Oligomeric Analogues of Polysulfur Nitride. 1. Reactions of Arylsulfenyl Chlorides with Bis(trimethylsilyl)sulfurdiimine

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Abstract: Reactions of [Me$_3$SiNSNSiMe$_3$] with [ArSCl] (Ar = 4-MePh, 4-ClPh, 4-NO$_2$Ph, 2-NO$_2$Ph, 2,4-(NO$_2$)$_2$Ph) afforded 1-aryl-4-trimethylsilyl disulfur dinitrides [ArSNSNSiMe$_3$] or 1,5-diaryl trisulfur dinitrides [ArSNSNSAr] with 1 or 2 equiv of [ArSCl], respectively. With 3 equiv of [ArSCl] (Ar = 4-MePh, 4-ClPh) the novel compounds, 1,7-diaryl tetrasulfurtrinitrido chloride [ArSNSNSNSAr][Cl], were obtained. Mixed 1,5-diaryl trisulfur dinitrides were obtained from the reaction of [ArSNSNSiMe$_3$] with [Ar^{1}SCl] (Ar $\neq$ Ar^1), whereas reactions of [ArSNSNSiMe$_3$] (Ar = 2-NO$_2$Ph, 2,4-(NO$_2$)$_2$Ph) with [SCl$_2$] resulted in the formation of 1,9-diaryl pentasulfur tetranitrides [ArSNSNSNSNSAr]. The latter compounds have the longest chain of consecutive sulfur and nitrogen atoms reported for nonpolymeric molecules. The compounds were investigated with UV, IR, and ^{1}H NMR spectroscopy. An increasing red shift was observed for the longest wavelength absorption in the UV-vis with increasing sulfur-nitrogen chain length, indicating extensive electron delocalization along the chain.

The metallic and superconducting behavior of polysulfur nitride, (SN)$_x$, has caused great interest in the physical and structural properties of this compound, which have been reviewed.[1] Recently it was shown that bromination of (SN)$_x$ increased the conductivity by an order of magnitude[2] and compounds of composition (SNBr$_{0-0.5}$)$_x$ were obtained.[2,3] A very similar compound was obtained by bromination of S$_4$N$_4$.[4] All these compounds have chains of unknown length consisting of alternating sulfur and nitrogen atoms.

These results created our interest in the preparation and properties of polysulfur nitride compounds with known chain lengths of the type [R(SN)$_n$R^1] (R = aryl, aryl-*N*; R^1 = aryl, aryl-*S*). At present the most common members of this group are the sulfurdiimines[5,6,7] [RNSNR^2] (R, R^2 = aryl), although members of the type [RSNSNSR] (R = aryl) are also well established.[8,9] It should be mentioned that the longest chains previously reported[10-12] are found in the compounds [R^{3}NSNSNSNR^3] (R^3 = *t*-Bu, Me$_3$Si, diphenylmethylene).

The facile displacement of the silyl groups of bis(trimethylsilyl)sulfurdiimine makes this compound a useful starting material for many sulfur-nitrogen containing compounds.[10,13,14] In this paper it is shown that reactions of bis(trimethylsilyl)sulfurdiimine[15] with arylsulfenyl chlorides [ArSCl] afforded convenient synthetic routes to both novel and known types of compounds with sulfur nitride chains of variable length.

Experimental Section

General Information. Reactions were carried out in an atmosphere of dry nitrogen. ^{1}H NMR spectra in CH$_2$Cl$_2$ (parts per million relative to CH$_2$Cl$_2$) were recorded on a Varian HA 100 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer IR spectrophotometer 283 and UV spectra on a Cary 17D. Melting and decomposition points were determined on a DTA apparatus, Du Pont Model 900, and were checked visually. Elemental analyses were performed by Childers Laboratories, Milford, N.J., and Chemical Analytical Services, University of Berkeley, and are summarized in Table I.

Chemicals. Sulfur dichloride was distilled directly before use (a few drops of PCl$_3$ added). Sodium bis(trimethylsilyl)amide was prepared according to the literature.[15] 4-Nitrophenyl- and 2,4-dinitrophenylsulfenyl chlorides were commercially available and were used without further purification. Solvents were dried and distilled prior to use and stored under nitrogen.

Preparation of [Me$_3$SiNSNSiMe$_3$]. This compound was prepared according to the literature[14] method with a few modifications. A 10% excess of [NaN(SiMe$_3$)$_2$] was used. The precipitate of NaCl was collected on a large frit under a nitrogen atmosphere and washed several times with dry ether. Purification of the compound by fractional distillation afforded [Me$_3$SiNSNSiMe$_3$] in 70% yield. Also a higher boiling fraction (90 °C, ~10 mmHg) of [(Me$_3$Si)$_3$N] was obtained as white crystals with a yield of about $1/20$ that of [Me$_3$SiNSNSiMe$_3$].

Preparation of [ArSCl] (Ar = 4-MePh, 4-NO$_2$Ph, 4-ClPh). Bis(4-tolyl)disulfide (0.1 mol) was dissolved in 25 mL of CHCl$_3$ and the solution was gently refluxed. Then SO$_2$Cl$_2$ (8.8 mL) in 10 mL of CHCl$_3$ was added dropwise with stirring. A rapid evolution of gas (SO$_2$) occurred. After the addition was completed (5–10 min) the mixture was refluxed for an additional 1 h. The solvent was distilled off with the oil bath at 110 °C, using a slight vacuum if necessary. The residue was distilled under vacuum. Only one fraction distilled, an orange oil, which turned red on cooling. *p*-Tolylsulfenyl chloride [4-MePhSCl] was obtained in almost quantitative yield (96%). [4-NO$_2$PhSCl], which solidified upon cooling, and [4-ClPhSCl][21] were obtained similarly. The compounds were identical with those reported earlier,[16] and satisfactory analytical data for C, H, and S or Cl were obtained.

Preparation of [2-NO$_2$PhSNSNSiMe$_3$]. A solution of [2-NO$_2$PhSCl] (0.57 g) in CH$_2$Cl$_2$ (10 mL) was added dropwise with stirring to [Me$_3$SiNSNSiMe$_3$] (0.62 g) in CH$_2$Cl$_2$ (10 mL). The yellow solution gradually turned orange-red in color. When the addition was completed (5–10 min), the mixture was set aside for 30 min. Solvent was removed under vacuum and the crude product was recrystallized from hexane or pentane in the cold. A small amount of a red, insoluble product, the bis-substituted sulfurdiimine, was removed by filtration. Cream-yellow crystals were obtained in 80% yield. [4-NO$_2$PhSNSNSiMe$_3$] (cream), [4-ClPhSNSNSiMe$_3$] (pale yellow), and [2,4-(NO$_2$)$_2$PhSNSNSiMe$_3$] (bright yellow) were obtained in a similar manner with similar yields.

Preparation of [2-NO$_2$PhSNSNSPhNO$_2$-2]. [2-NO$_2$PhSCl] (1.15 g) was added in one portion to a solution of [Me$_3$SiNSNSiMe$_3$] (0.62 g) in CH$_2$Cl$_2$ (5 mL). The solution rapidly turned red-brown in color and was set aside at ambient temperature. After 14 h a first fraction of large needles was collected on a filter and washed with CH$_2$Cl$_2$. A second fraction was obtained at −20 °C, yield 70%. These needles were dichroic with red facets and facets with a metallic appearance. The compounds [4-NO$_2$PhSNSNSPhNO$_2$-4] (red needles), [4-ClPhSNSNSPhCl-4] (orange needles, prepared in 7.5 mL of CH$_2$Cl$_2$/5 mL of hexane), and [2,4-(NO$_2$)$_2$PhSNSNSPh(NO$_2$)$_2$-2,4] (orange crystals, prepared in 10 mL of CH$_2$Cl$_2$) were obtained similarly with yields varying from 70 to 85%.

Preparation of [4-MePhSNSNSPhMe-4]. [4-MePhSCl] (1.58 g) was added in one portion to [Me$_3$SiNSNSiMe$_3$] (1.03 g) in 6 mL of CH$_2$Cl$_2$/6 mL of hexane and set aside. After 2 days a first fraction of crystals with a golden appearance (80 mg) was removed by filtration. This compound was [4-MePhSNSNSNSPhMe-4][Cl] and is described below. The supersaturated filtrate crystallized immediately

Table I. Analytical Results

Compd	Mp, °C	% C found (calcd)	% H found (calcd)	% N found (calcd)	% S found (calcd)	% Cl found (calcd)
4-ClPhSNSNSiMe$_3$	57–58	39.30 (30.04)	4.64 (4.73)	9.48 (10.12)	23.91 (23.16)	12.90 (12.80)
4-NO$_2$PhSNSNSiMe$_3$	96–98	37.84 (37.60)	4.55 (4.56)	14.30 (14.62)	22.71 (22.31)	
2-NO$_2$PhSNSNSiMe$_3$	99–103	37.47 (37.60)	4.40 (4.56)	14.87 (14.62)	22.58 (22.31)	
2,4(NO$_2$)$_2$PhSNSNSiMe$_3$	109–111	32.42 (32.51)	3.50 (3.64)	16.84 (16.86)	19.82 (19.29)	
4-MePhSNSNSPhMe-4	90–92	54.48 (54.87)	4.52 (4.60)	9.00 (9.14)	30.86 (31.39)	
4-ClPhSNSNSPhCl-4	161–162	41.64 (41.50)	2.43 (2.32)	7.95 (8.07)	27.30 (27.70)	
4-NO$_2$PhSNSNSPhNO$_2$-4	197–199	39.20 (39.12)	2.22 (2.19)	15.02 (15.21)	25.72 (26.11)	
2-NO$_2$PhSNSNSPhNO$_2$-2	222 dec	38.89 (39.12)	2.27 (2.19)	15.21 (15.21)	25.68 (26.11)	
2,4-(NO$_2$)$_2$PhSNSNSPh(NO$_2$)$_2$-4,2	235 dec	31.68 (31.44)	1.21 (1.32)	18.30 (18.33)	21.24 (20.98)	
4-NO$_2$PhSNSNSPhCl-4	150–151	40.14 (40.27)	2.22 (2.25)	11.53 (11.75)	26.86 (26.88)	8.82 (9.91)
2,4(NO$_2$)$_2$PhSNSNSPhMe-4	137–138	40.90 (40.82)	2.62 (2.64)	14.10 (14.65)	25.17 (25.15)	
(4-MePhSNSNSNSPhMe-4)Cl	126 dec	43.21 (43.34)	3.77 (3.64)	10.93 (10.83)	32.52 (33.06)	10.14 (9.14)
(4-ClPhSNSNSNSPhCl-4)Cl	145 dec	33.18 (33.61)	1.93 (1.88)	9.53 (9.80)	29.25 (29.91)	24.30 (24.80)
2-NO$_2$PhSNSNSNSNSPhNO$_2$-2	157 dec	31.24 (31.29)	1.95 (1.75)	18.21 (18.25)	34.58 (34.81)	
2,4-(NO$_2$)$_2$PhSNSNSNSNSPh(NO$_2$)$_2$-4,2	165 dec	26.05 (26.18)	1.08 (1.10)	20.17 (20.35)	28.85 (29.12)	

after filtration and red plates of [4-CH$_3$PhSNSNSPhCH$_3$-4] were obtained (0.8 g). Concentration of the mother liquor gave another fraction of [4-MePhSNSNSPhMe-4] as red needles (0.6 g). Total yield of [4-MePhSNSNSPhMe-4] was 1.4 g (91%). Both fractions, which had similar ^{1}H NMR resonances, were analytically pure but their x-ray powder data were different (however, the needles had a powder diagram very similar to [4-ClPhSNSNSPhCl-4], a compound with known structure[9]).

Preparation of [4-MePhSNSNSPh(NO$_2$)$_2$-2,4]. [4-MePhSCl] (0.79 g) was added to a solution of [2,4-(NO$_2$)$_2$PhSNSNSiMe$_3$] (1.6 g) in CH$_2$Cl$_2$ (5 mL) and the dark red mixture was set aside for 24 h. Red needles of [4-MePhSNSNSPh(NO$_2$)$_2$-2,4] were obtained at −20 °C in 55% yield. A second fraction (20%) could be obtained by addition of hexane. [4-NO$_2$PhSNSNSPhCl-4] was obtained as red needles by the same method. The second fraction, however, consisted of a mixture of [4-NO$_2$PhSNSNSPhCl-4], [4-NO$_2$PhSNSNSPhNO$_2$-4], and [4-ClPhSNSNSPhCl-4] according to ^{1}H NMR.

Preparation of [4-MePhSNSNSNSPhMe-4][Cl]. Three equivalents of [4-MePhSCl] (1.58 g) was added to [Me$_3$SiNSNSiMe$_3$] (0.69 g) in 7.5 mL of CH$_2$Cl$_2$/7.5 mL of hexane or 1 equiv of [4-MePhSCl] (0.53 g) was added to [4-CH$_3$PhSNSNSPhCH$_3$-4] (1.02 g) in the same solvent. Crystals were collected every 4 h. Fractions of large, golden needles and black-bronze, fine crystalline fractions, which had a metallic golden appearance upon compressing, were obtained. After 2 days 0.5–0.6 g (78–93% yield) of [4-MePhSNSNSNSPhMe-4][Cl] was obtained. The compound was slowly attacked by moisture in the air, and rapidly in solution. The reaction mixture was shown by ^{1}H NMR to contain only one other reaction product, presumably (4-CH$_3$PhS)$_2$, since the NMR spectrum was identical with the spectrum obtained from an original sample. The slow evolution of a gas (N$_2$) was evidenced by the fact that a pressure built up in the reaction flask.

Preparation of [4-ClPhSNSNSNSPhCl-4][Cl]. [4-ClPhSCl] (0.45 g) was added to a solution of [4-ClPhSNSNSPhCl-4] (0.87 g) in CHCl$_3$ (50 mL). According to the rate of color change this reaction appeared to proceed much more slowly than the above reaction. After 3 days blue-black plates of [4-ClPhSNSNSNSPhCl-4][Cl] were collected on a frit, yield 0.22 g (40%). The compound was fairly stable in air but decomposed rapidly in solution in the presence of moisture.

Preparation of [2-NO$_2$PhSNSNSNSNSPhNO$_2$-2]. SCl$_2$ (103 mg) in 0.94 mL of CH$_2$Cl$_2$ was added dropwise to a solution of [2-NO$_2$PhSNSNSiMe$_3$] (575 mg) in CH$_2$Cl$_2$ (10 mL). The mixture rapidly turned dark in color. After 4 h at ambient temperature the black bronze precipitate was collected on a filter and vacuum dried for 2 h, yield 300 mg (65%). A second fraction of 90 mg was obtained at −20 °C. Compressing the precipitate afforded golden-bronze surfaces with a metallic appearance. The compound was only slightly soluble in CH$_2$Cl$_2$ and gave dark purple-blue solutions. [2,4-(NO$_2$)$_2$PhSNSNSNSNSPh(NO$_2$)$_2$-2,4] was prepared similarly and isolated as a greenish-golden precipitate in 60% yield. The compound was only slightly soluble in CH$_2$Cl$_2$ and afforded dark blue solutions.

Results and Discussion

The use of [SO$_2$Cl$_2$] in the preparation of arylsulfenyl chlorides has many advantages over the use of chlorine gas,[16] since SO$_2$Cl$_2$ can be easily handled in exact quantities, the reactions proceed readily in boiling chloroform, and no substitution on the aryl ring was observed. This resulted in yields of 80–90% (aryl = 4-CH$_3$Ph, 4-ClPh, 4-NO$_2$Ph).

I. Disulfur Dinitride Compounds. The first 1-aryl-4-trimethylsilyl disulfur dinitrides of formula [ArSNSNSiMe$_3$] (Ar = 4-ClPh, 4-NO$_2$Ph, 2-NO$_2$Ph, 2,4-(NO$_2$)$_2$Ph) were obtained from the reaction of equimolar amounts of [Me$_3$SiNSNSiMe$_3$] and [ArSCl], according to

$$\mathrm{Me_3SiNSNSiMe_3 + ArSCl \rightarrow ArSNSNSiMe_3 + Me_3SiCl} \quad (1)$$

Only one other similar alkyl derivative has been reported, [Cl$_3$CSNSNSiMe$_3$], which was prepared in an analogous reaction.[13] According to ^{1}H NMR the reactions proceeded almost quantitatively, although a small amount of bis-substituted product was formed (0–10%). The rate of the reaction was mainly determined by the position of substituents on the phenyl ring. The ortho-substituted [2-NO$_2$PhSCl] and [2,4-(NO$_2$)$_2$PhSCl] reacted much more slowly than the para-substituted compounds, although in all cases reactions were complete in ~10 min at 30 °C. (This steric protection of the sulfenyl chloride group is also reflected in the high stability of [2-NO$_2$PhSCl] and [2,4-(NO$_2$)$_2$PhSCl] to hydrolysis, compared with the slow hydrolysis of the para-substituted [ArSCl] compounds.)

The 1-aryl-4-trimethylsilyl disulfur dinitrides were reasonably stable in air and very soluble in common organic solvents. These new compounds are of interest since they still contain a reactive trimethylsilyl group (see sections II and IV).

Two different configurations are likely for the 1-aryl-4-trimethylsilyl disulfur dinitrides, a trans,trans or a cis,trans configuration (Figure 1). A cis,cis configuration is excluded for steric reasons because of the bulky trimethylsilyl group. In the case of the dialkyl- and diarylsulfurdiimines[5,17,18] the common configuration in cis,trans, although in solution a small amount of the trans,trans isomer was also present. In view of this we assume that the 1-aryl-4-trimethylsilyl disulfur dinitrides also will adopt the cis,trans configuration.

Although ^{1}H NMR (Table II) confirmed the presence of the aryl and one silyl group on the -SNSN- moiety, no further structural conclusions could be obtained. UV and IR results will be discussed below (Table III).

Table II. ^{1}H NMR Data[a]

Compd	Aryl H, Me[b]	$\mathrm{Me_3Si}$
$\mathrm{Me_3SiNSNSiMe_3}$		−5.08
$\mathrm{4\text{-}ClPhSNSNSiMe_3}$	2.18, 2.05	−5.02
$\mathrm{4\text{-}NO_2PhSNSNSiMe_3}$	2.33, 2.88	−4.99
$\mathrm{2\text{-}NO_2PhSNSNSiMe_3}$	3.00, 3.09, 2.43, 2.06	−4.96
$\mathrm{2,4\text{-}(NO_2)_2PhSNSNSiMe_3}$	3.35, 3.83, 3.17	−4.95
4-MePhSNSNSPhMe-4	2.04, 1.91, −2.97	
4-ClPhSNSNSPhCl-4	2.06	
$\mathrm{4\text{-}NO_2PhSNSNSPhNO_2\text{-}4}$	2.25, 2.94	
$\mathrm{2\text{-}NO_2PhSNSNSPhNO_2\text{-}2}$	2.86, 3.04, 2.46, 2.10	
$\mathrm{4\text{-}NO_2PhSNSNSPhCl\text{-}4}$	2.18, 2.89, 2.08	
$\mathrm{2,4\text{-}(NO_2)_2PhSNSNSPhMe\text{-}4}$	2.89, 3.82, 3.17[c] 2.13, 1.96, −2.94[d]	
(4-MePhSNSNSNSPhMe-4)Cl	2.29, 2.04, −2.90	
(4-ClPhSNSNSNSPhCl-4)Cl	Too insoluble	
$\mathrm{2\text{-}NO_2PhSNSNSNSNSPhNO_2\text{-}2}$	2.86, 3.03, 2.48, 2.11	
$\mathrm{2,4\text{-}(NO_2)_2PhSNSNSNSNSPh(NO_2)_2\text{-}4,2}$	3.05, 3.84, 3.23	
4-MePhSCl	2.29, 1.92, −2.92	
4-ClPhSCl	2.29, 2.06	
$\mathrm{4\text{-}NO_2PhSCl}$	2.28, 2.90	
$\mathrm{2\text{-}NO_2PhSCl}$	2.71, 3.01, 2.51, 2.14	
$\mathrm{2,4\text{-}(NO_2)_2PhSCl}$	2.90, 3.84, 3.28	

[a] In $\mathrm{CH_2Cl_2}$ (ppm relative to $\mathrm{CH_2Cl_2}$). [b] Resonances are given in the sequence ortho H, meta H, para H or $\mathrm{-CH_3}$. [c] $\mathrm{2,4\text{-}(NO_2)_2Ph}$ group. [d] 4-MePh group.

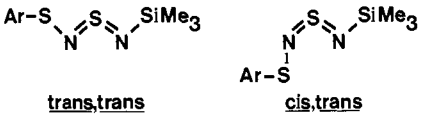

Figure 1. Proposed configurations of $[\mathrm{ArSNSNSiMe_3}]$.

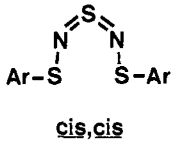

Figure 2. Proposed configuration for [ArSNSNSAr].

II. Trisulfur Dinitride Compounds. The symmetrically substituted 1,5-diaryl trisulfur dinitrides were obtained from the reaction of [ArSCl] with $[\mathrm{Me_3SiNSNSiMe_3}]$ in a 2:1 ratio (Ar = 4-MePh, 4-ClPh, $\mathrm{4\text{-}NO_2Ph}$, $\mathrm{2\text{-}NO_2Ph}$, $\mathrm{2,4\text{-}(NO_2)_2Ph}$) according to

$$\mathrm{Me_3SiNSNSiMe_3 + 2ArSCl \rightarrow ArSNSNSAr + 2Me_3SiCl} \tag{2}$$

Previously the 4-chlorophenyl[8] and the 2-nitrophenyl[19] derivatives have been reported. However, our synthesis is more general, affording the symmetrically substituted compounds with a wide variety of aryl groups in high yields (70–90%), and also allowing the synthesis of the mixed aryl derivatives $[\mathrm{ArSNSNSAr^1}]$ (Ar ≠ $\mathrm{Ar^1}$). These latter compounds were prepared from [ArSCl] ($\mathrm{Ar\text{-}4\text{-}CH_3Ph}$, 4-ClPh) and $[\mathrm{Ar^1SNSNSiMe_3}]$ ($\mathrm{Ar^1}$ = $\mathrm{2,4\text{-}(NO_2)_2Ph}$, $\mathrm{4\text{-}NO_2Ph}$) according to

$$\mathrm{Ar^1SNSNSiMe_3 + ArSCl \rightarrow Ar^1SNSNSAr + Me_3SiCl} \tag{3}$$

The yields in this reaction were sometimes lower owing to the simultaneous formation of [ArSNSNSAr] and $[\mathrm{Ar^1SNSNSAr^1}]$. Since no disproportionation was formed in a solution of pure $[\mathrm{4\text{-}NO_2PhSNSNSPhCl\text{-}4}]$ or of $[\mathrm{4\text{-}NO_2PhSNSNSPhNO_2\text{-}4}]$ and [4-ClPhSNSNSPhCl-4] under similar conditions, this aryl exchange must occur between ArSCl and $[\mathrm{Ar^1SNSNSiMe_3}]$ or $[\mathrm{Ar^1SNSNSAr}]$.

^{1}H NMR data of the compounds are given in Table II. Reactions 2 and 3 were followed with ^{1}H NMR spectroscopy and it was found that the rate of substitution of the second trimethylsilyl group was much slower than the first substitution. This explained the facile isolation of the monosubstituted compounds $[\mathrm{ArSNSnSiMe_3}]$. Especially in the case of $[\mathrm{2,4\text{-}(NO_2)_2PhSCl}]$ the reaction took many hours to go to completion.

The crystal structure of one compound [4-ClPhSNSNSPhCl-4] has been reported, and most likely the other 1,5-diaryl trisulfur dinitrides will have a similar (cis,cis) configuration (Figure 2). The UV and IR data are summarized in Table III and will be discussed below.

III. Tetrasulfur Trinitride Compounds. A unique and rather unexpected reaction took place between [ArSCl] (Ar = 4-MePh, 4-ClPh) and [ArSNSNSAr] or between $[\mathrm{Me_3SiNSNSiMe_3}]$ and three equimolar amounts of [ArSCl], which is essentially the same. In the case of Ar = 4-MePh golden needles, with a highly metallic appearance, were ob-

Table III. IR and UV–Vis Results

Compd	Vibrations of the S–N moiety[a] (KBr pellets)	UV adsorptions, nm[b] ($\mathrm{CHCl_3}$ solution)
$\mathrm{Me_3SiNSNSiMe_3}$		273
$\mathrm{4\text{-}ClPhSNSNSiMe_3}$	1196, 656, 463, 345	383, ~280
$\mathrm{4\text{-}NO_2PhSNSNSiMe_3}$	1194, 655, 455, 345	394, ~326
$\mathrm{2\text{-}NO_2PhSNSNSiMe_3}$	- - -, 655, 462, 335, 1060	409, ~353
$\mathrm{2,4\text{-}(NO_2)_2PhSNSNSiMe_3}$	1202, 648, 459, 329, 1054	413, ~361
4-MePhSNSNSPhMe-4	1139, 653, 483, 331	448, ~300, ~255
4-ClPhSNSNSPhCl-4	1138, 659, 482, 328	449, ~305, ~265
$\mathrm{4\text{-}NO_2PhSNSNSPhNO_2\text{-}4}$	1144, 663, 464, 330	458, ~352, ~288
$\mathrm{2\text{-}NO_2PhSNSNSPhNO_2\text{-}2}$	1139, 651, 488, 362	476, ~400
$\mathrm{2,4\text{-}(NO_2)_2PhSNSNSPh(NO_2)_2\text{-}4,2}$	1139, - - -, 483, 364	476, ~395, 342, ~280
$\mathrm{4\text{-}NO_2PhSNSNSPhCl\text{-}4}$	1146, 658, 483, 327	455, ~360, 297
$\mathrm{2,4(NO_2)_2PhSNSNSPhMe\text{-}4}$	1139, 660, 486, 341	474, ~360
(4-MePhSNSNSNSPhMe-4)Cl[d]	1082, 723, 500, 357, 977	582, ~480, 396,[c] ~285
(4-ClPhSNSNSNSPhCl-4)Cl[d]	1078, 730, 482, - - -, 970	565, ~475, 387,[c] ~284
$\mathrm{2\text{-}NO_2PhSNSNSNSNSPhNO_2\text{-}2}$	1109, 657, 485, 342, 1060	580, 424, ~290
$\mathrm{2,4\text{-}(NO_2)_2PhSNSNSNSNSPh(NO_2)_2\text{-}4,2}$	1091	587, ~425, ~360

[a] The first column is assigned to asymmetric (NSN) vibrations, the second column to the bending vibrations. [b] Extinction coefficients of the lowest energy adsorptions vary from 1 to 3 × 10^4; the other adsorptions have considerably smaller values for this coefficient. [c] Extinction coefficients ~2 × 10^4. [d] Nujol.

tained in high yield and analyzed as [4-MePhSNSNSNSPhMe-4][Cl]. The reaction was slow (several hours to 2 days) and proceeded according to

$$\begin{aligned} &2(\text{4-MePhSNSNSPhMe-4}) + \text{4-MePhSCl} \\ &\quad \rightarrow (\text{4-MePhSNSNSNSPhMe-4})\text{Cl} \\ &\qquad + (\text{4-MePhS})_2 + \mathrm{N}_2 \end{aligned} \tag{4}$$

The formation of $(\text{4-MePhS})_2$ in this reaction was verified by the fact that the ^{1}H NMR resonances of this product (2.09, 1.80, and −2.99 ppm relative to $\mathrm{CH_2Cl_2}$) in $\mathrm{CH_2Cl_2}$ were identical with the ^{1}H NMR resonances of an original sample.

We assume that these novel 1,7-bisaryl tetrasulfur trinitride compounds consist of a chain of alternating sulfur and nitrogen atoms with the aryl groups attached to the ends of the chain. This is supported by the low energy of the absorption in the visible (565 and 582 nm) which indicates extensive electron delocalization over the chain (see last section).

IV. Pentasulfur Tetranitride Compounds. The first 1,9-bisaryl pentasulfur tetranitride compounds were prepared by reacting [$\mathrm{ArSNSNSiMe_3}$] (Ar = 2-$\mathrm{NO_2}$Ph, 2,4-$\mathrm{(NO_2)_2}$Ph) with $\mathrm{SCl_2}$ in $\mathrm{CH_2Cl_2}$ solution according to

$$\begin{aligned} &2\mathrm{ArSNSNSiMe_3} + \mathrm{SCl_2} \rightarrow \mathrm{ArSNSNSNSNSAr} \\ &\qquad\qquad 2\mathrm{Me_3SiCl} \end{aligned} \tag{5}$$

We assume that these compounds also have a chain of alternating sulfur and nitrogen atoms, which was supported by the fact that they were identical with the compounds obtained from [$\mathrm{Me_3SiNSNSNSNSiMe_3}$] and 2[ArSCl].[20]

The strong absorptions in the visible (Table III) were evidenced in the golden metallic appearance of the compounds upon compressing, and are discussed in the next section.

V. UV-Vis and IR Results. The compounds described in this paper can be divided into five categories, based upon their composition and their UV-vis adsorption with the longest wavelength (Table III): [$\mathrm{Me_3SiNSNSiMe_3}$] ($\lambda_{\max}$ 273 nm); [$\mathrm{ArSNSNSiMe_3}$] ($\lambda_{\max}$ 383-413 nm); [ArSNSNSAr] ($\lambda_{\max}$ 448-476 nm); [ArSNSNSNSAr][Cl] ($\lambda_{\max}$ 565-582 nm); and [ArSNSNSNSNSAr] ($\lambda_{\max}$ 580-587 nm).

Comparison of the wavelength of these absorptions shows an increasing red shift with increasing length of the sulfur-nitrogen chain. These findings are interpreted as a result of increasing electron delocalization over these chains. Since electron-withdrawing substituents on the aryl ring increased the red shift slightly, this electron delocalization apparently also involved the aryl ring. The length of the sulfur-nitrogen chain in compounds of formula [ArSNSNSNSAr][Cl] would suggest a value for $\lambda_{\max}$ more intermediate between those of [ArSNSNSAr] and [ArSNSNSNSNSAr]. A positive charge on the chain induced by the chlorine atom, however, might cause an additional red shift to the wavelength of 565-582 nm. Infrared data of the characteristic vibrations of the sulfur-nitrogen chain are summarized in Table III. The significant lowering in energy of the ν_{as}(NSN) going from the [$\mathrm{ArSNSNSiMe_3}$] compounds (ν_{as} 1194-1202 $\mathrm{cm^{-1}}$) to the [ArSNSNSAr] compounds (ν_{as} 1138-1146 $\mathrm{cm^{-1}}$) may be due to the difference in geometry. The first most probably have a cis,trans configuration, whereas the latter have a cis,cis configuration as discussed earlier. Another explanation is a weakening of the double bond character of the sulfurdiimine moiety because of increased electron delocalization, which is also consistent with the further lowering to ~1100 and ~1080 $\mathrm{cm^{-1}}$ in the even more delocalized [ArSNSNSNSNSAr] compounds and [ArSNSNSNSAr]Cl compounds.

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References and Notes

(1) G. B. Street and R. L. Greene, *IBM J. Res. Dev.*, **21**, 99 (1977).

(2) G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene, and J. J. Mayerle, *J. Chem. Soc., Chem. Commun.*, 407 (1977); M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, M. J. Moran, C. K. Chiang, M. J. Cohen, A. G. Heeger, and D. L. Peebles, *Ibid.*, 473 (1977).

(3) C. Bernard, A. Herold, M. Lelaurain, and G. Robert, *C. R. Acad. Sci., Ser. C*, **283**, 625 (1976).

(4) G. B. Street, R. L. Bingham, J. I. Crowley, and J. Kuyper, *J. Chem. Soc., Chem. Commun.*, 464 (1977).

(5) J. Kuyper and K. Vrieze, *J. Organomet. Chem.*, **86**, 127 (1975).

(6) E. S. Levchenko and Z. I. Shokol, *Zh. Org. khim.*, **5**, 472 (1969); *J. Gen. Chem. USSR* (*Engl. Transl.*), 459 (1969).

(7) H. H. Hörhold and J. Beck, *J. Prakt. Chem.*, **311**, 621 (1969).

(8) J. Weiss and H. Piechaczek, *Z. Naturforsch. B*, **18**, 1139 (1963).

(9) F. P. Olsen and J. C. Barrick, *Inorg. Chem.*, **12**, 1353 (1973).

(10) R. Appel and M. Montenarh, *Z. Naturforsch. B*, **30**, 847 (1975).

(11) W. Lidy, W. Sundermeyer, and W. Verbeek, *Z. Anorg. Allg. Chem.*, **406**, 228 (1974).

(12) E. M. Holt and S. L. Holt, *J. Chem. Soc., Chem. Commun.*, 36 (1973).

(13) H. W. Roesky, W. Schaper, W. Grosse-Böwing, and M. Dietl, *Z. Anorg. Allg. Chem.*, **416**, 306 (1975).

(14) O. J. Scherer und R. Wies, *Z. Naturforsch. B*, **25**, 1486 (1970).

(15) U. Wannagat and H. Kuckerts, *Angew. Chem.*, **74**, 117 (1962).

(16) A. Schöberl and A. Wagner in Houben-Weyl, "Methoden der Organischen Chemie", Vol. 9, Georg Thieme Verlag, Stuttgart, 1955.

(17) J. Kuyper and K. Vrieze, *J. Organomet. Chem.*, **74**, 289 (1974).

(18) J. Kuyper, P. H. Isselman, F. C. Mylhoff, A. Spelbos, and G. Renes, *J. Mol. Struct.*, **29**, 247 (1975).

(19) H. C. Buchholt, A. Senning, and P. Kelly, *Acta Chem. Scand.*, **23**, 1279 (1969).

(20) J. Kuyper and G. B. Street, to be published.

(21) This compound could equally well be obtained from equimolar amounts of 4-ClPhSH and $\mathrm{SO_2Cl_2}$.