SnN}(\text{CH₃})₂ 167 \text{kJ mol⁻¹}).\)

Thus, other cyclic derivatives should be easy available from the reaction of tin-nitrogen compounds with inorganic halides. It should be added that in addition the formation of a tin-halogen bond is favoured.


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The molecule is also a dimer in solution but monomeric in the gas phase. Another interesting feature of the structure is, that the molecule has nearly a planar form in the solid state. All the S–N bonds are of different length, the N–S–N and S–N–S bond angles being 116.8° and 118.1°, respectively. The bond lengths are intermediate between that expected for a single (1.74 Å) and a double bond (1.54 Å). Comparing the Sn–S–N angle of 103.2° with the N–S–N angle of 116.8° a significantly difference is observed, which is caused by different electron density. This illustrates that it is to some extent justified to assign a formal oxidation number of +2 for the sulfur bonded to tin and a formal oxidation number of −4 for the sulfur atom located between the two nitrogen atoms. Recent work has shown that COF₂ or SOF₂ react at room temperature with the tin compound under insertion and elimination of dimethyltindifluoride.

The five-membered sulfur-nitrogen oxide shown above is a red oil at room temperature. The chemistry of this compound is essentially that associated with the SO group, which undergoes a number of the normal reactions of organic sulfur oxides.

Iminosulfur oxides and isocyanates react under evolution of SO₂ and CO₂ respectively. The structure of the fluorosulfonyl derivative has been determined by X-ray analysis.

The interesting feature of this structure is, that the exocyclic N–S bond adjacent to the five membered ring with a bond length of 1.603 Å is greater than the O₂S–N bond with distance of 1.586 Å.

These structural data confirm that the compound is partly ionic and might be assumed having an intermediate between the covalent and ionic form shown below.
By using the well-known compound \( \text{S}_3\text{N}_2\text{Cl}_2 \) as a starting material and nitrogen-tin derivatives we were able to isolate bicyclic compounds \( 9 \)–\( 10 \).

![Diagram of bicyclic compounds](image)

The question however, whether isomer 1 or 2 is formed has been established by X-ray analysis\(^{11}\). It is found that the formation of the five-membered ring is favoured. By comparing the data of the \( \text{S}_3\text{N}_2\text{Cl}^+ \) cation\(^{12}\) with the \( \text{N}–\text{S}_3\text{N}_2 \) part of \( \text{P}_3\text{N}_3\text{F}_5\text{NS}_3\text{N}_2 \) we observe that, the \( \text{S}–\text{S} \) distance is considerably longer 2.200 \( \text{Å} \) than in the cation 2.136 \( \text{Å} \). The electron density is apparently much higher. A further point of interest is, that the 6\( \pi \)-electron \( \text{S}_2\text{N}_2 \) part is not substantially influenced. It was confirmed by calculations on \( \text{S}_3\text{N}_2\text{Cl}^+ \) that the ring may formally be regarded as a pseudo-aromatic 6\( \pi \)-electron system\(^{13}\). Many compounds with \( \text{S}–\text{N} \) bonds may, of course, be synthesized from silicon-nitrogen derivatives. Typical of these is \( (\text{CH}_3)_3\text{Si}–\text{N}=\text{S}=\text{N}=\text{Si}(\text{CH}_3)_3 \). On reaction with \( \text{CH}_3\text{SiCl}_3 \) and the corresponding tin derivative the bicyclic silicon-sulfur-nitrogen compound is formed\(^{14}\).

![Diagram of cyclic compounds](image)

The molecule has exact \( \text{D}_3 \)-symmetry\(^{5}\). A related compound is obtained by using \( (\text{CH}_3)_3\text{SiCl}_2 \).\(^{15}\) The eight-membered ring was confirmed by X-ray analysis\(^{16}\). Both compounds are sensitive to moisture but can be sublimed without reduced pressure.

The products shown in the figures below resulted from the reaction of \( (\text{CH}_3)_3\text{Si}–\text{N}=\text{S}=\text{N}=\text{Si}(\text{CH}_3)_3 \) with \( \text{FSO}_2–\text{N}=\text{S}=0 \) in methylenechloride\(^{17}\).
The ionic species can be formally regarded as being formed according to the following equation:

\[ 2 \text{S}_4\text{N}_4\text{O}_2^- \rightarrow \text{S}_4\text{N}_4^+ + \text{S}_4\text{N}_4\text{O}_2^- \]

The ionic compound crystallizes with a monoclinic cell, space group P2_1/c and four units of S5N5+ per cell. The shape of the S5N5+ cation observed, differs greatly from the heart-shaped ion reported for S5N5+AlCl4-.

The ring is almost planar and the bond distance across the ring are the same within experimental error. The S-N bond lengths are in the range 1.543–1.580 Å and are normal for a delocalized S-N system, compared with the values of 1.548–1.566 Å in the S5N5+ ion.

The S5N5O4+ anion contains an S5N5 ring with two terminal oxygens on two of the sulfur atoms. Within experimental error, the ion shows m symmetry. The nitrogen atom situated between the two SO2 groups is displaced by 0.64 Å out of the mean plane at the rest of the ring as a consequence of the nearly tetrahedral angles at these two sulfur atoms. The bond distances to this nitrogen atom indicate some multiple bonding and suggest that the negative charge is delocalized over the SO2-N-SO2 system. The bond distances in the diimide N-S-N unit are very short, indicating substantial multiple bonding in this part of the ring whereas the bonds joining this unit to the SO2-N-SO2 portion of the ring lie within the range of S-N single bonds.

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