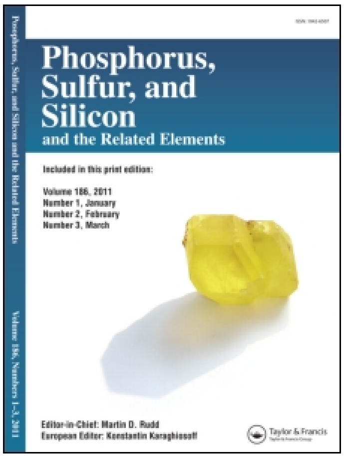

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Cyclotrisulfimide - Synthesis and Properties

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CYCLOTRISULFIMIDE - SYNTHESIS AND PROPERTIES

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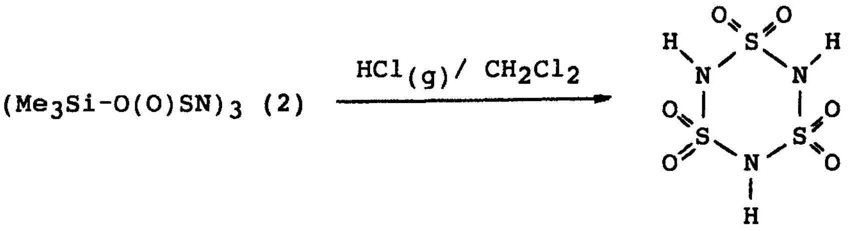
Abstract Cyclotrisulfimide (1,3,5,2,4,6- trithiatriazine-1,1,3,3,5,5-hexoxide) **(1)** has been synthesized successfully from persilylated sulfanuric acid **(2)** and hydrogen chloride in dichloromethane and has been isolated in pure form.
Correlations of infrared and ^{15}N-NMR spectra support assignment of the imide structure of **(1)**. Ring cleavage appears to characterize reactions of **(1)** with solvolytic reagents. Thermal decomposition of **(1)** has been studied by TG accompanied by TLC methods. Reaction with diazomethane in dioxane yields the N,N,N-trimethyl derivative **(3)**. Hitherto unknown **(2)** has been prepared from the trisilver salt of **(1)** using trimethylchlorosilane. The compound **(2)** has been characterized by IR, ^{15}N-NMR and by X-ray crystallography. In the structure the S_3N_3 ring adopts a flattened chair conformation with the silyl groups being axial.

RESULTS AND DISCUSSION

Repeated attempts to obtain cyclotrisulfimide (1,3,5,2,4,6 - trithiatriazine-1,1,3,3,5,5-hexoxide) **(1)** have failed since 1891 [1-5]. Only diluted aqueous solutions could be handled at low temperature without rapid decomposition [1-7].

In the reaction of the persilylated sulfanuric acid **(2)** with hydrogen chloride we were able to isolate **(1)** in a state of purity.



(1)

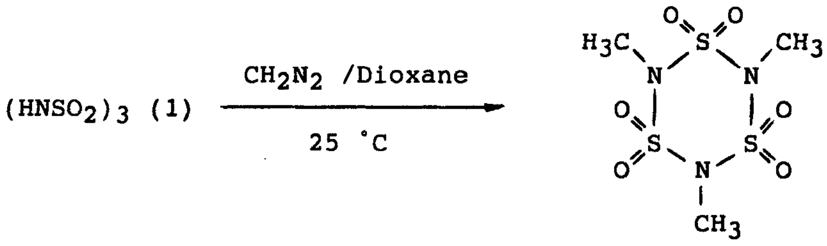
At room temperature **(1)** is a stable but moisture sensitive tribasic acid ($pK_1 = 1.7$, $pK_2 = 2.1$, $pK_3 = 4.4$, det. by potentiometric titration) soluble in polar solvents.

IR of **(1)** (nujol / hexachlorobutatiene mulls) : 3370 m, 3181 vs, 2601w, 1460 vs, 1390 m, 1311 m, 1247 w, 1227 s, 1187 vs, 1087 w, 887 vs, 639 m, 529 s (cm^{-1})

^{15}N-NMR (sulfolane) : +141,5 ppm (downfield to NH_3 (l) at 25 °C)

Both, IR group frequencies ν (NH) at 3181 cm^{-1}, ν (SO_2 asym) at 1460 - 1390 cm^{-1} and ν (SO_2 sym) at 1227-1187 cm^{-1} as well as the ^{15}N chemical shift for **(1)** are strongly diagnostic for the imide structure. of the compound in both solid state and solution. as shown below the assessment is supported by analogous spectroscopical results for **(3)**, the structure of which is known by X-ray cristallography [8].

In accordance to literature results [7] hydrolytical decomposition of **(1)** yielding sulfuric acid, sulfamic acid and sulfamide is observed and analyzed by TLC methods. The rate of hydrolysis increases with increasing acidity and concentration, respectively.
In non aqueous solutions (THF, dioxane, acetonitrile, sulfolane etc.) rapid formation of polymeric sulfimides is observed even with the exception of water. The decomposition rate depends on temperature and concentration as well. At elevated temperature (> 65 °C) thermal decomposition of **(1)** is observed in the solid state. TLC investigations of the residues indicate the formation of polymeric sulfimides.
Reaction of **(1)** with diazomethane in dioxane yields the N,N,N-trimethyl derivative **(3)**.



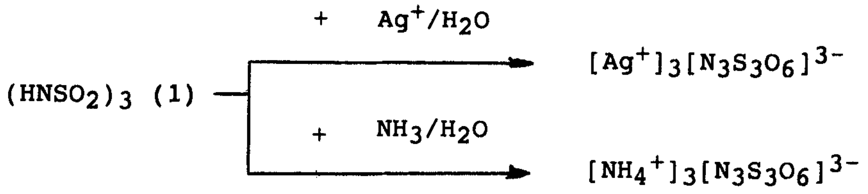
(3)

(60 % yield)

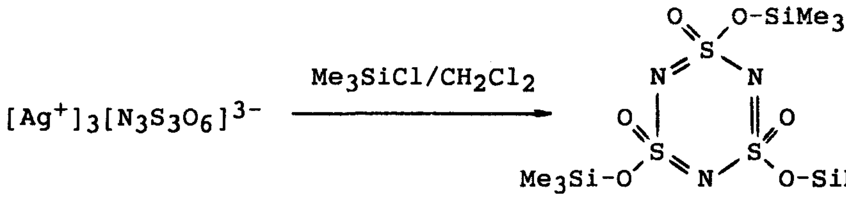
IR of **(3)** (in KBr) : 3400 v, 3055 vw, 2985 w, 1463 s, 1423 vs, 1410 vs, 1230 s, 1210 vs, 1190 s,960 s,940 s, 840 vs, 700 s, 650 s, 580 m, 550 vs, 490 s (cm^{-1})

^{15}N-NMR (THF) : +140,8 ppm (downfield to NH_3 (l) at 25 °C)

(1) also reacts with aqueous ammonia to give the triammonium salt, but with silver nitrate the scarcely soluble trisilver salt is precipitated.



The hitherto unknown **(2)** has been prepared in high yield by reaction of trisilver cyclotrisulfimide with trimethylchlorosilane.



(2)

(90 % yield)

(2) was purified by recristallation from cyclohexane yielding white crystals (m.p.93 °C) which are extremely moisture sensitive.

IR of **(2)** (in CCl_4) : 3960 w, 1300 s, 1260 s, 1140 s, 1000 s, 975 s, 865 vs, 825 vs, 615 w, 660 m (cm $^{-1}$)

^{15}N-NMR (THF) : +151,6 ppm (downfield to NH_3 (l) at 25 °C)

The crystal structure of **(2)** has been determinated by X-ray cristallography at 100K. In the structure the S_3N_3 ring adopts a flattened chair conformation with the silyl groups beeing axial.

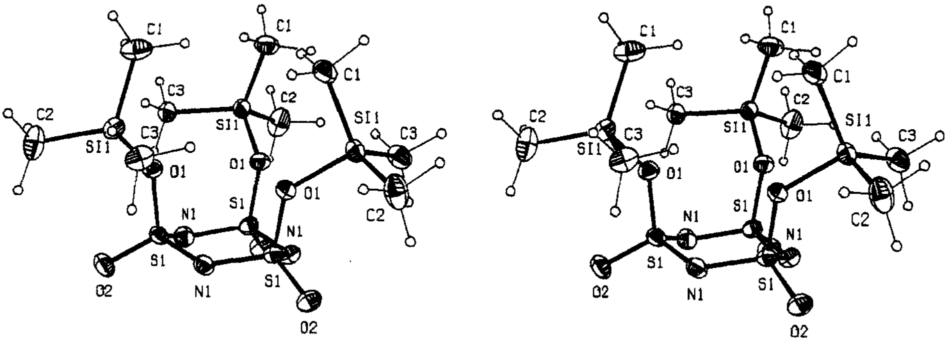


FIGURE 1 : Molecular structure of (**2**). The thermal ellipsoids are drawn at the 50% probability level, the hydrogen atoms are drawn with an arbitrary radius[9].

The bond lengths and angles (table 1) are not significantly different within the ring and are nearly the same as those in α-sulfanuric chloride [10].

TABLE 1 : Selected bond distances (Å) and angles (°) in (**2**)

S - O1	1,43 Å	S - N - S	120 °
S - O2	1,53	N - S - N	112
S - N	1,58	O - S -O	111

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REFERENCES

1. W.Traube, Ber.dtsch.chem.Ges. 25, 2472 (1892)
2. W.Traube, Ber.dtsch.chem.Ges. 26, 610 (1893)
3. A.Hantsch u. B.Stuer, Ber.dtsch.chem.Ges. 38, 1022 (1905)
4. R. Appel u. G.Berger, Z.anorg.allg.Chemie. 327, 114 (1964)
5. A.C.Hazell Acta.Chem.Soed. 26(6), 2542 (1972)
6. G.Heinze, A.Meuwsen Z.anorg.allg.Chemie. 275, 49 (1954)
7. H.A.Lehmann, G.Kempe, Z.anorg.allg.Chemie 306, 273 (1960)
8. A.C.Hazell, Acta Cryst. B 30, 2724 (1974)
9. C.K.Johnson: ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee,USA , 1965.
10. A.C.Hazell, G.A.Wiegers, A.Vos, Acta Cryst. 20, 186 (1966)