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Oligomeric Sulfur Nitrides. 2. Synthesis and Structure of 1,7-Di-4-tolyltetrasulfurtrinitrogen Chloride

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Bis(trimethylsilyl)sulfur diimide reacts with *p*-tolyl- or *p*-chlorophenylsulfenyl chloride to yield the corresponding 1,7-diaryltetrasulfurtrinitrogen cation. The course of the reaction is best explained by two consecutive additions of a sulfur–chlorine bond to a sulfur–nitrogen double bond, followed by the elimination of nitrogen gas and a diaryl disulfide. The crystal and molecular structure of one of the compounds, 1,7-di-4-tolyltetrasulfurtrinitrogen chloride, has been determined from three-dimensional X-ray counter data. The material crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a cell of dimensions $a = 8.536$ (2) Å, $b = 12.776$ (4) Å, $c = 8.413$ (2) Å, $\alpha = 78.51$ (1)°, $\beta = 87.04$ (1)°, and $\gamma = 80.05$ (1)°. Least-squares refinement has led to a conventional R factor of 0.061. The seven-membered SN chain assumes a cis,trans,trans,cis geometry, apparently to maximize the electrostatic interactions between itself and the chloride counterions. The values of the various S–N bond lengths indicate appreciable delocalization of charge over the entire chain.

Introduction

The discovery of the unusual electronic properties of poly(sulfur nitride)[1] and its brominated derivative[2] has generated a great deal of interest in the structural properties of this and related materials. To provide insight into the chemical and structural aspects of sulfur–nitrogen chains we have investigated the preparation and properties of small oligomeric analogues of $(SN)_x$. In an earlier paper[3] the syntheses of several new compounds possessing sulfur–nitrogen chains were described. One of these compounds, of composition (4-tolyl-SNSNSNS-tolyl-4)(Cl), was particularly interesting because of its visual resemblance to $(SN)_x$. In this paper we report the structure of this novel sulfur–nitrogen compound as well as the results of our investigation of the reactions leading to its formation.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Solvents were dried prior to use. ^{1}H NMR spectra were recorded in CH_2Cl_2 solution with a Varian HA-100 NMR spectrometer.

Preparation of (4-tolyl-SNSNSNS-tolyl-4)(Cl). 4-Tolylsulfenyl chloride (10 mmol) was added to bis(trimethylsilyl)sulfur diimide (4 mmol) in dry benzene (100 mL). The solution slowly darkened in color and was set aside for several days. When sufficient crystals had formed, they were collected on a filter and vacuum-dried. The filtrate was concentrated to 25 mL and set aside. After several days a second fraction was obtained. The crystals had a metallic golden appearance and were moisture sensitive. Needle-shape crystals as long as 2 cm could be obtained by carrying out the reaction in more dilute solution.

Preparation of (4-ClPh-SNSNSNS-PhCl-4)(Cl). The preparation of 1,7-bis(4-chlorophenyl)tetrasulfurtrinitrogen chloride was similar to that of the 4-tolyl compound. However, the reaction took several weeks to go to completion at room temperature, since the 1,5-bis(4-chlorophenyl)trisulfur dinitride initially formed not only reacted much slower but, in addition, crystallized from the benzene solution. Steel blue crystals were obtained in 85% yield after 4 weeks. Satisfactory analyses were obtained for both compounds.

Quantitative Determination of Nitrogen. During the formation of 1,7-di-4-tolyltetrasulfurtrinitrogen chloride a slow increase of the pressure in the reaction vessel was observed, due to the evolution of N_2. In order to determine the amount of N_2 evolved the reaction was carried out in CH_2Cl_2, since it proceeded similarly but much faster in that solvent. Di-4-tolyltrisulfur dinitride (0.92 g, 3.0 mmol) was dissolved in dry CH_2Cl_2 (25 mL) and the flask attached to a gas buret. Excess 4-tolylsulfenyl chloride (0.51 g) was added. After 24 h the gas evolution had ceased and 18.5 mL or 0.77 mmol (theroetical yield, 0.75 mmol) was collected. Filtration of the reaction solution gave 0.5 g of 1,7-di-4-tolyltetrasulfurtrinitrogen chloride. The ^{1}H NMR spectrum of the filtered solution showed it to contain more of this compound, in addition to 4-tolylsulfenyl chloride, which had been added in excess, and 4-tolyl disulfide. No other compounds were detected by ^{1}H NMR.

Isolation of the Product Disulfides. The benzene filtrates obtained from the reactions previously described were evaporated in air. After 1 day the residues were each extracted with 50 mL of pentane. The solutions thereby obtained were filtered and set aside at −25 °C. The light yellow crystals that subsequently precipitated were quickly filtered on a precooled frit, as they were quite soluble in pentane at room temperature. Isolation of a second fraction gave a total yield of 50–75% of di-4-tolyl or bis(4-chlorophenyl) disulfide. The ^{1}H NMR spectra of these compounds were identical with those of the products in the reaction solutions before they were exposed to air. Satisfactory analytical data were also obtained.

The same compounds could be prepared by reaction of the corresponding arylsulfenyl chlorides (6 mmol) with tris(trimethylsilyl)amine (2 mmol) in CH_2Cl_2. The reaction goes to completion after a few hours, with the disulfide and trimethylsilyl chloride being formed quantitatively. Gas evolution was also observed. Collection of this gas afforded 0.97 mmol of nitrogen.

Air Decomposition of (4-tolyl-SNSNSNS-tolyl-4)(Cl). Crystals of di-4-tolyltetrasulfurtrinitrogen chloride exposed to air slowly turned red. Extraction of the decomposition products with CH_2Cl_2, followed by evaporation of the CH_2Cl_2 and recrystallization of the resulting residue from hot hexane, gave 4-tolyl-SNSNS-tolyl-4.

Unit Cell and Intensity Data. Because of the insolubility of the compound, the crystals used for data collection were those obtained directly from the reaction medium. After observing a capillary-mounted crystal decompose in the X-ray beam, it became apparent that this would be a greater problem than moisture sensitivity and that several crystals would be necessary for data collection. In fact, a total of 5 crystals, all of them needles of approximate dimensions 0.15 × 0.15 × 0.25 mm, were used. The general procedure was to select a suitable crystal, mount it on the end of a glass fiber with nail enamel, spray it with a lacquer to protect it against moisture, and transfer it to an Enraf-Nonius CAD-4 automatic diffractometer. After the crystal was optically aligned, machine location, centering, and indexing of ca. 12 reflections were used to obtain the unit cell and orientation matrix. The compound crystallizes in the triclinic system with unit cell parameters $a = 8.536$ (2) Å, $b = 12.776$ (4) Å, $c = 8.413$ (2) Å, $\alpha = 78.51$ (1)°, $\beta = 87.04$ (1)°, and $\gamma = 80.05$ (1)°. There are two formula units per unit cell. A density of 1.44 (2) g·cm^{-3} determined by flotation in acetonitrile–carbon tetrachloride agrees well with the calculated value of 1.45 g·cm^{-3}. Although graphite-monochromatized Mo Kα radiation was used for data collection, the cell parameters quoted above were determined by a least-squares refinement of the setting angles of 15 high-angle reflections determined with Ni-filtered Cu Kα_1 radiation (λ 1.540 56 Å).

Data of the form $(h, \pm k, \pm l)$ were collected using θ–2θ scans to $2\theta = 40°$. The scan range was calculated according to the formula $\Delta\theta = (0.85 + 0.35 \tan \theta)$ and was extended by 25% on each side of the scan range for background measurement. The scan rate, based on the intensity measured during a fast prescan, was computed such that 5000 counts were to be obtained, if possible, in a maximum scan time of 90 s. An aperture with a height of 4 mm and a variable width of $(3.0 + 2.1 \tan \theta)$ mm was placed in front of the scintillation counter at a distance of 173 mm from the crystal. The intensities of three standard reflections were monitored after every 50 reflections. Data

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Table I. Final Atomic Positional and Thermal Parameters for $(CH_3C_6H_4)_2S_4N_3^+Cl^-$ [a,b]

atom	x	y	z	β_{11}[c] (or B, Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.1967 (2)	−0.0900 (2)	0.9065 (2)	224 (5)	80 (2)	127 (4)	−13 (2)	−24 (3)	−11 (2)
S(1)	0.1387 (2)	−0.2156 (1)	0.5558 (2)	195 (4)	54 (2)	104 (4)	−25 (2)	−22 (3)	−3 (2)
S(2)	0.0375 (3)	−0.1353 (2)	0.2412 (2)	209 (4)	65 (2)	101 (4)	−39 (2)	−31 (3)	−7 (2)
S(3)	0.1624 (3)	0.0603 (2)	0.1781 (2)	236 (5)	63 (2)	106 (4)	−45 (2)	−39 (3)	7 (2)
S(4)	0.2755 (2)	0.0562 (1)	0.4821 (2)	161 (4)	61 (2)	125 (4)	16 (2)	33 (3)	14 (2)
N(1)	0.0509 (7)	−0.2278 (5)	0.3956 (7)	185 (13)	59 (5)	100 (11)	−24 (6)	−6 (9)	−5 (6)
N(2)	0.1250 (7)	−0.0477 (4)	0.2925 (7)	195 (13)	52 (5)	101 (11)	−33 (6)	−29 (9)	0 (5)
N(3)	0.2486 (7)	0.1140 (4)	0.2921 (7)	180 (13)	60 (5)	107 (11)	−24 (6)	−31 (9)	1 (6)
C(1)	0.1762 (14)	−0.6616 (6)	0.9886 (11)	448 (29)	46 (6)	195 (19)	−30 (10)	51 (18)	30 (8)
C(2)	0.1604 (10)	−0.5478 (7)	0.8770 (10)	5.2 (2)					
C(3)	0.0663 (12)	−0.5219 (8)	0.7441 (12)	6.4 (2)					
C(4)	0.2366 (11)	−0.4690 (7)	0.9135 (11)	5.8 (2)					
C(5)	0.0559 (11)	−0.4192 (7)	0.6429 (12)	6.3 (2)					
C(6)	0.2287 (9)	−0.3673 (6)	0.8133 (10)	4.7 (2)					
C(7)	0.1408 (9)	−0.3444 (6)	0.6772 (9)	3.7 (2)					
C(8)	0.6010 (12)	0.3636 (8)	0.7622 (14)	238 (20)	112 (9)	390 (28)	−47 (10)	−69 (18)	−127 (13)
C(9)	0.5157 (10)	0.2882 (7)	0.6891 (11)	5.2 (2)					
C(10)	0.4983 (10)	0.1899 (7)	0.7731 (10)	4.9 (2)					
C(11)	0.4580 (11)	0.3198 (7)	0.5342 (11)	5.7 (2)					
C(12)	0.4229 (9)	0.1188 (6)	0.7089 (10)	4.4 (2)					
C(13)	0.3834 (10)	0.2515 (7)	0.4641 (10)	5.3 (2)					
C(14)	0.3665 (9)	0.1516 (6)	0.5517 (9)	3.7 (2)					

[a] Atoms are labeled as indicated in Figure 2. [b] Estimated standard deviations in the least significant figure(s) are given in parentheses. [c] The form of the anisotropic thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; values for the anisotropic thermal parameters only are × 10^4.

were collected until the intensities of these standards had declined by ~10%, at which point a new crystal was mounted and the precedure repeated. In this way, the intensities of 1550 reflections were measured.

The data were reduced as previously described,[4,5] with the value of ϵ in the expression for $\sigma(F_o^2)$ taken to be 0.05. The intensities collected with each crystal were scaled to account for the ~10% decline in the intensities of the standard reflections. The intensities of the standards measured at the beginning of data collection for each crystal were also used to place the intensities measured with different crystals onto a common scale. The intensities of 122 reflections ($0kl = 0\bar{k}l$) that were measured twice were averaged. The averaging residual, defined as $R = \sum|F_i^2 - \overline{F_i^2}|/\sum\overline{F_i^2}$, was 0.039. Given that approximately half the averaged intensities were measured with each of two different crystals, the low residual is a good indication that the scaling produced a quite consistent data set.

Solution and Refinement of the Structure. The structure was solved with MULTAN,[6] employing 220 reflections with $E > 1.39$. The intensity statistics indicated the space group to be centrosymmetric, hence $P\bar{1}$ (C_i^1, No. 2).[7] An E map computed with the phases obtained from the set with the highest combined figure of merit revealed all nonhydrogen atoms of the cation. A difference Fourier map computed following a few cycles of full-matrix least-squares refinement of the atomic positional parameters readily revealed the position of the chloride anion. Refinement of all the nonhydrogen atom positional and isotropic thermal parameters converged at $R = 0.114$. At this point anisotropic temperature factors were assigned to all but the carbon atoms of the phenyl rings. In addition, the phenyl hydrogen atoms were placed in idealized positions (C–H = 0.96 Å) and assigned isotropic thermal parameters equal to those of the carbon atoms to which they were attached. Refinement converged at $R = 0.061$ and $R_W = 0.083$ based on 139 parameters and 1355 observations for which $F^2 \geq 2\sigma(F^2)$. The error in an observation of unit weight was computed to be 2.7 electrons. The change in any parameter during the final cycle of refinement was at most 0.006 that of its standard deviation. The methyl hydrogen atoms could barely be detected above background in the final difference Fourier map, so further refinement was considered unnecessary.

The quantity minimized in the full-matrix least-squares refinement is $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes. The weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$. The discrepancy indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o)^{1/2}$. The scattering factors for the nonhydrogen atoms were taken from ref 8. Corrections for the anomalous dispersion of Cl^- and S were applied to the calculated structure factors.[9] The scattering factors of hydrogen were those of Stewart, Davidson, and Simpson.[10] The crystallographic programs used were those cited in ref 4.

Table II. Interatomic Distances (Å) and Angles (deg) in $(CH_3C_6H_4)_2S_4N_3^+Cl^-$

Distances[a]

S(1)–N(1)	1.622 (6)	C(3)–C(5)	1.405 (12)
S(1)–C(7)	1.753 (7)	C(4)–C(6)	1.394 (11)
S(2)–N(1)	1.567 (6)	C(5)–C(7)	1.376 (11)
S(2)–N(2)	1.585 (6)	C(6)–C(7)	1.356 (10)
S(3)–N(2)	1.589 (6)	C(8)–C(9)	1.537 (11)
S(3)–N(3)	1.564 (6)	C(9)–C(10)	1.341 (10)
S(4)–N(3)	1.631 (6)	C(9)–C(11)	1.376 (11)
S(4)–C(14)	1.758 (7)	C(10)–C(12)	1.401 (11)
C(1)–C(2)	1.555 (10)	C(11)–C(13)	1.397 (12)
C(2)–C(3)	1.363 (12)	C(12)–C(14)	1.390 (10)
C(2)–C(4)	1.378 (11)	C(13)–C(14)	1.368 (10)

Angles[a]

N(1)–S(1)–C(7)	101.2 (3)	C(5)–C(7)–C(6)	120.2 (7)
N(1)–S(2)–N(2)	103.1 (3)	C(5)–C(7)–S(1)	123.5 (7)
N(2)–S(3)–N(3)	103.6 (3)	C(6)–C(7)–S(1)	116.4 (6)
N(3)–S(4)–C(14)	100.8 (3)	C(8)–C(9)–C(10)	121.1 (8)
S(1)–N(1)–S(2)	120.4 (4)	C(8)–C(9)–C(11)	120.3 (8)
S(2)–N(2)–S(3)	126.0 (4)	C(10)–C(9)–C(11)	118.6 (8)
S(3)–N(3)–S(4)	120.1 (4)	C(9)–C(10)–C(12)	122.3 (8)
C(1)–C(2)–C(3)	121.0 (9)	C(9)–C(11)–C(13)	121.2 (8)
C(1)–C(2)–C(4)	120.7 (9)	C(10)–C(12)–C(14)	118.3 (7)
C(3)–C(2)–C(4)	118.2 (8)	C(11)–C(13)–C(14)	119.3 (8)
C(2)–C(3)–C(5)	120.2 (9)	C(12)–C(14)–C(13)	120.2 (7)
C(2)–C(4)–C(6)	122.1 (8)	C(12)–C(14)–S(4)	114.7 (5)
C(3)–C(5)–C(7)	120.2 (9)	C(13)–C(14)–S(4)	125.1 (6)
C(4)–C(6)–C(7)	119.0 (7)		

[a] See footnote b of Table I.

Table I contains the final positional and thermal parameters for all atoms, with their standard deviations derived from the inverse matrix of the last least-squares cycle. Bond distances and angles are listed in Table II.

Results and Discussion

Formation of 1,7-Diaryltetrasulfurtrinitrogen Chloride. The novel compounds 1,7-diaryltetrasulfurtrinitrogen chloride, (Ar-SNSNSNS-Ar)$^+$Cl$^-$, were prepared by the reaction of Ar-SNSNS-Ar with ArSCl (Ar = 4-tolyl or 4-chlorophenyl) or by the reaction of $(CH_3)_3$Si-NSN-Si$(CH_3)_3$ with ArSCl. In the latter case, Ar-SNSNS-Ar was formed as an intermediate product. In order to obtain further understanding of the remarkable formation of the 1,7-diaryltetrasulfurtrinitrogen

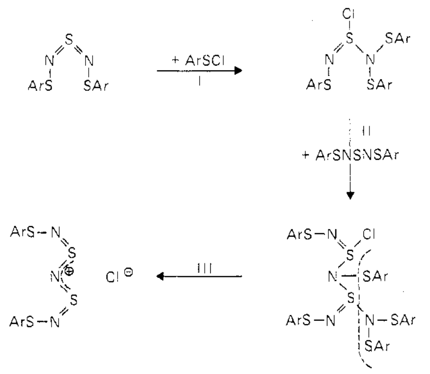

Figure 1. Proposed scheme for the formation of (Ar-SNSNSNS-Ar)(Cl), where Ar = 4-CH$_3$- or 4-ClPh.

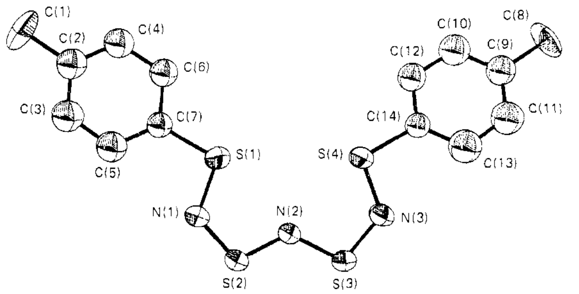

Figure 2. The di-4-tolyltetrasulfurtrinitrogen cation. The 50% probability ellipsoids are depicted.

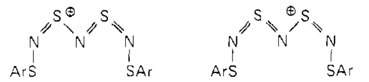

Figure 3. The two major resonance structures of the cation.

cation, the chemistry leading to it has been studied more extensively.

Proton NMR data taken during the course of the reaction, together with identification of the isolated products, show that the reaction leading to the formation of the title compound is given by the overall equation

$$4(\text{Ar-SNSNS-AR}) + 2\text{ArSCl} \rightarrow 2(\text{Ar-SNSNSNS-Ar})\text{Cl} + 3\text{Ar}_2\text{S}_2 + \text{N}_2 \quad (1)$$

The reaction goes to completion, as indicated by the virtually quantitative yield of products. Since the probable driving force for the reaction is the tendency of arylsulfenyl chlorides, ArSCl, to add to double bonds,[11] the course of the reaction can be explained by two consecutive additions of a sulfur–chlorine bond to a sulfur–nitrogen double bond, as shown in Figure 1. At least one intermediate product in the reaction of eq 1 was relatively stable. This was indicated by the appearance of transient peaks (resonances at 2.65 and −2.04 ppm relative to CH_2Cl_2, in addition to a peak partially obscured by the aryl resonances of the other compounds present) in the ^{1}H NMR spectrum taken in CH_2Cl_2, which vanished as the reaction neared completion.

The occurrence of the addition of ArSCl to Ar-SNSNS-Ar was substantiated by the reaction between 2,4-(NO_2)PhSCl and 4-tolyl-SNSNS-tolyl-4, which proceeded as shown in eq 2. When an excess of 4-tolyl-SNSNS-tolyl-4 is used, all of

$$2,4\text{-}(\text{NO}_2)_2\text{PhSCl} + \text{4-tolyl-SNSNS-tolyl-4} \rightarrow \text{4-tolyl-SNSNS-Ph}(\text{NO}_2)_2\text{-4,2} + (\text{4-tolyl})\text{SCl} \quad (2)$$

the 2,4-$(NO_2)_2$PhSCl is consumed to produce 4-tolyl-SNSNS-Ph$(NO_2)_2$-4,2. The (4-tolyl)SCl formed in the reaction undergoes further reaction with the excess 4-tolyl-SNSNS-tolyl-4 in the manner shown in eq 1. We assume that the intermediate in the reaction of eq 2 is a compound of the type formed in step I of Figure 1, in this case by the addition of 2,4-(NO_2)PhSCl to the sulfur–nitrogen double bond of 4-tolyl-SNSNS-tolyl-4 and subsequent elimination of (4-tolyl)SCl. That no further reaction takes place to yield a tetrasulfurtrinitrogen cation is probably due to the strong electron-withdrawing effect exerted by the nitro groups. We were able to obtain the 1,7-diaryltetrasulfurtrinitrogen chlorides only with aryl = 4-tolyl or 4-ClPh and not with aryl = 2- or 4-NO_2Ph. Furthermore, when aryl = 4-ClPh, reaction 1 proceeds much more slowly than when the less electronegative 4-tolyl group is involved. Addition of 4-NO_2PhSCl to 4-ClPh-SNSNS-PhCl-4 also proceeded according to eq 2, since the peaks of all the expected products were found in the ^{1}H NMR spectrum of the reaction solution.

In the case of Ar = 4-tolyl or 4-ClPh the newly formed S–Cl bond of step I, Figure 1 can add to a sulfur–nitrogen double bond of Ar-SNSNS-Ar. Subsequent elimination of Ar_2S_2 and N_2, possibly via the intermediate formation and disproportionation of $(ArS)_3N$, would then result in the formation of the title compound. An intramolecular migration of the central arylsulfenyl group is likely involved in the formation of the intermediate $(ArS)_3N$. Both inter- and intramolecular migrations of N-bonded arylsulfenyl groups have previously been

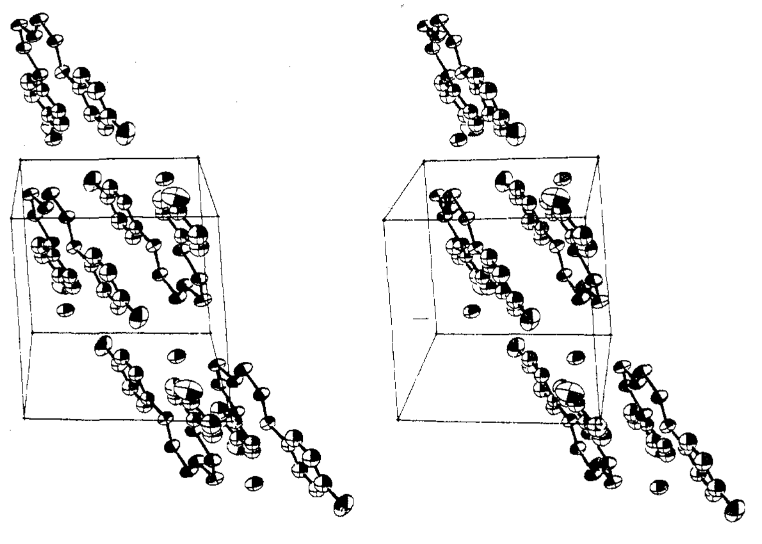

Figure 4. A stereoscopic view of the crystal packing. The origin of the cell is at the upper left rear corner. The *a* axis runs horizontally from left to right and *c* vertically from top to bottom. The *b* axis completes the right-handed coordinate system.

reported.[12] It should be mentioned that reaction of $((CH_3)_3Si)_3N$ with 4-tolylsulfenyl chloride at 30 °C proceeds according to eq 3. Again, one might assume the formation of an unstable $(ArS)_3N$ intermediate, which disproportionates to give the observed products. Tris(arylthio)amines have never been isolated.

$$2((CH_3)_3Si)_3N + 6(4\text{-tolyl})SCl \rightarrow 3(4\text{-tolyl})_2S_2 + N_2 + 6(CH_3)_3SiCl \quad (3)$$

Description of the Structure. The atom labeling scheme and the anisotropic thermal ellipsoids of the di-4-tolyltetrasulfurtrinitrogen cation is shown in Figure 2. Bond distances and angles are listed in Table II. The packing of the material is depicted in Figure 4.

Crystals of this unusual compound consist of discrete di-4-tolyltetrasulfurtrinitrogen cations and chloride anions. There is no crystallographic symmetry imposed on the cation, although there is an approximate mirror plane perpendicular to the long axis of the ion and containing N(2). The central portion of the cation, S(1)–S(4), is close to, but shows some significant deviations from, planarity. The equation of the best plane containing these seven atoms is $0.799X - 0.517Y - 0.307Z = 0.227$, where X, Y, and Z are coordinates (in Å) in a right-handed orthogonal axis system. X is along the crystallographic a axis, Y is in the ab plane, and Z is along c^*. The deviations (in Å) of the atoms from this plane are as follows: S(1), 0.06; S(2), −0.06; S(3), 0.06; S(4), −0.07; N(1), 0.01; N(2), −0.03; N(3), 0.04. The planes of the phenyl rings attached to S(1) and S(4) make dihedral angles with this plane of 14.4° and 4.1°, respectively. Thus the entire cation is close to being planar. Another, and perhaps more informative, view of the deviation from strict planarity of the S_4N_3 moiety is to consider the plane defined by atoms S(2)–N(2)–S(3). On one side of this three-atom segment, atom N(3) lies in the plane while S(4) deviates from it by only 0.03 Å. On the other side, a slight rotation about the N(2)–S(2) bond moves N(1) and S(1) out of the plane by 0.16 and 0.26 Å, respectively.

The most striking feature of the cation is the apparent delocalization of the π electrons over the entire S_4N_3 moiety, as indicated by the appreciable divergence of the various bond lengths from values expected on the basis of the most simple resonance structures of the compound, shown in Figure 3. On the basis of those structures, the bond orders of the pairs of bonds N(1)–S(1) and N(3)–S(4), N(2)–S(2) and N(2)–S(3), and N(1)–S(2) and N(3)–S(3) would be expected to be 1, 1.5, and 2, respectively. The average lengths of the preceding sets of bonds, in the same order, are 1.627 (8), 1.587 (8), and 1.566 (8) Å and may be compared to the values of ~1.69 and ~1.54 Å found for what are nominally single[13] and double [14,15] bonds, respectively, in similar compounds. Resonance structures complementing those of Figure 3 can be formulated in which electron donation from S(1) to N(1) or from S(4) to N(3) gives double-bond character to those respective bonds and places the positive charge on the sulfur atom involved. The appreciable delocalization indicated by the above is consistent with the metallic appearance of the compound. We point out that the material does not exhibit metallic electrical behavior.

One of the more interesting questions concerning this compound was the relationship between the configuration of the S–N chain and that of $(SN)_x$. As can be seen in Figure 2, the horseshoe configuration about the four bonds in the segment N(1)–N(3) is cis,trans,trans,cis, which differs from the cis,trans,cis,trans geometry of polythiazyl. It differs also from the cis,cis geometry of the shorter S_3N_2 chain of 1,5-bis(p-chlorophenyl)-2,4-diaza-1,3,5-trithiapenta-2,3-diene.[16] Since there are no steric factors preventing the cation from taking the $(SN)_x$ configuration, one is inclined to assume that the compound is forced into its configuration in order to achieve maximum packing efficiency between cations and anions. Such a configuration allows each anion to be surrounded by six partially positive sulfur atoms from three different cations. Four of them are at distances less than 3.3 Å from the anion while two others are at ~3.75 Å. Thus, two sulfur atoms (S(2) and S(3)) are situated at distances of 3.056 (3) and 3.237 (3) Å from the anion while the same two sulfur atoms on a different cation are at distances of 3.124 (3) and 3.266 (3) Å. Two different types of sulfur atoms (S(1) and S(4)) from a third cation, at distances of 3.720 (3) and 3.771 (3) Å, complete the sphere of sulfurs. All of this can be seen in Figure 4, which shows the packing of the ions in the unit cell. Not surprisingly, the anion approaches most closely those atoms (S(2) and S(3)) that would be predicted to be most positive on the basis of the two resonance structures shown in Figure 2. The short S---Cl ionic distances are slightly longer than those in chlorothiodithiazyl chloride.[17]

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Registry No. (4-tolyl-SNSNSNS-tolyl-4)(Cl), 67180-32-9; (4-ClPh-SNSNSNS-PhCl-4)(Cl), 67180-33-0; (4-tolyl)SCl, 933-00-6; (4-ClPh)SCl, 933-01-7; $(CH_3)_3Si\text{-}NSN\text{-}Si(CH_3)_3$, 18156-25-7.

Supplementary Material Available: Table III listing structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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