dissociation is considered (333 K, CH_4/C_2H_6 in the ratio 4:1) while C_2H_6 is more abundant in the photochemical process (diffuse daylight, 293 K, CH_4/C_2H_6 in the ratio 1:3). Thus the cleavage of the methyl-nickel bond may occur through two different pathways. However, more investigations are still necessary to understand these results.

In conclusion, it is tempting to write that the surprising production of a Ni(I) complex $[Ni(PMe_3)_4]BPh_4$ by homolysis of the Ni-C bond in $[Ni(CH_3)(PMe_3)_4]BPh_4$ can be predicted by the X-ray structure of $[Ni(CH_3)(PMe_3)_4]BPh_4$ since the molecule lies on the geometrical reaction path going from the trigonal bipyramid (C_{3v}) to the tetrahedron. However no simple mechanistic interpretation of the production of a mixture of CH_4 and C_2H_6 can now be proposed.

Registry No. I, 52166-20-8; $[Ni(PMe_3)_4]PF_6$, 77342-02-0; $Ni(PMe_3)_4$, 28069-69-4; $NiCl_2(PMe_3)_2$, 19232-05-4.

Supplementary Material Available: A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4,
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Thermal Decomposition of (Triphenylphosphoranediyl)aminocyclotrithiazene and (Triphenylarsoranediyl)aminocyclotrithiazene, $Ph_3E{=}NS_3N_3$ (E = P, As). Preparation and Structure of (Triphenylphosphoranediyl)amine (Thiosulfinyl)amine Sulfide, $Ph_3P{=}NSN{=}S{=}S$, and a Novel Synthesis of Disulfur Dinitride

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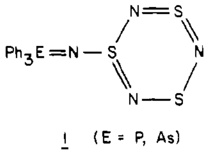
The thermolysis of (triphenylphosphoranediyl)aminocyclotrithiazene, $Ph_3P{=}NS_3N_3$, produces the open-chain (thiosulfinyl)amine derivative $Ph_3P{=}NSN{=}S{=}S$, the structure of which has been determined by X-ray crystallography. The crystals are monoclinic, of space group $P2_1/c$, with $a = 12.573$ (1) Å, $b = 11.170$ (1) Å, $c = 14.816$ (2) Å, $\beta = 115.96$ (1)°, $V = 1872.2$ Å^3, and D_{calcd} (for $Z = 4$) = 1.37 g cm^{-3}. The structure was solved by direct methods and was refined by full-matrix least-squares procedures to a final $R = 0.040$ and $R_w = 0.062$ for 1747 reflections with $I > 3\sigma(I)$. The structure consists of an open-chain $Ph_3P{=}NSN{=}S{=}S$ sequence with the sulfur and nitrogen atoms lying in a nearly planar cis-trans arrangement. The short terminal sulfur-sulfur bond (1.908 (2) Å) indicates a bond order significantly greater than one. The two S-N bonds of the terminal S_3N group are almost equal (1.592 (4) and 1.587 (4) Å). In contrast to the behavior of $Ph_3P{=}NS_3N_3$ the thermal decomposition of $Ph_3As{=}NS_3N_3$ leads to the elimination of S_2N_2. When the thermolysis is carried out in acetonitrile solution, S_2N_2 rapidly dimerizes to S_4N_4, but when the reaction is performed in the solid state at ca. 130 °C/10^{-3} torr, S_2N_2 can be isolated and converted to the $(SN)_x$ polymer.

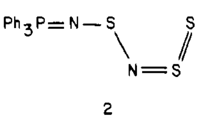
Introduction

The rapid and often violent thermal decomposition of many binary sulfur nitride molecules and ions $S_xN_y^{n\pm}$ is a well-known but little understood feature of their chemistry. One thermolytic process, namely, the cracking of S_4N_4 vapor over silver (or glass) wool, has been extensively studied since it is the conventional source of S_2N_2, the molecular precursor of the $(SN)_x$ polymer.[2] However, despite much research, the mechanism of the reaction remains in doubt. Many neutral species other than S_2N_2 (e.g., S_4N_2, S_3N_3, SN, S_2) can also be produced,[3] and the balance between them is a delicate function of temperature and pressure.

Recently we demonstrated the facile thermal interconversion of the three binary SN anions $S_4N_5^-$, $S_3N_3^-$, and S_4N^-,[4] and this discovery has prompted us to investigate more generally the thermal decomposition of other sulfur nitride derivatives. We have begun by examining the thermal degradation of the group 5 imine derivatives of cyclotrithiazene (**1**). The reactions depend on the group 5 element (P or As) involved, but both processes indicate the importance of the loss of N_2S or S_2N_2 as primary decomposition pathways. In this paper we discuss possible mechanisms for these reactions and report the preparation and structure of the open-chain (thiosulfinyl)amine sulfide species **2**, as well as a novel method for preparing S_2N_2 and $(SN)_x$.[5]



1 (E = P, As)



2

Experimental Section

Reagents and General Procedures. *N*-(Trimethylsilyl)(triphenylphosphoranediyl)amine,[6] (triphenylarsoranediyl)amine,[7] and tetrasulfur tetranitride[8] were all prepared according to literature methods. The phosphoranediylaminocyclotrithiazene $Ph_3P{=}NS_3N_3$ was prepared by the reaction of $Ph_3P{=}NSiMe_3$ with S_4N_4.[9] Triphenylphosphine (Baker) and triphenylarsine (Eastman) were commercial products and were used as received. All the solvents employed were of reagent grade and were dried before use: dichloromethane by distillation from P_2O_5 and acetonitrile by distillation from P_2O_5 followed by distillation from calcium hydride. All reactions were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox and silica gel. Infrared spectra were recorded on Nujol mulls (CsI win-

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[1] (a) University of Calgary. (b) University of Arkansas.

[2] For a recent review of the $(SN)_x$ polymer and its preparation, see: Labes, M. M.; Love, P.; Nichols, L. F. *Chem. Rev.* **1979**, *79*, 1.

[3] For example, see: (a) Smith, R. D. *J. Chem. Soc., Dalton Trans.* **1978**, 478. (b) Smith, R. D.; Wyatt, J. R.; De Corpo, J. J.; Weber, D.; Saalfeld, F. E. *Inorg. Chem.* **1978** *17*, 1639. (c) Louis, E. J.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1976**, 425.

[4] (a) Chivers, T.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1979**, 752. (b) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773.

[5] For a preliminary communication of part of this work, see: Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1980**, 35.

[6] (a) Birkhofer, L.; Ritter, A.; Richler, P. *Chem. Ber.* **1963**, *96*, 2750. (b) Birkhofer, L.; Ritter, A. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 417.

[7] (a) Appel, R.; Wagner, D. *Angew. Chem.* **1960**, *72*, 209. (b) Ross, B. W.; Marzi, W. B. *Chem. Ber.* **1975**, *108*, 1518. (c) Richler, W. Yamamoto, Y.; Schmidbaur, H. *Ibid.* **1977**, *110*, 1312.

[8] Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.

[9] Ruppert, I.; Bastian, V.; Appel, R. *Chem. Ber.* **1974**, *107*, 3426.

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dows) on a Perkin-Elmer 467 grating spectrophotometer, UV-visible spectra were recorded on a Cary 15 spectrophotometer, and ^{31}P NMR spectra were obtained with use of a Varian XL-200 spectrometer. The Raman spectrum of $Ph_3P{=}NS_3N$ was obtained on a powdered sample with use of a Jarrel-Ash Model 25-100 double monochromator with a Coherent Radiation Model CR-4 argon laser. Routine EI (70 ev) mass spectra were run on a Varian CH5 mass spectrometer. Chemical analyses were performed by M.H.W. Laboratories, Phoenix, AZ.

Preparation of $Ph_3As{=}NS_3N_3$.[10] **(a) From Triphenylarsine and S_4N_4.** Triphenylarsine (6.12 g, 20.0 mmol) and S_4N_4 (1.84 g, 10.0 mmol) were stirred together as a slurry in 10 mL of CH_2Cl_2 under an atmosphere of nitrogen. After 3 weeks, 200 mL of CH_2Cl_2 was added to the mixture to dissolve all the solid material. Ethanol (200 mL) was then added to the solution, which was slowly evaporated in vacuo, thereby producing bright orange-red microcrystals of $Ph_3As{=}NS_3N_3$ (3.70 g, 8.07 mmol, 81%). The product so obtained may be crystallized from CH_2Cl_2/CH_3CN as red prisms, which decompose with decrepitation ≥142 °C. The infrared spectrum of $Ph_3As{=}NS_3N_3$ (1600–250 cm^{-1}) shows bands at 1478 (w), 1439 (s), 1334 (w), 1310 (w), 1280 (vw), 1180 (w), 1069 (vw), 1022 (s), 1002 (m), 998 (m), 985 (vs), 935 (vs), 854 (vw), 843 (w), 749 (m), 741 (m), 733 (s), 690 (s), 648 (m), 624 (w), 500 (m), 482 (ms), 462 (ms), 453 (m), 395 (m), 338 (ms), 332 (m), and 301 (m) cm^{-1}. The UV-visible spectrum (in CH_2Cl_2) exhibits bands at 488 ($\epsilon \approx 4.0 \times 10^3$ L mol^{-1} cm^{-1}) and 336 nm ($\epsilon \approx 3.4 \times 10^3$ L mol^{-1} cm^{-1}).

(b) From $Ph_3As{=}NH$ and S_4N_4.[12] Solid S_4N_4 (1.15 g, 6.23 mmol) was added in one portion, under nitrogen, to a stirred solution of $Ph_3As{=}NH$ (3.00 g, 9.25 mmol) in 50 mL of acetonitrile. After a short induction time (~5 min) the solution turned deep red and a heavy orange precipitate formed. After this mixture was stirred for 24 h at room temperature, the orange solid was filtered from the solution, washed with 2 × 20 mL of CH_3CN, and recrystallized as described above (yield = 2.03 g, 4.43 mmol, 71% on the basis of S_4N_4).

Thermolysis of $Ph_3P{=}NS_3N_3$ in Acetonitrile. A slurry of $Ph_3P{=}NS_3N_3$ (2.00 g, 4.83 mmol) in 200 mL of acetonitrile was heated to reflux, producing an orange-red solution which rapidly deepened in color with continued heating. After 4 h at reflux, the solution was allowed to cool slowly to room temperature, whereupon a few crystals of c-S_8 were formed. These crystals (52 mg) were filtered off, and the filtrate was evaporated in vacuo to leave a gluey red residue. This paste was extracted with 3 × 50 mL of warm toluene, and the extracts were concentrated and eluted down a 700 × 35 mm Bio-Beads S-X8 column. The main cherry red fraction, which was preceded by a yellow-orange impurity, was reduced to dryness in vacuo to give a powdery red solid, which was recrystallized from 50 mL of hot acetonitrile as deep red crystals (with a green metallic luster) of $Ph_3P{=}NS_3N$, **2** (0.675 g, 1.75 mmol, 36%), mp 116–118 °C. The infrared spectrum of $Ph_3P{=}NS_3N$ (1600–250 cm^{-1}) shows bands at 1587 (vw), 1481 (w), 1438 (ms), 1435 (m), 1301 (vw), 1159 (vw), 1109 (vs), 1075 (vs), 1030 (w), 1026 (w), 998 (m), 917 (m), 855 (w), 847 (vw), 759 (m), 746 (ms), 724 (s), 690 (m), 668 (w), 591 (s), 550 (s), 527 (s), 497 (m), 467 (m), 397 (vw), 323 (m), and 282 (vw) cm^{-1}. Its UV-visible spectrum (in CH_2Cl_2) exhibits bands at 491 ($\epsilon \approx 1.4 \times 10^4$ L mol^{-1} cm^{-1}) and 314 nm ($\epsilon \approx 2.3 \times 10^3$ L mol^{-1} cm^{-1}). ^{31}P NMR spectrum ($CDCl_3$, external H_3PO_4): δ 23.1 (s).

Thermolysis of $Ph_3As{=}NS_3N_3$ in Acetonitrile. A slurry of $Ph_3As{=}NS_3N_3$ (0.500 g, 1.09 mmol) in 100 mL of acetonitrile was heated to a gentle reflux under an atmosphere of nitrogen. With continued heating over a period of 48 h, the wine red color of the solution slowly faded to a light orange, and the analysis (on silica, eluting solvent CH_2Cl_2/hexane (1:1)) showed the complete decomposition of the starting material into a mixture of S_4N_4, Ph_3AsS, and some Ph_3As and c-S_8. The solvent was then removed in vacuo, and the residue was extracted in 20 mL of warm toluene and eluted down a 35 × 400 mm Bio-Beads S-X8 column. Good separation of S_4N_4 from the other components was achieved, and upon evaporation of the S_4N_4 fraction, 0.099 g (0.54 mmol, 99%) of crystalline S_4N_4 (identified by its infrared spectrum) was obtained. The combined weight of the c-S_8, Ph_3As, and Ph_3AsS isolated amounted to 0.329 g (89% on the basis of a mass balance of Ph_3As and sulfur formed as in eq 3).

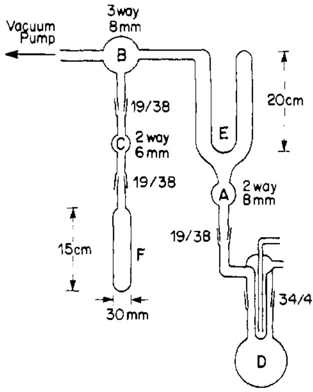

Figure 1. Apparatus used for the solid-state thermal decomposition of $Ph_3As{=}NS_3N_3$.

Solid-State Decomposition of $Ph_3As{=}NS_3N_3$.[13] The apparatus used for this reaction is shown in Figure 1. A vacuum of 10^{-3} torr was routinely obtained by connecting the apparatus to a standard mechanical pump connected in series with an oil diffusion pump. Because N_2 gas is evolved in the course of the thermolysis, the actual pressure of the apparatus during the thermolysis was undoubtedly greater than 10^{-3} torr, but we have no estimate of its exact value. In a typical experiment 2.00 g (4.37 mmol) of $Ph_3As{=}NS_3N_3$ (recrystallized from CH_2Cl_2/ethanol, dried in vacuo, and finely powdered) was added to the 100-mL flask (D) and the whole apparatus pumped down to 10^{-3} torr. Cooling water (~5 °C) was passed through the lower condenser, and liquid nitrogen was added to the upper cold finger (E). The thermolysis flask was then slowly heated by means of an oil bath to a bath temperature of 130–135 °C. A yellow crystalline sublimate soon appeared on the water-cooled condenser, and a pale yellow film slowly developed on the liquid-nitrogen finger (E). A magnetic stir bar which had been placed in the thermolysis flask was stirred occasionally in order to agitate the powdered $Ph_3As{=}NS_3N_3$ and promote efficient thermal contact with the walls of the flask. Over a period of approximately 12 h, all the $Ph_3As{=}NS_3N_3$ was consumed, leaving a yellow/pink sublimate on the water-cooled condenser and a tan film on the liquid-nitrogen finger. Tap A was then closed, and the liquid nitrogen in the cold finger was blown off with a stream of air. When most of the liquid nitrogen had evaporated, acetone was added to the finger producing a temperature of ca. −40 °C. Pumping was continued for about 30 min, during which time the volatile yellow impurities were rapidly removed, and the tan film was transformed into a greyish white micrycrystalline deposit of S_2N_2. When the temperature of the acetone was ca. −10 °C, tap B was closed off from the vacuum pump, and the cylindrical crystallization/polymerization flask was immersed in an ice bath. The acetone was then drawn off from the cold finger, which was allowed to warm to room temperature. Sublimation and crystallization of S_2N_2 into the ice-ccoled flask (F) was then allowed to proceed in a static vacuum for a period of 48 h. Final polymerization and annealing was carried out by closing tap C and leaving the S_2N_2 crystals at room temperature for 72 h and then by heating them in vacuo at 75 °C for 2 h. The lustrous golden crystals (1–3 mm in length) of $(SN)_x$ (yield 144 mg, 36%) prepared in this way are comparable to those obtained from the pyrolysis of S_4N_4.[13] Anal. Calcd for $(SN)_x$: S, 69.59; N, 30.41. Found: S, 69.33; N, 30.84 (C, 0.0; H, 0.0) $\sigma(300\ K) = 1 \times 10^3\ \Omega^{-1}\ cm^{-1}$; $\sigma(4\ K) = 14 \times 10^3\ \Omega^{-1}\ cm^{-1}$. The absence of S_4N_4 in the polymer was confirmed by analysis of its X-ray powder diffraction pattern.

The yellow/pink sublimate left on the water-cooled condenser was dissolved in CH_2Cl_2 and analyzed by TLC (on silica, eluting solvent

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[10] The reported procedure for preparing $Ph_3As{=}NS_3N_3$[11] cites the use of boiling benzene as a reaction solvent. While small quantities of the product can be obtained in this way, the elevated temperature causes considerable thermal degradation. We therefore describe herein two convenient high-yield methods for preparing this compound.

[11] Holt, E. M.; Watson, K. J. *J. Chem. Soc., Dalton Trans.* **1977**, 514.

[12] The mechanism of this reaction differs significantly from that involving $Ph_3P{=}NSiMe_3$ and S_4N_4.[9] Consistent with a mechanism involving a nucleophilic attack on S_4N_4, the reaction of $Ph_3P{=}^{14}NSiMe_3$ with $S_4{}^{15}N_4$ yields $Ph_3P{=}^{14}NS_3{}^{15}N_3$. By contrast, the reaction of $Ph_3As{=}^{14}NH$ with $S_4{}^{15}N_4$ leads to incorporation of ^{15}N into the exocyclic position. The possiblity of nitrene involvement is being investigated.

[13] The procedure for the purification, crystallization, and polymerization of S_2N_2 described in this experiment has been adapted from: Mikulski, C. M.; Russo, P. J.; Saran, M. S.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6358.

CH_2Cl_2/hexane, 1:1) and found to consist of c-S_8, Ph_3As, S_4N_4, and a small amount of Ph_3AsS. The mixture was partially separated by chromatography (as described above) to yield 241 mg (1.31 mmol, 60%) of S_4N_4 and 1.42 g (95%) of a mixture of c-S_8, Ph_3As, and Ph_3AsS (yields are based on a mass balance with use of the stoichiometry of eq 3 (a, b, or c)).

X-ray Measurements (at 22 ± 1 °C). Crystals of $Ph_3P{=}NS_3N$ suitable for X-ray work were obtained by slowly cooling a saturated solution in acetonitrile to 0 °C. The crystal used for all data collection was bounded by eight faces, parallel to the −1,1,2, −1,−1,2, 1,−1,0, −1,1,0, 1,1,0, −1,−1,0, 0,0,−1, and 3,0,−8 planes at face-to-center distances of 0.189, 0.189, 0.117, 0.117, 0.1035, 0.1035, 0.171, and 0.198 mm (all ±0.009 mm). The crystal was mounted on a glass fiber with the c axis parallel to the ϕ axis of the diffractometer. A least-squares refinement of 13 values of $(2 \sin \theta)/\lambda$ for 2θ values between 67 and 78° (λ(Cu Kα_1) = 1.5405 Å) gave cell constants for $S_3N_2PC_{18}H_{15}$ (fw = 386.49) of a = 12.573 (1) Å, b = 11.170 (1) Å, c = 14.816 (2) Å, β = 115.96 (1)°, V = 1872.2 Å^3, and D_{calcd}(for Z = 4) = 1.37 g cm^{-3}. The space group is $P2_1/c$.

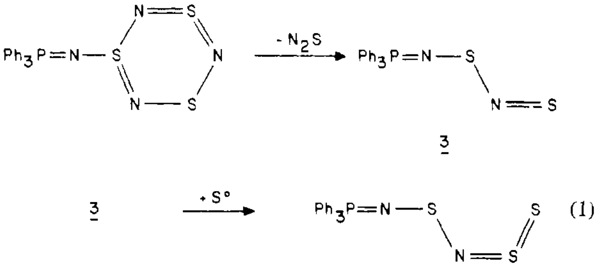
A GE XRD-5 manually operated quarter-circle diffractometer was used with Ni-filtered Cu Kα (λ = 1.5418 Å) radiation. For the intensity data a θ–2θ scan of 2° in 2θ was made at a speed of 2° min^{-1}; 10-s background counts were made at each end of the scan. A total of 2068 reflections ($2\theta < 100°$) were scanned, and 1772 ($I > 3\sigma(I)$) were used for the solution of the structure. Twenty-five of the strongest reflections were subsequently excluded from the refinement because they had obviously saturated the scintillation counter, and five were removed because of human error in the manual data collection. Two reflections, measured periodically during the 5-day data collection, indicated a nonlinear decay which could be approximated by a series of four linear decay curves. A simple correction was made for each of the four regions of the data set; the total decay was less than 10%. The crystal has a μ value of 32.2 cm^{-1}, and absorption correction with summation points every 0.0035 cm gave a range of intensity correction factors from 0.74 to 0.67.

The structure was solved by symbolic addition methods and refined by Fourier (local version of FORDAP) and full-matrix least-squares (local versions of ORFLS) techniques. Neutral-atom scattering factors were taken from ref 14, and real and imaginary anomalous dispersion corrections were made for phosphorus and sulfur.[15] Least-squares weights of $w = 1/(2F_{min} + F_o + 2F_o^2/F_{max})$ for the 1747-reflection, 217-parameter full-matrix refinement gave a final R = 0.040, R_w = 0.062, and a standard deviation of an observation of unit weight of 0.56 and showed no dependence of $\Delta F/\sigma(F)$ on either F or $\sin \theta$. The final refinement included 15 phenyl hydrogen atoms located at calculated positions (C–H = 0.95 Å, isotropic B = 5.0) for the calculation of the structure factors, but these positions and thermal factors were not refined. A final difference map showed no peaks greater than 0.2 e Å^{-3}. A listing of observed and calculated structure factors and tables containing the anisotropic thermal parameters of all the atoms and the bond length and valence angle information related to the phenyl carbon atoms are available as supplementary material.

Results and Discussion

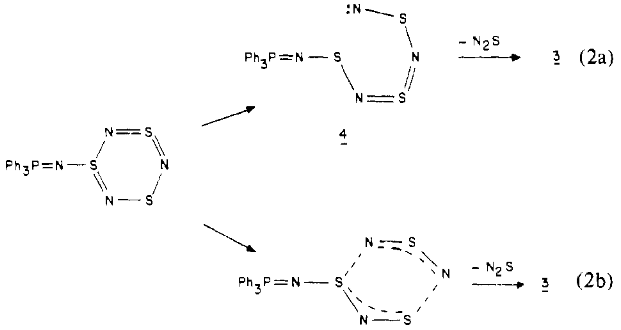
Thermolysis of $Ph_3E{=}NS_3N_3$ (E = P, As). During our studies of the reductive degradation of S_4N_4 with triphenylphosphine,[16] we had often noted the presence of a deep red pigment which intensified on heating. The analysis of these solutions also indicated the presence of a deeply colored component which was not $Ph_3P{=}NS_3N_3$, but attempts to isolate it were unsuccessful. However, on the basis of our experience with the thermal interconversions of the anions $S_4N_5^-$, $S_3N_3^-$, and S_4N^-,[4] it occurred to us that this red pigment might also be the product of a thermolytic transformation. Examination of the thermolysis of $Ph_3P{=}NS_3N_3$ in acetonitrile showed this supposition to be correct, the initially orange solution being converted over a period of several hours into a deep red solution. Subsequent workup of this solution afforded dark red crystals of $Ph_3P{=}NSN{=}S{=}S$ (**2**).

The formation of **2** can be regarded on a simple basis as the result of a two-step process, the first involving the loss of an NSN fragment from the cyclotrithiazene ring to yield an open-chain intermediate (**3**, eq 1). Empirically the reaction



closely resembles the decomposition pathways followed by the $S_4N_5^-$ and $S_3N_3^-$ ions[4] and the open-chain trithiadiazene $C_6F_5SN{=}S{=}NSC_6F_5$,[17] all of which proceed via the elimination of N_2S. The second step can be viewed as the reaction of elemental sulfur (formed by the rapid in situ disproportionation of N_2S) with **3**. This latter step corresponds to that proposed for the conversion of $S_3N_3^-$ to S_4N^- and stresses the importance of the SN=S=S group as a structural unit in the products of the thermal degradation of SN compounds.[18]

While eq 1 provides a framework for rationalizing the formation of **2**, several questions remain unanswered. For example, the manner in which the NSN moiety is eliminated from the S_3N_3 ring may be stepwise (eq 2a) or concerted (eq



2b). In the former case an open-chain nitrene (**4**) is produced, the same intermediate as we proposed in the formation of $Ph_3P{=}NS_3N_3$ from the reaction of S_4N_4 with triphenylphosphine.[16] The concerted route cannot rigorously be regarded as a symmetrical process (as it is in the elimination of N_2S from $S_4N_5^-$ and $S_3N_3^-$), but it has been pointed out by Laidlaw and Trsic[19] that under such circumstances (an asymmetric elimination) the disproporitionation of NSN to N_2 and S^0 could be very rapid.[20]

The thermolysis of $Ph_3As{=}NS_3N_3$ is significantly different from that of its phosphorus analogue. In acetonitrile solution, no equivalent of **2** is formed. Instead, the products are S_4N_4, triphenylarsine, c-S_8, and triphenylarsine sulfide. At least on an empirical level this result can be rationalized with the use of a reaction mechanism similar to that described above. Thus

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(14) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(15) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 7.

(16) (a) Bojes, J.; Chivers, T.; MacLean, G.; Oakley, R. T.; Cordes, A. W. *Can. J. Chem.* **1979**, *57*, 3171. (b) Bojes, J.; Chivers, T.; Cordes, A. W.; MacLean, G.; Oakley, R. T. *Inorg. Chem.* **1981**, *20*, 16.

(17) Golloch, A.; Kuss, M. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1972**, *27B*, 1280.

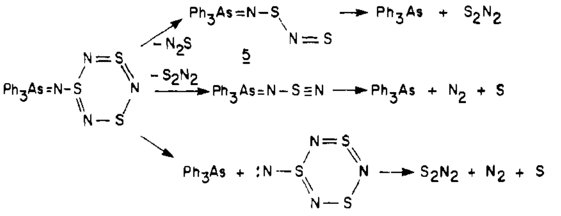
(18) It is also interesting to note that previous ESR studies on the solid-state decomposition of $Ph_3P{=}NS_3N_3$[9] indicated the formation of a free-radical species whose structure was proposed to be N_2S^- (although the sulfur content of the radical was not established). Competing disproportionation reaction are obviously important; in our own solution work small quantities of the S_4N^- ion were observed in addition to **2**.

(19) Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1981**, *20*, 1792.

(20) Our attempts to observe the NSN molecule in the gas phase have been unsuccessful. Quadrupole mass spectroscopic studies[21] of the vapors produced by heating $Ph_3P{=}NS_3N_3$ to 100 °C show only nitrogen molecules and sulfur atoms.

(21) Westwood, N. P. C., private communication.

the degradation can be viewed as beginning with the expulsion of an N_2S fragment from the S_3N_3 ring to yield an open-chain intermediate (**5**, eq 3a). In contrast to its phosphorus counterpart (**3**) this species immediately eliminates S_2N_2 which, in solution and in the presence of triphenylarsine, spontaneously dimerizes to S_4N_4.[22] The different thermal stabilities of **3** and **5** can be attributed to the relative weakness of the As=N bond in the latter. A comparison of the parent cyclotrithiazene structures **1** (E = P, As) demonstrates the point; in $Ph_3P{=}NS_3N_3$[23] the P=N bond (1.645 Å) is significantly shorter than a P—N single bond (e.g., 1.77 Å in $PO_3NH_3^-$[24]), whereas the As=N distance in $Ph_3As{=}NS_3N_3$[11] (1.837 Å) approaches the single bond value of 1.87 Å.[25]



(3a)

(3b)

(3c)

The above interpretation is not unique. Other decomposition pathways such as those depicted in eq 3b,c are equally plausible, but on the basis of our present evidence, we cannot differentiate between them. However, regardless of the order of their elimination, the two principal sulfur–nitrogen fragments of the reaction are NSN (as N_2 and S^0) and S_2N_2. This conclusion has important consequences, since the present decomposition represents the first reported example of an uncatalyzed thermolysis which produces S_2N_2. Although the conventional route to S_2N_2 (from S_4N_4 over silver wool)[2] can undoubtedly be optimized in terms of S_2N_2 formation, it is a potentially hazardous procedure which is not particularly amenable to large scale preparations. It is therefore surprising that simpler alternative routes to S_2N_2 have not been developed. Recently, Banister and co-workers reported the isolation of S_2N_2 by cracking S_4N_3Cl over silver wool, but here again both a catalyst and high temperatures (ca. 300 °C) were necessary.[26]

We have therefore investigated the vacuum-line thermolysis of $Ph_3As{=}NS_3N_3$ in order to assess the usefulness of the reaction as a synthetic route to S_2N_2. Our results indicate that, while the decomposition to S_2N_2 is a remarkably specific process (yield = 96% measured in the form of $(SN)_x$ and S_4N_4), dimerization of the product to S_4N_4 is a competing side reaction, the extent of which is pressure dependent. For example, mass spectroscopic studies have shown that, when the thermolysis is carried out at 10^{-6} torr, vaporization (at a probe temperature of 85 °C) precedes decomposition, and no S_4N_4 is produced.[27] However, in our synethetic work a higher pressure of ca. 10^{-3} torr has been used, and under these conditions a temperature of 130–135 °C is necessary to induce decomposition at a reasonable rate.[28] Because the thermolysis takes place in the solid state rather than in the gas phase, surface reactions are appreciable and cause the dimerization of more than half the S_2N_2 produced. Nonetheless, despite the lowered yield of the dimer, the method appears to be both reliable and convenient, and the S_2N_2 formed is relatively free of the contaminants[3] so often found in other methods. The purification and polymerization of the S_2N_2 to $(SN)_x$ with use

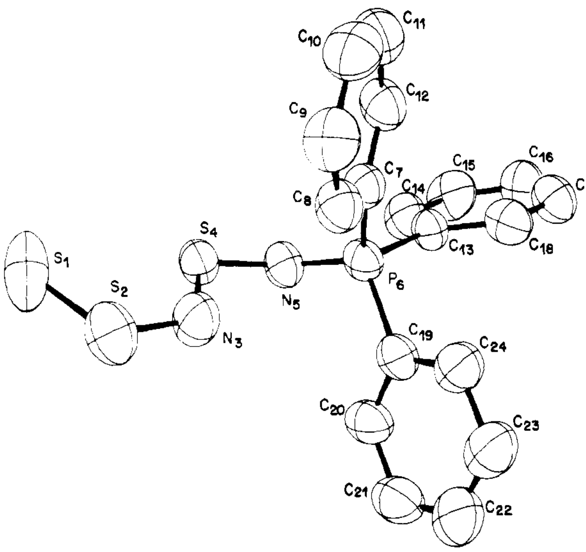


Figure 2. ORTEP drawing (50% probability ellipsoids) of the $Ph_3P{=}NS_3N$ molecule, showing the atomic numbering scheme.

Table I. Final Positional Parameters for $Ph_3P{=}NS_3N$ ($\times 10^4$) with Esd's in Parentheses

atom	*x*	*y*	*z*
S(1)	1258 (1)	10859 (1)	−2762 (1)
S(2)	1022 (1)	9181 (1)	−2703 (1)
N(3)	1974 (3)	8618 (3)	−1681 (2)
S(4)	2947 (1)	9431 (1)	−851 (1)
N(5)	3761 (2)	8577 (3)	64 (2)
P(6)	3256 (1)	7546 (1)	516 (1)
C(7)	1920 (3)	7938 (3)	609 (2)
C(8)	823 (3)	7761 (4)	−183 (3)
C(9)	−186 (3)	8166 (4)	−137 (3)
C(10)	−101 (4)	8743 (4)	711 (4)
C(11)	984 (4)	8933 (4)	1506 (3)
C(12)	2004 (3)	8539 (4)	1463 (3)
C(13)	4403 (3)	7278 (3)	1761 (2)
C(14)	5425 (4)	7947 (4)	2133 (3)
C(15)	6300 (4)	7745 (4)	3089 (4)
C(16)	6151 (4)	6888 (4)	3677 (3)
C(17)	5157 (4)	6202 (4)	3315 (3)
C(18)	4281 (3)	6386 (4)	2359 (3)
C(19)	3002 (3)	6152 (3)	−165 (2)
C(20)	3636 (3)	5947 (4)	−714 (3)
C(21)	3517 (5)	4855 (5)	−1196 (3)
C(22)	2771 (5)	3996 (4)	−1141 (4)
C(23)	2140 (4)	4196 (4)	−599 (3)
C(24)	2255 (4)	5280 (4)	−104 (3)

Table II. Selected Interatomic Distances (Å) and Angles (Deg) for $Ph_3P{=}NS_3N$ with Esd's in Parentheses

atoms	dist	atoms	angle
S(1)-S(2)	1.908 (2)	S(1)-S(2)-N(3)	111.4 (2)
S(2)-N(3)	1.592 (4)	S(2)-N(3)-S(4)	120.9 (2)
N(3)-S(4)	1.587 (4)	N(3)-S(4)-N(5)	107.7 (2)
S(4)-N(5)	1.607 (4)	S(4)-N(5)-P(6)	124.0 (2)
N(5)-P(6)	1.598 (3)	N(5)-P(6)-C(7)	114.3 (2)
P(6)-C(7)	1.799 (4)	N(5)-P(6)-C(13)	105.2 (2)
P(6)-C(13)	1.800 (5)	N(5)-P(6)-C(19)	113.2 (2)
P(6)-C(19)	1.807 (4)	C(7)-P(6)-C(13)	108.6 (2)
S(1)-S(4)	3.131 (2)	C(7)-P(6)-C(19)	108.1 (2)
		C(13)-P(6)-C(19)	

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[22] As is observed generally when solutions of S_2N_2 are exposed to nucleophiles. See, for example: Becke-Goehring, M. *Adv. Inorg. Chem. Radiochem.* **1960**, *2*, 169.

[23] Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1357.

[24] (a) Hobbs, E.; Corbridge, D. E. C.; Raistrick, B. *Acta Crystallogr.* **1953**, *6*, 621. (b) Cruickshank, D. W. J. *Ibid.* **1964**, *17*, 671.

[25] Weiss, J.; Eisenhuth, W. *Z. Anorg. Allg. Chem.* **1967**, *350*, 9.

[26] Banister, A. J.; Hauptmann, Z. V. *J. Chem. Soc., Dalton Trans.* **1980**, 731.

[27] As in the mass spectrum of $Ph_3P{=}NS_3N_3$,[10] no parent ion is observed for $Ph_3As{=}NS_3N_3$. The largest mass fragment observed is Ph_3As^+, which is also the base peak.

[28] Even when heated excessively (e. g., above its melting point of 142 °C) the decomposition of $Ph_3As{=}NS_3N_3$ is not violent. Nonetheless we recommend that proper precautionary measures be taken when carrying out this thermolysis.

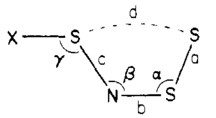
Table III. Structural Parameters of the XSN=S=S Unit in Various Molecules[a]

structural parameter	X		
	S	$Ph_3P=N$	pip[b]
a	1.914 (3)	1.908 (2)	1.912 (3)
b	1.625 (5)	1.592 (4)	1.569 (7)
c	1.572 (6)	1.587 (4)	1.657 (6)
d	3.141 (3)	3.131 (2)	3.194
mean SN	1.598	1.590	1.613
α	111.0 (3)	111.4 (2)	114.9 (1)
β	120.5 (4)	120.9 (2)	119.2 (4)
γ	110.5 (3)	107.7 (2)	105.7 (1)

[a] *a-d* refer to the bond lengths (Å) and α, β, and γ to the bond angles (deg) shown in 6. [b] pip refers to the substituted piperidine in 7.

of standard procedures affords lustrous crystals of the polymer which have conductivity characteristics (see Experimental Section) within the limits reported elsewhere.[2,29]

Molecular Structure of $Ph_3P=NS_3N$. The crystal structure of **2** consists of discrete molecules of $Ph_3P=NS_3N$, the molecular structure of which is shown in Figure 2. The atomic coordinates of all the atoms are given in Table I, and pertinent bond lengths and angles are presented in Table II. The molecule consists of an open-chain PNSNSS sequence, the nitrogen and sulfur atoms all being coplanar to within 0.04 Å. The phosphorus atom is rotated away from this plane, producing an N(3)-S(4)-N(5)-P(6) torsion angle of 136.4 (3)°. Such a structural unit, with a "sickle-shaped" cis-trans configuration of the XS_3N group (see **6**) is also observed in the S_4N^- anion and in another neutral amino derivative (**7**).[4,30,31] The principal structural parameters of the XS_3N unit in these three molecules are shown for comparison in Table III. The short terminal S=S bonds suggest significant multiple-bond character (cf. 1.860 Å in $S=SF_2$,[32] 1.882 Å in S_2O,[33] and 1.828 Å in $S_2I_4^{2+}$ [34]), and recent Hartree-Fock-Slater SCF calculations on the S_4N^- anion indicate a bond order equivalent to $^5/_4\sigma$ plus $^1/_4\pi$.[4b] Although the mean S=N distances in all three molecules are similar, the individual values vary considerably. In **2** the two SN bonds are almost equal, whereas in **7** and S_4N^- they diverge significantly from their mean, the difference being in opposite senses. The calculated energy difference between S_4N^- structures containing equal and unequal bond lengths has been estimated at less than 10 kcal mol^{-1}, so the existence of all three structural possibilities for the XS_3N system ($b \simeq c$ in **2**, $b > c$ in S_4N^- and $b < c$ in **7**) is not remarkable. The infrared spectrum of **2** is relatively complex (see Experimental Section), but the Raman spectrum is simple and shows three strong bands characteristic of the SN=S=S group: ν(S=S) = 589 cm^{-1}, ν(S=N) = 722 and 921 cm^{-1}. In the Raman spectrum of S_4N^-,[4] these vibrations are observed at 592, 710, and 892 cm^{-1}, and in S_3N^- [35] they occur at 576, 686, and 896 cm^{-1}. The ν(P=N) band in the infrared spectrum of **2** occurs at 1075 cm^{-1}, similar to the value of 1081 cm^{-1} in $Ph_3P=NS_3N_3$. By contrast, the P=N bond distances differ significantly (1.598 (3) and 1.645 (10) Å[23]), the length of **2** being more nearly equal to the mean P=N distance of 1.59 Å found in $(Ph_3P=N)_2S_4N_4$.[26]



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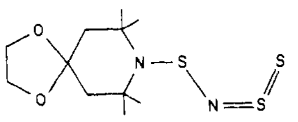

7

Conclusion

The results of this work provide a basis for understanding the mechanisms of the thermal decomposition of conjugated SN rings and chains. The loss of the N_2S fragment is particularly prevalent in the systems studied thus far, and this finding rekindles speculation on the possible existence of such a species.[36,37] The decomposition pathway involving the elimination of S_2N_2 from $Ph_3As=NS_3N_3$ under relatively mild conditions is perhaps of greater significance. In this reaction the experimental conditions have been adjusted to provide a convenient method for producing S_2N_2 in small quantities. It is likely that further work on the thermochemistry of other conjugated SN molecules will yield even more efficient routes for the large scale synthesis of S_2N_2 and hence $(SN)_x$.

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Registry No. $Ph_3P=NS_3N$, 73845-61-1; $Ph_3P=NS_3N_3$, 33082-06-3; $Ph_3As=NS_3N_3$, 63212-45-3; Ph_3As, 603-32-7; S_4N_4, 28950-34-7; $Ph_3As=NH$, 24507-56-0; S_2N_2, 25474-92-4; $(SN)_x$, 56422-03-8.

Supplementary Material Available: A listing of the calculated and observed structure factors for $Ph_3P=NS_3N$, Table S1 giving the thermal parameters for the $Ph_3P=NS_3N$ structure, and Table S2 giving the bond distances and angles within the phenyl groups (11 pages). Ordering information is given on any current masthead page.

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(31) The structural parameters quoted for the S_4N^- ion have been adjusted following a rerefinement of the original data set: Chivers, T.; Cordes, A. W.; Oakley, R. T.; Swepston, P. N., to be published.

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