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Spirocyclic Phosphathiazenes: Central Role of $(Ph_2PN)_4(SN_2)$ in Thermal Transformations of Unsaturated PNS Heterocycles and a Comparison of the Crystal and Molecular Structures of the 6,6- and 8,8-Spirocycles $(Ph_2PN)_4(SN_2)$ and $(Ph_2PN)_4(S_3N_4)$

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The 6,6-spirocycle $(Ph_2PN)_4(SN_2)$ (**2**) is obtained from the solid-state thermolysis of $(Ph_2PN)_2(NSX)$ (**1** (X = Cl, Br, I, N_3, or NR_2, where $R_2 = Me_2$, Et_2, or C_5H_{10})), $(Ph_2PN)_2(SN)^+Br_3^-$, $(Ph_2PN)_4(SN)_2$, or the related 8,8-spirocycle $(Ph_2PN)_4(S_3N_4)$ (**4**) at temperatures in the range 150–245 °C. In the case of X = NR_2, the 12-membered rings $(Ph_2PN)_4(NSNR_2)_2$ have been isolated and shown to be intermediates in the thermal transformation **1** → **2**. The molecular structures of **2** and **4** are compared, with particular reference to the remarkable stability of **2**. Crystal data: **2**·0.5CH_3CN, triclinic, space group $P\bar{1}$, $a = 13.691$ (1) Å, $b = 18.168$ (2) Å, $c = 19.032$ (2) Å, $\alpha = 104.572$ (8)°, $\beta = 92.867$ (7)°, $\gamma = 97.613$ (8)°, $V = 4525$ (1) Å^3, $Z = 4$, the asymmetric unit consisting of two independent molecules of **2** and one molecule of CH_3CN; **4**·0.7CH_2Cl_2·0.2CH_3CN, orthorhombic, space group $Pna2_1$, $a = 24.927$ (5) Å, $b = 9.249$ (1) Å, $c = 20.263$ (5) Å, $V = 4672$ (2) Å^3, $Z = 4$. The final residual factors were $R = 0.038$ and $R_w = 0.051$ for **2** and $R = 0.051$ and $R_w = 0.060$ for **4**. The reaction of **1** (X = Cl) with an excess of sodium azide in acetonitrile at 23 °C yields, as major products, the 6,6-spirocycle (**2**), a 12-membered ring $(Ph_2PN)_4(SN)_2$ (**7**), and the new PNS heterocycle **9**, tentatively identified as a 6,8-spirocycle.

Introduction

We have reported briefly on the thermal conversion of the 6-membered ring $(Ph_2PN)_2(NSX)$ (**1** (X = I)) to the 6,6-spirocycle $(Ph_2PN)_4(SN_2)$ (**2**),[1] a transformation that has been shown to occur via the 12-membered ring $(Ph_2PN)_4(NSX)_2$ (**3**) for X = NMe_2 (Figure 1).[2] A more detailed investigation of the thermal decomposition of a variety of cyclophosphathiazenes (heterocycles containing phosphorus (V), nitrogen, and sulfur in a formal oxidation state of +3 or +4) has now revealed that **2** is the final product of all these thermolyses.

In this paper, we present the full details of our studies of the formation of **2** and we discuss the reasons for its remarkable stability (toward oxygen, moisture, and heat) in the context of a comparison of the X-ray crystal structure with that of the related 8,8-spirocycle $(Ph_2PN)_4(S_3N_4)$ (**4**).[3] The structures of **2** and **4** are also compared with those of the related monocyclic compounds **1** and 1,3-$(Ph_2PN)_2(SN)_2$ (**5**), respectively. Finally, we describe the reaction of **1** (X = Cl) with sodium azide, which yields the 12-membered ring $(Ph_2PN)_4(SN)_2$ (**7**) and a new PNS ring system tentatively identified as the 6,8-spirocycle **9** in addition to the 6,6-spirocycle **2** as the major products.

Experimental Section

Reagents. The compounds $(Ph_2PN)_2(SNX)$ (**1** (X = Cl, Br, I, NR_2))[4], $(Ph_2PN)_2(SN)^+Br_3^-$ (**6**),[4] and $(Ph_2PN)_4(SN)_2$ (**7**)[5] were prepared by literature procedures. All solvents were dried and distilled before use: acetonitrile (P_2O_5 and CaH_2), methylene dichloride, and chloroform (P_2O_5). Sodium azide (Fisher) was used as received.

Instrumentation. Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. Raman spectra were obtained on solid samples in glass capillaries by using a Jarrell-Ash Model 25-100 double monochromator calibrated with indene. A Coherent Radiation CR3 argon ion laser was used to produce exciting lines at 488.0 and 514.5 nm. ^1H and ^{31}P NMR spectra were recorded with a Varian XL-200 spectrometer. ^{31}P NMR chemical shifts are reported relative to external 85% H_3PO_4. Mass spectra were obtained with a Varian CH-5 instrument operating at 70 eV. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary, and by MHW Laboratories, Phoenix, AZ.

Thermolysis Experiments. The procedures used for the thermolyses of PSN heterocycles were similar, and only one example is described in detail. The results of the other thermolysis experiments are summarized in Table I.

Preparation of $(Ph_2PN)_4(SN_2)$ (2). (a) Thermolysis of $(Ph_2PN)_2$(NSI). Solid $(Ph_2PN)_2$(NSI) (108 mg, 0.19 mmol) was heated at ca. 150 °C for 2 h in a Schlenk tube under a dynamic vacuum (10^{-3} torr). The pale brown solid residue was recrystallized from acetonitrile to give colorless crystals of $(Ph_2PN)_4(SN_2)$ (72 mg, 0.08 mmol), mp 231 °C, after pumping under vacuum for several hours. Anal. Calcd for $C_{48}H_{40}N_6P_4S$: C, 67.28; H, 4.71; N, 9.81. Found: C, 67.40; H, 4.62; N, 9.89. Infrared spectrum (Nujol): 1435 s, 1187 vs, 1165 vs, 1154 sh, s, 1118 vs, 1102 vs, 720 s, 690 s, 539 vs, cm^{-1}. Raman spectrum: 1113 m, 1024 w, 994 vs, 681 m, 614 w, 584 w, 205 w cm^{-1}. Mass spectrum: *m/e* 856 (M^+, 100%), 444 [$(Ph_2PN)_2(SN)^+$, 25%]. $\{^1H\}^{31}P$ NMR ($CDCl_3$): δ +17.9.

(b) Reaction of $(Ph_2PN)_2$(NSCl) with Sodium Azide. A mixture of sodium azide (0.40 g, 6.1 mmol) and $(Ph_2PN)_2$(NSCl) (1.00 g, 2.1 mmol) in acetonitrile (30 mL) was stirred at 23 °C for 24 h. Filtration of this solution gave a powdery yellow solid and a dark red-brown filtrate. The solid was treated with methylene dichloride (5 × 5 mL), and after removal of the solvent, the extract was fractionally recrystallized from CH_3CN–CH_2Cl_2 (3:1) to give $(Ph_2PN)_4(SN)_2$ (**7**) (70 mg, 0.08 mmol) and a pale yellow solid (100 mg), tentatively identified as the 6,8-spirocycle **9** (see Results and Discussion). Anal. Calcd for $C_{48}H_{41}N_7P_4S_2$: C, 63.78; H, 4.57; N, 10.84; P, 13.70; S, 7.09. Found: C, 64.69, 64.78; H, 4.82, 4.74; N, 10.32, 10.51; P, 13.25; S, 6.96. Infrared spectrum (Nujol): 1435 s, 1228 sh, s, 1218 s, 1194 s, 1174 s, 1108 v, 1070 m, 1028 m, 890 m, 860 m, 726 m, 699 s, 580 m, 554 m, 543 m, 528 m, 508 s cm^{-1}. Mass spectrum: *m/e* 856 [$(Ph_2PN)_4(SN_2)^+$, 28%], 490 [$(Ph_2PN)_2(SN)_2^+$, 21%], 444 [$(Ph_2PN)_2(SN)^+$, 100%]. $\{^1H\}^{31}P$ NMR ($CDCl_3$): δ +4.0 (s), +1.3 (s), −1.2 (s) in the approximate intensity ratio 2:1:1.

The products in the filtrate were separated by chromatography on a Bio-Beads S-X8 column (20 × 100 mm) using toluene as eluant. The four fractions collected yielded $(Ph_2PN)_4(SN_2)$ (**2**) (125 mg, 0.15 mmol), $(Ph_2PN)_4(S_3N_4)$ (**4**) (30 mg, 0.03 mmol), S_4N_4 (10 mg), and 1,3-$(Ph_2PN)_2(SN)_2$ (**5**) (10 mg),[6] identified by comparison of their infrared spectra with those of authentic samples.

Preparation of $(Ph_2PN)_4(S_3N_4)$ (4). $Me_3SiNSNSiMe_3$ (0.155 g, 0.75 mmol) was added to $(Ph_2PN)_2$(NSCl) (0.720g, 1.5 mmol) in methylene dichloride (25 mL). After 6 h at 23 °C, solvent was removed in vacuo and acetonitrile (ca. 8 mL) was added to the red-brown semisolid residue. The precipitate was recrystallized from methylene dichloride containing a small amount of acetonitrile to give yellow crystals of $(Ph_2PN)_4(S_3N_4)$ (0.145 g, 0.15 mmol), mp 150 °C dec to a red liquid. Anal. Calcd for $C_{49.1}H_{42}N_{8.2}P_4S_3Cl_{1.4}$: C, 57.96; H, 4.17; N, 11.31. Found: C, 58.82, 58.54; H, 4.17, 4.03; N, 11.36, 11.40. The calculated formula contains 0.7 CH_2Cl_2 and 0.2 CH_3CN as determined by X-ray crystallography. Infrared spectrum (Nujol): 1430 s, 1310 s, 1293 s, 1280 s, 1268 s, 1104 vs, 1035 s, 1021 s, 927 s, 732 s, 720 s, 695 s, 540 s, 521 vs, 500 s, 492

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[1] Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 700.

[2] Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702.

[3] Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1982**, 982.

[4] Chivers, T.; Rao, M. N. S. *Inorg. Chem.* **1984**, *23*, 3605.

[5] Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 186.

[6] Burford, N.; Chivers, T.; Richardson, J. F. *Inorg. Chem.* **1983**, *22*, 1482.

0020-1669/85/1324-2237$01.50/0

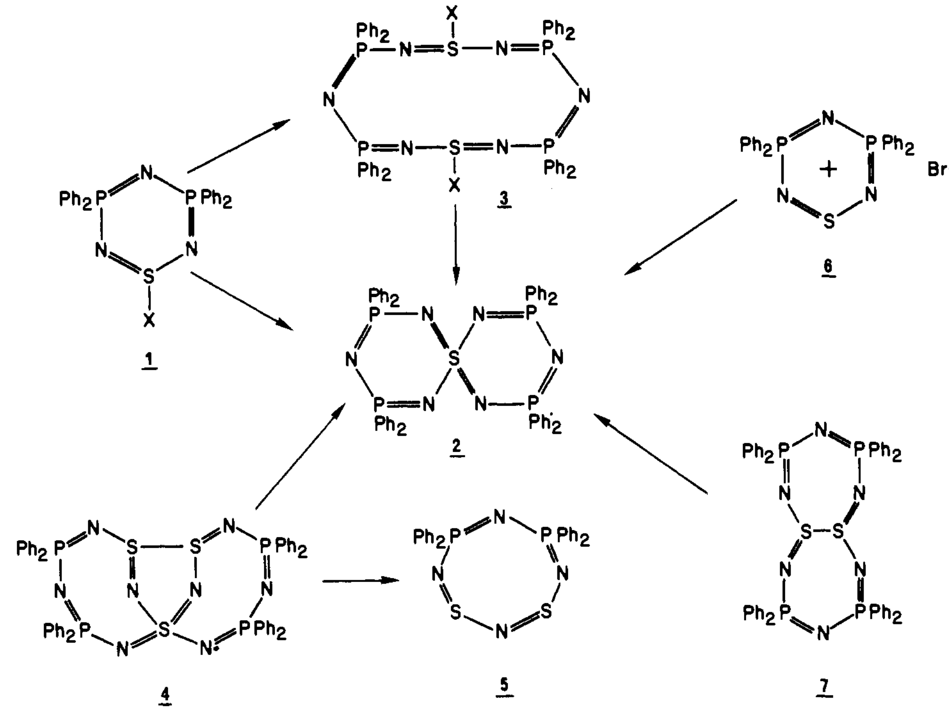

Figure 1. Reaction scheme for thermal transformations of cyclophosphathiazenes represented by valence-bond structures for consistency.

Table I. Thermal Decomposition of Unsaturated PSN Heterocycles

compd (mg)	reacn conditions, °C/h	yield of **2**, mg	other products (mg)[a]
$(Ph_2PN)_2(NSCl)$ (75)	210/2	25	$(Ph_2PN)_4$ (15)
$(Ph_2PN)_2(NSBr)$ (30)	245/0.5	*b*	
$(Ph_2PN)_2(NSI)$ (108)	150/2	72	
$(Ph_2PN)_2(SN)^+Br_3^-$ (60)	240/1[c]	20	
$(Ph_2PN)_2(NSNMe_2)$ (70)	185/0.5	40	
$(Ph_2PN)_2(NSNEt_2)$ (200)	165/2.5	100	$(Ph_2PN)_4(NSNEt_2)_2$ (25)
$(Ph_2PN)_2(NSNC_5H_{10})$ (275)	200/1	140	$(Ph_2PN)_4(NSNC_5H_{10})_2$ (20)
$(Ph_2PN)_4(NSNMe_2)_2$ (35)	180/2	20	
$(Ph_2PN)_4(NSNEt_2)_2$ (250)	245/1	100	
$(Ph_2PN)_4(NSNC_5H_{10})_2$ (50)	220/2	15	$(C_5H_{10}N)_2S$
$(Ph_2PN)_4(SN)_2$ (165)	240/0.5	105	S_8 (5)
$(Ph_2PN)_4(S_3N_4)$ (75)	170/0.5	15	1,3-$(Ph_2PN)_2(SN)_2$ (30)

[a] Weights correspond to isolated products that were identified by comparison of their infrared spectra with those of authentic samples. [b] Not isolated; identified by infrared and ^{31}P NMR spectra. [c] At lower temperatures, ca. 155 °C, the major thermolysis product is $(Ph_2PN)_2(NSBr)$.

s cm^{-1}. Raman spectrum: 1113 m, 1023 w, 993 vs, 946 m, 477 w, 370 s, 308 m, 245 vs cm^{-1}. Mass spectrum: *m/e* 856 [$(Ph_2PN)_4(SN_2)^+$, 2%], 490 [$(Ph_2PN)_2(SN)_2^+$, 69%], 444 [$(Ph_2PN)_2(SN)^+$, 100%]. $\{^1H\}^{31}P$ NMR ($CDCl_3$): δ +1.8 (s, 1 P), +5.4 (s, 1 P). UV–visible spectrum (CH_3CN), λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 274 (0.9×10^4), 347 (1.3×10^4).

Preparation of $(Ph_2PN)_4(NSNR_2)_2$. (a) $(Ph_2PN)_4(NSNMe_2)_2$. A solution of $(Ph_2PN)_2(NSNMe_2)$ (780 mg) in acetonitrile (25 mL) was allowed to stand at 230 °C for several days.[7] Colorless needles (200 mg) were deposited and were identified as $(Ph_2PN)_4(NSNMe_2)_2$ by X-ray crystallography;[2] mp 175 °C dec. Anal. Calcd for $C_{52}H_{52}N_8P_4S_2$: C, 63.91; H, 5.38; N, 11.47. Found: C, 62.39; H, 5.38; N, 11.22. $\{^1H\}^{31}P$ NMR ($CDCl_3$): δ +5.0. Infrared spectrum (Nujol): 1438 s, 1328 vs, 1301 s, 1277 s, 1154 s, 1141 s, 1128 vs, 1110 sh, 1090 vs, 1078 sh, 1035 s, 757 s, 730 vs, 705 vs, 550 vs, 535 vs cm^{-1}.

(b) $(Ph_2PN)_4(NSNEt_2)_2$. Diethylamine (0.5 mL) in methylene dichloride (5 mL) was added to a solution of $(Ph_2PN)_2(NSCl)$ (1.12 g, 2.34 mol) in methylene dichloride (25 mL) during 20 min. After 3 h at 23 °C, solvent was removed in vacuo and the reddish semisolid residue was treated with acetonitrile (30 mL). The insoluble material was a mixture of $(Ph_2PN)_4(NSNEt_2)_2$ and $Et_2NH_2^+Cl^-$. The latter was removed by washing with water or ethanol. The acetonitrile filtrate deposited white crystals of $(Ph_2PN)_4(NSNEt_2)_2$ (0.70 g, 0.68 mol) on standing at 23 °C for 3 h. Anal. Calcd for $C_{56}H_{60}N_8P_4S_2$: C, 65.09; H, 5.87; N, 10.85. Found: C, 65.70; H, 5.88; N, 10.98. Infrared spectrum (Nujol): 1438 s, 1285 s, 1266 vs, 1119 s, 1080 s, 1070 s, 725 s, 703 s, 555 s cm^{-1}. The product was insufficiently soluble in common solvents to obtain a ^{31}P NMR spectrum.

(c) $(Ph_2PN)_4(NSNC_5H_{10})_2$. Solid $(Ph_2PN)_2(NSNC_5H_{10})$ (120 mg) was heated at 140 °C for 0.5 h under a dynamic vacuum (10^{-3} torr). The residue was extracted with acetonitrile (10 mL), and the filtrate deposited white crystals of $(Ph_2PN)_4(NSNC_5H_{10})_2$ (20 mg) on standing. Anal. Calcd for $C_{58}H_{60}N_8P_4S_2$: C, 65.89; H, 5.73; N, 10.60. Found: C, 64.92; H, 5.61; N, 10.57. $\{^1H\}^{31}P$ NMR ($CDCl_3$): δ +4.7. Infrared spectrum (Nujol): 1438 s, 1120 s, 1080 vs, 1067 s, 1063 sh, s, 725 s, 701 s, 551 s, 524 sh, s cm^{-1}.

X-ray Analysis. The crystal data and experimental conditions are given in Table II. The data were collected by using the $\omega/2\theta$ scan technique on an Enraf-Nonius CAD 4F automated diffractometer fitted with a low-temperature device. The cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry of 25 accurately centered reflections. The final choice of the space groups was based on an examination of the intensities measured during the data collection, the distribution of *E* values, and the successful solution of the structures. Three standard reflections measured every 1500 s of X-ray exposure time showed no decomposition of the crystals had occurred during the data acquisition period. The data were corrected for background, Lorentz, and polarization effects, but absorption corrections were not considered necessary.

The structures were solved by a combination of direct methods (MULTAN 78)[8] and a series of structure factor and difference Fourier

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(7) After precipitation of the dimers $(Ph_2PN)_4(NSNR_2)_2$, these acetonitrile solutions deposit two other white crystalline solids. $R_2NH_2^+$-$[(Ph_2PN)_2(NSO_2)]^-$ and $(Ph_2PN)_2(NS(O)NPPh_2NPPh_2NH_2)$. These products apparently result from the aerial hydrolysis of **1** (X = NR_2) and **3** (X = NR_2), respectively, and their structures have been determined by X-ray crystallography: Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1531.

Table II. Crystal Data

formula	$C_{48}H_{40}N_6P_4S\cdot 0.5CH_3CN$	$C_{48}H_{40}N_8P_4S_3\cdot 0.7CH_2Cl_2\cdot 0.2CH_3CN$
formula wt	889.4	1015.5
cryst description	colorless blocks	pale yellow blocks
space group	$P\bar{1}$	$Pna2_1$
a, Å	13.691 (1)	24.927 (5)
b, Å	18.168 (2)	9.249 (1)
c, Å	19.032 (2)	20.263 (5)
α, deg	104.572 (8)	90
β, deg	92.867 (7)	90
γ, deg	97.613 (8)	90
V, Å^2	4525 (1)	4672 (2)
Z	4	4
D_c, g cm^{-3}	1.29	1.47
D_m, g cm^{-3}	1.30 (1)	
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
temp, °C	23 (2)	−100 (5)
max θ, deg	25	29
scan range $\Delta\omega$, deg	1.5(0.74 + 0.347 tan θ)	1.5(0.80 + 0.347 tan θ)
scan speed, deg min^{-1}	0.6–6.6	0.5–6.6
octants, collcd	$-h,\pm k,\pm l$	$+h,-k,+l$
cryst dimens, mm	0.45 × 0.43 × 0.27	0.40 × 0.32 × 0.29
μ(Mo Kα), cm^{-1}	2.57	4.55
no. of unique data	8420	6359
no. of obsd data ($I > 3\sigma(I)$)	5627	2377
no. of data used in final cycle[b]	7290	5455
no. of variables in final cycle	1090	606
GOF	1.90	0.86
R, R_w[c]	0.038, 0.051	0.051, 0.060

[a] Graphite monochromator. [b] Observed data plus those for which $I_c > 3\sigma(I_o)$ [c] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

syntheses. Refinement was carried out by block-diagonal least-squares techniques based on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weighting scheme used for both structures was $w = [\sigma^2(F_o) + 0.001F_o^2]^{-1}$, where $\sigma(F_o)$ was derived from counting statistics. All computations were performed by using the XRAY 76 system of programs[9] implemented on a Honeywell computer with a MULTICS operating system. Scattering factors for the non-hydrogen atoms were those of Cromer and Mann,[10] and those for H were taken from ref 11. Anomalous dispersion corrections were included for non-hydrogen atoms.[12]

The structure of $(Ph_2PN)_4(SN_2)$ (**2**) consists of two crystallography independent molecules of the spirocyclic compound and one molecule of CH_3CN solvate. Refinement of this structure proceeded smoothly with all H atoms being clearly revealed in a difference Fourier synthesis. H atoms were included in the model in ideal positions (sp^2, C–H = 0.95 Å; sp^3, C–H = 1.00 Å), with each isotropic thermal parameter set to 1.1 times that of the C atom to which it is bonded, but were not refined. The highest peak in the final difference Fourier synthesis was of electron density 0.20 e Å^{-3} at fractional coordinates (0.1711, 0.9593, 0.3990) and is of no chemical significance. The refinement of $(Ph_2PN)_4(S_3N_4)$ (**4**) was straightforward except for the solvate. A molecule of CH_2Cl_2 was readily located from a difference Fourier synthesis but was found to have excessively large thermal parameters. Refinement of an occupancy factor for the atoms of the CH_2Cl_2 solvate indicated a maximum of 0.7 molecule was present. A subsequent difference Fourier map of the same region revealed a CH_3CN molecule, which was found to have an occupancy factor of 0.2. In the final cycles the occupancy factors were set to these values, and all H atoms, except those of the CH_3CN molecule, were included in idealized positions (as above). The final difference Fourier synthesis showed a maximum peak of 0.15 e Å^{-3} at fractional coordinates (0.0102, 0.9734, 0.3500), which is of no chemical significance. The R factor calculated for the inverted model of **4** was not significantly different from that reported herein.

Results and Discussion

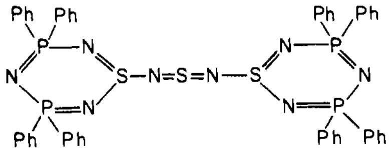
Formation of $(Ph_2PN)_4(SN_2)$ (2). The 6,6-spirocycle **2** is formed by the thermolysis of a variety of cyclophosphathiazenes: the 6-membered rings $(Ph_2PN)_2(NSX)$ (**1** (X = Cl, Br, I, or NR_2, where R_2 = Me_2, Et_2, or C_5H_{10})) and $(Ph_2PN)_2(SN)^+Br_3^-$ (**6**), the 12-membered ring $(Ph_2PN)_4(SN)_2$ (**7**), and the tricyclic compound $(Ph_2PN)_4(S_3N_4)$ (**4**) (see Figure 1). Details of the reaction conditions for these thermal decompositions are given in Table I.

We have demonstrated for **1** (X = NR_2) that this transformation occurs via ring expansion to give a 12-membered ring $(Ph_2PN)_4(NSX)_2$ (**3**) the structure of which has been determined by X-ray crystallography for X = NMe_2.[2] This ring-opening reaction, **1** → **3**, occurs at 23 °C in acetonitrile solutions for X = NMe_2 or NEt_2 or on heating of solid samples (ca. 140 °C for X = NC_5H_{10}). By contrast, the phenyl derivative (**1** (X = Ph)) exhibits high thermal stability and can be recovered unchanged after 1 h at 220 °C.

The marked difference in the influence of the exocyclic groups attached to sulfur on the stability of the P_2SN_3 ring can be attributed to electronic effects. Ab initio MO calculations demonstrate that the LUMO for the $P_2SN_3^+$ ring is *strongly antibonding with respect to the NSN segment of the ring.*[13] This finding provides a rationale for the facile ring-opening reactions observed for **1** under the influence of reducing agents or nucleophiles, since such processes would tend to populate the LUMO; e.g., **1** + $Me_3SiNSNSiMe_3$ → **4** (see below) and **1** + Ph_3Sb → **7**.[5] In a similar way the strong π-donor property of an Me_2N substituent is expected to result in a weakening of the endocyclic S–N bonds and, hence, ring opening via S–N bond cleavage.[14,15]

Unlike the case for 1,5-$(Me_2N)_2S_4N_4$,[16] there are no short cross-ring contacts between exocyclic Me_2N groups and the remote sulfur atoms in $(Ph_2PN)_4(NSNMe_2)_2$ (**3** (X = NMe_2)). Nevertheless, the conversion **3** → **2** occurs via loss of $(R_2N)_2S$ (see Table I). Thus the formation of the spirocycle **2** involves breaking three S–N bonds (two endocyclic and one exocyclic) and the formation of two new S–N bonds. Similarly, the conversion **7** → **2**, with elimination of sulfur, necessitates the breaking of two S–N bonds and the cross-ring S–S bond and the production of two new S–N bonds.

Formation and Thermolysis of $(Ph_2PN)_4(S_3N_4)$ (4). The reaction between **1** (X = Cl) and $Me_3SiNSNSiMe_3$ in a 2:1 molar ratio produced the 8,8-spirocycle **4** instead of the expected product **8**. The formation of **4** can be viewed to occur via double insertion



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(8) MULTAN 78 is a system of programs for the automatic solution of crystal structures from X-ray diffraction data: Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. "MULTAN 78"; University of York: York, England, 1978.

(9) Stewart, J. M., Ed. Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(11) Stewart, R. F.; Davidson, E.; Simpson, W. *J. Chem. Phys.* **1965**, *42*, 3175.

(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.

(13) Burford, N.; Chivers, T.; Hojo, M.; Laidlaw, W. G.; Richardson, J. F.; Trsic, M. *Inorg. Chem.* **1985**, *24*, 709.

(14) A related phenomenon, the existence of both folded (R = Me_2N) and planar (R = Ph) structures for 1,5-$RC(NSN)_2CR$, has been explained in terms of the effect of the π-donor properties of the Me_2N group on the π-electronic structure of the $C_2S_2N_4$ ring.[15]

(15) (a) Ernest, I.; Hollick, W.; Rihs, G.; Schomburg, D.; Shoham, G.; Wenkert, D.; Woodward, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1540. (b) Boutique, J. P.; Riga, J.; Verbist, J. J.; Delhalle, J.; Fripiat, J. G.; Haddon, R. C.; Kaplan, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 312. (c) Gleiter, R.; Bartetzko, R.; Cremer, D. *J. Am. Chem. Soc.* **1984**, *106*, 3437. (d) Millefiori, S.; Millefiori, A.; Granozzi, G. *Inorg. Chim. Acta* **1984**, *90*, L55. (e) Oakley, R. T. *Can. J. Chem.* **1984**, *62*, 2763.

(16) Roesky, H. W.; Pelz, C.; Gieren, A.; Hadicke, E. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1437. Roesky, H. W.; Rao, M. N. S.; Graf, C.; Gieren, A.; Hadicke, E. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 592.

Table III. Positional Parameters (×10^5 for S, P; ×10^4 for N, C) for the Non-Hydrogen Atoms of $(Ph_2PN)_4(SN_2)\cdot0.5CH_3CN$

atom	*x/a*	*y/b*	*z/c*
S(1A)	39735 (9)	60729 (6)	73683 (6)
P(1A)	41755 (8)	67412 (7)	61951 (6)
P(2A)	23769 (8)	59805 (7)	63861 (6)
P(3A)	42279 (9)	67111 (7)	88819 (6)
P(4A)	49497 (9)	53671 (7)	82972 (6)
N(1A)	4597 (2)	6518 (2)	6903 (2)
N(2A)	3023 (2)	6498 (2)	5973 (2)
N(3A)	2975 (2)	5634 (2)	6946 (2)
N(4A)	3748 (3)	6644 (2)	8085 (2)
N(5A)	4765 (3)	6016 (2)	8990 (2)
N(6A)	4576 (3)	5454 (2)	7520 (2)
C(1A)	5155 (3)	3664 (2)	4555 (2)
C(2A)	5607 (3)	4132 (3)	5194 (3)
C(3A)	5067 (5)	4441 (3)	5760 (3)
C(4A)	4073 (5)	4290 (3)	5692 (3)
C(5A)	3608 (4)	3839 (4)	5059 (4)
C(6A)	4146 (4)	3522 (3)	4490 (3)
C(11A)	−4497 (3)	2236 (2)	3646 (2)
C(12A)	−4402 (4)	1895 (3)	4210 (3)
C(13A)	−4620 (4)	1095 (3)	4082 (3)
C(14A)	−4945 (4)	660 (3)	3388 (3)
C(15A)	−5070 (5)	1002 (4)	2839 (3)
C(16A)	−4843 (4)	1787 (3)	2969 (3)
C(21A)	8311 (3)	4833 (3)	4259 (2)
C(22A)	8500 (3)	4815 (3)	4973 (3)
C(23A)	9015 (4)	5456 (4)	5476 (3)
C(24A)	9345 (4)	6103 (4)	5271 (4)
C(25A)	9170 (4)	6121 (3)	4561 (4)
C(26A)	8653 (4)	5496 (3)	4065 (3)
C(31A)	−1481 (3)	3489 (3)	3140 (2)
C(32A)	−960 (4)	3744 (3)	2629 (3)
C(33A)	−281 (5)	3341 (5)	2263 (4)
C(34A)	−121 (5)	2688 (5)	2396 (4)
C(35A)	−626 (6)	2402 (4)	2896 (4)
C(36A)	−1320 (4)	2815 (3)	3260 (3)
C(41A)	−3263 (3)	3148 (2)	527 (3)
C(42A)	−3411 (4)	3222 (3)	−172 (3)
C(43A)	−2685 (7)	3071 (4)	−659 (3)
C(44A)	−1829 (7)	2840 (4)	−420 (6)
C(45A)	−1685 (5)	2788 (4)	266 (5)
C(46A)	−2388 (4)	2941 (3)	745 (3)
C(51A)	−5079 (3)	2411 (3)	803 (2)
C(52A)	−4879 (4)	1754 (3)	978 (3)
C(53A)	−5494 (5)	1056 (3)	705 (3)
C(54A)	−6294 (5)	1015 (4)	246 (4)
C(55A)	−6507 (4)	1655 (5)	65 (3)
C(56A)	−5896 (4)	2355 (3)	343 (3)
C(61A)	3751 (3)	4685 (2)	1738 (2)
C(62A)	3244 (4)	5004 (3)	1272 (3)
C(63A)	2239 (6)	5034 (4)	1300 (4)
C(64A)	1755 (5)	4738 (4)	1787 (5)
C(65A)	2221 (5)	4409 (4)	2242 (4)
C(66A)	3233 (4)	4380 (3)	2216 (3)
C(71A)	−4404 (4)	5545 (3)	1608 (3)
C(72A)	−4231 (5)	6175 (3)	2210 (3)
C(73A)	−3788 (6)	6880 (4)	2133 (4)
C(74A)	−3515 (7)	6918 (5)	1443 (5)
C(75A)	−3645 (7)	6302 (5)	866 (5)
C(76A)	−4102 (5)	5629 (4)	949 (3)
S(1B)	−2817 (8)	12356 (6)	73469 (6)
P(1B)	4222 (9)	17433 (7)	61652 (7)
P(2B)	−2727 (9)	27658 (7)	72909 (7)
P(3B)	4535 (9)	7644 (7)	85205 (6)
P(4B)	−14907 (9)	2697 (7)	79809 (6)
N(1B)	−23 (3)	1089 (2)	6543 (2)
N(2B)	317 (3)	2600 (2)	6585 (2)
N(3B)	−473 (3)	2076 (2)	7682 (2)
N(4B)	595 (2)	1069 (2)	7808 (2)
N(5B)	−618 (3)	355 (2)	8598 (2)
N(6B)	−1234 (2)	655 (2)	7327 (2)
C(1B)	238 (3)	8493 (3)	4717 (2)
C(2B)	55 (4)	9085 (3)	5285 (3)
C(3B)	655 (5)	9305 (3)	5931 (3)
C(4B)	1445 (5)	8937 (4)	6011 (3)
C(5B)	1636 (4)	8355 (4)	5456 (4)
C(6B)	1026 (4)	8119 (3)	4809 (3)
C(11B)	−1695 (3)	8339 (2)	3961 (2)
C(12B)	−2187 (4)	8780 (3)	3617 (3)
C(13B)	−3173 (5)	8826 (4)	3696 (4)
C(14B)	−3682 (5)	8433 (5)	4112 (4)
C(15B)	−3226 (5)	7994 (4)	4446 (4)
C(16B)	−2225 (4)	7944 (3)	4387 (3)
C(21B)	−391 (3)	6401 (2)	2077 (2)
C(22B)	−51 (4)	6098 (3)	1424 (3)
C(23B)	−566 (6)	5449 (4)	927 (4)
C(24B)	−1406 (6)	5095 (4)	1093 (4)
C(25B)	−1757 (5)	5363 (5)	1724 (5)
C(26B)	−1257 (4)	6038 (4)	2216 (3)
C(31B)	1454 (4)	6980 (3)	2912 (2)
C(32B)	1526 (4)	6403 (3)	3259 (3)
C(33B)	2438 (6)	6242 (4)	3462 (3)
C(34B)	3266 (5)	6638 (5)	3312 (4)
C(35B)	3219 (5)	7207 (5)	2969 (4)
C(36B)	2302 (5)	7371 (3)	2772 (3)
C(41B)	−818 (3)	8478 (3)	669 (3)
C(42B)	−822 (4)	8637 (4)	0 (4)
C(43B)	−1087 (6)	8075 (6)	−632 (4)
C(44B)	−1357 (6)	7335 (6)	−605 (5)
C(45B)	−1332 (6)	7151 (4)	37 (6)
C(46B)	−1068 (4)	7730 (4)	693 (3)
C(51B)	−1333 (4)	9884 (3)	1494 (3)
C(52B)	−2214 (5)	9763 (4)	1787 (3)
C(53B)	−2860 (8)	10302 (8)	1831 (6)
C(54B)	−2666 (12)	10908 (10)	1570 (9)
C(55B)	−1805 (10)	11024 (6)	1288 (8)
C(56B)	−1112 (5)	10522 (4)	1239 (4)
C(61B)	1914 (3)	731 (3)	2420 (2)
C(62B)	2437 (4)	1174 (3)	2041 (3)
C(63B)	2670 (5)	1957 (3)	2299 (4)
C(64B)	2406 (6)	2310 (4)	2927 (4)
C(65B)	1912 (7)	1905 (5)	3344 (4)
C(66B)	1643 (5)	1102 (3)	3083 (3)
C(71B)	2528 (3)	9357 (2)	1611 (2)
C(72B)	3254 (4)	9167 (3)	2033 (3)
C(73B)	4071 (4)	8893 (3)	1719 (4)
C(74B)	4161 (5)	8817 (4)	989 (5)
C(75B)	3451 (6)	8993 (4)	577 (4)
C(76B)	2630 (4)	9260 (3)	868 (3)
C(7)	2434 (5)	9857 (4)	4392 (4)
C(8)	3238 (7)	9457 (5)	4229 (4)
N(7)	3915 (6)	9141 (5)	4092 (5)

of an SN group from the sulfur diimide bridge into each of the 6-membered rings of **8**. This process could take place in a stepwise or concerted manner and would result in a 6- → 8-membered-ring expansion with the bridging sulfur atom becoming the spirocyclic center.[17] The presence of the inter-ring S–S bond in **4** is discussed below.

The thermolysis of **4** produces 1,3-$(Ph_2PN)_2(SN)_2$ (**5**) as the major product, with smaller amounts of the spirocycle **2**.

Comparison of the Molecular and Crystal Structures of 2 and 4. ORTEP drawings of the spirocyclic molecules **2** and **4** are shown in Figures 2 and 3, respectively. Positional parameters can be found in Tables III and IV, and important bond lengths and bond angles are summarized in Tables V and VI.

We begin this comparison with some general comments about the structures of **2** and **4** in the context of π-electron-precise and π-electron-rich heterocycles.[18] The spirocycle **2** consists of two almost planar P_2SN_3 rings.[19] Assuming the sulfur atom formally

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(17) It is, of course, possible that the initial ring expansion reaction involves the monosubstituted product $(Ph_2PN)_2(NSNSNSiMe_3)$. We attempted to prepare this intermediate by conducting the reaction of **1** (X = Cl) with $Me_3SiNSNSiMe_3$ in a 1:1 molar ratio but were unable to purify the product.

(18) Chivers, T. *Acc. Chem. Res.* **1984**, *17*, 166.

Table IV. Positional Parameters (×10^5 for S, P; ×10^4 for N, C) for the Non-Hydrogen Atoms of $(Ph_2PN)_4(S_3N_4)\cdot 0.7CH_2Cl_2\cdot 0.2CH_3CN$

atom	*x/a*	*y/b*	*z/c*
S(1)	11964 (6)	−1359 (16)	85153[a]
S(2)	15098 (6)	10223 (15)	72975 (8)
S(3)	9818 (6)	−10990 (16)	72340 (8)
P(1)	24582 (6)	−8011 (16)	74153 (8)
P(2)	22721 (6)	−4174 (16)	88568 (8)
P(3)	25 (6)	6048 (16)	73280 (9)
P(4)	884 (6)	440 (17)	87673 (8)
N(1)	1361 (2)	1240 (5)	8065 (3)
N(2)	2098 (2)	511 (5)	7123 (2)
N(3)	2515 (2)	−983 (6)	8191 (3)
N(4)	1643 (2)	−609 (6)	9010 (3)
N(5)	1074 (2)	−1435 (5)	8003 (3)
N(6)	392 (2)	−617 (6)	7017 (3)
N(7)	−148 (2)	555 (6)	8084 (3)
N(8)	709 (2)	287 (6)	8954 (3)
C(1)	3115 (2)	−485 (6)	7073 (3)
C(2)	3489 (3)	−1595 (7)	7096 (3)
C(3)	4008 (3)	−1403 (7)	6851 (3)
C(4)	4151 (3)	−68 (7)	6597 (4)
C(5)	3783 (3)	1058 (7)	6575 (3)
C(6)	3261 (3)	843 (7)	6814 (3)
C(11)	2243 (2)	−2521 (7)	7093 (3)
C(12)	2216 (3)	−2752 (7)	6415 (3)
C(13)	2067 (3)	−4098 (9)	6164 (3)
C(14)	1943 (2)	−5208 (7)	6602 (4)
C(15)	1966 (2)	−4997 (7)	7271 (4)
C(16)	2122 (2)	−3653 (7)	7521 (3)
C(21)	2446 (2)	1473 (6)	8984 (3)
C(22)	2265 (3)	2196 (7)	9537 (3)
C(23)	2381 (3)	3660 (7)	9626 (3)
C(24)	2665 (3)	4413 (8)	9146 (4)
C(25)	2856 (3)	3671 (8)	8602 (3)
C(26)	2756 (3)	2213 (7)	8520 (3)
C(31)	2603 (2)	−1449 (6)	9490 (3)
C(32)	3159 (3)	−1523 (8)	9466 (3)
C(33)	3440 (3)	−2374 (8)	9918 (3)
C(34)	3166 (3)	−3117 (7)	10398 (3)
C(35)	2602 (3)	−3029 (7)	10434 (3)
C(36)	2325 (2)	−2197 (7)	9980 (3)
C(41)	−608 (2)	393 (6)	6858 (3)
C(42)	−585 (3)	187 (7)	6177 (3)
C(43)	−1060 (3)	98 (7)	5822 (3)
C(44)	−1550 (3)	166 (7)	6147 (3)
C(45)	−1569 (3)	332 (8)	6820 (3)
C(46)	−1093 (2)	464 (7)	7185 (3)
C(51)	247 (2)	2385 (6)	7122 (3)
C(52)	239 (2)	3490 (7)	7590 (3)
C(53)	420 (2)	4857 (6)	7434 (3)
C(54)	613 (2)	5146 (7)	6805 (3)
C(55)	627 (3)	4079 (7)	6334 (3)
C(56)	440 (3)	2693 (7)	6487 (3)
C(61)	−91 (2)	−1835 (6)	8905 (3)
C(62)	−422 (3)	−2550 (7)	8466 (3)
C(63)	−578 (3)	−3986 (7)	8587 (4)
C(64)	−401 (3)	−4665 (7)	9147 (4)
C(65)	−72 (3)	−3959 (8)	9594 (4)
C(66)	90 (3)	−2543 (7)	9467 (3)
C(71)	−258 (2)	1021 (7)	9401 (3)
C(72)	2 (3)	1726 (7)	9908 (3)
C(73)	−283 (3)	2430 (8)	10397 (3)
C(74)	−839 (3)	2447 (7)	10385 (3)
C(75)	−1106 (3)	1771 (9)	9873 (4)
C(76)	−817 (3)	1028 (8)	9392 (4)
C(7)	3934 (5)	8991 (12)	4228 (6)
Cl(1)	3900 (1)	8971 (3)	5096 (1)
Cl(2)	3738 (1)	10673 (3)	3902 (2)
C(8)	3844 (15)	9529 (45)	3869 (21)
C(9)	3837 (19)	96 (54)	4535 (25)
N(9)	3833 (13)	713 (38)	5070 (18)

[a] Coordinate fixed to define the origin.

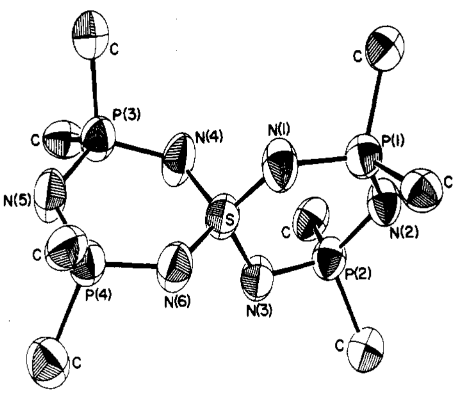

Figure 2. ORTEP drawing (50% probability ellipsoids) of $(Ph_2PN)_4(SN_2)$ (**2**) (molecule A), showing the atomic numbering scheme. For clarity, only α-C atoms of phenyl rings are shown.

contributes one π-electron to each ring, the individual P_2SN_3 rings are 6-π-electron systems isoelectronic with $P_2SN_3^+$ in **1**. In contrast to **1** (X = Cl), however, spirocycle **2** exhibits high stability toward heat and nucleophilic reagents. There are important differences between **1** and **2** that account for their dissimilar reactivities. In **2** the sulfur atom is four-coordinate and in a formal oxidation state of +6 whereas the sulfur atom in **1**, in solution, is two-coordinate.[20] Consequently, sulfur must utilize d orbitals in the π system of **2** whereas the sulfur p_z orbital makes the primary contribution to the π system of **1**.[13] The result will be

Table V. Selected Bond Lengths (Å) and Angles (deg) for $(Ph_2PN)_4(SN_2)\cdot 0.5CH_3CN$

	molecule A	molecule B
	Distances	
S(1)–N(1)	1.555 (4)	1.552 (4)
S(1)–N(3)	1.560 (3)	1.562 (4)
S(1)–N(4)	1.565 (3)	1.557 (4)
S(1)–N(6)	1.553 (4)	1.558 (3)
N(1)–P(1)	1.604 (4)	1.608 (4)
P(1)–N(2)	1.587 (3)	1.590 (4)
N(2)–P(2)	1.584 (4)	1.587 (4)
P(2)–N(3)	1.609 (4)	1.611 (4)
N(4)–P(3)	1.592 (4)	1.600 (4)
P(3)–N(5)	1.593 (4)	1.587 (4)
N(5)–P(4)	1.589 (3)	1.595 (4)
P(4)–N(6)	1.594 (4)	1.606 (4)
	Angles	
N(1)–S(1)–N(3)	111.9 (2)	113.2 (2)
N(1)–S(1)–N(4)	110.1 (2)	108.4 (2)
N(1)–S(1)–N(6)	107.0 (2)	105.0 (2)
N(3)–S(1)–N(4)	108.7 (2)	108.9 (2)
N(3)–S(1)–N(6)	106.7 (2)	110.2 (2)
N(4)–S(1)–N(6)	112.5 (2)	111.2 (2)
S(1)–N(1)–P(1)	125.3 (2)	125.1 (2)
N(1)–P(1)–N(2)	116.3 (2)	115.4 (2)
P(1)–N(2)–P(2)	120.1 (2)	120.6 (2)
N(2)–P(2)–N(3)	116.3 (2)	116.4 (2)
P(2)–N(3)–S(1)	121.4 (2)	124.4 (2)
S(1)–N(4)–P(3)	125.5 (3)	123.0 (2)
N(4)–P(3)–N(5)	117.0 (2)	116.8 (2)
P(3)–N(5)–P(4)	119.6 (2)	119.7 (2)
N(5)–P(4)–N(6)	117.0 (2)	116.9 (2)
P(4)–N(6)–S(1)	126.8 (2)	123.5 (2)

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(19) Schmidpeter, A.; Eiletz, H. *Phosphorus, Relat. Group V Elem.* **1976**, *6*, 113. Schmidpeter, A.. Eiletz. H.; van Seyerl, J.; Huttner, G. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 911. The anion $(Ph_2PN)_4(PN_2)^-$, formally isoelectronic with **2**, has been prepared, but it has not been possible to grow crystals suitable for an X-ray structural determination (Schmidpeter, A., private communication). As suggested by Schmidpeter et al., the anion probably has a structure similar to that of **2** with phosphorus, instead of sulfur, as the spirocyclic center.

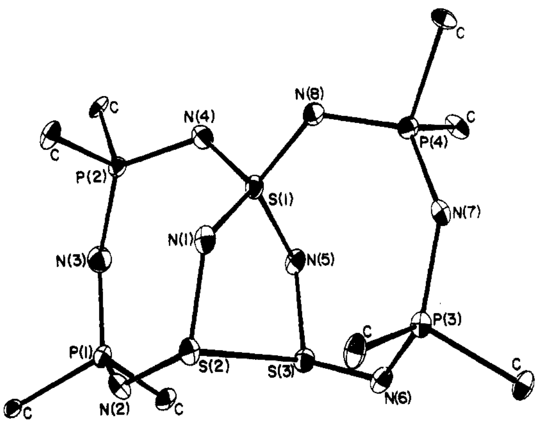

Figure 3. ORTEP drawing (50% probability ellipsoids) of $(Ph_2PN)_4(S_3N_4)$ (**4**), showing the atomic numbering scheme. For clarity, only α-C atoms of phenyl rings are shown.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $(Ph_2PN)_4(S_3N_4)\cdot 0.7CH_2Cl_2\cdot 0.2CH_3CN$

	Distances		
S(1)–N(1)	1.620 (5)	N(3)–P(2)	1.569 (6)
S(1)–N(4)	1.560 (5)	P(2)–N(4)	1.609 (5)
S(1)–N(5)	1.617 (5)	N(5)–S(3)	1.606 (6)
S(1)–N(8)	1.557 (5)	S(3)–N(6)	1.599 (5)
N(1)–S(2)	1.611 (5)	N(6)–P(3)	1.618 (5)
S(2)–S(3)	2.366 (2)	P(3)–N(7)	1.578 (5)
S(2)–N(2)	1.581 (5)	N(7)–P(4)	1.578 (5)
N(2)–P(1)	1.622 (5)	P(4)–N(8)	1.608 (5)
P(1)–N(3)	1.587 (6)		
	Angles		
N(1)–S(1)–N(4)	113.7 (3)	P(1)–N(3)–P(2)	141.5 (4)
N(1)–S(1)–N(5)	105.7 (3)	N(3)–P(2)–N(4)	120.3 (3)
N(1)–S(1)–N(8)	108.8 (3)	P(2)–N(4)–S(1)	122.7 (3)
N(4)–S(1)–N(5)	109.7 (3)	S(1)–N(5)–S(3)	120.4 (3)
N(4)–S(1)–N(8)	105.1 (3)	N(5)–S(3)–S(2)	91.6 (2)
N(5)–S(1)–N(8)	114.0 (3)	N(6)–S(3)–S(2)	107.2 (2)
S(1)–N(1)–S(2)	120.3 (3)	N(5)–S(3)–N(6)	116.9 (3)
N(1)–S(2)–S(3)	91.6 (2)	S(3)–N(6)–P(3)	129.7 (3)
N(2)–S(2)–S(3)	104.8 (2)	N(6)–P(3)–N(7)	120.1 (3)
N(1)–S(2)–N(2)	117.8 (3)	P(3)–N(7)–P(4)	140.4 (3)
S(2)–N(2)–P(1)	130.9 (3)	N(7)–P(4)–N(8)	121.7 (3)
N(2)–P(1)–N(3)	119.4 (3)	P(4)–N(8)–S(1)	125.5 (3)

a higher energy LUMO (π^*), which, together with the higher coordination number of sulfur, will render **2** less susceptible to ring-opening reactions. In summary, the electronic structure of **2** resembles that of a cyclophosphazene rather than a cyclophosphathiazene due to the high oxidation state of sulfur.

Examples of the tendency of π-electron-rich cyclophosphathiazenes to reduce their antibonding electrons by the formation of *intra-ring* S–S bonds include the 12-membered ring $(Ph_2PN)_4(SN)_2$ (**7**)[5,21] and the 8-membered rings 1,5-$(R_2PN)_2(SN)_2$ (R = Me,[22] Ph[6]). By contrast, the formation of an intra-ring S–S bond in 1,3-$(Ph_2PN)_2(SN)_2$ (**5**) is geometrically unfavorable and this heterocycle adopts a monocyclic structure in which the thiazene segment of the ring is planar. It has been successfully treated as a 10-π-electron system in which the HOMO is a π^* orbital.[6] Spirocycle **4** can be viewed as two 1,3-$P_2S_2N_4$ rings fused at a common (spirocyclic) sulfur atom. Alternatively, **4** can be considered to result formally from the insertion of a 3-π-electron SN moiety into each of the 6-π-electron rings of **2**. Both viewpoints lead to the conclusion that the 8-membered rings in **4** would be 9-π-electron systems in the absence of the S–S bond [d(S(2)–S(3)) = 2.366 (2) Å]. It seems reasonable to suggest, therefore, that this *inter-ring* S–S bond reduces the antibonding electron density in the two 8-membered rings.[23] The formation of dimers via weak *intermolecular* S–S bonds is a feature of the solid-state structures of 7-π-electron S–N rings, e.g. $S_3N_2^{+}\cdot$,[24] $PhCN_2S_2\cdot$,[25] and $Ph_2C_2N_3S\cdot$.[26]

We turn now to a comparison of the structural details for **2** and **4** (see Table VII). In light of the previous discussion, a comparison with their monocyclic relatives $(Ph_2PN)_2(NSX)$ (**1** (X = Cl, I, NMe_2, Ph))[13] and 1,3-$(Ph_2PN)_2(SN)_2$ (**5**),[6] respectively, is also informative.

Spirocycle **2** has four short, equal S–N bond lengths of ca. 1.56 Å [cf. d(S–N) for **1**: 1.55 (X = Cl,[3] I[1]), 1.59 (X = NMe_2),[13] and 1.62 Å (X = Ph)[13]].[27] Unlike the case for **1** (X = Cl, I), however, there is no significant difference between P–N(P) (1.59 Å) and P–N(S) (1.60 Å) bond lengths, which are typical values for cyclophosphazenes.[28] The endocyclic bond angles (112° at S, 117° at P, and 123° at N) and the approximate planarity of the rings in **2** bear a close resemblance to those found for **1** (X = NMe_2) (see Table VII).[13] These data suggest that the polarization of π-electron density toward the PNP and NSN units of the ring, which is observed for **1** (X = Cl, I), is not operative in the P_2SN_3 rings of **2**. Thus the molecular structure of **2**, as well as the electronic structure (vide supra), resembles that of a cyclophosphazene rather than a cyclophosphathiazene.

In spirocycle **4** there are two S–N bond lengths of ca. 1.56 Å and two of ca. 1.62 Å for the spirocyclic sulfur atom. The average d(S–N) value is 1.59 Å (cf. 1.58 Å in 1,3-$(Ph_2PN)_2(SN)_2$ (**5**)).[6] There is a significant difference between P–N(P) and P–N(S) distances for **4** (1.585 (5) and 1.610 (5) Å, respectively, which has also been observed for **5**.[6] The central S_3N_2 ring of **4** is approximately planar and forms angles of 88.0 and 88.8° with the best planes through the two 8-membered ($P_2S_2N_4$) rings. The two phosphorus atoms are on opposite sides of the best planes for the $P_2S_2N_4$ rings (cf. **5**).[6] Unlike the $P_2S_2N_4$ ring of **5**, however, in which the NSNSN unit is almost planar, the $P_2S_2N_4$ rings in **4** are distinctly puckered due to the presence of the spirocyclic center and the inter-ring S–S bond. The spirocyclic sulfur and one of the nitrogen atoms attached to it from each ring (N(1) and N(5)) are on opposite sides of the best planes. As a result of this puckering, the average bond angles at sulfur and nitrogen are significantly smaller in **4** compared to those in **5** (Table VII).

Spectroscopic Data for 2 and 4. The ^{31}P NMR spectra show a single peak at +17.9 ppm for **2** and two equally intense peaks at +1.8 and +5.4 ppm for **4**, consistent with the structures determined above. These values are typical for 6- and 8-membered cyclophosphazenes, respectively.[28] However, no coupling was observed between the inequivalent phosphorus atoms in **4** although ^2J(P–N–P) values of 40–50 Hz are typical for cyclotetraphosphazenes.[28]

The high stability of the 6,6-spirocycle (**2**) is manifested in its mass spectrum, which is dominated by the molecular ion peak. In contrast, no molecular ion is observed for **4**; the major fragment ions are 5^+ and 6^+. It should be recalled that **5** is also the major

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(20) Electrochemical studies have shown that **1** is completely ionized to $(Ph_2PN)_2(SN)^+$ and Cl^- ions in acetonitrile solutions (ca. 10^{-3}M): Chivers, T.; Hojo, M., unpublished results quoted in ref 13.

(21) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.

(22) Burford, N.; Chivers, T.; Codding, P. W.; Oakley, R. T. *Inorg. Chem.* **1982**, *21*, 982.

(23) The 8-membered rings in **4** are distinctly puckered, compared to the thiazene unit in **5**, due to the presence of the inter-ring S–S bond and the spirocyclic sulfur center. Consequently, it is not accurate, strictly speaking to distinguish between σ and π electrons.

(24) (a) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784. (b) Krebs, B.; Henkel, G.; Pohl, S.; Roesky, H. W. *Chem. Ber.* **1980**, *113*, 226. (c) Thewalt, U.; Burger, M. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 293.

(25) Vegas, A.; Perez-Salazar, A.; Banister, A. J.; Hey, R. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1812.

(26) Cordes, A. W.; Hayes, P. J.; Josephy, P. D.; Koenig, H.; Oakley, R. T.; Pennington, W. T. *J. Chem. Soc., Chem. Commun.* **1984**, 573. Hayes, P. J.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1326.

(27) As indicated in Table V there are no significant differences in corresponding bond lengths for molecules A and B of **2**, but there are small differences in some of the bond angles. Average values of bond lengths and bond angles are used in the structural comparison of **2** and **4**.

(28) Krishnamurthy, S. S.; Sau, A. C.; Woods, M. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41.

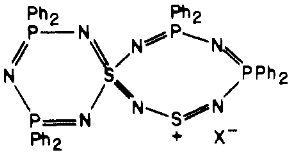
Table VII. Comparison of Bond Lengths (Å) and Bond Angles (deg) in **2**, **4**, $(Ph_2PN)_2(NSNMe_2)$ (**1** (X = NMe_2)), and 1,3-$(Ph_2PN)_2(SN)_2$ (**5**)

	$(Ph_2PN)_4(SN_2)$	$(Ph_2PN)_2(NSNMe_2)$[a]	$(Ph_2PN)_4(S_3N_4)$	1,3-$(Ph_2PN)(SN)_2$[b]
Bond Lengths[c]				
d(S–N, spirocyclic)	four at 1.56		two at 1.56, two at 1.62	
d(S–N, other)		1.59	1.58–1.61	1.58
d[P–N(P)]	1.588 (4)	1.59	1.578 (6)	1.585 (3)
d[P–N(S)]	1.600 (4)	1.61	1.615 (6)	1.610 (4)
Endocyclic Bond Angles[c]				
S (spirocyclic)	112		114	
S (other)		112	117	120
P	117	118	120	118
N (range)	120–127	120–126	120–141	126–144

[a] Data taken from ref 13. [b] Data taken from ref 6. [c] Average values.

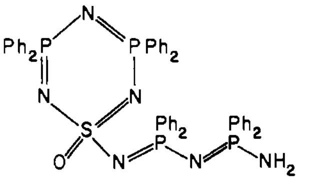
product from the thermal decomposition of **4**.

Reaction of $(Ph_2PN)_2(NSCl)$ (1 (X = Cl)) with Azide Ion. Surprisingly, spirocycle **2** is also produced when **1** (X = Cl) is treated with an excess of sodium azide in acetonitrile *at room temperature*. The latter reaction yields a complex mixture of cyclophosphathiazenes, which include the 12-membered ring **7** and a new compound tentatively identified (vide infra) as a 6,8-spirocycle (**9**) as major products. In addition, small amounts of the 8,8-spirocycle **4**, the 8-membered ring 1,3-$(Ph_2PN)_2(SN)_2$ (**5**), and S_4N_4 were isolated.



9

We have been unable to grow crystals of **9** suitable for X-ray analysis, consequently the proposed structure is based on complete elemental analyses,[29] spectroscopic data (mass and ^{31}P NMR spectra), and chemical evidence. The major peaks in the mass spectrum occur at *m/e* 856, 490, and 444, corresponding to ions of the 6,6-spirocycle **2**, the 8-membered ring **5**, and the 6-membered ring **6**, respectively. The mass spectrum of the 8,8-spirocycle shows the same peaks, but the intensity of the 490 peak relative to that of the 444 peak is much higher for **4**. The ^{31}P NMR spectrum of **9** consists of three singlets in the approximate intensity ratio 2:1:1 and bears a striking resemblance to that of $(Ph_2PN)_2(NS(O)NPPh_2NH_2)$ (**10**).[7] Finally, the decomposition of **9** to the 6,6-spirocycle **2** was observed to occur (^{31}P NMR spectrum). This transformation would involve the elimination of NSX, a process that is known to occur readily for 8-membered cyclophosphathiazenes containing adjacent thiazyl groups.[21]



10

The 12-membered ring **7** can be considered to result from the reduction of **1** (X = Cl) by azide ion[30] (cf. conversion of **1** (X = Cl) to **7** by Ph_3Sb).[5] To account for the simultaneous production of **9**, we propose that **1** (X = N_3), formed via nucleophilic substitution, acts as a source of the nitrene **1** (X = N). The reaction of the nitrene with $(Ph_2PN)_2(SN)^+X^-$[29] could then lead to **9** via a ring expansion reaction similar to that involved in the formation of the 8,8-spirocycle (vide supra). We have no direct evidence for the existence of the nitrene, however, and this aspect of the proposed mechanism, together with related ring expansion reactions of **1**, is the subject of continuing investigations.[31]

Summary and Conclusions

The 6,6-spirocycle **2** plays a central role, as the final product, in the thermal decomposition of a variety of cyclophosphathiazenes containing sulfur in the +3 or +4 oxidation state. For 6-membered rings (**1**) this reaction has been shown to occur via the 12-membered ring **3** when X = NR_2, and other nucleophiles, e.g. $Me_3SiNSNSiMe_3$ and N_3^-, also promote ring-opening reactions of **1**. These examples demonstrate that the presence of two- or three-coordinate sulfur in these ring systems results in a much higher reactivity than is observed for the corresponding cyclophosphazenes. The next challenge is to determine whether this greater reactivity can be exploited for the preparation of even larger rings or linear polymers containing a backbone of P, N, and S atoms.

Acknowledgment. We thank the NSERC (Canada) for financial support.

Supplementary Material Available: Listings of thermal parameters for non-hydrogen atoms (Tables S-I and S-VI), positional and thermal parameters for hydrogen atoms (Tables S-II and S-VII), bond lengths (Tables S-III and S-VIII) and bond angles (Tables S-IV and S-IX) associated with phenyl rings, structure factor amplitudes (Tables S-V and S-X), and best planes (Table S-XI) for **2** and **4** (75 pages). Ordering information is given on any current masthead page.

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(29) In order to have an even number of electrons the 6,8-spiroycle must either be a cation or contain one three-coordinate nitrogen atom. The identity of X^- in **9** is, however, uncertain. The obvious choice, Cl^-, is ruled out by the chemical analyses, which total 100% for C, H, N, P, and S. The calculated analytical data agree well with the experimental values if X = H, but there is no evidence for =NH in the IR spectrum of **9**.

(30) The reduction of cyclothiazyl halides, $S_3N_2Cl^+Cl^-$ and $(NSCl)_3$, to $(SN)_x$ and S_4N_4 by sodium azide has been reported recently: Kennett, F. A.; MacLean, G. K.; Passmore, J.; Rao, M. N. S. *J. Chem. Soc., Dalton Trans.* **1982**, 851.

(31) We have prepared the azide **1** (X = N_3) from **1** (X =Cl) and trimethylsilyl azide and have observed that it decomposes readily at 100 °C to give **2**. Attempts to trap the nitrene **11** have been thwarted by the extreme moisture sensitivity of this azide.