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Account

The general course of reactions and structural correlations in S–N chemistry discussed in terms of a carbon and sulfur(IV) equivalence

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Abstract

The comparability of the thiazyl ($^{\bullet}S{\equiv}N$) and cyano ($^{\bullet}C{\equiv}N$) groups is discussed in terms of the element displacement principle, supported by the chemical behaviour of comparable compounds. Based on the hypothetical tautomeric equilibrium $H_2N{-}S{\equiv}N \leftrightarrow HN{=}S{=}NH$ postulated in analogy to $H_2N{-}C{\equiv}N \leftrightarrow HN{=}C{=}NH$ with due consideration paid to the isolated intermediates $ClS{\equiv}N$ and $[S_4N_3]Cl$, possible reaction steps during the synthesis of S_4N_4 are outlined and evaluated critically. In addition halogenation, ring contraction and ring expansion reactions of S_4N_4 are included as well in the discussion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: S_4N_4-synthesis; Halogenations; Conversions; S_2Cl_2-reaction; Reaction schemes; Detected and assumed intermediates

1. Introduction

Attempts to interpret synthetic reactions, molecular structures and chemical properties of S–N compounds in analogy to other combinations of elements such as N–O did not result in a satisfactory match, even though a large number of experimentally sound data were available for such an endeavour.

Review articles [1–4] dealt primarily with the large structural complexity of S–N compounds and their chemical behaviour, but did not attempt a systematic correlation to related chemical systems. The review article by Chivers [5], where synthetic routes to S–N rings are classified according to reaction type, and then molecular and electronic structures are interpreted based on spectroscopic studies, and where the chemical behaviour of rings is discussed, or the proposal by Bannister [6], to view S–N cycles as electron rich Hückel aromatic rings injected new ideas however and summarized the application of molecular orbital (MO) bonding concepts to SN rings [7]. The MO calculations are however restricted to compounds, where structural parameter and spectroscopic data, in particular those from electronic and photo electron spectroscopy form the basis for quantitative calculations. Generally valid predictions and explanations for the highly differentiated, complex reaction chemistry is normally not available. Intuitatively simple comparisons such as of $S{\equiv}N$ versus $N{\equiv}O^+$ [8(a)] fail in particular where the chemical behaviour of their derivatives is concerned. In a comprehensive and detailed article R.T. Oakley [8(b)] discussed the structural, physical, and chemical properties of sulfur-nitrogen compounds with the intention 'to explore and develop relationships that exists between molecular structure, electronic structure, and chemical reactivity in compounds containing formally unsaturated =S=N– link ages'. He comes to the conclusion that 'Even now many fundamental issus remain unresolved. The observation that iodine oxidizes $S_3N_3^-$ to S_4N_4, for example, still represents a veritable Pandora's box for those who would venture a mechanistic interpretation'.

In the light of the 1982 published 'Periodic System of Functional Groups' [9] an attempt will be made here, to confer an uniform basis upon sulfur-nitrogen chemistry and to indicate the existing relationships. In accord with its chemical behaviour the sp^3d hybridised sulfur will be related to carbon (sp^2-, sp-hybridised) and it will

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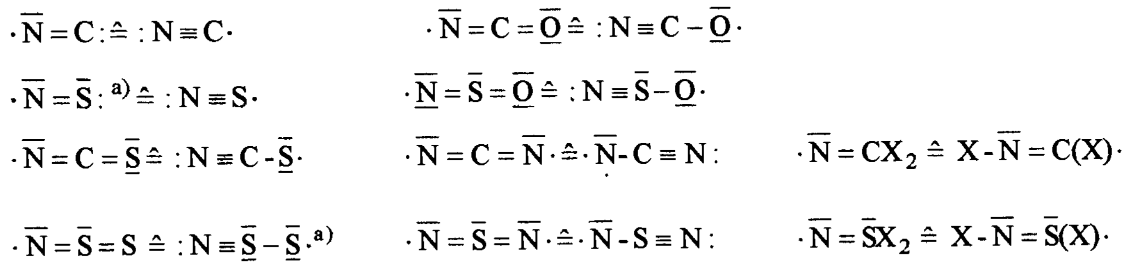
be labelled as an electron rich paracarbon. Consequently the chemistry of the S≡N group is to be compared with that of the C≡N group. The following isomeric parahalogen and parachalcogen pairs illustrate this relationship [10]:



$$\cdot\overline{N}=C: \triangleq :N\equiv C\cdot \qquad \cdot\overline{N}=C=\underline{\overline{O}} \triangleq :N\equiv C-\underline{\overline{O}}\cdot$$

$$\cdot\overline{N}=\overline{S}:^{a)} \triangleq :N\equiv S\cdot \qquad \cdot\underline{\overline{N}}=\overline{S}=\underline{\overline{O}} \triangleq :N\equiv \overline{S}-\underline{\overline{O}}\cdot$$

$$\cdot\overline{N}=C=\underline{\overline{S}} \triangleq :N\equiv C-\underline{\overline{S}}\cdot \qquad \cdot\overline{N}=C=\overline{N}\cdot \triangleq \cdot\overline{N}-C\equiv N: \qquad \cdot\overline{N}=CX_2 \triangleq X-\overline{N}=C(X)\cdot$$

$$\cdot\overline{N}=\overline{S}=S \triangleq :N\equiv\underline{\overline{S}}-\underline{\overline{S}}\cdot^{a)} \qquad \cdot\overline{N}=\overline{S}=\overline{N}\cdot \triangleq \cdot\overline{N}-S\equiv N: \qquad \cdot\overline{N}=\overline{S}X_2 \triangleq X-\overline{N}=\overline{S}(X)\cdot$$

[a)] Compounds with these groups have not yet been synthesized.

In contrast to the carbon containing moieties the groups containing paracarbon are bent or non planar as a result of the additional free electron pair at the S atom.

1.1. The binary neutral sulfur nitrides S_4N_4, S_2N_2, $(SN)_x$ and S_4N_2

If binary paraelements are derived from the pair of elements S and N using nitrogen as a base element and sulfur as a ligand or vice versa, the following parahalogens are obtained: S=N–, N≡S– and also paranitrogen, N≡S≡. Thereby the thionitrosyl, S=N–, has to be compared with the nitrosyl, O=N–, as well as with the isonitrile group, :C=N–.

Whereas a great many stable nitrosyl compounds exist, thionitrile compounds are known merely as intermediates [11], or as unstable substances that can persevere only in solution or at low temperatures [12]. Thus the thionitriles can be compared with the very reactive and partly unstable isonitriles, rather than with covalent nitrosyl compounds. It is remarkable, that thionitrosylhalides and also parahalides such as S=N–X (X = halogene, CN, SCN, CF_3, CF_3S...) have not yet been prepared. There is no parahalogen N≡O– analogous to the covalent N≡S–. Nevertheless, similarities do exist between the $[N\equiv S]^+$ and $[N\equiv O]^+$ cations [3].

All attempts to correlate the structures of the binary SN compounds with the basic parahalogen building block S=N–, which is analogous with O=N–, were unseccessful. However, the parahalogen N≡S–, that may be compared with the parahalogen N≡C–, can serve as a building block for this type of compounds. The sp^3d^1 hybridized S atom becomes a paracarbon and differs formal from carbon only by an additional pair of valence electrons and the type of its hybridization. If N appears as a ligand for these two elements (S and C), the comparable parahalogens N≡C– and N≡S– are obtained.

Cyano (-C≡N) as well as the thiazyl derivatives show similarities in view of trimerisation reactions observed for the corresponding halogen compounds. Some differences in chemical bahaviour and reactivity e.g. between ClCN and ClSN stem, to a large extent, from differences in hybridization for sulfur and carbon respectively. The sp hybridized carbon in linear ClCN requires addition of e.g. $HCl-BF_3$ [13] (as catalyst) or absorption on either graphitic surfaces of charcoal [14] or on zeolithes (molecular sieves) [15] to induce trimerisation resulting in sp^2 hybridization on carbon. ClSN trimerisation on the other hand proceeds spontaneously with a concommittant change from sp^2 to sp^3 on sulfur, implying considerably less structural reorganisation for sulfur than for carbon.

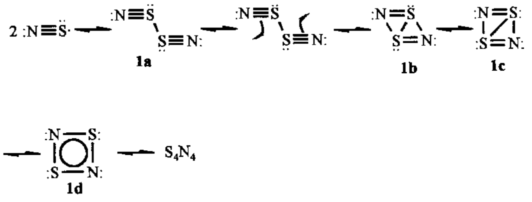
A chemical similarity is also noted in the ability to polymerize for both CN and SN. Polythiazyl (SN). represents the first example of a polymeric metal with typical metallic properties exhibiting even superconductivity at 0.2 K [16]. The more common β-form of $(SN)_x$ consists of infinite molecular chains with alternating S and N atoms and a slight deviation from planarity for both S and N. Dicyanogen on the other hand exhibits even more variations in this polymeric forms. The closest structural analogue to polythiazyl appears to be polycyanogen, prepared from $(CN)_2$ in tetrahydrofuran in the presence of butyl lithium. The dark, solid material consists according to spectroscopic measurements of non-linear chains with an alternating Arrangement of CN substituted carbon atoms. It exhibits semiconductor properties [17a].

Additional evidence for an equivalency of the –C≡N and –S≡N groups is provided by the reactions of $(S_2N)^+(AsF_6)^-$ with CH_3CN giving $(CH_3CSNSN)^+$ $(AsF_6)^-$ or RC≡CH yielding $(RCSNSCH)^+(AsF_6)^-$ (R = H, CH_3), respectively. In the latter case N is replaced by pseudo nitrogen (HC≡) [17b]. If these reactions are transformed to S≡N– chemistry, then X–S≡N should react with $(S_2N)^+(AsF_6)^-$ to give $(XSSNSN)^+$ $(AsF_6)^-$. This was clearly demonstrated in 1987 by the preparation of $(FSSNSN)^+(AsF_6)^-$ from F–S≡N and $(S_2N)^+(AsF_6)^-$ [18].

It is well known, that N≡C dimerizes to the stable (N≡C)$_2$ and the same can be expected to happen with N≡S. However, unlike the linear cyanogen, (N≡S)$_2$ is, of course, bent. Taking the angle of 117°, as determined for N≡S–F [19], as a basis, then N≡S–S≡N may have the structure **1a**. (see Scheme 1)

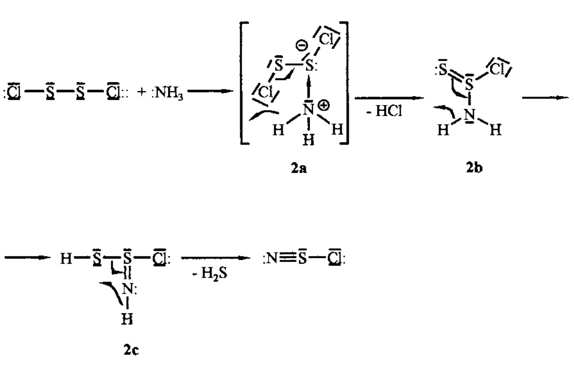
The pronounced differences in electronegativity and size of N and S, as well as their relative proximity lead to a mutual interaction between the nucleophilic N and electrophilic S of opposite N≡S– fragments. An intermediate state **1b** develops and this rearanges by the formation of proper bonds between N and S leading to the rectangular ring **1c** which finally provides the stable 6π-Hückel aromat **1d**. This cyclisation can be compared with the photochemically induced cyclisation of butadiene to bicyclo-[1,1,0]-butane [20] according to Fig. 1

Of crucial importance for the chemical behaviour of **1e** is a transanular S–S interaction. This ring is isovalent and isostructural (square planar) with the S_4^{++} ring (S^+ corresponds to a paranitrogen). S_4N_4 is formed from two S_2N_2 molecules, by stacking them in such a way, that the two N atoms find themselves above the two S atoms and vice versa. By opening –S–N bonds, one at a time, two S_2N_2 rings dimerise into S_4N_4 [21] through a disrotatory synchronous reaction, the transanular S–S interaction remaining intact (for orbital interaction see [5,21]). The Electron Impact Mass Spectra of $S_4N_4$and S_2N_2 show that $S_2N_2^+$ and SN^+ peaks appear with high intensity [22] implying that both **1c** and SN are important intermediates in the chemistry of S_4N_4.



Scheme 1.

Fig. 1.



Scheme 2.

1.2. Sulfur nitride, S_4N_4: possible reactions during its synthesis

S_4N_4 plays a central role in S–N chemistry. Although it has been known since 1835 and is easily synthetically accessible, very little is known about the reaction mechanism that lead to its formation. It is formed, when ammonia, NH_3, is introduced into solutions of sulfur chlorides, such as SCl_2, S_2Cl_2, or SCl_4 in inert organic solvents (benzene, CCl_4). The highest yields are obtained using an equimolar mixture of SCl_2 and SCl_4. Irrespective of the sulfur chloride used as a starting material, two compounds, Cl–S≡N and $[S_4N_3]^+Cl^-$, are always formed as intermediates, i.e. these two compounds are certainly present in the reaction mixture [23]. Subsequently an attempt will be made to suggest possible reaction pathways, based on the two isolated and unambiguously characterised intermediates.

1.3. The formation of ClS≡N from SCl_2, S_2Cl_2 or SCl_4 and NH_3

Since ClSN is formed in a very early stage of the synthesis of S_4N_4, it can be viewed as a primary reaction product. Its formation from SCl_4 and NH_3 is easily understandable since both inter- and intra-molecular condensations may lead to ClSN according to

$$SCl_4 + 2NH_3 \xrightarrow[-\,NH_4Cl]{} H_2N{-}SCl_3 \xrightarrow[-\,2NH_4Cl]{+\,NH_3} ClS{\equiv}N$$

However, difficulties are encountered when attempting to understand its formation from SCl_2 or S_2Cl_2, since in this case S^{II} or S^{I} have to be oxidized to S^{IV} without seemingly any oxidizing agent available for the formation of sulfenic acids.

The formation of ClSN from SCl_2 or S_2Cl_2 and NH_3 becomes reasonable if the following equilibria are considered:

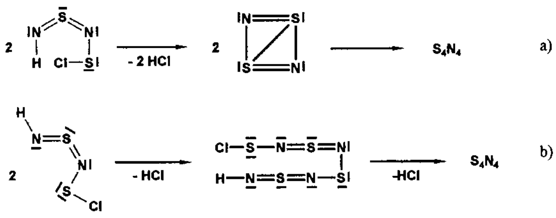
$$2\,SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

$$SCl_2 + Cl_2 \rightleftharpoons SCl_4$$

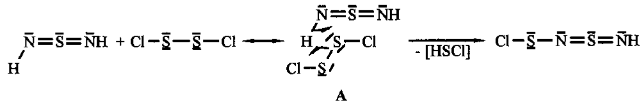
The formation of ClSN from ClSSCl and NH_3 is postulated in the following outline: Scheme 2

In this scheme a nucleophilic attack of NH_3 on sulfur takes place with the formation of a coordinative S–N bond. The intermediate stage **2a** is transformed into **2b** with the formation of HCl and by proton migration gives **2c**. A further proton migration leads to the generation of H_2S and the formation of N≡SCl

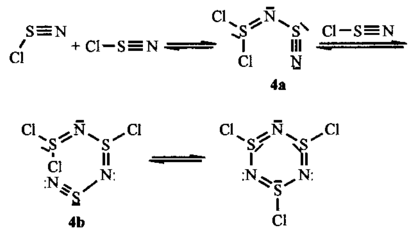
Side reactions between H_2S or NH_4HS and sulfur chlorides may then be responsible for the formation of elementary sulfur.



Scheme 3.



Scheme 4.



Scheme 5.

1.4. The direct reaction of ClSN and NH_3 to S_4N_4

The NSCl, formed in the above schemes may then react with NH_3 to $H_2N–S≡N$ which is very likely to rearange into HN=S=NH [10].

$$ClSN + NH_3 \xrightarrow[-HCl]{} H_2NS{\equiv}N \rightleftharpoons HN{=}S{=}NH$$

Had S_2Cl_2 or $SCl_2 + SCl_4$ been used at the outset, then the following condensation can occur:

$$ClSCl + HN{=}S{=}NH \xrightarrow[-HCl]{} ClSN{=}S{\equiv}NH$$

Therefore the formation of S_4N_4 can be accomplished in two ways: Scheme 3

The first route leads to a cycliszation of the bent *cis*-ClSN=S=NH to S_2N_2 (see Scheme 3a). Then two S_2N_2 rings rearrange as mentioned in Scheme 1 to form S_4N_4 [21]. In the second case, the S–Cl group can assume a *trans*-position relative to the H atom. A linear condensation occurs, that may develop into a bicondensation. Through further HCl evolution (see S_8 formation [24]) S_4N_4 is formed (Scheme 3b). In the case where ClSSCl is employed, the N atom of HN=S=NH acts as a nucleophile towards the sulfur, the intermediate **A** produced as a transient, decomposes as shown in Scheme 4:

The eliminated HSCl decomposes forthwith into sulfur and HCl The formation of S_4N_4 follows the reaction route given in Scheme 3.

Only recently HNSNH was synthesized by three different routes and characterized by matrix-IR spectroscopy. Additionally the decomposition of the unstable molecule could be elucidated. Starting from the compounds made for the first time AgNSNAg and TlNSNTl as well as from known INSNI [25] which was made by a more efficient, reproducible process and in good yields from KNSNK and ICl in CH_2Cl_2 or $(CH_3)_3SiNSNSi(CH_3)_3$ and ICl in C_4F_8, reactions with HX (X = Cl, I) provides in all three cases unstable HNSNH. It decomposes mainly to S_4N_4 and ammonium salts. In addition small amounts of N_2 could be detected. The over all reaction of INSNI and HI including decomposition of the primary formed HNSNH takes place according to

$$4INSNI + 8HI \rightarrow S_4N_4 + 2NH_4I + 7I_2 + N_2$$

At a 1:1 molar ratio of the educts also unstable HNSNI is formed preliminary. The complicated temptatively by the following assumed steps

$$\begin{array}{lcl}
4INSI + 8HI & \rightarrow & 4HNSNH + 8I_2 \\
2HNSNH & \rightarrow & 2HN{=}S{=}N{-}SN + 2NH_3 \\
2HN{=}S{=}N{-}SN & \rightarrow & S_4N_4 + HN{=}NH \\
HN{=}NH & \rightarrow & 1/2H_2NNH_2 + 1/2N_2 \\
1/2H_2NNH_2 + I_2 & \rightarrow & 2HI + 1/2N_2 \\
2NH_3 + 2HI & \rightarrow & 2NH_4I \\
\hline
4INSNI + 8HI & \rightarrow & S_4N_4 + 2NH_4I + 7I_2 + N_2
\end{array}$$

Although according to quantum mechanical calculations, $H_2N–S≡N$ is about 5 kcal mol^{-1} thermodynamically less stable than HNSNH it presumably appears as an intermediate in chemical and decomposition process [26].

1.5. Formation of $[S_4N_3]Cl$ in the course of the synthesis of S_4N_4

In the course of the synthesis of S_4N_4 by Becke–Göhring et al. [23], the presence of $[S_4N_3]Cl$ in addition to ClSN was unequivocally ascertained. The formation of this species can occur in one of three ways:

1. In preliminary stages of the $(ClSN)_3$ formation
2. By way of $[S_3N_2Cl]^+Cl^-$ and
3. In a direct process.

1.5.1. From S_2Cl_2 and preliminary stages of $Cl_3S_3N_3$

Whereas linear Cl–C≡N will not trimerize in the absence of suitable catalysts the initially formed bent Cl–S≡N molecule is capable of trimerisation at 20°C, even in dilute solution, presumably according to Scheme 5:

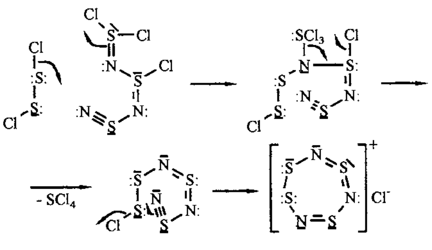
Now $[S_4N_3]Cl$ can be directly formed according to Scheme 6 via stage **4b** by the addition of S_2O_2 and the elimination of SCl_4:

1.5.2. *Via $[S_3N_2Cl]^+Cl^-$ as a-preliminary-stage*

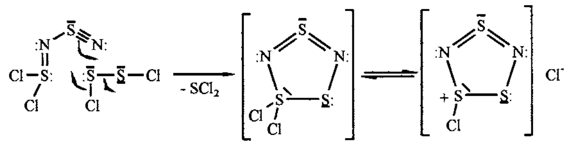
The synthesis of $[S_3N_2Cl]^+Cl^-$ is reported to proceed as shown [23,27]:

$$2ClSN + S_2Cl_2 \rightarrow [S_3N_2Cl]Cl + SCl_2$$

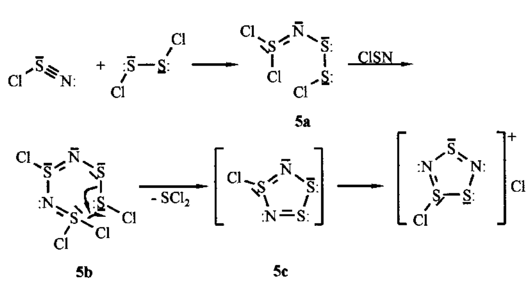
Considering the proved stoichiometry it is appropriate to assume that in the synthesis of S_4N_4 either a dimerization of ClSN occurs to yield **4a** which thereupon reacts with S_2Cl_2 as follows Scheme 7. Or a direct addition occurs of ClSCl to ClSN resulting in **5a** and this reacts further with another ClSN to give initially **5b** and **5c** and finally affords $[S_3N_2Cl]^+Cl^-$ with the elimination of SCl_2 according to Scheme 8:



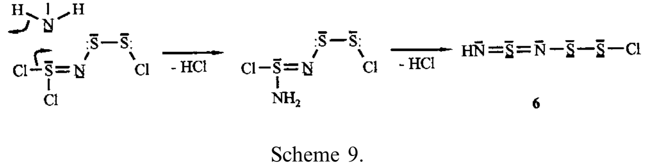
Scheme 6.



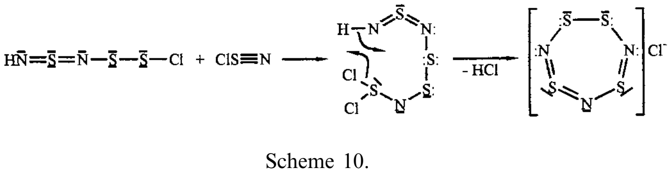
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

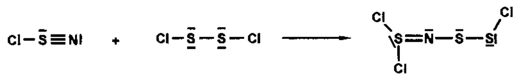
This last mechanism Scheme 8 is preferred on account of its simplicity.

When heated to 80–95°C $[S_3N_2Cl]Cl$ furnishes $[S_3N_2]_2^{+\,+}(Cl^-)_2$, which in turn forms various products at 130–150°C, among them ClSN and SCl_2 and ultimately $[S_4N_3]Cl$ [27]. Because of its complexity the above process–if it occurs at all–is certainly insignificant for the production of $[S_4N_3]Cl$. This assumption is the more justified in view of the reaction that occurs under reflux between $[S_3N_2Cl]Cl$ and S_2Cl_2 dissolved in CCl_4 [28] to yield quantitatively $[S_4N_3]Cl$.

1.5.3. *The direct formation of $[S_4N_3]Cl$*

The proposed reaction routes are the outcome of an early ammonolysis and may have the following sequence:

1. The addition of S_2Cl_2 to Cl–S≡N

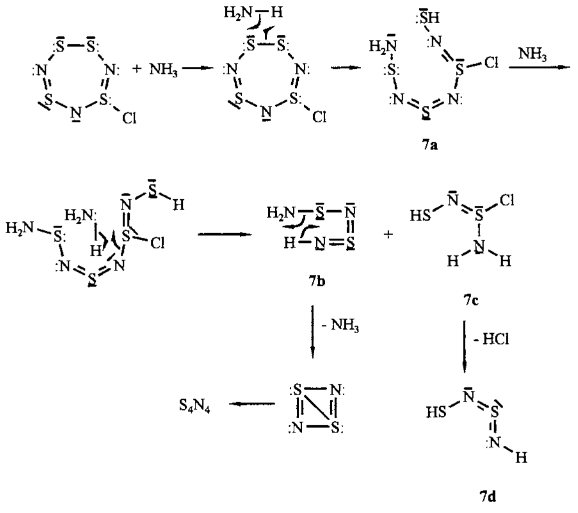


2. A nucleophilic attack of NH_3 on the most electrophilic sulfur and stabilization of the intermediates by repeated elimination of HCl: (Scheme 9) **6** may also be formed from HN=S=NH and S_2Cl_2 with HCl elimination.
3. Addition of ClSN to **6** as shown in Scheme 10:

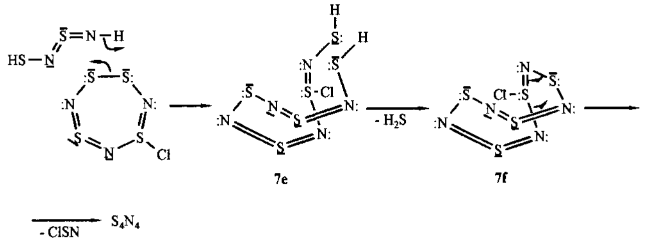
1.6. *Conversion of $[S_4N_3]Cl$ into S_4N_4 by means of NH_3*

One may envisage initial nucleophilic attack by NH_3 on the S–S bond of $[S_4N_3]Cl$ to open the ring and give **7a**. In the second reaction step a repeated nucleophilic attack is postulated by NH_3 on the S^{IV} atom. By HCl elimination and chain cleavage the intermediates H_2N-S-N=S=NH, (**7b**), and HSN=S(Cl)NH_2, (**7c**), can be formed. The question, whether NH_3 reacts in the opposite sequence is really immaterial since in both instances identical intermediates are produced. Whereas **7b** itself can form S_2N_2, which gives S_4N_4, as has been discussed already (see Scheme 11).

The second intermediate, **7d**, can react further with S_4N_3Cl. Hereby **7d** nucleophilically attacks the S–S bond with its NH group and splits the ring **7e** creating an additional S–H group. With the elimination of H_2S the intermediate S_5N_5Cl, **7f**, is formed, but this is unstable and changes into S_4N_4 eliminating ClSN. The following Scheme 12 gives the possible reaction sequence:



Scheme 11.



Scheme 12.

1.7. Critical evaluation of the possible reaction route

In addition to the indicated reactions that may lead to ClSN, it is worth noting that ClSSCl also is able to react in the form of $S{=}SCl_2$ [10]. Elimination of HCl gives **2b** and this may react to give ClSN, as indicated in Scheme 2. The crucial point of the addition reaction route is the reactivity of ClSN that may participate in two kinds of competing reactions, i.e. both ammonolysis and oligomerization. Presumably both reaction types are responsible for the formation of S_4N_4. The respective contribution of each possibly depends on the temperature and on the ClSN and NH_3 concentration. At low temperatures, ClSN in solution trimerizes to produce the cyclic $Cl_3S_3N_3$, probably in stages by way of the linear dimeric **4a** and trimeric **4b** molecules. At higher temperatures (about 100°C) a dissociation in the opposite direction sets in to give ClSN [29]. Since in the synthesis of S_4N_4 the temperature of 50°C is not to be exceeded, it may be assumed that the $Cl_3S_3N_3$ ring is in equilibrium with the open-chain fragments **4a** and **4b** (see Scheme 5).

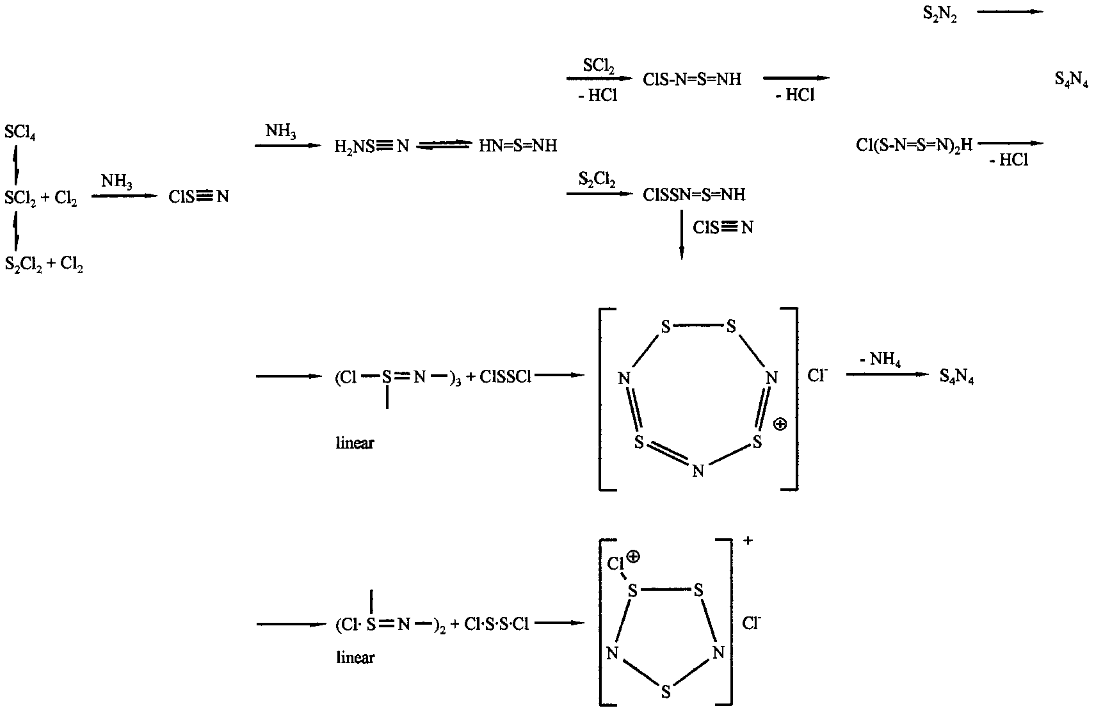
According to Scheme 6, **4b** is initially added to ClSSCl and affords $[S_4N_3]^+Cl^-$. At the same time, the monomeric ClSN or the dimeric **4a** may according to Scheme 8 or Scheme 7 condense to $[S_3N_2Cl]^+Cl^-$. However, since $[S_3N_2Cl]^+Cl^-$ is transformed into S_4N_3Cl [27] only at 130 to 150°C in vacuo via the intermediate $(S_3N_2Cl)_2$ or by being refluxed in CCl_4- such conditions do not exist in the synthesis of S_4N_4- these reaction steps are most improbable, all the more go as the occurence of $[S_3N_2Cl]^+Cl^-$ or $(S_3N_2Cl)_2$ has as yet not been proved during the S_4N_4 synthesis. A further possibility for the formation of S_4N_3Cl is the condensation of **4a** with NH_3 or of HN=S=NH with S_2Cl_2 to give HN=S=NSSCl and this compound then reacts with ClSN to form S_4N_3Cl according to Scheme 10. Consequently the synthesis of S_4N_4 can well be understood by means of two reaction routes. After the formation of ClSN the production of $[S_4N_3]Cl$ may follow according to Scheme 6 without the participation of NH_3. Alternatively it may be transformed into $[S_4N_3]Cl$ by way of HN=S=NH as intermediate with the employment of NH_3 according to Scheme 10. A direct synthesis of S_4N_4 can be accomplished by Scheme 3. The presence of SN cations as intermediates during the S_4N_4 synthesis appears to be unlikely, because their electrophilic nature would require an acidic medium; the reaction medium in the S_4N_4 synthesis however is basic. Similarly 'longlived' SN-radicals do not appear to play an important role either. Intense colours or abrupt colour changes are only observed when the temperatures of the reactions get out of control. The best yields of S_4N_4 results when the reaction mixture shows a salmon red colour. Scheme 13 once again summarizes the discussed reaction paths.

2. Reduction and halogenation of S_4N_4

It is quite simple to explain the reaction of S_4N_4 with $SnCl_2$ in a boiling mixture of C_2H_5OH and benzene that results in $S_4(NH)_4$. In this reaction a reduction takes place of S^{IV} to S^{II} and a concomitant hydrogenation of the nitrogen atoms to NH groups.

In this combined operation of reduction and hydrogenation the cage structure of S_4N_4 is converted to the crown structure of cyclooctasulfur and at the time the alternating NH groups function as pseudochalogens and occupy sulfur positions in the S_8 ring.

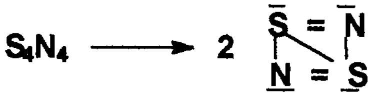
The fluorination of S_4N_4 with AgF_2 in CCl_4 at 25°C proceeds in a similar fashion [30]. Here both transanular S–S bonds are opened and the four S atoms are fluorinated to give four S–F groups. At the same time the cage conformation is altered and four alternating S=N double bonds are formed with retention of the eight membered ring. Since the ≡S–F group is isovalent with nitrogen, one should compare the structure of $N_4(SF)_4$ with that of N_8 which is non existant. However, if N is superseded by pseudonitrogen, (≡CH), cyclooctatetraene, is arrived at. Exactly like $F_4S_4N_4$ this has localized double bonds [d(C=C) = 1.34 Å, d(C–C) = 1.48 Å, comp. d(S=N) = 1.54 Å, d(S–N) =



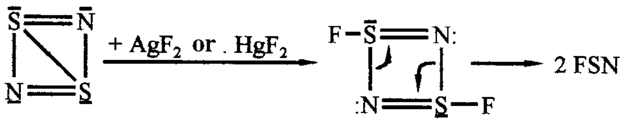
Scheme 13.

1.66 Å and in its boatkonformation has a similar structure to the S_4N_4 frame of $F_4S_4N_4$ (see Scheme 14).

The fluorination of S_4N_4 with AgF_2 or with HgF_2 in boiling CCl_4 leads to NSF_3 or to NSF within 1.5 or 5–6 h, respectively. Under these conditions S_4N_4 may dissociate initially according to



followed by fluorination at the transanular S–S bond of the four membered ring and dissociation of the strained ring to 2 FSN:



8

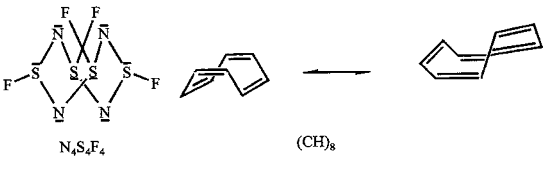
AgF_2 alone is then capable of fluorinating FSN to F_3SN. NS_2F_2 that has been described in a previous publication [31] and not observed since, might have been **8**, which according to its structure and stability might be compared with cylobutadiene. Since the decomposition of S_4N_4 starts at 250°C, one can assume that FSN is not formed through this intermediate step.

The chlorination of S_4N_4 is analogous to the preparation of $F_4S_4N_4$. In this case primarily $Cl_4S_4N_4$ is formed via $Cl_2S_4N_4$ but it is thermally unstable. Evidently the lower electronegativity of chlorine is insufficient for the formation of localized double bonds. Following the delocalization of the p-electrons, the ring skeleton has to become planar; the strain that then appears in the ring, causes the ring opening and formation of $Cl_3S_3N_3$ and ClSN which can be detected in solution even after eight days [32]

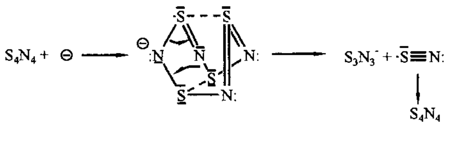
3. The conversion of S_4N_4 to $S_3N_3^-$ or $S_4N_5^-$

I. The reduction of $S_4N_4$with potassium leads to the transfer of one electron to the S_4N_4 cage. Consequently the number of p-electrons increases to **13** and for S_4N_4 – the cage structure changes to a more planar conformation for the anion radical. Subsequently SN is eliminated and stable $S_3N_3^-$ is formed.

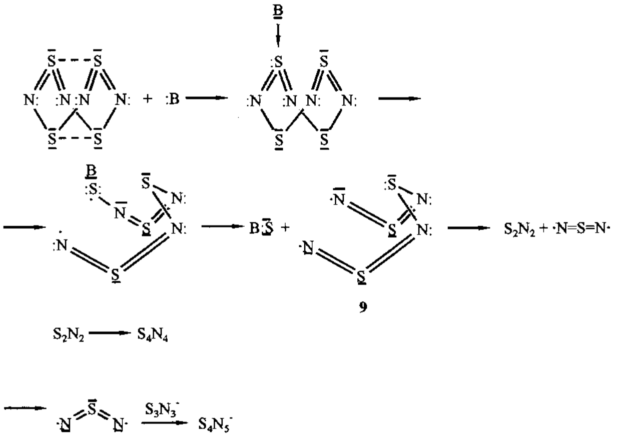
As previously mentioned, SN tetramerizes again to the starting compound S_4N_4. The electrochemical reduction of S_4N_4 proceeds analogously and so does the reduction with $NaNH_2$ or Na_2S (the oxidation products are H_2NNH_2 and S_8). Azides with a large cation (Cs^+, R_4N^+) are ionized in a polar solvent and so N_3^- reacts as a reducing agent and transfers one electron to S_4N_4,



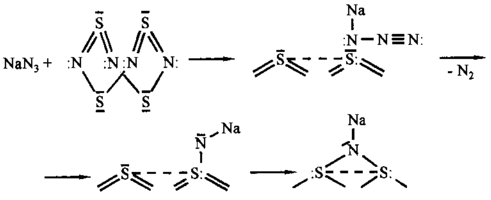
Scheme 14.



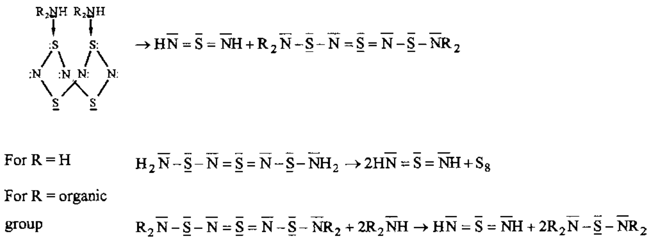
Scheme 15.



Scheme 16.



Scheme 17.



Scheme 18.

whereby $S_4N_4^-$ and N_2 are formed as intermediates. The anion decomposes according to Scheme 15 into $[S_3N_3]^-$ and S_4N_4:

II. The reaction carried out similarly with the nucleophilic agents KCN, $(C_6H_5)_3P$, NH_3, R_2NH, Na_2S (in excess) and with the azides MN_3 (M = Li, Na, K) do not proceed uniformly. Two reactions yielding different products in variable ratios may occur simultanously where nucleophilic reducing agents such as e.g. $(C_6H_5)_3P$, KCN or Na_2S (in excess) are employed.

(a) A nucleophilic attack of the Lewis base on S of the S_4N_4 cage with simultaneous cleavage of the appropriate SN bond. The bent chain thus formed then eliminates the sulfurized Lewis base (Ph_3PS, SCN, S_x) and intermediate **9** forms. Subsequently this decomposes to the biradical $^{\bullet}N{=}S{=}N^{\bullet}$ and S_2N_2 which in turn is converted to S_4N_4.

(b) Analogously the reduction of S_4N_4 proceeds via the nucleophile to $S_4N_4^-$ and this decomposes to $S_3N_3^-$ as indicated in Scheme 15.

The biradical $^{\bullet}N{=}S{=}N^{\bullet}$ reacts with $S_3N_3^-$ by bridging two S atoms to give the bicycle $S_4N_5^-$. This product has indeed been observed. The following reaction (Scheme 16) illustrates the above mentioned processes (a) and (b), step by step:

III. In the reactions of S_4N_4 with MN_3 (M=Li, Na, K), NH_3, R_2NH additional reaction paths have to be considered, namely

(a) the addition of the undissociated MN_3 without alternation of the S_4N_4 cage. Hereby MN_3 initially nucleophilically attacks the sulfur, eliminates N_2, and forms $M[S_4N_5]$, according to Scheme 17.

(b) The ammonolysis of S_4N_4 then leads to HNSNH and this in turn forms $S_4N_5^-$ via a reaction sequence as elaborated in Scheme 18. In this manner S_8 is formed initially as a byproduct with NH_3 and with R_2NH as a byproduct R_2NSNR_2. The formation of HNSNH is illustrated in the reaction steps presented in Scheme 18:

4. Syntheses leading to $S_4N_5^-$

Most procedures describing the preparation of $S_4N_5^-$ use S_4N_4 as, the starting material, which already has a cage structure. However, $S_4N_5^-$ can also be synthesized in good yield, by methanolysis of either $(CH_3)_3SiN{=}S{=}N{-}Si(CH_3)_3$ [33] or $(CH_3)_3C{-}N{=}S{=}NSi(CH_3)_3$ [34]. In this case the cage has first to be formed from smaller building blocks. The formation of $S_4N_5^-$ from $[(CH_3)_3SiN]_2S$ and CH_3OH can be explained by the following reaction sequence in a rather simple manner according to Scheme 19

Using these partial equations as a basis, the stoichiometry of the methanolysis can be presented as follows

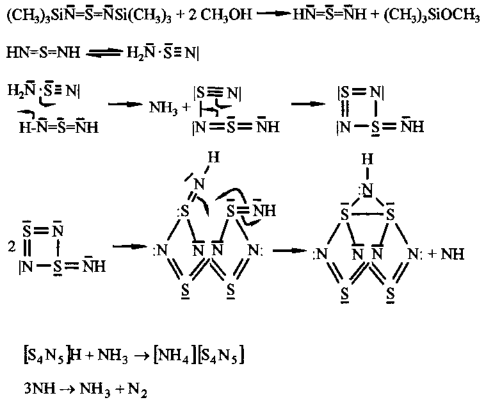
$$\begin{array}{ll}
12x & (CH_3)_3Si{-}N{=}S{=}N{-}Si(CH_3)_3 + 2CH_3OH \\
 & \rightarrow HN{=}S{=}NH + 2(CH_3)_3SiOCH_3 \\
6x & 2HNSNH \rightarrow HNS_2N_2 + NH_3 \\
3x & 2HNS_2N_2 \rightarrow (HN)_2S_4N_4 \\
3x & (HN)_2S_4N_4 \rightarrow H[N_5S_4] + NH \\
3x & H[S_4N_5] + NH_3 \rightarrow NH_4[S_4N_5] \\
 & 3NH \rightarrow NH_3 + N_2
\end{array}$$

$$12(CH_3)_3SiNSNSi(CH_3)_3 + 24CH_3OH$$

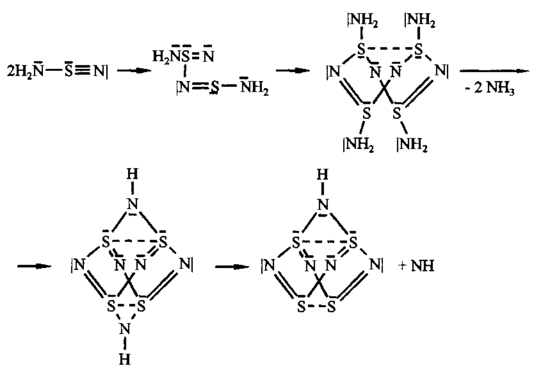
$$\rightarrow 3NH_4[S_4N_5] + 24(CH_3)_3SiOCH_3 + NH_3 + N_2$$

This stoichiometry is completely in accord with experimental findings [33]. The conversion of HN=S=NH formed during the methanolysis of $(CH_3)_3SiN{=}S{=}N\text{–}Si(CH_3)_3$, can be assumed to take place more directly, without the additional interim stages, as follows: (Scheme 20).

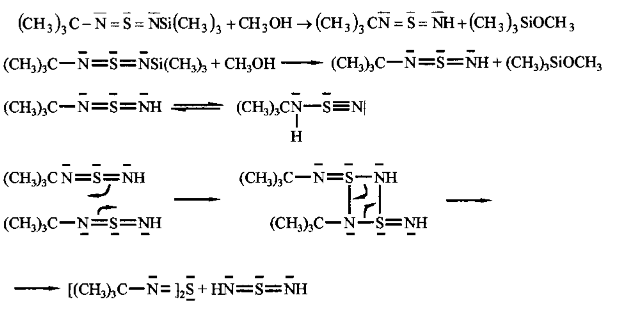
The reaction steps, presented in Scheme 20 differ from those indicated in Scheme 19 in so far as the aminothiazyl form of HNSNH immediately reacts to form a four membered ring which dimerizes to $(NH_2)_4S_4N_4$, as assumed also in the case of S_2N_2. By elimination of two moles of NH_3 the unknown closed polyhedron $H_2[S_4N_6]$ is formed, which obviously is not stable and converts to $H[S_4N_5]$ by eliminating NH; NH then decomposes, as indicated in Scheme 19 into NH_3 and N_2. The decomposition of the highly symmetrical $H_2[S_4N_6]$ to $H[S_4N_5]$ is difficult to understand.



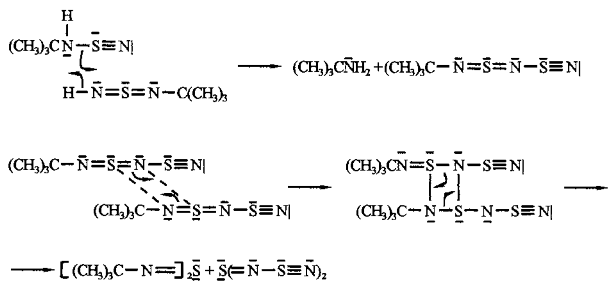
Scheme 19.



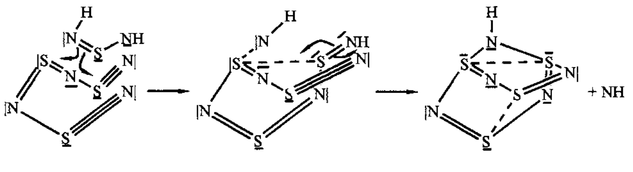
Scheme 20.



Scheme 21.



Scheme 22.



Scheme 23.

The methanolysis of $(CH_3)_3CN{=}S{=}N\text{–}Si(CH_3)_3$ [34] takes a more complex course, resulting in smaller yields of $S_4N_5^-$ and a more complex, overall stoichiometry. The following reaction scheme explains the formation of $S_4N_5^-$ and of all other observed reaction products (Scheme 21).

It is obvious that this analogous equilibrium of carbodiimide/cyanamide is apparently of predominant importance in the binary S–N chemistry and is of eminent significance for the understanding of the formation of $S_4N_5^-$ (Scheme 22).

$(CH_3)_3C\text{–}N{=}S{=}NH$ synproportionates via the above mentioned tetrahedral ring to $[(CH_3)_3CN{=}]_2S$ and HN=S=NH which condensates with $S({=}N\text{–}S{=}N)_2$ formed in Scheme 22 according to Scheme 23.

The mechanisms of Schemes 19, 22 and 23 differ only insignificantly – above all the step leading to the cage formation is in both cases nearly identical. The following stoichiometry results from this mechanism (Schemes 22 and 23). It completely coincides with that attained experimentally [34].

$$17(CH_3)_3C\text{–}N{=}S{=}N\text{–}Si(CH_3)_3 + 17CH_3OH$$
$$\rightarrow 17(CH_3)_3C\text{–}M{=}S{=}N\text{–}H + 17(CH_3)_3SiOCH_3$$
$$12(H_3C)_3C\text{–}N{=}S{=}NH$$
$$\rightarrow 6(CH_3)_3C\text{–}N{=}S{=}N\text{–}S{\equiv}N + 6(CH_3)_3CNH_2$$
$$6(CH_3)_3CN{=}S{=}N\text{–}S{=}N$$
$$\rightarrow 3S{=}(N\text{–}S{\equiv}N)_2 + 3(CH_3)_3CN{=}S{=}NC(CH_3)_3$$
$$4(CH_3)_3CN{=}S{=}NH$$
$$\rightarrow 2HN{=}S{=}NH + 2(CH_3)_3CN{=}S{=}NC(CH_3)_3(CH_3)_3$$
$$CN(H)\text{–}S{\equiv}N + NH_3$$
$$\rightarrow (CH_3)_3CNH_2 + HN{=}S{=}NH$$
$$3S{=}(N\text{–}S{\equiv}N)_2 + 3HN{=}S{=}NH \rightarrow 3[S_4N_5]H + 3NH$$

$$3NH \rightarrow N_2 + NH_3$$

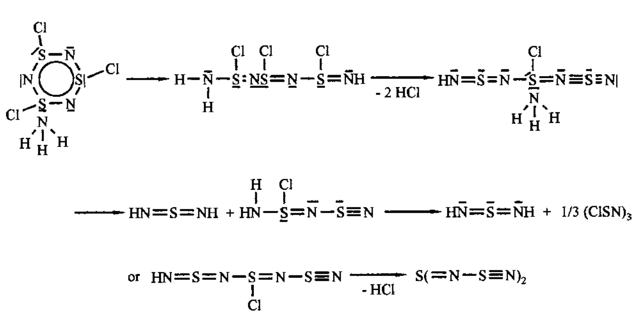
$$3[S_4N_5]H + 3(CH_3)_3CNH_2)$$
$$\rightarrow 3[(CH_3)_3CNH_3]^+[S_4N_5]^-$$

$$17(CH_3)_3CN{=}S{=}N\text{–}Si(CH_3)_3 + 17CH_3OH$$
$$\rightarrow 3[(CH_3)_3CNH_3]^+[S_4N_5]^- + 4(CH_3)_3CNH_2$$
$$+ 5(CH_3)_3CN{=}S{=}NC(CH_3)_3 + N_2$$
$$+ 17(CH_3)_3SiOCH_3$$

The reaction pathways (Schemes 22 and 23) contain two more reaction steps, namely ammonolysis and the synproportionation of $(CH_3)_3CN(H)SN$ according to Scheme 19.

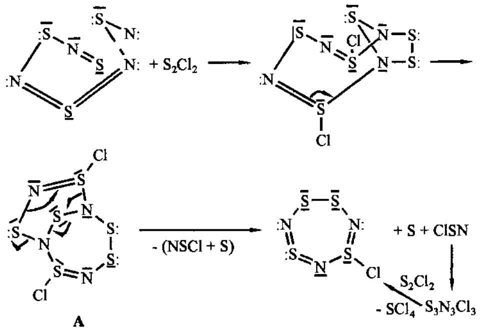
5. Reactions of $Cl_3S_3N_3$ with NH_3

Ammonolysis of $Cl_3S_3N_3$ [35] leads to $S_4N_5^-$, but probably not via $N_3S_3(NH_2)_3$, that then decomposes to $3N{\equiv}SNH_2$. Here it has to be assumed, that in the first reaction step NH_3 nucleophilically attacks sulfur on the opposite side of the Cl position and first forms an adduct that further reacts by ring opening– and elimination of HCl (according to Scheme 24).

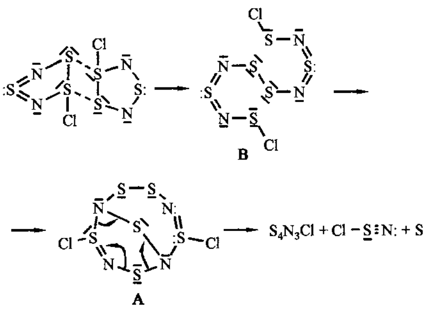


Scheme 24.

These intermediate compounds may then react further to furnish $S_4N_5^-$, as indicated for HN=S=NH in Scheme 15 or for $S(NSN)_2$ in reaction Scheme 19, respectively.



Scheme 25.



Scheme 26.

6. Preparation of $[S_4N_3]Cl$ from S_4N_4 and S_2O_2 or by heating of $(S_3N_2)_2Cl_2$

The reaction of S_4N_4 with S_2Cl_2 probably initiated by fixation of S_2Cl_2 via electrophilic attack of sulfur to an N-atom, followed by the addition of chlorine to the adjacent sulfur atom. The second S–Cl residue is added to the opposite S–N bond similarly, whereby a composite bicyclic molecule is formed consisting of a 5-membered and an 8-membered ring. This bicycle rearranges to the condensed ring A, which transforms to $[S_4N_3]Cl$ by elimination of ClSN and sulfur·$Cl_3S_3N_3$, formed from ClSN, reacts likewise with an excess of S_2Cl_2 to generate $[S_4N_3]Cl$ as stated in Scheme 6. The following reaction (Scheme 25) illustrates the suggested reaction sequence.

By heating $(S_3N_2Cl)_2$ initial ring opening is followed by linkage of both 5-membered rings and the formation of a chain intermediate B. This then rearranges to the bi-ring A, which decomposes to S_4N_3Cl, ClSN and sulfur, as indicated in Scheme 25, according to Scheme 26.

The objective of this discussion has been to present firmly established results of the chemistry of S–N compounds in the light of a strictly applied, topological comparison between SN and CN and to point out possible connections between corresponding representatives of both classes. It is however not surprising that similarities do not extend to structural details, best manifested in the SN-cage structures, where the elctronrich thiazyl is capable to form shapes, which hitherto have not been observed for CN-units. The reactions pathways suggested here are admittedly of speculative character but never the less consistent with experiences and observations in the chemistry of SN compounds, and underscore in nearly all reactions the greater complexity encountered in this area. The suggestions made are intended to stimulate discussions and to form a potential basis for further experimental investigations.

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