

Bu_3PCuI_4 , was prepared by standard methods.⁴² All reactions were carried out under an atmosphere of dry nitrogen.

Synthesis of Metallophosphazenes II. The syntheses of the metallophosphazenes II were all carried out in an identical manner; the following procedure is typical. Hexachlorocyclotriphosphazene (I, 5.0 g, 0.014 mol) and $[\text{n-Bu}_3\text{PCuI}]_4$ (4.0 g, 0.0025 mol) were stirred together in THF (150 mL) at -80°C . The Grignard reagent (25 mL of a 3 M solution in THF or ether) was added dropwise over a period of ≈ 30 min. The reaction mixture was then stirred for 16 h, and the temperature was allowed to rise slowly to $\approx 25^\circ\text{C}$. These complexes II were not isolated but were allowed to react with alkyl halides, as described in the next section.

Reaction of II with Alkyl Halides. Initially, all the reactions listed in Table VI were monitored by ^{31}P NMR spectroscopy. A 3-mL aliquot of the solution in THF, prepared as previously described, was withdrawn under a blanket of dry nitrogen and introduced into a nitrogen-filled NMR tube. The alkyl halide (2 mL) was then added carefully and the mixture allowed to stand for 25 h. At the end of this time, the ^{31}P NMR of the mixture was scanned. A spectrum such as that in part a in Figure 1 indicated that no reaction had taken place. A spectral pattern as shown in spectrum d in Figure 1 indicated that a reaction had occurred. Only when a reaction was observed by ^{31}P NMR monitoring, was that reaction repeated on a large scale and were the products isolated. This was done in the following manner.

Isolation of Products. A solution of II in THF, prepared as described previously, was cooled to 0°C and the alkyl halide (0.07 mol) added dropwise over ≈ 30 min. This mixture was stirred for 48 h, and the temperature was allowed to rise to 25°C . The solvent was then removed under reduced pressure, and the products were dissolved in toluene (250 mL). The organic layer was then washed with aqueous HCl (10% solution, 250 mL) and dried over MgSO_4 , and the solvent was removed under reduced pressure to leave the crude product. This

was purified by filtration of a solution in CH_2Cl_2 through neutral alumina, followed by recrystallization from hexane to leave the product as white crystals.

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Registry No. I, 940-71-6; II (R = CH_3), 75083-25-9; II (R = C_2H_5), 75083-26-0; II (R = $n\text{-C}_3\text{H}_7$), 75083-27-1; II (R = $n\text{-C}_4\text{H}_9$), 75083-28-2; II (R = $i\text{-C}_3\text{H}_7$), 75083-29-3; II (R = $i\text{-C}_4\text{H}_9$), 75083-30-6; II (R = $t\text{-C}_4\text{H}_9$), 75083-31-7; II (R = C_3H_5), 75083-32-8; III (R = R' = CH_3), 6204-32-6; III (R = CH_3 , R' = C_2H_5), 72474-25-0; III (R = CH_3 , R' = $n\text{-C}_3\text{H}_7$), 72474-26-1; III (R = CH_3 , R' = $n\text{-C}_4\text{H}_9$), 72474-27-2; III (R = CH_3 , R' = $i\text{-C}_3\text{H}_7$), 72474-28-3; III (R = CH_3 , R' = $i\text{-C}_4\text{H}_9$), 75067-44-6; III (R = CH_3 , R' = $t\text{-C}_4\text{H}_9$), 72474-20-5; III (R = R' = C_2H_5), 75067-45-7; III (R = C_2H_5 , R' = $n\text{-C}_3\text{H}_7$), 75067-46-8; III (R = C_2H_5 , R' = $n\text{-C}_4\text{H}_9$), 75067-47-9; III (R = C_2H_5 , R' = $i\text{-C}_3\text{H}_7$), 75067-48-0; III (R = C_2H_5 , R' = $i\text{-C}_4\text{H}_9$), 75067-49-1; III (R = C_2H_5 , R' = $t\text{-C}_4\text{H}_9$), 75067-50-4; III (R = R' = $n\text{-C}_3\text{H}_7$), 75067-51-5; III (R = $n\text{-C}_3\text{H}_7$, R' = $n\text{-C}_4\text{H}_9$), 75067-52-6; III (R = $n\text{-C}_3\text{H}_7$, R' = $i\text{-C}_3\text{H}_7$), 75067-53-7; III (R = $n\text{-C}_3\text{H}_7$, R' = $i\text{-C}_4\text{H}_9$), 75067-54-8; III (R = $n\text{-C}_3\text{H}_7$, R' = $t\text{-C}_4\text{H}_9$), 75067-55-9; III (R = R' = $n\text{-C}_4\text{H}_9$), 75082-97-2; III (R = $n\text{-C}_4\text{H}_9$, R' = $i\text{-C}_3\text{H}_7$), 75067-56-0; III (R = $n\text{-C}_4\text{H}_9$, R' = $i\text{-C}_4\text{H}_9$), 75067-57-1; III (R = $n\text{-C}_4\text{H}_9$, R' = $t\text{-C}_4\text{H}_9$), 75067-58-2; III (R = C_3H_5 , R' = CH_3), 72474-22-7; III (R = C_3H_5 , R' = C_2H_5), 75067-59-3; III (R = C_3H_5 , R' = $n\text{-C}_3\text{H}_7$), 75067-60-6; III (R = C_3H_5 , R' = $n\text{-C}_4\text{H}_9$), 75067-61-7; III (R = C_3H_5 , R' = $i\text{-C}_3\text{H}_7$), 72474-29-4; III (R = C_3H_5 , R' = $i\text{-C}_4\text{H}_9$), 75067-62-8; III (R = C_3H_5 , R' = $t\text{-C}_4\text{H}_9$), 72474-21-6; III (R = R' = C_3H_5), 72474-23-8; CH_3I , 74-88-4; $\text{C}_2\text{H}_5\text{I}$, 75-03-6; $n\text{-C}_3\text{H}_7\text{I}$, 107-08-4; $n\text{-C}_4\text{H}_9\text{I}$, 542-69-8; $\text{C}_3\text{H}_5\text{Br}$, 106-95-6; $[\text{n-Bu}_3\text{PCuI}]_4$, 28132-72-1.

Supplementary Material Available: Table II, dialkylphosphazene infrared data, Table IV, dialkylphosphazene ^1H NMR data, and Table V, dialkylphosphazene ^{13}C NMR data (26 pages). Ordering information is given on any current masthead page.

(42) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* 1963, 7, 9.

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Reaction of Triphenylphosphine with Tetrasulfur Tetranitride: Synthesis and Structure of 1,5-Bis(triphenylphosphinimino)cyclotetrathiazene, $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$

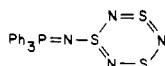
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The reaction of triphenylphosphine with S_4N_4 in acetonitrile yields 1,5-bis(triphenylphosphinimino)cyclotetrathiazene, $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$, as well as smaller amounts of the tetrasulfur pentanitride salt of the tris(triphenylphosphinimino)sulfonium cation, $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+$. The crystal and molecular structure of $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ has been determined by single-crystal X-ray diffraction. The crystals of $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ are monoclinic, of space group $P2_1/c$, with $a = 10.306$ (1) Å, $b = 19.473$ (5) Å, $c = 17.804$ (1) Å, $\beta = 94.03(1)^\circ$, $V = 3564.1$ Å³, $Z = 4$, and $D_{\text{calc}} = 1.37$ g cm⁻³. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final $R = 0.043$ and $R_w = 0.060$ for 3303 reflections with $I > 3\sigma(I)$. The structure consists of a 1,5-disubstituted S_4N_4 cage, the two exocyclic triphenylphosphinimino ligands being oriented in equatorial and axial directions, with the mean $d(\text{P}-\text{N}) = 1.592$ Å and $\angle\text{P}-\text{N}-\text{S} = 122.6^\circ$. The asymmetry of the ligand orientation distorts the S_4N_4 unit from the ideal C_{2v} symmetry. The otherwise symmetry-related S-N bonds fall into two classes: (i) $d(\text{S}-\text{N}) = 1.630$ (4)–1.675 (4) Å and (ii) $d(\text{S}-\text{N}) = 1.583$ (4)–1.613 (4) Å. The substituted sulfur atoms are separated by 3.727 (2) Å, but the two unsubstituted sulfurs remain only 2.452 (2) Å apart, indicating significant σ bonding between these two atoms.

Introduction

The reaction of triphenylphosphine with tetrasulfur tetranitride was first reported in 1961 by Krauss and Jung, who described the preparation of triphenylphosphinimino-cyclotetrathiazene, $\text{Ph}_3\text{P}=\text{N}-\text{S}_3\text{N}_3$ (1), in 11% yield.² This compound



1

had been described earlier by Fluck, Becke-Goehring, and Dehoust,³ who isolated it in low yield as a side product of the reaction of triphenylphosphine ylide and S_4N_4 . No attempt was made at the time to rationalize the formation of 1, nor were any other products (apart from Ph_3PS) observed. Later, however, Fluck and Reinisch examined the reaction of PhPCl_2 with S_4N_4 ,⁴ and although they were unable to isolate any sulfur-containing compound, they did suggest a mechanism

(2) Krauss, H.-L.; Jung, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1961, 16B, 624.

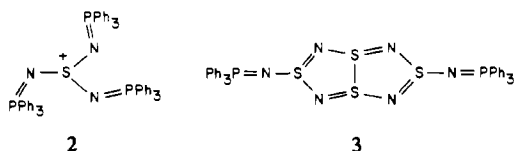
(3) Fluck, E.; Becke-Goehring, M.; Dehoust, G. *Chem. Ber.* 1961, 312, 60.

(4) Fluck, E.; Reinisch, R. M. *Z. Anorg. Allg. Chem.* 1964, 328, 165.

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involving nucleophilic attack by the phosphine on S_4N_4 , followed by ring opening to give, as an intermediate, the α,ω -diphosphiniminotrithiadiazene $Cl_2PhP=NSN=S=NSN=PPhCl_2$. Their proposal was based in part on the observation of a similar open-chain compound during the reaction of S_4N_4 with organic diazo compounds.⁵ The molecular structure of **1** was confirmed by Holt and Holt in 1970,⁶ but since that time no further work on the reaction has been reported.

Recent results from our laboratory on the nucleophilic degradation of S_4N_4 have demonstrated that, regardless of the nucleophile employed, the principal products of such reactions are the $S_4N_5^-$ and $S_3N_3^-$ anions.⁷ The apparent discrepancy between our findings and those of Krauss and Jung prompted us to reinvestigate the reaction of S_4N_4 with triphenylphosphine. We have found that, in agreement with our earlier conclusions, the $S_4N_5^-$ anion is also formed in this reaction, as the salt of the novel sulfonium cation $(Ph_3P=N)_3S^+$ (**2**). Of more significance, however, is the fact that when the reaction is carried out in acetonitrile, as opposed to benzene, the major reaction product is 1,5-bis(triphenylphosphinimino)-cyclotetrathiazene, $(Ph_3P=N)_2S_4N_4$ (**3**), the first 1,5-disub-



stituted S_4N_4 ring.⁸ Herein we provide a full account of the preparation of **1-3** from the reaction of triphenylphosphine with S_4N_4 and describe the crystal and molecular structure of **3**.¹⁰

Experimental Section

Reagents and General Procedures. Tetrasulfur tetranitride,¹¹ *N*-(trimethylsilyl)triphenylphosphinimine,¹² and tetra-*n*-butylammonium tetrasulfur pentanitride¹³ were all prepared according to literature methods. Triphenylphosphine (Baker) and sulfur dichloride (Ventron) were commercial products. The former was purified by recrystallization from ethanol; the latter, by distillation in the presence of PCl_3 . All the solvents employed were of reagent grade, and all were dried before use: benzene by distillation from calcium hydride, acetonitrile by distillation from P_2O_5 followed by distillation from calcium hydride, and dichloromethane (for spectroscopic work) and dichloroethane by distillation from P_2O_5 . All distillations of solvents and all reactions were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox and silica gel. Infrared spectra ($4000-250\text{ cm}^{-1}$) were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. UV-visible spectra were obtained with use of a Cary 15 spectrophotometer. Chemical analyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Müllheim, West Germany, and by MHW Laboratories, Phoenix, AZ.

Reaction of Triphenylphosphine with S_4N_4 in Benzene. Tetrasulfur tetranitride (1.50 g, 8.15 mmol) was added to a solution of triphenylphosphine (4.26 g, 16.3 mmol) in 100 mL of benzene, and the resulting mixture was stirred at room temperature under an atmosphere

of nitrogen. After ca. 15 min an orange-red color was generated, and after ca. 2 h the color had darkened to a wine red and a flocculent orange-yellow precipitate was present. After 24 h the mixture was filtered and the insoluble solid washed with $2 \times 20\text{ mL}$ of benzene and sucked dry. This solid was recrystallized by slow evaporation of a CH_2Cl_2 /methanol solution to give pale yellow needles of $(Ph_3P=N)_3S^+S_4N_5^-$ (**2**) (1.00 g, 0.91 mmol, 23% yield based on nitrogen), which slowly darken to a gray-brown color on heating above $120\text{ }^\circ\text{C}$ and melt to a dark blue liquid at $172-174\text{ }^\circ\text{C}$. Anal. Calcd for $C_{54}H_{45}N_8P_3S_5$: C, 61.23; H, 4.28; N, 10.58; P, 8.77; S, 15.13. Found: C, 61.03; H, 4.20; N, 10.80; P, 8.06; S, 16.06. The infrared spectrum of **2** ($1600-250\text{-cm}^{-1}$ region) shows bands at 1588 w , 1482 w , 1439 s , 1339 vw , 1315 w , 1188 vw , 1182 w , 1160 w , 1115 vs , 1055 vs , 1025 m , 998 m , 956 s^* , 916 m^* , 860 w , 781 m , 754 m , 722 s , 693 s , 665 vw^* , 647 w^* , 618 w^* , 600 w^* , 543 s , 501 m , 457 w , 438 m^* , 415 w , 405 vw , 358 vw , and $300\text{ w}^*\text{ cm}^{-1}$ (bands labeled with an asterisk are assigned to vibrations of the $S_4N_5^-$ anion^{7a,c,13}). The UV-visible spectrum of **2** (in CH_2Cl_2) shows bands at $\sim 345\text{ nm}$ (sh) ($\epsilon \sim 3.3 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$) and $<290\text{ nm}$ (actual λ_{max} obscured by $\pi \rightarrow \pi^*$ transition on phenyl rings).

Evaporation of the original filtrate gave a dark red crystalline mass, which was transferred to a Soxhlet extractor and extracted with 300 mL of ether for 24 h. Evaporation of the ether extracts then yielded a crystalline mixture of Ph_3PS and $Ph_3P=NS_3N_3$ **1** (combined weight 3.60 g), from which the latter was separated by washing the solid mixture with the minimum quantity ($2 \times 100\text{ mL}$) of acetonitrile necessary to dissolve away the Ph_3PS . The crude $Ph_3P=NS_3N_3$ (1.00 g, 2.40 mmol, 29%) was recrystallized from CH_2Cl_2 /acetonitrile as dark orange prisms which darken on heating $>125^\circ$ and melt to a deep red liquid at $130\text{ }^\circ\text{C}$ (lit.² mp $128\text{ }^\circ\text{C}$). The infrared spectrum is consistent with that reported earlier.¹⁴ The UV-visible spectrum (in CH_2Cl_2) shows bands at 478 nm ($\epsilon \sim 4.4 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$) and 330 nm ($\epsilon \sim 3.7 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$) [lit.^{2,3} λ_{max} 485 nm ($\epsilon 5.4 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$)].

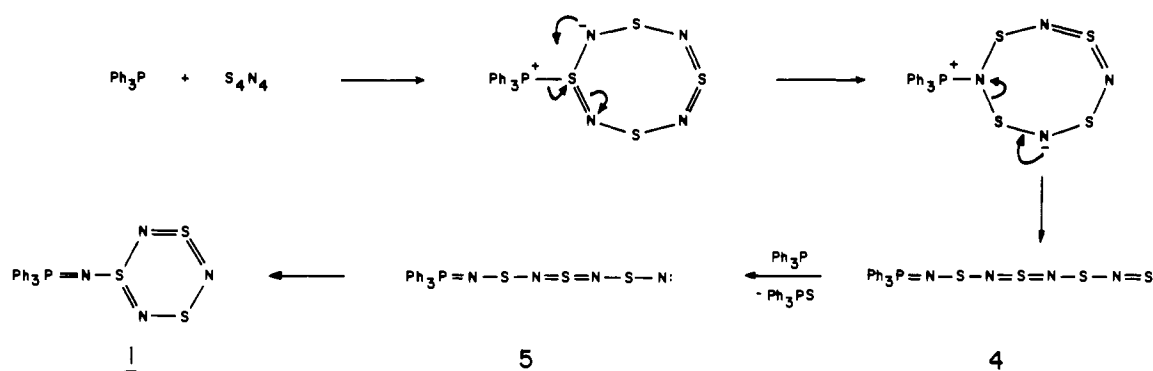
Reaction of Triphenylphosphine with S_4N_4 in Acetonitrile. Tetrasulfur tetranitride (1.00 g, 5.43 mmol) and triphenylphosphine (2.85 g, 10.9 mmol) were added, as solids, to 60 mL of acetonitrile, and the slurry so formed was stirred vigorously at room temperature under an atmosphere of nitrogen. As the S_4N_4 slowly dissolved, a red color was generated in the solution and, after 2-3 h, a salmon-pink precipitate began to form. After 24 h the orange solution was filtered from the solid material, and the latter was transferred to a beaker and thoroughly washed with $5 \times 100\text{ mL}$ of ether (until the extracts were colorless). The ether-insoluble part (1.57 g) was then further extracted with $5 \times 100\text{ mL}$ of acetonitrile (until the extracts were colorless). The remaining insoluble solid, $(Ph_3P=N)_2S_4N_4$ (**3**) (1.09 g, 1.48 mmol, 41% yield based on nitrogen), could be recrystallized by dissolving it in a minimum (40 mL) of dichloromethane at room temperature and adding the saturated solution to 250 mL of acetonitrile. The small, yellow, crystalline blocks of **3** so obtained darken (to red) on heating above $120\text{ }^\circ\text{C}$ and melt to a deep red liquid at $151\text{ }^\circ\text{C}$. Anal. Calcd for $C_{36}H_{30}N_6P_2S_4$: C, 58.67; H, 4.11; N, 11.41; P, 8.41; S, 17.40. Found: C, 58.56; H, 4.18; N, 11.46; P, 8.36; S, 17.48. The infrared spectrum ($1600-250\text{-cm}^{-1}$ region) shows bands at 1558 w , 1482 w , 1440 s , 1320 vw , 1308 w , 1185 vw , 1144 s , 1116 vs , 1071 s , 1026 w , 998 w , 967 vs , 919 vs , 858 vw , 852 vw , 788 m , 767 m , 759 m , 747 m , 725 s , 696 m , 691 m , 638 m , 619 vw , 600 vw , 550 m , 540 m , 537 m , 529 m , 499 m , 487 m , 462 m , 462 m , 447 w , 443 sh , 415 w , 400 vw , and 387 w cm^{-1} . The UV-visible spectrum of **3** (in CH_2Cl_2) shows a broad band with $\lambda_{\text{max}} <290\text{ nm}$ (the actual peak is obscured by the $\pi \rightarrow \pi^*$ transition of the phenyl rings).

Evaporation of the original acetonitrile filtrate yielded 1.54 g of a pale red crystalline solid which, after recrystallization from ether, gave Ph_3PS (1.25 g, 4.25 mmol), identified by its infrared spectrum. No $Ph_3P=NS_3N_3$ (**1**) was observed. The original ether extracts were evaporated to give 0.680 g of a crystalline mass, which consisted almost entirely of Ph_3PS plus a small quantity ($<25\text{ mg}$) of S_4N_4 . The final acetonitrile washings were evaporated to leave a sticky crystalline solid which, after recrystallization from CH_2Cl_2 /methanol, was identified by its infrared spectrum (vide supra) as $(Ph_3P=N)_3S^+S_4N_5^-$ (**2**) (0.47 g, 0.44 mmol, 16% yield based on nitrogen).

Reaction of $Ph_3P=NSiMe_3$ with Sulfur Dichloride. *N*-(Trimethylsilyl)triphenylphosphinimine (6.17 g, 17.6 mmol) was added,

- (5) Fluck, E. Z. *Anorg. Allg. Chem.* **1961**, *312*, 195.
 (6) Holt, E. M.; Holt, S. L. J. *Chem. Soc. D* **1970**, 1704; *J. Chem. Soc., Dalton Trans.* **1974**, 1990.
 (7) (a) Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* **1978**, *17*, 3668. (b) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1977**, 453. (c) Bojes, J.; Chivers, T. *Inorg. Chem.* **1978**, *17*, 318. (d) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1978**, 391.
 (8) The structure of the recently isolated $S_4N_4Cl_2$, an important intermediate in the chlorination of S_4N_4 , may well be related to that of **3**, but no structural information has yet been reported (see ref 9).
 (9) Zborilova, L.; Gebauer, P. Z. *Anorg. Allg. Chem.* **1979**, *448*, 5; *Z. Chem.* **1979**, *19*, 76.
 (10) For the preliminary communication of this work, see: Bojes, J.; Chivers, T.; MacLean, G.; Oakley, R. T.; Cordes, A. W. *Can. J. Chem.* **1979**, *57*, 3171.
 (11) Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.
 (12) Birkofer, L.; Ritter, A. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 417.
 (13) (a) Scherer, O. J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 485. (b) Flues, W.; Scherer, O. J.; Weiss, J.; Wolmershäuser, G. *Ibid.* **1976**, *15*, 379.

Scheme I



as a solid, to a solution of sulfur dichloride (0.909 g, 8.8 mmol) in 25 mL of dichloroethane. The dark red solution so formed was then heated under reflux for 16 h. The solvent was then removed in vacuo to leave a red gluey mass to which was added 50 mL of benzene, and the whole mixture was shaken vigorously for 2–3 min. An insoluble powdery solid soon separated, and it was then filtered off and washed with 2×30 mL of benzene and sucked dry. This material was recrystallized from hot CH_2Cl_2 /benzene as colorless crystalline blocks of $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{Cl}^-$ (4.45 g, 4.97 mmol, 85%), dec pt $>250^\circ\text{C}$. Anal. Calcd for $\text{C}_{34}\text{H}_{45}\text{N}_3\text{P}_3\text{SCl}$: C, 72.35; H, 5.06; N, 4.69; P, 10.37; S, 3.58; Cl, 3.95. Found: C, 72.37; H, 5.15; N, 4.40; P, 10.07; S, 3.32; Cl, 4.41. The infrared spectrum of $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{Cl}^-$ (1600–250- cm^{-1} region) exhibits the same cation bands observed for $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{S}_4\text{N}_5^-$ (vide supra) with no anion bands.

Preparation of $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{S}_4\text{N}_5^-$ by Metathesis. A solution of $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{Cl}^-$ (102 mg, 0.114 mmol) in 5 mL of CH_3CN was added to a solution of *n*- $\text{Bu}_4\text{N}^+\text{S}_4\text{N}_5^-$ (50 mg, 0.114 mmol) in 5 mL of acetonitrile. A canary yellow crystalline precipitate was rapidly produced. After 5 min this solid was filtered from the solution, washed with ether, and sucked dry (weight 0.074 g). A second crop of yellow needles (0.013 g) was obtained upon evaporation of the filtrate. The infrared spectrum of this solid (total yield 0.091 g, 0.86 mmol, 75%) was identical with that of $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{S}_4\text{N}_5^-$ obtained from the $\text{Ph}_3\text{P}/\text{S}_4\text{N}_4$ reaction.

X-ray Measurements for $(\text{Ph}_3\text{P}=\text{N})_3\text{S}_4\text{N}_4$. Crystals suitable for X-ray work were obtained by the slow addition of acetonitrile to a saturated solution of $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ in dichloromethane. The parallelepiped crystal used for all data collection measured $0.038 \times 0.018 \times 0.065$ mm (all ± 0.01 mm) in the [001], [100], and [010] directions. The crystal was mounted on a glass fiber with the *b* axis parallel to the ϕ axis of the diffractometer.

Crystal Data (at $22 \pm 1^\circ\text{C}$). For $\text{C}_{36}\text{H}_{30}\text{N}_6\text{P}_2\text{S}_4$ ($M_r = 736.86$) the crystals are monoclinic. A least-squares refinement of 16 values of $2(\sin \theta)/\lambda$ for 2θ values between 81 and 89° ($\lambda(\text{Cu K}\alpha_1) = 1.5405 \text{ \AA}$) gave $a = 10.306$ (1) \AA , $b = 19.473$ (5) \AA , $c = 17.804$ (1) \AA , $\beta = 94.03$ (1) $^\circ$, $V = 3564.1 \text{ \AA}^3$, and D_{calcd} (for $Z = 4$) of 1.37 g cm^{-3} . The crystal had a μ value of 34.7 cm^{-1} . Systematic absences uniquely indicated the space group $P2_1/c$; four molecules per unit cell in this space group imposes no crystallographic symmetry on the component molecules.

Intensity data were collected with the use of a GE XRD manually operated diffractometer using Ni-filtered $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation and a θ - 2θ scan of 2.0° in 2θ at a scan speed of 2° min^{-1} . Stationary-crystal, stationary-counter background readings were taken for 10 s at each end of the scan. All reflections (3660) with $2\theta < 100^\circ$ were scanned. Of these, 3349 had $I > 3\sigma(I)$ and were used for the solution of the structure. A total of 46 of these reflections were subsequently excluded from use in the refinement; 39 of the highest scan counts were removed because they had saturated the scintillation counter, and 7 reflections were removed because of obvious human error in the data collection. Two reflections measured periodically during the 12-day collection period indicated a linear decay due to crystal decomposition. A simple correction was made to adjust for this decay.¹⁵ An absorption correction with summation points every

(15) A decrease in intensities of the check reflections, linear with respect to X-ray exposure, was attributed to crystal decomposition. The total decay was 11.5% for the first 2200 reflections measured ($2\theta < 90^\circ$). The linear decay was 32% for the last set of reflections measured ($2\theta > 90^\circ$).

0.005 cm gave a range of correction factors (for I) of 0.74–0.55.

The structure was solved by direct methods and refined by Fourier and full-matrix least-squares procedures. Neutral-atom scattering factors were taken from ref 16, and real and imaginary anomalous dispersion corrections (from ref 17) were made for sulfur and phosphorus. Least-squares weights of $a = (2F_{\text{min}} + F_o + 2F_o^2/F_{\text{max}})^{-1}$ for the 3303-reflection, 433-parameter, full-matrix refinement gave final $R_1 = 0.043$ and $R_2 = 0.060$, a standard deviation of an observation of unit weight of 0.47, and no dependence of $\Delta F/\sigma(F)$ on either F or $\sin \theta$. The final refinement included the 30 phenyl hydrogen atoms at calculated positions ($\text{C}-\text{H} = 0.95 \text{ \AA}$, $\beta_{\text{iso}} = 5.0 \text{ \AA}^2$) for the calculation of the structure factors; these hydrogen positions were not refined. The final difference Fourier map showed no peaks above background noise. A table of observed and calculated structure factors and tables containing the anisotropic thermal parameters and bond length and valence angle information related to the phenyl carbon atoms are available as supplementary material.

Results and Discussion

We have examined the reaction of triphenylphosphine with S_4N_4 under a variety of conditions, using different solvents (benzene, acetonitrile, dichloroethane, and ethanol), molar ratios (2:1 and 1:1 of $\text{Ph}_3\text{P}:\text{S}_4\text{N}_4$), and temperatures (20 – 80°C). We limit our description here to the reactions carried out in benzene and acetonitrile at ambient temperature using a 2:1 molar ratio of $\text{Ph}_3\text{P}:\text{S}_4\text{N}_4$, since the yields of the observed products are maximized under these conditions. The effect of temperature on the reaction is critical. We have reported elsewhere that both the S_4N_5^- ion¹⁸ and $\text{Ph}_3\text{P}=\text{NS}_3\text{N}_3$ ¹⁹ are readily susceptible to thermal degradation. Thus, low (ambient) reaction temperatures are imperative if thermally initiated decomposition of the products is to be avoided. The problem of immediate concern is to understand, if only partially, the mechanism of the formation of the different products. We suggest that the reaction begins with the nucleophilic attack of triphenylphosphine at a sulfur (*not* nitrogen²⁰) atom of the S_4N_4 cage^{3–5} (see Scheme I). Electron transfer, followed by a 1,2 shift of phosphorus from sulfur to nitrogen²¹ and ring opening, then leads to an open-chain intermediate 4 (cf. the reaction of S_4N_4 with azide ion^{7c}). Loss of a terminal sulfur atom from 4 would produce a nitrene intermediate 5, which could cyclize to give 1. Nitrene intermediates were also proposed by Fluck and co-workers,^{3–5} although Kresze²¹ and others²² discounted their involvement in the nucleophilic degradation of sulfur diimides. One might expect an inter-

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(18) Chivers, T.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1979**, 752.

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(22) Minami, T.; Miki, H.; Matsumoto, H.; Ohshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1968**, *26*, 3049.

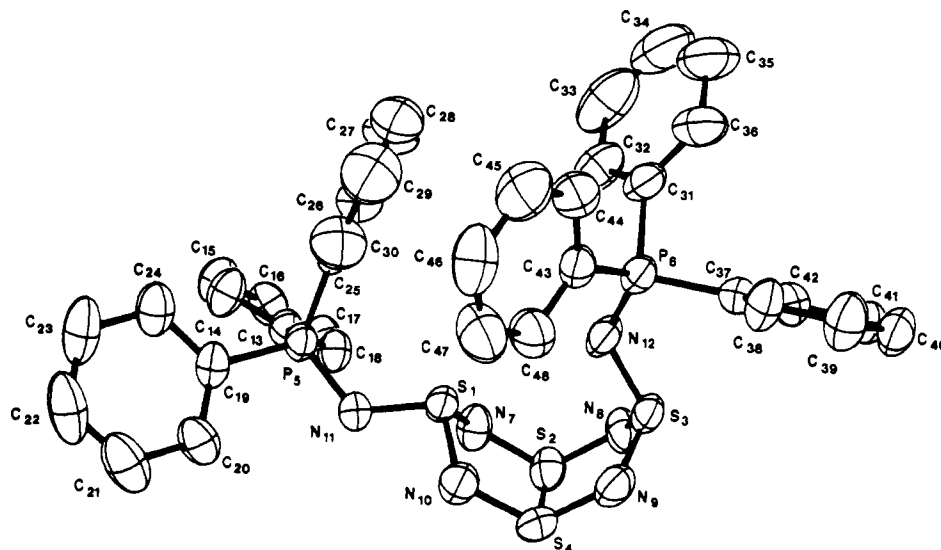


Figure 1. ORTEP plot (50% probability ellipsoids) for $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ showing the atomic numbering scheme.

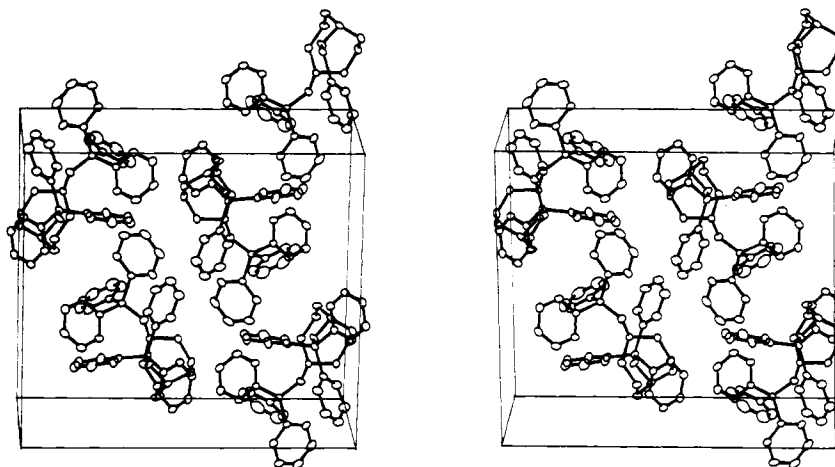
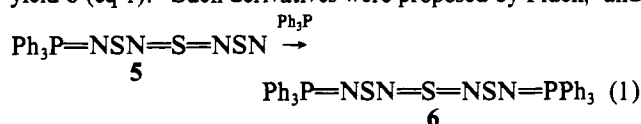
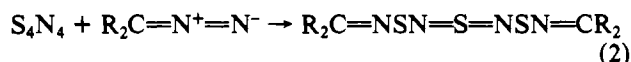


Figure 2. Molecular packing in $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ as viewed down the b axis.

mediate such as **5** to react readily with triphenylphosphine to yield **6** (eq 1). Such derivatives were proposed by Fluck,⁴ and



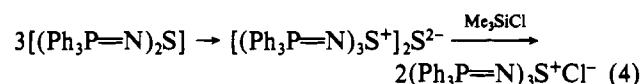
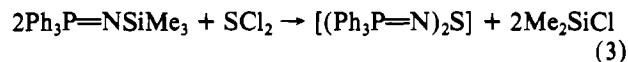
in the reaction of S_4N_4 with diazo compounds, analogous open-chain compounds are produced (eq 2).^{5,23} We have been



unable to confirm the existence of **6**; presumably it would be susceptible to further degradation by triphenylphosphine (interestingly, **1** itself does not react with triphenylphosphine).

The formation of **2**²⁴ appears to involve the initial formation of the bis(imino) sulfide $(\text{Ph}_3\text{P}=\text{N})_2\text{S}$, a probable product of the sequential degradation of intermediates such as **4** and **6** with triphenylphosphine. We have attempted the preparation

of $(\text{Ph}_3\text{P}=\text{N})_2\text{S}$ by the reaction of $\text{Ph}_3\text{P}=\text{NSiMe}_3$ and SCl_2 (cf. the preparation of $(\text{Ph}_2\text{C}=\text{N})_2\text{S}$ from $\text{Ph}_2\text{C}=\text{NH}$ and SCl_2 ²⁵). However, the product isolated in high yield is $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{Cl}^-$,²⁶ formed presumably by the disproportionation of the initially produced $(\text{Ph}_3\text{P}=\text{N})_2\text{S}$. Metathesis of the sulfide ion with Me_2SiCl accounts for the presence of the chloride ion (eq 3 and 4). In the $\text{Ph}_3\text{P}/\text{S}_4\text{N}_4$ reaction, this latter step cannot occur; instead, the sulfide ion apparently reacts with S_4N_4 to afford S_4N_5^- , as observed elsewhere.^{7c}



Finally, we note that the formation of **3** can be viewed as the addition of an $-\text{N}=\text{S}=\text{N}-$ unit to the symmetrical linear compound **6** (cf. the conversion of S_3N_3^- to S_4N_5^- by reaction with S_4N_4),^{7c} but, in the absence of any mechanistic evidence, further speculation is inappropriate.

Crystal and Molecular Structure of $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$. The final atomic coordinates for the $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ structure are

(23) Grushkin, B. U.S. Patent 3 616 393, 1971; U.S. Patent 3 615 409, 1971.

(24) The identity of the S_4N_5^- ion was confirmed chemically by preparing the compound by cation exchange, using $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+\text{Cl}^-$ and $n\text{-Bu}_4\text{N}^+\text{S}_4\text{N}_5^-$ (see Experimental Section). The identity of the new sulfonium ion $(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+$ has been confirmed by an X-ray crystal structure determination of **2** by Dr. M. Extnie of the Molecular Structure Corp. The important structural parameters of the cation are as follows: $d(\text{S}-\text{N}) = 1.635$ (4) Å, $d(\text{P}-\text{N}) = 1.597$ (4) Å, $\angle\text{NSN} = 102.1$ (2)°, $\angle\text{SNP} = 119.2$ (3)°. The S_4N_5^- anion is disordered, and a comparison of it with the $\text{Bu}_4\text{N}^+\text{S}_4\text{N}_5^-$ structure^{13b} is unwarranted.

(25) Hunger, K. *Chem. Ber.* **1967**, *100*, 2214.

(26) A related compound $[(\text{Ph}_3\text{P}=\text{N})_3\text{S}^+][\text{Cl}^-]$ (on the basis of analytical data) with a red color was previously claimed to be one of the products of the reaction of triphenylphosphine with $\text{S}_4\text{N}_3\text{Cl}$: Prakash, H.; Sisler, H. H. *Inorg. Chem.* **1968**, *7*, 2200.

Table I. Final Nonhydrogen Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$

atom	x	y	z
S(1)	7881 (1)	1185 (1)	1600 (1)
S(2)	9108 (1)	933 (1)	3032 (1)
S(3)	6573 (1)	582 (1)	3384 (1)
S(4)	8147 (1)	-65 (1)	2363 (1)
P(5)	8242 (1)	2028 (1)	348 (1)
P(6)	4214 (1)	1148 (1)	2801 (1)
N(7)	9014 (4)	1383 (2)	2286 (2)
N(8)	7966 (3)	953 (2)	3600 (2)
N(9)	6950 (4)	-91 (2)	2900 (2)
N(10)	8002 (4)	332 (2)	1587 (2)
N(11)	8592 (4)	1372 (2)	856 (2)
N(12)	5761 (4)	1123 (2)	2842 (2)
C(13)	9400 (4)	2708 (2)	549 (2)
C(14)	9598 (5)	3214 (3)	31 (3)
C(15)	10454 (5)	3749 (3)	205 (3)
C(16)	11101 (5)	3775 (2)	908 (3)
C(17)	10922 (5)	3271 (3)	1419 (3)
C(18)	10073 (4)	2731 (2)	1250 (2)
C(19)	8354 (4)	1769 (2)	-611 (2)
C(20)	8956 (5)	1155 (2)	-758 (3)
C(21)	9110 (6)	965 (3)	-1498 (4)
C(22)	8675 (7)	1383 (4)	-2072 (3)
C(23)	8063 (7)	1991 (3)	-1939 (3)
C(24)	7878 (5)	2189 (3)	-1202 (3)
C(25)	6659 (4)	2374 (2)	450 (2)
C(26)	6493 (5)	2977 (3)	834 (3)
C(27)	5246 (8)	3209 (4)	957 (4)
C(28)	4201 (7)	2831 (6)	0701 (5)
C(29)	4351 (6)	2232 (5)	321 (5)
C(30)	5577 (5)	1996 (3)	191 (4)
C(31)	3674 (4)	2008 (2)	3000 (3)
C(32)	4462 (6)	2559 (3)	2878 (3)
C(33)	4052 (10)	3220 (3)	3077 (5)
C(34)	2896 (12)	3301 (4)	3402 (5)
C(35)	2111 (8)	2768 (4)	3506 (4)
C(36)	2482 (6)	2113 (3)	3297 (4)
C(37)	3490 (4)	620 (2)	3488 (2)
C(38)	2592 (5)	112 (2)	3297 (2)
C(39)	2072 (6)	-273 (2)	3853 (3)
C(40)	2488 (5)	-172 (2)	4596 (3)
C(41)	3380 (5)	324 (3)	4799 (2)
C(42)	3873 (4)	728 (2)	4246 (2)
C(43)	3556 (4)	895 (2)	1883 (2)
C(44)	2321 (5)	1096 (3)	1596 (3)
C(45)	1863 (6)	864 (3)	893 (3)
C(46)	2582 (7)	438 (3)	480 (3)
C(47)	3782 (6)	222 (3)	773 (3)
C(48)	4269 (5)	458 (3)	1469 (3)

given in Table I. The thermal parameters are available as supplementary material. Selected bond lengths and bond angles are summarized in Table II; the structural parameters of the phenyl groups are available as supplementary material. Figure 1 shows an ORTEP drawing of $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ and the atomic numbering scheme. The structure consists of discrete molecules of a 1,5-disubstituted S_4N_4 cage, the two exocyclic triphenylphosphinimino ligands being oriented in axial and equatorial directions. There are no unusual intermolecular contacts (see Figure 2, which shows a unit cell diagram).

The different orientation of the two $\text{Ph}_3\text{P}=\text{N}$ ligands is an interesting feature of the present structure. By way of comparison, there are only two structural reports of S_4N_4 derivatives possessing ligands bound to a tetravalent sulfur: these are $\text{F}_4\text{S}_4\text{N}_4$ ²⁷ and $(\text{CF}_3\text{NO})_4\text{S}_4\text{N}_4$ ²⁸. In both instances the eight-membered ring adopts a distorted S_4 (tub) conformation, with the ligands located in equatorial positions. There are no transannular S-S interactions. The preference for equatorial ligands is also observed in $\text{Ph}_3\text{P}=\text{NS}_3\text{N}_3$ ⁶ and $\text{Ph}_3\text{As}=\text{NS}_3\text{N}_3$ ²⁹ and in the two heterocyclic derivatives $\text{RAs}(\text{N}=\text{S}=\text{N})_2$ (R = Ph, mesityl), both 1,5-disubstituted eight-membered rings,³⁰ the two ligands are also bound equatorially. The conformational asymmetry of the two ligands in $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ causes several distortions of the S_4N_4 unit. The angle sums at S(1) and S(3) (see Table III) are different, the larger value for $\sum\angle\text{S}(3)$ probably reflecting the greater steric crowding experienced by the axial $\text{Ph}_3\text{P}=\text{N}$ ligand. For the same reason, the dihedral angle of the N(9)-S(3)-N(8) plane with the plane of the four endocyclic nitrogens is greater than the corresponding angle for the N(10)-S(1)-N(7) plane (Table IV). The other two N-S-N dihedral angles are almost

Table II. Selected Bond Lengths (Å) and Angles (Deg) with Esd's in Parentheses for $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$

Bond Lengths			
S(1)-N(7)	1.675 (4)	P(5)-C(25)	1.787 (4)
S(1)-N(10)	1.666 (4)	P(6)-C(31)	1.806 (5)
S(3)-N(8)	1.630 (4)	P(6)-C(37)	1.801 (4)
S(3)-N(9)	1.632 (4)	P(6)-C(43)	1.794 (4)
S(2)-N(7)	1.588 (4)	S(1)-S(3)	3.727 (2)
S(2)-N(8)	1.605 (4)	S(2)-S(4)	2.452 (2)
S(4)-N(9)	1.613 (4)	N(7)-N(8)	2.773 (8)
S(4)-N(10)	1.583 (4)	N(9)-N(10)	2.771 (8)
S(1)-N(11)	1.599 (4)	N(8)-N(9)	2.570 (8)
S(3)-N(12)	1.621 (4)	N(7)-N(10)	2.577 (8)
P(5)-N(11)	1.592 (4)	S(1)-S(2)	2.809 (2)
P(6)-N(12)	1.592 (4)	S(1)-S(4)	2.792 (2)
P(5)-C(13)	1.799 (4)	S(3)-S(2)	2.814 (2)
P(5)-C(19)	1.792 (4)	S(3)-S(4)	2.818 (2)
Bond Angles			
N(7)-S(1)-N(10)	101.0 (2)	N(11)-P(5)-C(19)	106.8 (2)
N(8)-S(3)-N(9)	104.0 (2)	N(11)-P(5)-C(25)	114.6 (2)
N(7)-S(2)-N(8)	120.6 (2)	N(12)-P(6)-C(31)	109.9 (2)
N(9)-S(4)-N(10)	120.2 (2)	N(12)-P(6)-C(37)	114.4 (2)
S(1)-N(7)-S(2)	118.8 (1)	N(12)-P(6)-C(43)	110.3 (2)
S(1)-N(10)-S(4)	118.6 (1)	C(13)-P(5)-C(19)	108.1 (2)
S(2)-N(8)-S(3)	120.9 (2)	C(13)-P(5)-C(25)	107.4 (2)
S(3)-N(9)-S(4)	120.5 (2)	C(19)-P(5)-C(25)	108.9 (2)
N(7)-S(1)-N(11)	102.4 (2)	C(31)-P(6)-C(37)	104.5 (2)
N(10)-S(1)-N(11)	100.2 (2)	C(31)-P(6)-C(43)	109.3 (2)
N(8)-S(3)-N(12)	105.2 (2)	C(37)-P(6)-C(43)	108.3 (2)
N(9)-S(3)-N(12)	109.9 (2)	N(7)-N(8)-N(9)	89.9 (4)
S(1)-N(11)-P(5)	123.7 (2)	N(8)-N(9)-N(10)	90.2 (4)
S(3)-N(12)-P(6)	121.4 (2)	N(9)-N(10)-N(7)	89.9 (4)
N(11)-P(5)-C(13)	110.9 (2)	N(10)-N(7)-N(8)	90.0 (4)

Table III. Structural Parameters of $\text{Ph}_3\text{P}=\text{NS}$ Units in $\text{Ph}_3\text{P}=\text{NS}_3\text{N}_3$ and $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ ^a

	$(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$		
	$\text{Ph}_3\text{P}=\text{NS}_3\text{N}_3$	axial	equatorial
$d(\text{P}-\text{N})$, Å	1.645 (10)	1.592 (4)	1.592 (4)
$d(\text{S}-\text{N})$, Å	1.602 (10)	1.621 (4)	1.599 (4)
$\sum\angle\text{S}$, deg	318.6 (5)	319.1 (2)	303.6 (2)
$\angle\text{PNS}$, deg	121.0 (6)	121.4 (2)	123.7 (2)

^a Here and elsewhere in this paper integers quoted in parentheses refer to esd's for single-valued parameters and indicate ranges of results for the averages of chemically equivalent bonds.

Table IV. Dihedral Angles with Respect to the N(7)-N(8)-N(9)-N(10) Plane^a

plane	N(7)-S(1)-N(10)	N(8)-S(3)-N(9)	N(7)-S(2)-N(8)	N(9)-S(4)-N(10)
dihedral angle, deg	113.4 (2)	121.9 (2)	86.2 (2)	85.1 (2)

^a Planar to within 0.002 (4) Å; $\chi^2 = 1.6$.

NS_3N_3 ,²⁹ and in the two heterocyclic derivatives $\text{RAs}(\text{N}=\text{S}=\text{N})_2$ (R = Ph, mesityl), both 1,5-disubstituted eight-membered rings,³⁰ the two ligands are also bound equatorially. The conformational asymmetry of the two ligands in $(\text{Ph}_3\text{P}=\text{N})_2\text{S}_4\text{N}_4$ causes several distortions of the S_4N_4 unit. The angle sums at S(1) and S(3) (see Table III) are different, the larger value for $\sum\angle\text{S}(3)$ probably reflecting the greater steric crowding experienced by the axial $\text{Ph}_3\text{P}=\text{N}$ ligand. For the same reason, the dihedral angle of the N(9)-S(3)-N(8) plane with the plane of the four endocyclic nitrogens is greater than the corresponding angle for the N(10)-S(1)-N(7) plane (Table IV). The other two N-S-N dihedral angles are almost

(27) Wieggers, G. A.; Vos, A. *Proc. Chem. Soc., London* 1962, 387.(28) Emel'us, H. J.; Forder, R. A.; Poulet, R. J.; Sheldrick, G. M. *J. Chem. Soc. D* 1970, 1483.(29) Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc., Dalton Trans.* 1977, 514.(30) Alcock, N. W.; Holt, E. M.; Kuyper, J.; Mayerle, J. J.; Street, G. B. *Inorg. Chem.* 1979, 18, 2235.

Table V. Cross-Ring S-S Distances in Bridged S₄N₄ Cages

molecule	bridging unit	d(S-S), Å	ref
S ₄ N ₄		2.59-2.60	32
S ₅ N ₆	-N=S=N-	2.425	33
S ₅ N ₆ (CH ₂) ₄	-N=S(CH ₂) ₄ =N-	2.433	34
S ₄ N ₅ ⁻	-N ⁻	2.71	13b
S ₄ N ₅ ⁺ ^a	-N ⁺	4.01	35a

^a In S₄N₅Cl.

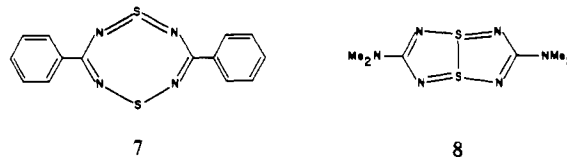
equal. Similar steric interactions probably account for the large $\sum \Delta S$ value found in Ph₃P=N-S₃N₃. Differences are also observed in the otherwise chemically equivalent endocyclic bonds. Thus, the mean length³¹ of N(10)-S(1) and N(7)-S(1) (1.671 (9) Å) is longer than that of N(9)-S(3) and N(8)-S(3) (1.631 (1) Å), and to a lesser extent the N(9)-S(4) and N(8)-S(2) bonds (mean 1.609 (8) Å) are longer than the N(10)-S(4) and N(7)-S(2) bonds (mean 1.586 (4) Å). However, the average endocyclic S-N distance (1.62 Å) is quite close to that found in S₄N₄ itself (1.625 (12) Å).³² The two Ph₃P=N ligands themselves have similar structural parameters (Table IV). All the phenyl groups are planar to within 0.02 Å.

Perhaps the most striking feature of the present structure is the partially opened S₄N₄ cage. Substitution at S(1) and S(3) opens the S(1)-S(3) distance to 3.727 (2) Å (cf. d(S-S) in S₄N₄ = 2.59-2.60 Å³²). However, at the unsubstituted sulfurs, the cross-ring interaction remains intact; the S(2)-S(4) distance (2.452 (2) Å) is in fact shorter than that in S₄N₄. A similar situation is observed in S₅N₆³³ and in S₅N₆(CH₂)₄,³⁴ where one S-S linkage is replaced by bridging N=S=N and N=S(CH₂)₄=N units respectively (see Table V). By contrast, in S₄N₅⁻, the cross-ring S-S distance is lengthened to 2.71 Å,^{13b} and in S₄N₅⁺, the separation corresponds to a typical nonbonded contact.^{35a}

The above information provides support for existing experimental^{33b} and theoretical³⁵ evidence in favor of at least a partial S-S bond in S₄N₄. We suggest that the variations in the unique S-S bond in (Ph₃P=N)₂S₄N₄, S₅N₆, and S₄N₅⁻ reflect the ability of the different ligands (Ph₃P=N, N=S=N, N⁻) to withdraw π*-electron density from the S₄N₄ unit. Thus, extending the bonding model of S₄N₄ proposed by Gleiter,³⁶ more effective π-acceptor ligands (e.g., N⁻) tend

to remove π* electrons from the S₄N₄ cage, thereby depopulating the orbitals involved in the S-S σ interaction. Conversely, the more electron-donating groups Ph₃P=N, N=S(CH₂)₄=N, and N=S=N transfer electron density onto the S₄N₄ cage, resulting in a strengthening of the S-S interaction. Consistent with this argument, oxidation of S₄N₄ to S₄N₄²⁺³⁷ and of S₄N₅⁻ to S₄N₅⁺ causes a complete loss of cross-ring bonding.^{35a}

Further support for this bonding scheme comes from the recently reported structures of the heterocycles **7** and **8**. In



these two molecules the structural effects of the electron-releasing NMe₂ groups and the electron-accepting aryl groups are dramatically apparent. In **7** the eight-membered C₂S₂N₄ ring is planar, while in **8** the ring is markedly puckerd (folded across the S-S contact) with an S-S distance of 2.428 Å.³⁸ Planarity, or the approach to it, may therefore be possible in certain 1,5-disubstituted S₄N₄ derivatives (e.g., S₄N₄Cl₂ or S₄N₄F₂⁹), and by judicious choice of the ligands attached to sulfur, regulation of the S-S distance should be feasible.

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Registry No. 1, 33082-06-3; 2, 72144-80-0; 3, 75266-62-5; (Ph₃P=N)₃S⁺Cl⁻, 75266-63-6; S₄N₄, 28950-34-7; Ph₃P, 603-35-0; Ph₃P=NSiMe₃, 13892-06-3; SCl₂, 10545-99-0; *n*-Bu₄N⁺S₄N₅⁻, 58894-68-1.

Supplementary Material Available: Listings of calculated and observed structure factors for (Ph₃P=N)₂S₄N₄, thermal parameters for the (Ph₃P=N)₂S₄N₄ structure (Table SI), and bond distances and angles within the phenyl rings of (Ph₃P=N)₂S₄N₄ (Table SII) (20 pages). Ordering information is given on any current masthead page.

- (31) Here and elsewhere, when mean values are quoted, the number in parentheses refers to the range of results, not to the esd.
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 (39) Since the submission of our manuscript a paper on the structures of sulfur-nitrogen cages has appeared: Bartetzko, R.; Gleiter, R. *Chem. Ber.* **1980**, *113*, 1138. On the basis of qualitative arguments based on MO theory, these authors predict that stable cage structures with short transannular S-S distances will occur if the substituents in the 1,5-positions of the S₄N₄ cage provide a high-lying filled b₂ orbital e.g., N=S=N in S₅N₆.³³ Our results for 1,5-(Ph₃P=N)₂S₄N₄ provide experimental support for this prediction, which is in agreement with our own conclusions (vide supra). Bartetzko and Gleiter also predict that substituents which provide low-lying empty orbitals should lead to structures with long transannular S-S interactions, e.g., N⁺ in S₄N₅⁺.^{35a}