1946 *Inorg. Chem.* **1984**, *23*, 1946–1952

Contribution from the Department of Chemistry,
The University of Calgary, Calgary, Alberta T2N 1N4, Canada

Oxidative Addition of Halogens to 1,3- and 1,5-$(Ph_2PN)_2(SN)_2$: X-ray Crystal Structure of 1,5-$(Ph_2PN)_2(NSBr)_2$ and a Comparison of the Crystal Structures of the 12-Membered Ring 1,3,7,9-$(Ph_2PN)_4(SN)_2$ and the Corresponding Dication $(Ph_2PN)_4(SN)_2^{2+}$

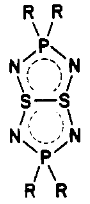
N. BURFORD, T. CHIVERS,* M. N. S. RAO, and J. F. RICHARDSON

Received September 2, 1983

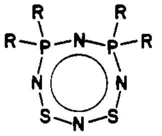
The 8-membered ring 1,5-$(Ph_2PN)_2(SN)_2$ undergoes an oxidative-addition reaction with Br_2 or SO_2Cl_2 to give 1,5-$(Ph_2PN)_2(NSX)_2$ (X = Br, Cl). The crystals of 1,5-$(Ph_2PN)_2(NSBr)_2$ are monoclinic, space group *Pn*, with $a = 11.476$ (3) Å, $b = 7.240$ (1) Å, $c = 16.914$ (4) Å, $\beta = 106.42$ (1)°, $V = 1347.9$ (5) Å^3, and $Z = 2$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to give a final $R = 0.043$ and $R_w = 0.047$. The structure consists of an 8-membered ring in a chair conformation with exocyclic bromine substituents in a trans configuration [d(S–Br) = 2.454 (7) and 2.440 (8) Å]. The average S–N and P–N bond lengths are 1.53 and 1.62 Å, respectively, and the average endocyclic bond angles at phosphorus, sulfur, and nitrogen are 119.3, 114.0, and 139.3°, respectively. In contrast, the reaction of 1,3-$(Ph_2PN)_2(SN)_2$ with SO_2Cl_2 results in a ring contraction to give $(Ph_2PN)_2(NSCl)$ while the reaction with Br_2 produces $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2$, (**7**, X = Br). The molecular structure of the dication in **7**, a 12-membered ring, is compared with that of the corresponding neutral compound 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (**9**) prepared from $(Ph_2PN)_2(NSCl)$ and Ph_3Sb. The crystal data are as follows: for **7**·CH_3CN, monoclinic, space group $P2_1/n$, $a = 16.956$ (3) Å, $b = 13.978$ (1) Å, $c = 23.796$ (4) Å, $\beta = 91.61$ (1)°, $V = 5638$ (1) Å^3, $Z = 4$; for **9**, triclinic, $P\bar{1}$, $a = 9.191$ (1) Å, $b = 11.724$ (1) Å, $c = 21.409$ (2) Å, $\alpha = 79.29$ (1)°, $\beta = 89.01$ (1)°, $\gamma = 75.30$ (1)°, $V = 2191.5$ (6) Å^3, $Z = 2$. The final residual factors were $R = 0.051$ and $R_w = 0.051$ for **7** and $R = 0.046$ and $R_w = 0.024$ for **9**. The reactions of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ with iodine or excess bromine produce the 6-membered rings $(Ph_2PN)_2(NSI)$ and $[(Ph_2PN)_2(SN)]^+[Br_3^-]$, respectively. The compound 1,3-$(Ph_2PN)_2(SN)_2$, but not the 1,5-isomer, readily undergoes a cycloaddition reaction with norbornadiene to give a symmetrical S,S-bonded adduct on the basis of ^1H and ^{13}C NMR data.

Introduction

We have recently reported the preparation and structural identification of two isomers of the 8-membered $P_2S_2N_4$ ring, **1** and **2**.[1] The structural parameters and spectroscopic properties of **2** are consistent with a 10-π-electron eight-center system, i.e. a π-electron-rich ring.[2] For example, this dark orange isomer exhibits a strong visible absorption band at 460 nm attributed to the HOMO(π^*) → LUMO(π^*) transition.[1] In contrast, the 1,5-isomer, **1**, is pale yellow and has a bicyclic structure in which the two halves of the molecule are folded about a cross-ring S–S bond (d(S–S) = 2.528 (1) Å).[1] The methyl derivative of **1** has a similar structure.[3] In effect the two π^* electrons of a planar 10-π-electron eight-center ring are converted to a pair of S–S σ-bonding electrons in the butterfly structure **1**.[3,4]



1



2

In view of this fundamental difference between the electronic structures of the structural isomers **1** and **2**, it was of interest to compare their chemical reactivity. π-Electron-rich inorganic heterocycles are known to be readily oxidized by halogens and to undergo cycloaddition reactions with certain olefins.[2] We have, therefore, commenced this comparison by investigating the reactions of **1** and **2** with halogens and with norbornadiene (NBD). In this paper we describe the synthesis (X = Cl, Br) and X-ray structural determination (X = Br) of the mixed phosphazene–thiazyl ring 1,5-$(Ph_2PN)_2(NSX)_2$ (**3**). We also report the unexpected formation of the salt $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2$ (**7**, X = Br) from the reaction of **2** with Br_2. The structure of this 12-membered cyclic dication is compared with that of the corresponding neutral compound, 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (**9**) prepared from $(Ph_2PN)_2(NSCl)$ (**5**, X = Cl) and triphenylantimony.[5] The 6-membered P_2SN_3 ring, **5** or **8**, is re-formed when **9** is treated with halogens. The spectroscopic characterization of the NBD adduct of **2** is also described.

Experimental Section

Reagents and General Procedures. The isomers 1,3- and 1,5-$(Ph_2PN)_2(SN)_2$,[1] and $(Ph_2PN)_2(NSCl)$,[6] were prepared by literature procedures. Bromine (Fisher), chlorine (Matheson), iodine (Shawinigan), triphenylantimony (Eastman), and norbornadiene (Aldrich) were commercial products used as received. Acetonitrile was dried over P_2O_5 and calcium hydride and freshly distilled before use. Methylene dichloride was distilled from P_2O_5. All reactions were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox and silica gel. Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. ^{31}P NMR spectra were obtained on a Varian XL 200 spectrometer using 85% H_3PO as external reference. Chemical analyses were performed by M.H.W. Laboratories, Phoenix, AZ.

Preparation of 1,5-$(Ph_2PN)_2(NSBr)_2$ (3, X = Br). Liquid bromine (0.6 mmol) was added dropwise, by syringe, to a stirred solution of 1,5-$(Ph_2PN)_2(SN)_2$ (0.30 g, 0.6 mmol) in methylene dichloride (15 mL) at 23 °C. The yellow solution was cooled to −20 °C to produce yellow crystals of 1,5-$(Ph_2PN)_2(NSBr)_2$ (0.33 g, 0.5 mmol), mp 163–5 °C (dec). Anal. Calcd for $C_{24}H_{20}Br_2N_4P_2S_2$: C, 44.33; H, 3.10; Br, 24.57; N, 8.61. Found: C, 44.48; H, 3.13; Br, 24.80; N, 8.58. IR (Nujol): 1585 (w), 1475 (w), 1439 (w), 1310 (w), 1240 (vs), 1183 (s), 1170 (vs), 1156 (vs), 1120 (s), 1112 (s), 1029 (w), 1000 (m), 741 (w), 730 (s), 722 (s), 690 (s), 545 (s), 519 (m), 479 (w), 440 (w), 420 (w), 376 (w), 265 (w) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): +7.3 ppm.

Preparation of 1,5-$(Ph_2PN)_2(NSCl)_2$ (3, X = Cl). Sulfuryl chloride (0.6 mmol) was added dropwise, by syringe, to a stirred solution of

---

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

[2] Chivers, T. *Acc. Chem. Res.*, in press.

[3] Burford, N.; Chivers, T.; Codding, P. W.; Oakley, R. T. *Inorg. Chem.* **1982**, *21*, 982.

[4] Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Adv. Chem. Ser.* **1983**, *No. 232*, 81.

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

[6] Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1982**, 982. Optimum conditions involve the use of a 3:1 molar ratio of $Ph_2PCl–S_4N_4$ in acetonitrile at reflux for 3 h.

0020-1669/84/1323-1946$01.50/0

1,5-$(Ph_2PN)_2(SN)_2$ (0.30 g, 0.6 mmol) in methylene dichloride (15 mL) at 23 °C. The white precipitate, which formed immediately, was dissolved by addition of warm CH_2Cl_2 (50 mL). The pale green solution was cooled to −20 °C to produce white crystals (with a pale green tinge) of 1,5-$(Ph_2PN)_2(NSCl)_2$ (0.27 g, 0.5 mmol), mp 156–8 °C (dec). Anal. Calcd for $C_{24}H_{20}Cl_2N_4P_2S_2$: C, 51.34; H, 3.59; Cl, 12.63; N, 10.00. Found: C, 51.35; H, 3.80; Cl, 12.89; N, 9.98. IR (Nujol): 1580 (w), 1475 (m), 1437 (vs), 1312 (m), 1245 (vs), 1190 (vs), 1177 (vs), 1164 (vs), 1125 (vs), 1030 (m), 1000 (m), 851 (vw), 750 (m), 735 (vs), 724 (vs), 696 (vs), 645 (w), 546 (s), 527 (m), 480 (w), 438 (w), 421 (w), 383 (m), 331 (w), 290 (m) cm^{-1}.

Reaction of 1,3-$(Ph_2PN)_2(SN)_2$ with Bromine. (a) Liquid bromine (0.4 mmol) was added dropwise, by syringe, to a stirred solution of 1,3-$(Ph_2PN)_2(SN)_2$ (0.20 g, 0.4 mmol) in acetonitrile (20 mL) at 23 °C. The deep orange solution turned deep red-brown immediately and, after 30 min, became pale orange. The volume of the solution was reduced to 10 mL by removal of solvent in vacuo, and when the solution was cooled to −20 °C, orange crystals of $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2$ (**7**, X = Br) (0.11 g, 0.1 mmol) were obtained. Anal. Calcd for $C_{48}H_{40}Br_6N_6P_4S_2$: C, 42.13; H, 2.95; N, 6.14. Found: C, 42.27; H, 3.30; N, 6.18. IR (Nujol): 1583 (m), 1578 (vw), 1478 (m), 1438 (vs), 1307 (s), 1290 (s), 1260 (s), 1200 (vs), 1177 (vs), 1160 (s), 1127 (vs), 1117 (vs), 1027 (w), 1000 (m), 840 (m), 760 (m), 748 (s), 737 (vs), 720 (s), 696 (vs), 632 (w), 560 (vs), 547 (s), 535 (s), 506 (vs), 465 (w), 419 (m) 322 (vw) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): +12.0 ppm.

(b) The reaction mixture obtained by addition of bromine (1.0 mmol) to a solution of 1,3-$(Ph_2PN)_2(SN)_2$ (0.50 g, 1.0 mmol) in acetonitrile (25 mL) was heated at reflux for 16 h. A small amount of yellow precipitate, removed by filtration, was identified as $S_4N_3^+Br_3^-$ (infrared spectrum).[7] The filtrate produced a mixture of pale orange needles and yellow platelets identified as $[(Ph_2PN)_2(SN)]^+[Br_3^-]$ and $(Ph_2PN)_2(NSBr)$ (total yield 0.54 g), respectively, by their infrared spectra.[8] In a separate experiment, a solution of $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2$ warmed to 60 °C in acetonitrile produced orange crystals of $[(Ph_2PN)_2(SN)]^+[Br_3^-]$.

Reaction of 1,3-$(Ph_2PN)_2(SN)_2$ with Sulfuryl Chloride. Sulfuryl chloride (0.4 mmol) was added dropwise, by syringe, to a stirred solution of 1,3-$(Ph_2PN)_2(SN)_2$ (0.20 g, 0.4 mmol) in acetonitrile (20 mL). The deep orange solution turned yellow immediately. The volume of the solution was reduced to 10 mL by removal of solvent in vacuo. Pale yellow crystals of $(Ph_2PN)_2(NSCl)$ (0.15 g, 0.3 mmol), identified by infrared spectroscopy,[6] were obtained when the solution was cooled to −20 °C.

Reaction of 1,3-$(Ph_2PN)_2(SN)_2$ with Iodine. A solution of iodine (0.10 g, 0.4 mmol) in acetonitrile (20 mL) was added to a solution of 1,3-$(Ph_2PN)_2(SN)_2$ (0.20 g, 0.4 mmol) in acetonitrile (20 mL). The deep orange solution became black immediately. The volume of the solution was reduced to 10 mL, and cooling to −20 °C produced black crystals of $[(Ph_2PN)_4(SN)_2]^{2+}[I_3^-]_2$ (**7**, X = I) (0.16 g, 0.1 mmol).[9] Anal. Calcd for $C_{48}H_{40}I_6N_6P_4S_2$: C, 34.93; H, 2.44; I, 46.14; N, 5.09; P, 7.51; S, 3.88. Found: C, 35.61; H, 2.67; I, 43.79; N, 5.00; P, 8.32; S, 4.35. IR (Nujol): 1582 (m), 1574 (vw), 1474 (m), 1437 (vs), 1330 (w), 1305 (w), 1248 (vs), 1168 (vs), 1122 (vs), 1115 (vs), 1068 (vw), 1024 (w), 999 (m), 889 (s), 846 (w), 826 (m), 750 (s), 741 (m), 735 (s), 727 (s), 694 (vs), 588 (vw), 545 (vs), 533 (vs), 513 (vs), 503 (vs), 465 (w), 452 (w), 433 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): +18.8 ppm.

Preparation of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (9). Solid triphenylantimony (0.48 g, 1.4 mmol) was added in small amounts to a stirred suspension of $(Ph_2PN)_2(NSCl)$ (1.30 g, 2.7 mmol) in acetonitrile (25 mL). After 24 h at 23 °C, the bright yellow precipitate was removed by filtration and recrystallization from CH_2Cl_2–CH_3CN (1:1) to give yellow platelets of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (0.48 g, 0.5 mmol), mp 182–4 °C. Anal. Calcd for $C_{48}H_{40}N_6P_4S_2$: C, 64.85; H, 4.54; N, 9.46; S, 7.21; P, 13.94. Found: C, 64.98; H, 4.52; N, 9.26; S, 7.06; P, 14.18 (by difference). IR (Nujol): 1580 (vw), 1473 (m), 1433 (s), 1304 (w), 1273 (w), 1223 (s), 1173 (m), 1131 (m), 1118 (s), 1105 (s), 1078 (vs), 1064 (sh, s), 1026 (m), 997 (w), 792 (s), 781 (w), 761 (w), 737 (w), 724 (s), 718 (s), 692 (s), 568 (s), 553 (s), 530 (w), 520 (w), 510 (s), 450 (w), 429 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): +15.3 ppm. Workup of the filtrate produced Ph_3SbCl_2 and small amounts of 1,3- and 1,5-$(Ph_2PN)_2(SN)_2$ (infrared spectra).[1]

Reaction of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ with Bromine. Liquid bromine (0.31 g, 1.9 mmol) was added to a stirred solution of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (0.34 g, 0.38 mmol) in methylene dichloride (15 mL) at 23 °C. After 3 h, solvent was removed in vacuo, and the residue was dissolved in MeCN–CH_2Cl_2 (4:1) and cooled to −20 °C to give orange red crystals of $[(Ph_2PN)_2(SN)]^+[Br_3^-]$ (0.21 g, 0.31 mmol) identified by comparison of its infrared spectrum with that of an authentic sample.[8]

Reaction of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ with Iodine. Crystals of iodine (0.12 g, 0.45 mmol) were added to a stirred solution of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (0.40 g, 0.45 mmol) in methylene dichloride (20 mL) over a period of 15 min. After 4 h solvent was removed in vacuo, and the residue was treated with acetonitrile (15 mL). Red crystals of $(Ph_2PN)_2(NSI)$ (0.33 g, 0.58 mmol) were filtered off, and the filtrate yielded orange crystals of $(Ph_2PN)_2(NSI)\cdot MeCN$ (0.17 g, 0.28 mmol). Both products were identified by comparison of their infrared spectra with that of an authentic sample prepared from $(Ph_2PN)_2(NSCl)$ and potassium iodide in acetonitrile.[10]

Preparation of 1,3-$(Ph_2PN)_2(SN)_2\cdot$NBD (10). Norbornadiene (0.04 g, 0.4 mmol) was added dropwise to a solution of 1,3-$(Ph_2PN)_2(SN)_2$ (0.20 g, 0.4 mmol) in diethyl ether (20 mL). After 1 h, the orange solution became pale yellow, and a white precipitate was filtered off and recrystallized from CH_2Cl_2–CH_3CN to give colorless crystals of 1,3-$(Ph_2PN)_2(SN)_2\cdot C_7H_8$ (0.14 g, 0.2 mmol). Anal. Calcd for $C_{31}H_{28}N_4P_2S_2$: C, 63.90; H, 4.84; N, 9.62. Found: C, 63.72; H, 4.70; N, 9.68. ^1H NMR [$CDCl_3$; δ values vs. internal Me_4Si (multiplicity, J in Hz)]: δ 1.50 (AB), 3.22 (t, 1.6), 4.02 (d, 1.9), 6.10. $\{^1H\}^{31}C$ NMR ($CDCl_3$; δ values vs. internal Me_4Si): δ 44.2, 45.2, 82.7, 139.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): +6.2 ppm. IR (Nujol): 1438 (s), 1240 (vs), 1164 (w), 1130 (vs), 1113 (vs), 1098 (m), 1072 (w), 835 (vs), 750 (s), 729 (vs), 705 (m), 552 (m), 539 (s), 512 (s), 490 (w), 453 (w) cm^{-1}.

X-ray Structural Analyses. The crystal data and experimental conditions and results are summarized in Table I. Crystals of 1,5-$(Ph_2PN)_2(NSBr)_2$ and $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2\cdot CH_3CN$ are extremely air-/moisture-sensitive and were therefore mounted in a sealed capillary under an atmosphere of nitrogen. A crystal of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ was mounted on a glass fiber under normal conditions. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurately centered reflections. The space groups were determined by using the indexing routines of the diffractometer and by examination of the intensities measured during data collection. Where necessary, the final choice of space group was based on the distribution of E values calculated with use of a K curve.[11a] The intensity data were collected on an Enraf-Nonius CAD4F automated diffractometer using an ω–2θ scan and were corrected for Lorentz and polarization effects. With 1,5-$(Ph_2PN)_2(NSBr)_2$ and $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2\cdot CH_3CN$, absorption corrections were applied.[11b]

The structures were solved by direct methods[11c] and refined by using full-matrix least squares as described previously.[1] Atomic scattering factors were those of Cromer and Mann[12a] and were corrected for the real and imaginary parts of the anomalous dispersion.[12b] With each structure, phenyl H atoms were included in idealized positions (sp^2, C–H = 0.95 Å) and thermal parameters were set to 1.1 times

---

(7) Wolmershäuser, G.; Street, G. B. *Inorg. Chem.* **1978**, *17*, 2685.

(8) We have recently found that $(Ph_2PN)_2(NSCl)$ reacts with Br_2 or I_2 in methylene dichloride at 23 °C to give $[(Ph_2PN)_2(NS)]^+[X_3^-]$ (X = Br, I), which, on thermolysis at ca. 155 °C, produces $(Ph_2PN)_2(NSX)$: Chivers, T.; Rao, M. N. S. *Inorg. Chem.*, in press.

(9) The analytical data are low for iodine content and slightly high for C, H, P, and S, a result that can be attributed to facile loss of molecular I_2 from the salt (cf. $S_4N_3^+I_3^-$ dec. pt ca. 40 °C: Vincent, H.; Monteil, Y.; Berthet, M. P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 5). The infrared spectrum is very similar to that of **7** (X = Br), but there is an unexplained difference of ca. 7 ppm in the ^{31}P NMR chemical shift compared to that of **7** (X = Br).

(10) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 700.

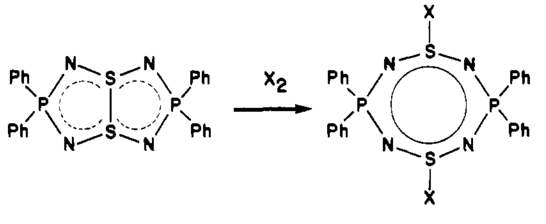
(11) Computing was performed at the University of Calgary with use of: (a) The X-RAY 76 package of crystallographic programs: Stewart, J. M., Ed. Technical Report TR-446; Computer Science Center: University of Maryland, *College Park, MD.* (b) A local modification of the program CADABS by P. Coppens et al., State University of New York at Buffalo Crystallographic Computing Programs. (c) The program MULTAN 78 by P. Main et al., University of York, England.

(12) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect A* **1968**, *A24*, 321. (b) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV, p 149.

Table I. Crystallographic Parameters

	$1,5\text{-}(Ph_2PN)_2(NSBr)_2$	$[(Ph_2PN)_4(NS)_2]^{2+}\text{-}[Br_3^-]_2\cdot CH_3CN$	$1,3,7,9\text{-}(Ph_2PN)_4(SN)_2$
fw	650.3	1409.4	888.9
space group	*Pn*	$P2_1/n$	*P*1
a, Å	11.476 (3)	16.956 (3)	9.191 (1)
b, Å	7.240 (1)	13.978 (1)	11.724 (1)
c, Å	16.914 (4)	23.796 (4)	21.409 (2)
α, deg	90	90	79.29 (1)
β, deg	106.42 (1)	91.61 (1)	89.01 (1)
γ, deg	90	90	75.30 (1)
V, $Å^3$	1348 (1)	5638 (1)	2191.5 (6)
Z	2	4	2
D_c, g cm^{-3}	1.60	1.66	1.35
radiation (λ, Å)	Mo Kα (0.710 69, graphite monochromator)		
temp, °C	23 (2)	23 (2)	23 (2)
scan range Δω, $1.5(a + 0.347 \tan \theta)^\circ$	$a = 0.56$	$a = 0.60$	$a = 0.58$
scan speed, deg min^{-1}	0.6-5.0	0.5-5.0	0.7-5.0
max θ, deg	30	20	25
reflcns scanned, obsd ($I > 3\sigma(I)$)	3917, 1199	5333, 1390	7676, 4559
octants collcd	$-h,+k,\pm l$	$-h,+k,\pm l$	$-h,\pm k,\pm l$
cryst dimens, mm	0.22 × 0.33 × 0.50	0.20 × 0.36 × 0.49	0.15 × 0.32 × 0.44
boundary planes	6; {010}, {101}	7; {010}, {101}, $(01\bar{1})$	6; {001}, {011}, $(\bar{1}00)$, (110)
μ(Mo Kα), cm^{-1}	34.72	47.51	3.10
min/max transmissn factors	0.47/0.65	0.33/0.59	
weighting formula, $[\sigma^2(F_o) + n(F_o)^2]^{-1}$	$n = 0.0003$	$n = 0.0002$	$n = 0.0$
no. observns used in final cycle[a]	2588	3283	6216
residual e.d., e $Å^{-3}$	1.36	0.83	0.46
GOF	1.34	1.04	1.61
R,R_w[b]	0.043, 0.047	0.051, 0.051	0.046, 0.024

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



1 3

Figure 1. Oxidative addition of halogens (X = Br, Cl) to $1,5\text{-}(Ph_2PN)_2(SN)_2$.

the effective isotropic thermal parameter of the bonded C atom. The methyl H atoms of the CH_3CN solvate molecule in the dication could not be located. In the final cycles the structures were refined as follows: $1,5\text{-}(Ph_2PN)_2(NSBr)_2$, the N, P, S, and Br atoms were refined with anisotropic thermal parameters and the C atoms were refined isotropically; $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2\cdot CH_3CN$, the phenyl rings were treated as rigid groups (C–C = 1.395 Å, C–C–C = 120°) with individual isotropic thermal parameters for the C atoms, all N and the remaining C atoms were refined isotropically, and the P, S, and Br atoms were refined anisotropically; $(Ph_2PN)_4(SN)_2$, all non-hydrogen atoms were refined anisotropically. The final difference Fourier maps in all cases showed minor residual peaks that were of no chemical significance.

Results and Discussion

Reactions of 1,3- and $1,5\text{-}(Ph_2PN)_2(SN)_2$ with Halogens. The electron-rich heterocycle, **2**, is more easily oxidized by halogens than its structural isomer, **1**, as might have been expected from a consideration of their electronic structures (vide supra).[1] Furthermore, the outcome of these oxidations is quite different. The halogens Br_2 or Cl_2 (as SO_2Cl_2) undergo a smooth oxidative addition with **1** at room temperature in methylene dichloride to give the bifunctional heterocycles $1,5\text{-}(Ph_2PN)_2(NSX)_2$ (**3**, X = Br, Cl; Figure 1). No reaction was observed between **1** and I_2 even at reflux in acetonitrile. By contrast, the 1,3-isomer, **2**, reacts with SO_2Cl_2 to give a high yield of the 6-membered ring $(Ph_2PN)_2(NSCl)$ (**5**, X = Cl),[6] whereas Br_2 or I_2 in acetonitrile at 23 °C converts **2** to the salts $[(Ph_2PN)_4(SN)_2]^{2+}[X_3^-]_2$ (**7**, X = Br or I) in which

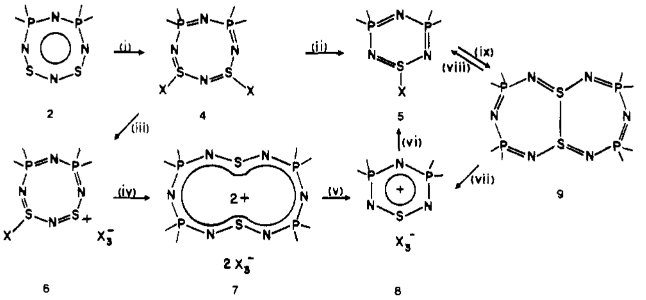


Figure 2. Reactions of $1,3\text{-}(Ph_2PN)_2(SN)_2$ and $1,3,7,9\text{-}(Ph_2PN)_4(SN)_2$ with halogens: (i) SO_2Cl_2, Br_2, or I_2; (ii) –NSX (X = Cl); (iii) X_2 (X = Br, I); (iv) –NSX; (v) 60 °C, X = Br; (vi) $-X_2$ (X = Br, I); (vii) excess Br_2; (viii) I_2; (ix) Ph_3Sb (X = Cl).

the dication is a 12-membered ring (vide infra). This difference in behavior is best explained by initial oxidative addition to give $1,3\text{-}(Ph_2PN)_2(NSX)_2$ (**4**) followed by elimination of NSX (see Figure 2).

The instability of **4** (X = Cl) with respect to loss of NSCl to give **5** (X = Cl) has a parallel in the chlorination of S_4N_4 to give $(NSCl)_3$ via $1,5\text{-}Cl_2S_4N_4$[13] and, probably, $(ClSN)_4$.[14] The different behavior observed for reactions of **2** with Br_2 or I_2 is attributed to the relative stability of the Br_3^- and I_3^- ions compared to Cl_3^- in the solid state.[15] We propose that **4** reacts with excess halogen to give **6**, which subsequently loses NSX (X = Br, I) to form the 12-membered dication $[(Ph_2PN)_4(SN)_2]^{2+}$ as a trihalide salt, **7**, via a dimerization reaction. The isolation of $S_4N_3^+Br^-$ from the reaction of **2** with Br_2 in boiling acetonitrile provides some evidence for the formation of the NSBr monomer.[16]

---

(13) (a) Zborilova, L.; Gebauer, P. *Z. Anorg. Allg. Chem.* **1979**, *448*, 5. (b) Zborilova, L.; Gebauer, P. *Z. Chem.* **1979**, *19*, 32. (c) Zak, Z. *Acta Crystallogr., Sect. B* **1981**, *B37*, 23.

(14) (a) Nelson, J.; Heal, H. G. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 429. (b) Alange, G. G.; Banister, A. J.; Bell, B. *J. Chem. Soc., Dalton Trans.* **1972**, 2399. (c) Vincent, H.; Monteil, Y. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 51.

(15) Downs, A. J.; Adams, C. J. "Comprehensive Inorganic Chemistry"; Pergamon Press: Oxford, 1973; Vol. 2, p 1536.

Table II. Atomic Coordinates for the Non-Hydrogen Atoms of 1,5-$(Ph_2PN)_2(NSBr)_2$ (×10^4 for Br, S, and P; ×10^3 for C and N)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Br(1)	6244[a]	−695 (5)	7892[a]	C(22)	354 (2)	404 (3)	494 (1)
Br(2)	6858 (1)	5684 (5)	5437 (1)	C(23)	277 (2)	491 (3)	428 (1)
S(1)	5917 (1)	−143 (11)	6414 (4)	C(24)	259 (2)	642 (2)	433 (1)
S(2)	7257 (6)	5197 (11)	6914 (4)	C(25)	296 (1)	739 (2)	507 (1)
P(1)	4809 (7)	3384 (11)	6567 (5)	C(26)	359 (2)	644 (4)	582 (1)
P(2)	8341 (6)	1586 (10)	6758 (4)	C(31)	952 (2)	35 (4)	763 (2)
N(1)	494 (2)	131 (3)	625 (1)	C(32)	963 (2)	134 (3)	840 (1)
N(2)	609 (2)	656 (3)	702 (1)	C(33)	1022 (3)	29 (4)	909 (2)
N(3)	826 (2)	366 (3)	714 (1)	C(34)	1079 (2)	−189 (2)	886 (1)
N(4)	718 (1)	51 (3)	633 (1)	C(35)	1044 (2)	−252 (3)	807 (1)
C(11)	402 (1)	316 (2)	736 (1)	C(36)	960 (3)	−142 (5)	752 (2)
C(12)	409 (2)	472 (3)	788 (1)	C(41)	915 (2)	161 (3)	604 (1)
C(13)	342 (1)	470 (2)	843 (1)	C(42)	995 (3)	309 (4)	605 (2)
C(14)	264 (2)	334 (3)	844 (1)	C(43)	1068 (2)	307 (3)	546 (2)
C(15)	253 (2)	165 (3)	783 (1)	C(44)	1047 (2)	216 (2)	488 (1)
C(16)	313 (2)	184 (3)	728 (1)	C(45)	960 (2)	78 (2)	476 (1)
C(21)	388 (2)	463 (4)	500 (1)	C(46)	892 (1)	59 (2)	532 (1)

[a] Restricted to define the origin.

At first sight it appears that the different stabilities of the isomeric mixed phosphazene–thiazyl rings, 1,5-$(Ph_2PN)_2(NSX)_2$ (**3**) and 1,3-$(Ph_2PN)_2(NSX)_2$ (**4**), may be related to the relative positions of the two thiazyl units. When these units occupy adjacent positions in the ring, loss of NSX occurs readily. However, if these units are separated by a phosphazene unit, the elimination of NSX does not take place, possibly because it would require the cleavage of a P–N as well as an S–N bond. To give further insight into the stability of mixed phosphazene–thiazyl rings we have investigated the reactions of the 12-membered ring, 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (**9**), with halogens.

Reactions of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (9) with Halogens. In contrast to 1,5-$(Ph_2PN)_2(SN)_2$, **9** reacts readily with iodine in methylene dichloride at room temperature (Figure 2). The product is not, however, the 12-membered mixed phosphazene–thiazyl ring $(Ph_2PN)_4(NSI)_2$ but the previously reported 6-membered ring $(Ph_2PN)_2(NSI)$ (**5**, X = I).[10] Similarly, the reaction of **9** with excess bromine produced $[(Ph_2PN)_2(SN)]^+[Br_3^-]$ (**8**, X = Br), and the 6-membered $P_2SN_3^+$ ring is also formed on gentle heating of the 12-membered dication, **7**, in acetonitrile. On the other hand it should be pointed out that the reverse reaction, i.e. dimerization of a 6-membered P_2SN_3 to a 12-membered $P_4S_2N_6$ ring, occurs readily at room temperature in acetonitrile *where the substituents on sulfur are electron-donating R_2N groups* (R = Me, Et, $(-CH_2-)_5$).[17] Thus, it appears that the stability of mixed phosphazene–thiazyl ring systems, $(Ph_2PN)_x(NSX)_y$, depends on the electronic influence of the substituents on sulfur as well as other factors such as ring size and the relative positions of the thiazyl units. Nevertheless in all the transformations of PNS heterocycles described so far, there is a definite preference for processes that involve breaking only S–N bonds. No examples of ring expansion or contraction requiring cleavage of P–N bonds have been observed.

Reaction of 1,3-$(Ph_2PN)_2(SN)_2$ with Norbornadiene. The 6-membered ring $(Ph_2PN)(SN)_2$ readily undergoes a cycloaddition reaction with norbornadiene to give an adduct in which the olefin is symmetrically bound to the sulfur atoms of the heterocyclic ring.[18] This mode of addition is expected since both the HOMO and LUMO of the 6-membered ring are primarily sulfur based. Since the characteristics of the HOMO and LUMO of **2** are almost identical with those of $(Ph_2PN)(SN)_2$ (see Figure 3), a similar cycloaddition reaction with olefins can be anticipated. The addition of norbornadiene to **2** resulted in the immediate formation of a pale yellow crystalline adduct, **10**, which, on the basis of ^1H and ^{13}C NMR data, is formed by symmetrical S,S addition to the heterocyclic ring. By contrast, the 1,5-isomer, **1**, does not form an adduct with norbornadiene.

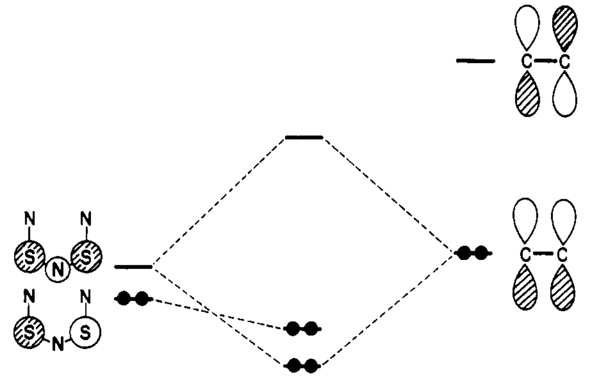
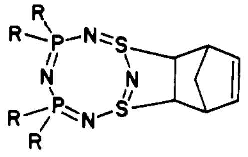


Figure 3. Qualitative symmetry correlation diagram for the interaction of the π-HOMO and LUMO of an $S_2N_3^-$ unit of 1,3-$(Ph_2PN)_2(SN)_2$ with the HOMO and LUMO of an electron-rich olefin.



10

Crystal and Molecular Structures of 1,5-$(Ph_2PN)_2(NSBr)_2$. The crystal structure of 1,5-$(Ph_2PN)_2(NSBr)_2$ (**3**, X = Br) consists of discrete molecular units with no unusual intermolecular contacts. The final atomic coordinates of the unique non-hydrogen portion of the molecule are given in Table II. Thermal parameters, parameters for the hydrogen atoms, and the list of structure factors are available as supplementary material. Selected bond lengths and angles are presented in Table III, and Figure 4 shows an ORTEP drawing with the atomic numbering scheme for the molecule.

The structure of **3** consists of an 8-membered ring in which the two phosphorus and four nitrogen atoms are planar to within 0.07 Å. The two sulfur atoms are displaced on either

---

(16) Wolmershäuser and Street have provided evidence for the involvement of NSBr as an intermediate in the formation of $S_4N_3^+Br^-$ from S_4N_4 and liquid Br_2 (see ref 7).

(17) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702.

(18) Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M. C.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282.

(19) For a more extensive discussion the cycloaddition reaction of olefins with S–N heterocycles, see: Liblong, S. W.; Oakley, R. T.; Cordes, A. W.; Noble, M. C. *Can. J. Chem.* **1983**, *61*, 2062.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 1,5-$(Ph_2PN)_2(NSBr)_2$

Distances			
S(1)-Br(1)	2.454 (7)	S(2)-N(3)	1.57 (2)
S(2)-Br(2)	2.440 (8)	P(1)-N(1)	1.61 (2)
S(1)-N(1)	1.51 (2)	P(1)-N(2)	1.68 (2)
S(1)-N(4)	1.57 (2)	P(2)-N(3)	1.65 (2)
S(2)-N(2)	1.47 (2)	P(2)-N(4)	1.54 (2)
Angles			
Br(1)-S(1)-N(1)	101.8 (10)	N(1)-P(1)-N(2)	118 (1)
Br(1)-S(1)-N(4)	105.3 (7)	P(1)-N(2)-S(2)	145 (2)
Br(2)-S(2)-N(2)	194.5 (8)	N(2)-S(2)-N(3)	112 (1)
Br(2)-S(2)-N(3)	195.2 (9)	S(2)-N(3)-P(2)	132 (1)
N(1)-S(1)-N(4)	116 (1)	N(3)-P(2)-N(4)	121 (1)
S(1)-N(1)-P(1)	137 (1)	P(2)-N(4)-S(1)	144 (1)

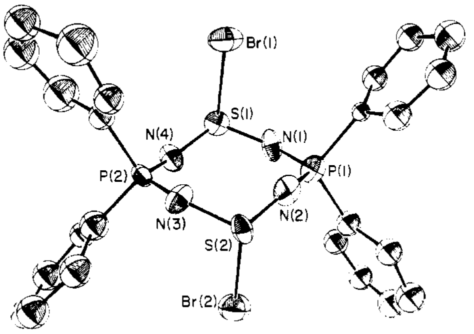


Figure 4. ORTEP drawing (50% probability ellipsoids) of 1,5-$(Ph_2PN)_2(NSBr)_2$ (**3**) (X = Br), showing the atomic numbering scheme.

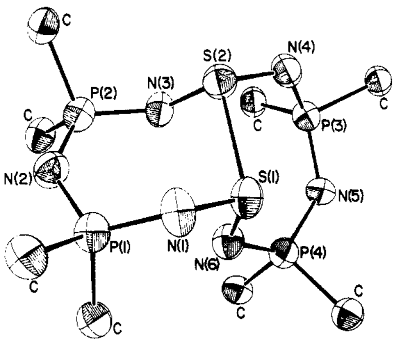


Figure 5. ORTEP drawing (50% probability ellipsoids) of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (**9**), showing the atomic numbering scheme. For clarity only the α-C atoms of the phenyl rings are shown.

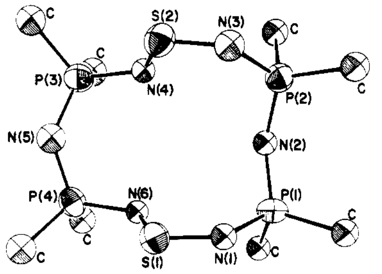
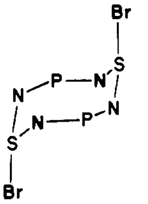


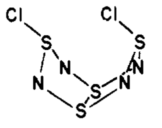
Figure 6. ORTEP drawing (50% probability ellipsoids) of $[(Ph_2PN)_4(SN)_2]^{2+}$ (**7**), showing the atomic numbering scheme. For clarity only the α-C atoms of the phenyl rings are shown.

side of this plane by 0.54 and 0.58 Å, respectively, to give a chair conformation. Although the P-N bond lengths span a wide range (1.54-1.68 Å), the average value (1.62 Å) is the same as that found for **1**.[1] In contrast, the average S-N bond distance (1.53 Å, range 1.47-1.57 Å) is significantly shorter than that in **1** (1.59 Å), suggesting that π bonding is mainly localized in the NSN units of **3**. The absence of the cross-ring S-S bond results in larger bond angles at phosphorus and nitrogen (average values 119 and 139°, respectively) compared to those found for **1** (110 and 121°).[1] The endocyclic bond angles at sulfur are 112.3 and 115.7°.

The most significant structural feature of **3** is the exocyclic S-Br bonds, which adopt a trans (axial, axial) configuration with respect to the 8-membered ring, **11**. This represents the first structural characterization of a thiazyl bromide, and the S-Br bond lengths are ca. 2.45 Å. There are few structurally characterized compounds containing covalent S-Br bonds with which to compare this value.[20-23] However, the S-Br distance in the cation $(BrS)CS_2N_2^+$ is 2.208 (4) Å[24] (cf. sum of covalent radii of sulfur and bromine 2.28 Å),[25] suggesting that the S-Br bond in **3** has an appreciable ionic contribution. Long sulfur-halogen bonds have also been observed for the lower homologue in the mixed phosphazene-thiazyl series, $(Ph_2PN)_2(NSX)$ (d(S-Cl) = 2.36 vs. 2.03 Å;[6] d(S-I) = 2.71 vs. 2.37 Å[10]).



11



12

The trans addition of the halogen substituents across the S-S bond is consistent with the mode of addition of Cl_2 to S_4N_4 to give 1,5-$Cl_2S_4N_4$.[13] In the latter case, the remaining S-S bond imposes a folded structure and the halogen atoms adopt an exo,endo configuration (**12**).[13c] Assuming a bromonium (or chloronium) ion is involved in the initial attack at the cross-ring bond of **1**, the symmetric S-S σ(MO) will facilitate the formation of a bridged intermediate. Subsequent attack by halide ion would be restricted to the other side of the ring leading to trans addition. It should be noted, however, that the bromination of S_4N_4 (unlike chlorination) produces either polymers of the type $(NSBr_{0.4})_x$, in which bromine is present as Br_3^- and/or intercalated Br_2 molecules,[26] or the salt $S_4N_3^+Br_3^-$.[7,27] Evidently 1,5-$Br_2S_4N_4$ is unstable at room temperature, while the heterocycle, **3**, is stable up to ca. 150 °C. Similarly 1,5-$(Ph_2PN)_2(NSCl)_2$ (dec pt ca. 155 °C) has much higher thermal stability than 1,5-$Cl_2S_4N_4$, which must be prepared at -60 °C to avoid decomposition via loss of NSCl.[13]

Crystal and Molecular Structures of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ and $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2{\cdot}CH_3CN$. The crystal structure

---

(20) Magee, P. S. "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1982; Vol. 4, Chapter 6, p 283.

(21) Attempts to prepare $(BrSN)_3$ by the reaction of $(ClSN)_3$ with BBr_3 in methylene dichloride at 0 °C produced $S_4N_4{\cdot}BCl_3$ in 83% yield. Anal. Calcd for $BCl_3N_4S_4$: B, 3.59; Cl, 35.28; N, 18.59; S, 42.55. Found: B, 3.61; Cl, 35.33; N, 18.38; S, 42.13: Chivers, T.; Proctor, J., unpublished results.

(22) The ionic compound $S_4N_3^+Br^-$ decomposes at 90-110 °C to release NSBr monomer: Peake, S. C.; Downs, A. J. *J. Chem. Soc., Dalton Trans.* **1974**, 859.

(23) The preparation of S_5N_5Br, which probably contains the $S_5N_5^+$ cation, has recently been reported: Zborilova, L.; Gegauer, P. *Z. Anorg. Allg. Chem.* **1981**, *483*, 44.

(24) Wolmershäuser, G.; Kruger, C.; Tsay, Y.-H. *Chem. Ber.* **1982**, *115*, 1126.

(25) Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977.

(26) Street, G. B.; Bingham, R. L.; Crowley, J. I.; Kuyper, J. *J. Chem. Soc., Chem. Commun.* **1977**, 464. Akhtar, M.; Chiang, C. K.; Heeger, A. J.; MacDiarmid, A. G. *Ibid.* **1977**, 846. Akhtar, M.; Chiang, C. K.; Heeger, A. J.; Milliken, J.; MacDiarmid, A. G. *Inorg. Chem.* **1978**, *17*, 1539.

(27) Mayerle, J. J.; Wolmershäuser, G.; Street, G. B. *Inorg. Chem.* **1979**, *18*, 1161.

Table IV. Atomic Coordinates of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ ($\times 10^4$) with Esd's in Parentheses

atom	*x/a*	*y/b*	*z/c*
S(1)	3010.5 (9)	7122.4 (7)	2806.9 (4)
S(2)	2817.0 (10)	5781.1 (7)	2118.7 (4)
P(1)	1703.5 (10)	9209.2 (8)	1897.3 (4)
P(2)	637.8 (10)	7502.7 (8)	1315.6 (4)
P(3)	1743.6 (10)	4289.4 (7)	3149.1 (4)
P(4)	891.7 (10)	6478.4 (7)	3665.8 (4)
N(1)	3127 (3)	8302 (2)	2320 (1)
N(2)	972 (3)	8743 (2)	1365 (1)
N(3)	1090 (3)	6375 (2)	1898 (1)
N(4)	2945 (3)	4557 (2)	2611 (1)
N(5)	1340 (3)	5076 (2)	3685 (1)
N(6)	1327 (3)	7341 (2)	3052 (1)
C(11)	293 (4)	9914 (3)	2400 (1)
C(12)	701 (4)	10300 (3)	2921 (2)
C(13)	−372 (5)	10845 (3)	3304 (2)
C(14)	−1849 (5)	11004 (3)	3168 (2)
C(15)	−2285 (4)	10639 (3)	2646 (2)
C(16)	−1220 (4)	10098 (3)	2260 (2)
C(21)	2432 (3)	10437 (3)	1507 (1)
C(22)	1735 (4)	11164 (3)	961 (2)
C(23)	2188 (5)	12170 (3)	684 (2)
C(24)	3343 (5)	12459 (3)	956 (2)
C(25)	4050 (4)	11756 (3)	1492 (2)
C(26)	3609 (4)	10746 (3)	1769 (2)
C(31)	1497 (4)	7085 (3)	599 (1)
C(32)	1602 (5)	5965 (3)	469 (2)
C(33)	2324 (6)	5610 (3)	−66 (2)
C(34)	2916 (5)	6388 (4)	−472 (2)
C(35)	2780 (5)	7512 (4)	−372 (2)
C(36)	2077 (4)	7869 (3)	173 (2)
C(41)	−1357 (3)	7720 (3)	1187 (1)
C(42)	−2068 (4)	6837 (3)	1417 (2)
C(43)	−3615 (4)	7045 (4)	1305 (2)
C(44)	−4420 (4)	8122 (4)	986 (2)
C(45)	−3731 (5)	8999 (4)	756 (2)
C(46)	−2206 (4)	8810 (3)	859 (2)
C(51)	52 (4)	4141 (3)	2783 (1)
C(52)	−1326 (4)	4485 (3)	3049 (2)
C(53)	−2618 (4)	4336 (3)	2777 (2)
C(54)	−2494 (5)	3834 (3)	2245 (2)
C(55)	−1112 (5)	3466 (3)	1983 (2)
C(56)	155 (4)	3627 (3)	2248 (2)
C(61)	2618 (3)	2786 (2)	3570 (1)
C(62)	2015 (4)	2388 (3)	4137 (2)
C(63)	2618 (5)	1244 (3)	4475 (2)
C(64)	3796 (4)	503 (3)	4242 (2)
C(65)	4393 (4)	876 (3)	3690 (2)
C(66)	3804 (4)	2031 (3)	3347 (2)
C(71)	−1108 (3)	7053 (3)	3689 (1)
C(72)	−1948 (4)	7491 (3)	3127 (2)
C(73)	−3495 (4)	7821 (3)	3136 (2)
C(74)	−4211 (4)	7739 (3)	3704 (2)
C(75)	−3403 (4)	7309 (3)	4260 (2)
C(76)	−1844 (4)	6958 (3)	4252 (2)
C(81)	1692 (3)	6710 (3)	4385 (1)
C(82)	1431 (4)	7844 (3)	4526 (2)
C(83)	2085 (5)	8033 (3)	5061 (2)
C(84)	3024 (5)	7098 (4)	5456 (2)
C(85)	3285 (5)	5984 (4)	5324 (2)
C(86)	2620 (4)	5783 (3)	4785 (2)

of 1,3,7,9-$(Ph_2PN)_4(SN)_2$ (**9**) consists of discrete molecular units with no unusual intermolecular contact. The final atomic coordinates are given in Table IV, and Figure 5 shows an ORTEP drawing with the atomic numbering scheme for the molecule. The crystal structure of $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2\cdot CH_3CN$ (**7**, X = Br) consists of cationic and anionic units. The final atomic coordinates are given in Table V, and Figure 6 shows an ORTEP drawing with the atomic numbering scheme for the dication. Thermal parameters, parameters for the hydrogen atoms, and the list of structure factors for **7** and **9** are available as supplementary material. Table VI compares the bond lengths and bond angles for the neutral 12-membered ring **9** with those of the related dication **7**.

Table V. Atomic Coordinates ($\times 10^4$) for Refined Atoms of $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2\cdot CH_3CN$

atom	*x/a*	*y/b*	*z/c*
Br(1)	4916 (1)	4921 (2)	4065 (1)
Br(2)	4745 (1)	3529 (2)	3254 (1)
Br(3)	4588 (2)	2350 (2)	2536 (1)
Br(4)	5111 (1)	7899 (2)	408 (1)
Br(5)	5542 (1)	9374 (2)	936 (1)
Br(6)	6005 (2)	10797 (2)	1522 (1)
S(1)	3771 (3)	6339 (4)	3442 (2)
S(2)	6238 (3)	5846 (4)	3480 (2)
P(1)	4171 (3)	6610 (4)	2288 (2)
P(2)	5879 (3)	6160 (4)	2313 (2)
P(3)	6057 (3)	7491 (4)	4152 (2)
P(4)	4355 (3)	7781 (4)	4166 (2)
N(1)	3781 (7)	6043 (9)	2830 (5)
N(2)	5102 (8)	6744 (9)	2351 (5)
N(3)	6125 (8)	5514 (9)	2879 (6)
N(4)	6071 (7)	6911 (9)	3547 (5)
N(5)	5210 (8)	7536 (10)	4402 (5)
N(6)	4187 (7)	7292 (9)	3543 (5)
N(7)	2016 (10)	6853 (12)	3498 (7)
C(1)	1564 (14)	6571 (17)	3798 (9)
C(2)	962 (14)	6201 (17)	4146 (9)

Table VI. Selected Bond Lengths (Å) and Angles (deg) for **7** (X = Br) and **9**

	$[(Ph_2PN)_4(SN)_2]^{2+}$-$[Br_3^-]_2\cdot CH_3CN$	$(Ph_2PN)_4(SN)_2$
	Distances	
S(1)–S(2)		2.385 (1)
S(1)–N(1)	1.51 (1)	1.596 (2)
S(1)–N(6)	1.52 (1)	1.599 (3)
S(2)–N(3)	1.51 (1)	1.603 (2)
S(2)–N(4)	1.52 (1)	1.594 (2)
P(1)–N(1)	1.67 (1)	1.624 (2)
P(1)–N(2)	1.59 (1)	1.580 (3)
P(2)–N(2)	1.55 (1)	1.582 (3)
P(2)–N(3)	1.67 (1)	1.614 (2)
P(3)–N(4)	1.65 (1)	1.626 (3)
P(3)–N(5)	1.57 (1)	1.584 (3)
P(4)–N(5)	1.58 (1)	1.583 (2)
P(4)–N(6)	1.65 (1)	1.613 (2)
Br(1)–Br(2)	2.750 (3)	
Br(2)–Br(3)	2.383 (4)	
Br(4)–Br(5)	2.512 (4)	
Br(5)–Br(6)	2.540 (4)	
	Angles	
N(1)–S(1)–N(6)	112.0 (7)	107.8 (1)
N(1)–S(1)–S(2)		102.7 (1)
N(6)–S(1)–S(2)		97.3 (1)
N(3)–S(2)–N(4)	112.3 (7)	109.5 (1)
N(3)–S(2)–S(1)		97.1 (1)
N(4)–S(2)–S(1)		101.8 (1)
N(1)–P(1)–N(2)	113.4 (7)	118.7 (1)
N(2)–P(2)–N(3)	115.5 (7)	120.5 (1)
N(4)–P(3)–N(5)	112.7 (7)	120.7 (1)
N(5)–P(4)–N(6)	111.3 (7)	118.4 (1)
S(1)–N(1)–P(1)	129.0 (8)	123.4 (2)
P(1)–N(2)–P(2)	140.6 (9)	134.0 (1)
P(2)–N(3)–S(2)	128.4 (9)	120.8 (2)
S(2)–N(4)–P(3)	125.2 (8)	126.5 (1)
P(3)–N(5)–P(4)	135.7 (9)	132.9 (1)
P(4)–N(6)–S(1)	124.9 (8)	121.5 (1)
Br(1)–Br(2)–Br(3)	178.7 (1)	
Br(4)–Br(5)–Br(6)	176.4 (1)	

The most obvious difference between **7** and **9** is the lack of a cross-ring S–S bond in the former. This difference is expected since the dication has two fewer electrons than the neutral compound (cf. 1,5-$(Ph_2PN)_2(NSBr)_2$ vs. 1,5-$(Ph_2PN)_2(SN)_2$). There are also significant differences in bond lengths between the two 12-membered rings. The average S–N bond length (1.52 Å) for the dication is substantially smaller than that observed for the neutral compound (1.60 Å).

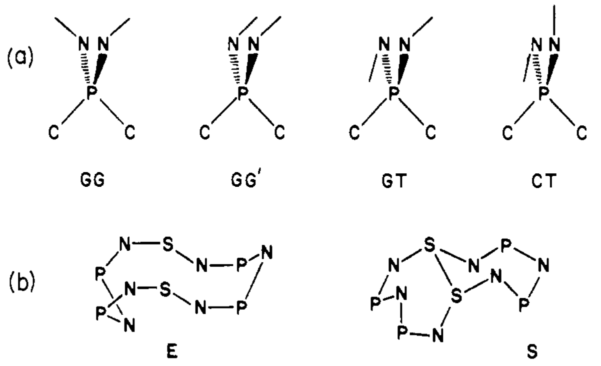


Figure 7. (a) Possible local geometries at phosphorus in cyclophosphazenes viewed along a vector connecting geminal nitrogen atoms, G = gauche, C = cis, T = trans. (b) Eclipsed (E) and staggered (S) arrangements of the PNSNP segments of the 12-membered $P_4N_2S_6$ rings in $(Ph_2PN)_4(SN)_2^{2+}$ and 1,3,7,9-$(Ph_2PN)_4(SN)_2$.

The average P–N bond lengths of the P–N–P units have the same value (1.58 Å) in both **7** and **9**, but $|d(\text{P–N})|$ for the P–N–S segments of the ring is 1.66 Å for the dication and 1.62 Å for the neutral compound. A similar trend of long, connecting P–N bonds and short S–N bonds has been observed for the related 6-membered heterocycle **5** (X = Cl,[6,28] I,[10] Ph[29]), and ab initio MO calculations indicate that π bonding is strongest in the PNP and NSN segments of these ring systems.[29] The absence of the cross-ring restriction results in larger average bond angles at nitrogen for the dication compared to the neutral compound (PNP = 137 vs. 133°; PNS = 127 vs. 123°). However, the bond angles at phosphorus move closer to the tetrahedral value in the dication (113.7 vs. 119.6°).

The conformations of the two 12-membered rings provide an interesting comparison in the context of the local conformation at the phosphorus (and sulfur) atoms using the terminology from Mizushima[30] adapted for cyclophosphazenes by Paddock and co-workers.[31] As indicated in Figure 7a the geometries at phosphorus can be distinguished by viewing the molecule along a vector connecting geminal nitrogen atoms. Unlike $(Me_2PN)_6$, which contains a mixture of GG, GT, and CT geometries,[32] all of the phosphorus centers in $(Ph_2PN)_4(SN)_2^{2+}$ have the more energetically favorable GG arrangement facilitated by the cis–trans geometry of the PNSNP sequence. The dication has pseudosymmetry through N(2) and N(5) so that the opposite S–N bonds are eclipsed (viewed down the S–S vector, see Figure 7b). Although the PNSNP units are also in a cis–trans arrangement in the neutral molecule 1,3,7,9-$(Ph_2PN)_4(SN)_2$, the opposite nitrogen atoms are staggered with respect to the S–S vector, due to the constraints imposed by the cross-ring S–S bond. Consequently, two opposite phosphorus centers adopt a GG′ conformation to accommodate the twisted structure.

The Br_3^- ion is known to adopt either symmetrical or unsymmetrical (nearly linear) structures depending on the nature of the cation.[33] In the case of $[(Ph_2PN)_4(SN)_2]^{2+}[Br_3^-]_2\cdot CH_3CN$, both forms of the anion are observed. For the unsymmetrical form the Br–Br bond lengths are 2.383 (4) and 2.750 (3) Å (BrBrBr = 178.7°) [cf. $Cs^+Br_3^-$ (d(Br–Br) = 2.440 and 2.698 Å),[34] and $S_4N_3^+Br_3^-$ (d(Br–Br) = 2.431 (2) and 2.677 (2) Å)[27]], while the symmetrical anion has d(Br–Br) = 2.512 (4) and 2.540 (4) Å (BrBrBr = 176.4 (1)° [cf. $[Me_3NH^+]_2Br^-Br_3^-$ (d(Br–Br) = 2.53 and 2.54 Å).[35] There is a weak interaction (d(S–Br) = 2.95 Å) between the sulfur atoms of the cation and one of the bromine atoms of a Br_3^- anion.

Conclusion

The PNS heterocycles described in this investigation can be considered as hybrids of the parent cyclophosphazene and cyclothiazene rings. The former are π-electron-precise molecules that exhibit a remarkable range of ring sizes. The heterocyclic ring is chemically robust, i.e. not easily oxidized or reduced, and reactions are frequently limited to the exocyclic substituents. By contrast, cyclothiazenes are π-electron rich; the heterocyclic ring is very labile, and they readily form cations (or anions). The hybrid PNS rings combine the properties of the parent systems, e.g. they are readily oxidized, and the characterization of $(Ph_2PN)_4(SN)_2^{2+}$ suggests that a series of PNS cations, $(Ph_2PN)_x(SN)_y^+$ ($x + y$ = 3–5, etc.; y is odd) and $(Ph_2PN)_x(SN)_y^{2+}$ ($x + y$ = 3–5, etc.; y is even), π-isoelectronic with the cyclophosphazenes, is possible. The extent of this series and of the sequence of mixed phosphazene–thiazyl rings, $(Ph_2PN)_x(NSX)_y$, may, however, be limited by the lower stability of rings containing adjacent SN units. The chemical reactivity of PNS heterocycles *containing two-coordinate sulfur* is dominated by the sulfur centers. The reasons for this preference will be discussed in a forthcoming publication.[29]

Acknowledgment. We thank the NSERC (Canada) for financial support and the Alberta Research Council for a scholarship to N.B.

Registry No. **1**, 85028-71-3; **2**, 85028-69-9; **3** (X = Br), 90133-20-3; **3** (X = Cl), 90133-21-4; **5** (X = Br), 90133-26-9; **5** (X = Cl), 84247-67-6; **5** (X = I), 88008-07-5; **7** (X = Br), 90133-23-6; **7** (X = I), 90133-27-0; **8** (X = Br), 90133-25-8; **9**, 86487-11-8; **10**, 90133-28-1; $(ClSN)_3$, 5964-00-1; BBr_3, 10294-33-4; $S_4N_4\cdot BCl_3$, 33490-44-7; bromine, 7726-95-6; sulfuryl chloride, 7791-25-5; iodine, 7553-56-2; triphenylantimony, 603-36-1; norbornadiene, 121-46-0.

Supplementary Material Available: Listings of thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, bond lengths and bond angles, and observed and calculated structure factors for **3** (X = Br), **7** (X = Br), and **9** (89 pages). Ordering information is given on any current masthead page.

---

(28) Pohl, S.; Petersen, O.; Roesky, H. W. *Chem. Ber.* **1979**, *112*, 1545.

(29) Burford, N.; Chivers, T.; Hojo, M.; Laidlaw, W. G.; Richardson, J. F.; Trsic, M., submitted for publication in *J. Am. Chem. Soc.*

(30) Mizushima, S. "Structure of Molecules and Internal Rotation"; Academic Press: New York, 1954.

(31) Dougill, M. W.; Paddock, N. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1022 and references cited therein.

(32) Oakley, R. T.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 3118.

(33) Reference 15, p 1549.

(34) Breneman, G. L.; Willett, R. D. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1073.

(35) Wiebanga, E. H.; Havinga, E. E.; Boswijk, K. H. *Adv. Inorg. Chem. Radiochem.* **1963**, *3*, 148.