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Hybrid Sulfanuric−Phosphazene Ring Systems: Synthesis, Spectroscopic Characterization, and X-ray Structures of *trans*-$Ph_4P_2N_4[S(O)R]_2$ (R = Ph, Me), *cis*-$Ph_4P_2N_4[S(O)Me]_2$, and $R_4P_2N_4(SNMe_2)_2$ (R = Ph, Et)

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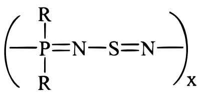
The reaction of the chair form of $Ph_4P_2N_4(SR)_2$ (R = Ph, Me) or the boat form of $Ph_4P_2N_4(SMe)_2$ with an excess of *m*-chloroperbenzoic acid in THF produces *trans*-$Ph_4P_2N_4[S(O)R]_2$ (**4a**, R = Ph; **4b**, R = Me) or *cis*-$Ph_4P_2N_4$-$[S(O)Me]_2$ (**4b**), respectively. The structures of *trans*-**4a**, *trans*-**4b**, and cis-**4b** were determined by X-ray crystallography, which revealed twist-boat conformations for the $P_2N_4S_2$ rings. The S−N bond distances decrease by ca. 0.06 Å and the ∠NSN bond angles increase by ca. 3−4° upon oxidation of the S(IV) centers to S(VI). Crystals data: *trans*-**4a**, monoclinic, $P2_1/n$, $a = 10.173(3)$ Å, $b = 18.030(3)$ Å, $c = 17.920(2)$ Å, $\beta = 91.47(1)°$, $V = 3285(1)$ Å^3, $Z = 4$; *trans*-**4b**, monoclinic, $P2_1/n$, $a = 10.616(2)$ Å, $b = 17.833(3)$ Å, $c = 14.133(5)$ Å, $\beta = 97.00(3)$ Å, $V = 2655(1)$ Å^3, $Z = 4$; *cis*-**4b**, monoclinic, $P2_1/n$, $a = 10.536(3)$ Å, $b = 17.219(2)$ Å, $c = 15.085(3)$ Å, $\beta = 109.45(2)°$, $V = 2580.5(9)$ Å^3, $Z = 4$. The reaction of $R_4P_2N_4(SCl)_2$ with 2 equiv of Me_3SiNMe_2 in THF at −78 °C yields $R_4P_2N_4(SNMe_2)$ (**5a**, R = Ph; **5b**, R = Et) in which the $P_2N_4S_2$ rings adopt chair (**5b**) or distorted chair (**5a**) structures. Crystals data: **5a**, triclinic, $P\bar{1}$, $a = 9.891(4)$ Å, $b = 10.123(6)$ Å, $c = 8.759(4)$ Å, $\alpha = 113.12(3)°$, $\beta = 111.82(3)°$, $\gamma = 64.28(4)°$, $V = 704.9(7)$ Å^3, $Z = 1$; **5b**, monoclinic, $P2_1/c$, $a = 8.144(2)$ Å, $b = 15.548(3)$ Å, $c = 8.250(2)$ Å, $\beta = 109.24(2)°$, $V = 986.3(4)$ Å^3, $Z = 2$. The thermolysis of **5b** at 80 °C yields $Et_4P_2N_4S_2$ as the final product.

Introduction

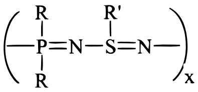
In addition to the fundamental interest in their structures and bonding, inorganic ring systems serve as precursors to linear polymers via ring-opening polymerization (ROP). Cyclophosphazenes $(NPCl_2)_x$ are known for a wide variety of ring sizes ($x = 3−17$), and ROP of the trimer at 250 °C produces the rubbery material $(NPCl_2)_n$.[1] Derivatives of this inorganic backbone polymer exhibit a wide range of useful properties.[1] By contrast, the isoelectronic sulfanuric system $[NS(O)Cl]_x$ is well characterized only for $x = 3$[2,3] and heating this trimer at 250−285 °C results in decomposition.[4] However, sulfanuric polymers poly(oxy)thiazenes, $[N{=}S(O)R]_n$ (R = alkyl, aryl), have been synthesized by a condensation route.[5]

Hybrid sulfanuric−phosphazene ring systems of the type $[NS(O)Cl]_x[NPCl_2]_y$ have been known since 1963,[6] and recently, the six-membered ring ($x = 1$, $y = 2$) was used to prepare hybrid polymers with an $NS^{VI}NPNP$ repeating unit by ROP at 165 °C.[7] For several years we have been interested in the synthesis and properties of polymers containing *alternating* PN and SN linkages such as **1**−**3**.



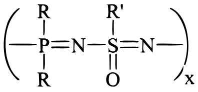
$$\left(-\overset{R}{\underset{R}{P}}{=}N-S{=}N-\right)_x$$

1



$$\left(-\overset{R}{\underset{R}{P}}{=}N-\overset{R'}{S}{=}N-\right)_x$$

2



$$\left(-\overset{R}{\underset{R}{P}}{=}N-\overset{R'}{\underset{O}{S}}{=}N-\right)_x$$

3

On the basis of ring strain considerations, six-membered heterocycles are the preferred precursors for ROP. However, the obvious sources of the polymers **1** and **2** are eight-membered rings of the type $R_4P_2N_4S_2$[8] and $R_4P_2N_4(SR')_2$.[9] The properties of polymer **1**, a hybrid of polyphosphazenes and the metallic conductor poly(sulfur nitride), $(SN)_x$, would be of especial interest, but the thermolysis of $Ph_4P_2N_4S_2$ at 250 °C yields the cyclic phosphazenes $(Ph_2PN)_n$ ($n = 3, 4$) and S_4N_4.[10] In view of the better atmospheric stability of S(VI) compared to S(IV) systems in the sulfanuric−phosphazene polymers reported by

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(1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Eaglewood Cliffs, NJ, 1992; Chapter 3.

(2) (a) Hazell, A. C.; Wiegers, G. A.; Vos, A. *Acta Crystallogr.* **1966**, *20*, 186. (b) Lork, E.; Behrens, U.; Steinke, G.; Mews, R. *Z. Naturforsch.* **1994**, *49b*, 437.

(3) The fragments $N_5S_5O_5Cl_4^+$, $N_5S_5O_5Cl_3^+$, and $N_4S_4O_3Cl_4^+$ have been observed in the mass spectrum of the reaction product from the synthesis of $[NS(O)Cl]_3$, but the cyclic tetramer ($x = 4$) or pentamer ($x = 5$) have not been isolated: Lin, T.-P.; Klingebiel, U.; Glemser, O. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1095.

(4) McKenney, R. L.; Fetter, N. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3569.

(5) (a) Roy, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 1530. (b) Roy, A. K.; Burns, G. T.; Lie, G. C.; Grigoras, S. *J. Am. Chem. Soc.* **1993**, *115*, 2604.

(6) For a review, see: van de Grampel, J. C. *Rev. Inorg. Chem.* **1981**, *3*, 1.

(7) (a) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044. (b) Ni, Y.; Park, P.; Liang, M.; Massey, J.; Waddling, C.; Manners, I. *Macromolecules* **1996**, *29*, 3401.

(8) (a) Burford, N.; Chivers, T.; Codding, P. W.; Oakley, R. T. *Inorg. Chem.* **1982**, *21*, 982. (b) Burford, N.; Chivers, T.; Richardson, J. F. *Inorg. Chem.* **1983**, *22*, 1482. (c) Chivers, T.; Dhathathreyan, K. S.; Liblong, S. W.; Parks, T. *Inorg. Chem.* **1988**, *27*, 1305. (d) Chivers, T.; Edwards, M.; Parvez, M. *Inorg. Chem.* **1992**, *31*, 1861.

(9) (a) Chivers, T.; Kumaravel, S. S.; Meetsma, A.; van de Grampel, J. C.; van der Lee, A. *Inorg. Chem.* **1990**, *29*, 4592. (b) Chivers, T.; Gao, X.; Hilts, R. W.; Parvez, M.; Vollmerhaus, R. *Inorg. Chem.* **1995**, *34*, 1180.

(10) Chivers, T.; Vollmerhaus, R. Unpublished results, 1992.

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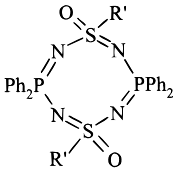
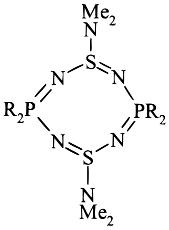
Manners et al.,[11] we have concentrated our efforts on eight-membered-rings of the type **4**. Here we report the synthesis and structural characterization of *trans*-**4a** and *cis*- and *trans*-**4b**, the first sulfanuric−phosphazene rings of this type.[12,13]



trans-**4a**, R' = Ph
trans-**4b**, R' = Me
cis-**4b**, R' = Me



5a, R = Ph
5b, R = Et

The known tendency of the Me_2N group to promote the formation of macrocycles from smaller PN−SN rings[14] suggests that ring-opening of the bifunctional systems **5** might lead to large ring systems and/or S(IV)-containing polymers of the type **2**. We have, therefore, prepared and structurally characterized **5a**,**b** and briefly investigated their thermal decomposition.

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled before use: tetrahydrofuran, diethyl ether, toluene, hexane (Na/benzophenone), acetonitrile and methylene chloride (P_4O_{10} and CaH_2). SO_2Cl_2 was distilled prior to use. CH_3I was purified by passing it through a column of alumina. The purification of *m*CPBA was performed by using literature procedures.[15] Other reagents were used as received: PCl_3, Ph_2PCl, Me_3SiN_3, $SOCl_2$, MeLi, $Li[N(SiMe_3)]_2$, PhSSPh, Me_3SiNMe_2. The compounds 1,5-$Ph_4P_2N_4S_2$,[8c] 1,5-$Ph_4P_2N_4(SPh)_2$,[9a] 1,5-$Ph_4P_2N_4(SMe)_2$,[9b] $Ph_4P_2N_4(SCl)_2$,[16] and $Et_4P_2N_4(SCl)_2$[17] were obtained from literature procedures. PhSCl was prepared by the reaction of PhSSPh with SO_2Cl_2. The handling of air- and moisture-sensitive reagents was performed under an atmosphere of argon or nitrogen using Schlenk techniques or a glovebox.

Instrumentation. ^{31}P NMR spectra were recorded on a Varian XL-200 instrument, and the chemical shifts are relative to an external standard, 85% H_3PO_4 in $CDCl_3$. ^1H NMR spectra were collected on a Bruker AM-200 spectrometer. Infrared spectra were obtained on a Mattson 4030 FTIR spectrophotometer. Elemental analyses and electron impact (70 eV) mass spectra (VG 7070F micromass spectrometer) were provided by the Analytical Services Laboratory of the Department of Chemistry, The University of Calgary.

Synthesis of *trans*-1,5-$Ph_4P_2N_4[S(O)Ph]_2$ (4a). A solution of *m*CPBA (0.146 g, 0.844 mmol) in THF (ca. 25 mL) was added dropwise to a pale yellow slurry of 1,5-$Ph_4P_2N_4(SPh)_2$ (0.136 g, 0.211 mmol) in THF (ca. 25 mL) at 25 °C. After 1 h the solvent was removed from the colorless solution by vacuum leaving a white solid which was dissolved in CH_2Cl_2 (ca. 75 mL) and treated with an equal volume of aqueous solution of $NaHCO_3$ (0.7 g, 8.4 mmol). The organic layer was isolated, dried with anhydrous $MgSO_4$, and passed through a column of silica. The solvent was removed under vacuum leaving an off-white solid, which was recrystallized by slow evaporation of a saturated $CHCl_3$ solution to give 1,5-$Ph_4P_2N_4[S(O)Ph]_2$ (0.153 mmol, 0.104 g, 73%). Mp: 233−235 °C. NMR (δ, ppm) ($CDCl_3$): $\{^1H\}^{31}P$ $+5.1$. MS (*m/e*): 676 (100%, M^+). IR (Nujol, cm^{-1}): 1458 s, 1374 s, 1240 s, 1218 s, 1148 vs [ν(S═O)], 1117 vs, 1023 m, 996 m, 870 m, 790 m, 747 m, 690 s, 558 m, 517 w, 449 w. The product was also recrystallized from CH_3CN to give 1,5-$Ph_4P_2N_4[S(O)Ph]_2 \cdot H_2O \cdot CH_3CN$. Anal. Calcd for $C_{38}H_{35}P_4N_5S_2O_2$: C, 63.41; H, 4.90; N, 9.73; Found: C, 63.34; H, 4.63; N, 9.90. NMR (δ, ppm) ($CDCl_3$): ^1H 7.6−7.9, 7.0−7.4 (m, C_6H_5, 30 H), 2.05 (s, CH_3CN, 3 H), 1.61 (s, H_2O, 2 H).

Synthesis of *trans*-1,5-$Ph_4P_2N_4[S(O)Me]_2$ (4b). *trans*-**4b** was prepared from *m*CPBA (0.052 g, 0.300 mmol) and the chair isomer of 1,5-$Ph_4P_2N_4(SMe)_2$ (0.078 g, 0.150 mmol) in THF (ca. 50 mL) at 25 °C by a procedure similar to that described for **4a**. The product was recrystallized from CH_3CN at −20 °C to give colorless needles of *trans*-1,5-$Ph_4P_2N_4[S(O)Me]_2$ (0.0272 g, 0.049 mmol, 35%). Mp: 256−257 °C (dec). Anal. Calcd for $C_{26}H_{26}P_2N_4S_2O_2$: C, 56.51; H, 4.74; N, 10.14. Found: C, 56.29; H, 4.74; N, 10.14. IR (Nujol, cm^{-1}) 1462 vs, 1376 vs, 1226 m, 1193 m, 1171 m, 1156 s, 1139 s [ν(S═O)], 1112 s, 1077 w, 1025 w, 977 w, 954 w, 845 w, 747 w, 725 w, 693 m, 686 w. NMR (δ, ppm) ($CDCl_3$): $\{^1H\}^{31}P$ $+4.2$; ^1H 7.8−8.0, 7.4−7.6 (M, C_6H_5, 20H), 2.8 (t, $^4J(^1H-^{31}P) = 1.7$ Hz, SCH_3, 6H). MS (*m/e*): 551 (100%, M^+).

Synthesis of *cis*-1,5-$Ph_4P_2N_4[S(O)Me]_2$ (4b). The boat isomer of 1,5-$Ph_4P_2N_4(SMe)_2$ (0.175 mmol) was prepared in THF (ca. 25 mL) by the reaction of 1,5-$Ph_4P_2N_4S_2$ with MeLi to give [1,5-$Ph_4P_2N_4S_2$-Me][Li] followed by the addition of an excess of MeI.[9b] The reaction mixture was then treated, in situ, with *m*CPBA (0.061 g, 0.350 mmol) in THF (ca. 25 mL). *cis*-**4b** was isolated by a procedure similar to that described for **4a**. The product was recrystallized from hot toluene to give *cis*-1,5-$Ph_4P_2N_4[S(O)Me]_2$ as a colorless crystalline solid (0.060 g, 0.108 mmol, 62%) Mp: 222 °C (dec). Anal. Calcd for $C_{26}H_{26}P_2N_4S_2O_2$: C, 56.51; H, 4.74; N, 10.14. Found: C, 55.70; H, 4.62; N, 9.78. IR (Nujol, cm^{-1}) 1461 vs, 1378 vs, 1260 w, 1225 m, 1128 s [ν(S═O)], 1171 m, 1024 m, 978 w, 841 w, 809 w, 752 w, 720 m, 696 m, 564 w, 543 m. NMR (δ, ppm) ($CDCl_3$): $\{^1H\}^{31}P$ $+3.4$; ^1H 7.4−8.3 (m, C_6H_5, 20H) 2.9 (t, $^4J(^1H-^{31}P) = 1.7$ Hz, SCH_3, 6H). MS (*m/e*): 551 (100%, M^+).

Preparation of 1,5-$Ph_4P_2N_4(SNMe_2)_2$ (5a). A solution of Me_2NSiMe_3 (0.083 g, 0.705 mmol) in THF (ca. 25 mL) was added dropwise to a stirred slurry of 1,5-$Ph_4P_2N_4S_2Cl_2$ (0.180 g, 0.320 mmol) in THF (ca. 25 mL) at −78 °C. A white precipitate formed, and the supernatant was decanted to give the crude product (0.183 g). 1,5-$Ph_4P_2N_4(SNMe_2)_2$ (0.046 g, 25%) was obtained by recrystallization from a mixture of CH_2Cl_2 and Et_2O cooled to −20 °C. Mp: 165−166 °C. IR (Nujol, cm^{-1}): 1462 s, 1435 s, 1377 s, 1260 w, 1183 w, 1157 m, 1137 s, 1112 s, 1075 s, 1042 m, 1023 m, 996 m, 909 m, 807 m, 766 w, 752 w, 718 m, 694 s, 640 w, 630 w, 536 s, 517 w, 502 m, 444 w, 427 w. NMR (δ, ppm) ($CDCl_3$): $\{^1H\}^{31}P$ 14.7; ^1H 2.61 (s, NCH_3, 12H), 7.8−8.0, 7.2−7.4 (m, C_6H_5, 20H). MS (*m/e*): 534 (25, $M^+ - NMe_2$), 490 (86, $M^+ - 2NMe_2$).

Preparation of 1,5-$Et_4P_2N_4(SNMe_2)_2$ (5b). A solution of Me_2NSiMe_3 (0.203 g, 1.73 mmol) in THF (ca. 25 mL) was added dropwise to stirred slurry of 1,5-$Et_4P_2N_4S_2Cl_2$ (0.269 g, 0.788 mmol) in THF (ca. 25 mL) at −78 °C. After 1 h the colorless solution was warmed to −30 °C and the solvent was removed by vacuum to give a pale pink solid. The product was recrystallized from a Et_2O/pentane solution to give colorless crystals of 1,5-$Et_4P_2N_4(NMe_2)_2$ (0.256 g, 0.662 mmol, 84%). Mp: 55−57 °C (dec). Anal. Calcd for $C_{12}H_{32}N_6P_2S_2$: C, 37.29; H, 8.35; N, 21.74. Found: C, 37.61; H, 8.45; N, 21.28. IR (Nujol, cm^{-1}) 1456 s, 1377 s, 1260 w, 1177 m, 1147 s, 1127 s, 1114 s, 1101 s, 1064 s, 1033 s, 994 m, 910 m, 797 m, 786 m, 751 m, 723 m, 701 m, 648 m, 629 s, 501 w, 443 w, 426 w, 398 w, 329 w, 281 w. NMR (δ, ppm) ($CDCl_3$): $\{^1H\}^{31}P$ 39.4; ^1H 2.39 (s, NCH_3, 12H), 1.77 [d of q, $^2J(^1H-^{31}P) = 17.6$ Hz, $^3J(^1H-^1H)$ 7.6 Hz, CH_2CH_3, 6H], 1.10 [d of t, $^3J(^1H-^{31}P) = 14.6$ Hz, $^3J(^1H-^1H) = 7.6$ Hz CH_2CH_3, 12H]. MS (*m/e*): 342 (4, $M^+ - NMe_2$), 298 (25, $M^+ - 2NMe_2$).

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(11) (a) Ni, Y.; Park, P.; Liang, M.; Massey, J.; Waddling, C.; Manners, I. *Macromolecules* **1996**, *29*, 3401. (b) For a review, see: Gates, D. P.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1997**, 2525.

(12) Macrocycles of the type $\{[NS(O)Cl][NPCl_2]\}_n$ ($n = 3, 6$) have been isolated and structurally characterized recently: Ni, Y.; Lough, A. J.; Rheingold, A. L.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 998.

(13) There is a brief report of the eight-membered ring $[NS(O)Cl][NPCl_2]_3$, but no structural information is available: Voswijk, C.; van de Grampel, J. C. *Rec. Trav. Chim. Pays-Bas* **1974**, *93*, 120.

(14) (a) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702. (b) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1985**, *24*, 2237.

(15) Traylor, T. G.; Lee, W. A.; Stynes, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 755.

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

(17) Brock, M.; Chivers, T.; Parvez, M.; Vollmerhaus, R. *Inorg. Chem.* **1997**, *36*, 485.

Table 1. Crystallographic Data for *trans*-**4a** and *cis*- and *trans*-**4b**

	trans-**4a**	*trans*-**4b**	*cis*−**4b**
formula	$C_{36}H_{30}O_2N_4P_2S_2$	$C_{26}H_{26}O_2N_4P_2S_2$	$C_{26}H_{26}O_2N_4P_2S_2$
fw	676.73	552.58	552.58
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	10.173(3)	10.616(2)	10.536(3)
b, Å	18.030(3)	17.883(3)	17.219(2)
c, Å	17.920(2)	14.133(5)	15.085(3)
β, deg	91.47(1)	97.00(3)	109.45(2)
V, Å^3	3285(1)	2655(1)	2580.5(9)
Z	4	4	4
T, °C	−73	−73	−73
λ, Å	0.710 69	0.710 69	0.710 69
d_{calcd}, g cm^{-3}	1.368	1.382	1.422
μ, cm^{-1}	2.89	3.41	3.51
R^a	0.045	0.049	0.045
$R_w{}^b$	0.043	0.049	0.042

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w\Delta^2/\sum wF_o2]^{1/2}$.

Table 2. Crystallographic Data for **5a**,**b**

	5a	**5b**
formula	$C_{28}H_{32}N_6S_2P_2$	$C_{12}H_{32}N_6P_2S_2$
fw	578.67	386.49
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	9.891(4)	8.144(2)
b, Å	10.123(6)	15.548(3)
c, Å	8.759(4)	8.250(2)
α, deg	113.12(3)	
β, deg	111.82(3)	109.24(2)
γ, deg	64.28(4)	
V, Å^3	704.9(7)	986.3(4)
Z	1	2
T, °C	−103	−103
λ, Å	0.710 69	0.710 69
d_{calcd}, g cm^{-3}	1.363	1.301
μ, cm^{-1}	3.32	4.38
R^a	0.032	0.038
$R_w{}^b$	0.031	0.040

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w\Delta^2/\sum wF_o{}^2]^{1/2}$.

X-ray Analyses. All measurements were made on a Rigaku AFC6S diffractometer. Crystallographic data are summarized in Tables 1 and 2.

***trans*-4a.** Crystals of *trans*-**4a** were obtained by slow evaporation of a saturated $CHCl_3$ solution. A colorless prismatic crystal (0.60 × 0.40 × 0.37 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.18 < 2\theta < 20.97°$. Scans of $(1.10 + 0.34 \tan\theta)°$ were made at a speed of 4.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 6027 reflections were measured, of which 3022 had $I > 3.00\sigma(I)$. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.[18] The structure was solved by direct methods[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. For all five structures, scattering factors were those of Cromer and Waber,[21] and allowance was made for anomalous dispersion.[22] All calculations were performed using teXsan.[23]

***trans*-4b.** Crystals of *trans*-**4b** were obtained from a CH_3CN solution at −20 °C. A colorless plate (0.60 × 0.30 × 0.09 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 17 carefully centered reflections in the range $18.19 < 2\theta < 27.62°$. Scans of $(1.47 + 0.34 \tan\theta)°$ were made at a speed of 4.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 4880 reflections were measured, of which 2271 had $I > 3.00\sigma(I)$. The solution and refinement of the structure followed the procedures described above for **4a**.

***cis*-4b.** Crystals of *cis*-**4b** were grown in a CH_2Cl_2−hexane solution of 23 °C. A colorless prismatic crystal (0.70 × 0.40 × 0.30 mm) was sealed in a glass capillary containing a small amount of the mother liquor (CH_2Cl_2/hexane). Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.15 < 2\theta < 21.43°$. Scans of $(1.84 + 0.34 \tan\theta)°$ were made at a speed of 16.0° min^{-1} to a maximum 2θ value of 55.1°. The intensities of 6173 reflections were measured, of which 3155 had $I > 3.00\sigma(I)$. The solution and refinement of the structure followed the procedures described for **4a**.

5a. Crystals of **5a** were obtained by layering a diethyl ether solution with pentane. A colorless prismatic crystal (0.70 × 0.45 × 0.30 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.17 < 2\theta < 21.72°$. Scans of $(1.73 + 0.34 \tan\theta)°$ were made at a speed of 16.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 2502 reflections were measured, of which 2006 had $I > 3.00\sigma(I)$. The solution and refinement of the structure followed the procedures described for **4a**.

5b. Crystals of **5b** were grown from a CH_2Cl_2/diethyl mixture at −20 °C. A colorless prismatic crystal (0.65 × 0.55 × 0.45 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.35 < 2\theta < 21.79°$. Scans of $(1.73 + 0.34 \tan\theta)°$ were made at a speed of 16.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 1829 reflections were measured, of which 1429 had $I > 3.00\sigma(I)$.

Results and Discussion

Synthesis and Spectroscopic Characterization of *trans*-$Ph_4P_2N_2[S(O)Ph]_2$ (4a) and *cis*- and *trans*-$Ph_4P_2N_4[S(O)Me]_2$ (4b). The reaction of the chair forms of $Ph_4P_2N_4(SPh)_2$ or $Ph_4P_2N_4(SMe)_2$[9b] with an excess of *m*-chloroperbenzoic acid (MCPBA) in THF at 25 °C produces *trans*-**4a** and *trans*-**4b** as air-stable, colorless crystalline solids. The products were characterized by ^1H and ^{31}P NMR, IR, and mass spectra. The trans-orientation of the exocyclic O atoms was established by X-ray crystallography (vide infra). The derivative **4a** melts without decomposition at ca. 235 °C, whereas *trans*-**4b** decomposes when it melts at 256−257 °C. The oxidation of $Ph_4P_2N_4(SPh)_2$ ($\delta(^{31}P)$ +30 ppm) with MCPBA was monitored by ^{31}P NMR spectroscopy, which revealed the formation of two intermediates (δ +12.1 and +10.5 ppm). Four equivalents of MCPBA were required for complete conversion to *trans*-**4a** (δ +5.1 ppm). It is likely that one of the intermediates is $Ph_4P_2N_4(SPh)[S(O)Ph]$, but we did not attempt to isolate this mono-oxidized product.[24]

Several routes are available for the synthesis of the S(IV) ring systems 1,5-$Ph_4P_2N_4(SR)_2$.[9] Interestingly, the reaction of $Li[Ph_4P_2N_4S_2Me]$ with MeI produces the boat form of $Ph_4P_2N_4(SMe)_2$ (**6**) initially. This conformer can be isolated, but it is readily converted to the chair form upon gentle warming in CH_2Cl_2. Since the oxidation of **6** (chair) yields *trans*-**4b**, we

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(18) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(19) SAPI91: Fan Hai-Fu. *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, 1991.

(20) DIRDIF94: Beuskens, P. T.; Admiraal, G.; Beuskens, G.; Bosman, W. P.; Garcia-Granda, R. S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1994.

(21) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71−98.

(22) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(23) teXsan: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.

(24) In related work we have structurally characterized the mono-oxidized $C_2N_4S_2$ ring (4-$BrC_6H_4)_2C_2N_4[S(O)C_6H_4CH_3$-4][$SC_6H_4CH_3$-4]: Chivers, T.; Hirsch, M.; Parvez, M. Unpublished results, 1997.

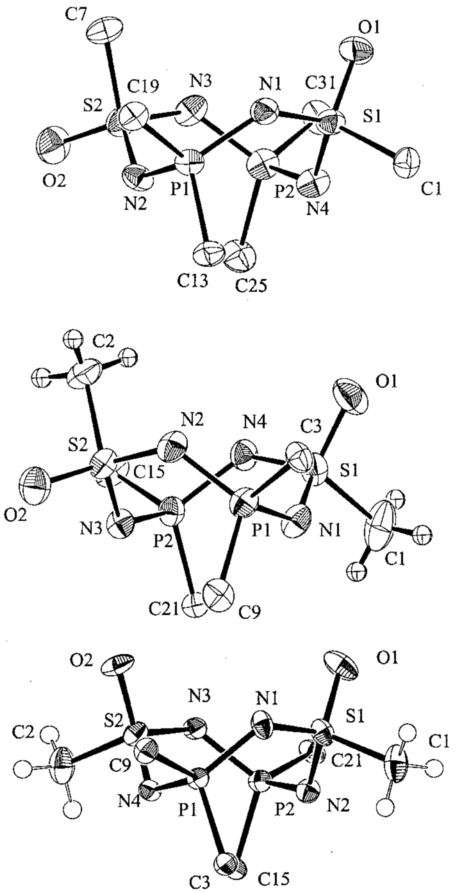
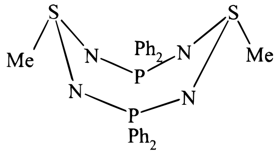
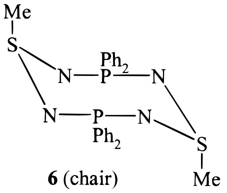


Figure 1. ORTEP drawings of *trans*-$Ph_4P_2N_4[S(O)R]_2$ (**4a**, R = Ph; **4b**, R = Me) and *cis*-$Ph_4P_2N_4[S(O)Me]_2$ (*cis*-**4b**). For clarity only the α-carbon atoms of Ph groups are shown.

surmised that treatment of **6** (boat) with MCPBA should produce **4b** with O atoms in cis (or endo) positions.



6 (boat)



6 (chair)

In view of the thermal instability of **6** (boat) the oxidation was carried out in situ and monitored by ^{31}P NMR spectroscopy. The disappearance of the resonance for **6** (boat) (δ +14.1 ppm) was accompanied by the growth of a major resonance for *cis*-**4b** at δ +3.4 ppm and a minor product (ca. 20% by integration) identified as *trans*-**4b** on the basis of the ^{31}P NMR chemical shift (+4.2 ppm). The isomer *cis*-**4b** was identified by ^{1}H and ^{31}P NMR, IR, and mass spectra and an X-ray structure determination (*vide infra*). It melts at 222 °C without decomposition.

X-ray Structures of *trans*-4a, *trans*-4b, and *cis*-4b. To compare the conformations of the $P_2N_4S_2$ ring, ORTEP drawings of *trans*-**4a**, *trans*-**4b**, and *cis*-**4b** are all shown in Figure 1. Selected bond distances and bond angles are found in Table 3.

The X-ray structural determinations confirmed that oxidation of the chair conformers of 1,5-$Ph_4P_2N_4(SR)_2$ (R = Ph, Me) with MCPBA produces the trans-isomers 1,5-$Ph_4P_2N_4[S(O)R]_2$ (**4a**, R = Ph; **4b**, R = Et) whereas oxidation of the boat form of 1,5-$Ph_4P_2N_4(SMe)_2$ produces *cis*-$Ph_4P_2N_4[S(O)Me]_2$ (*cis*-**4b**).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for *trans*-**4a**, *trans*-**4b**, and *cis*-**4b**

	trans-**4a**	*trans*-**4b**		*cis*-**4b**
S(1)−O(1)	1.445(3)	1.442(5)	S(1)−O(1)	1.438(3)
S(2)−O(2)	1.439(3)	1.444(5)	S(2)−O(2)	1.448(3)
S(1)−N(1)	1.561(4)	1.560(6)	S(1)−N(1)	1.577(3)
S(1)−N(4)	1.567(4)	1.574(5)	S(1)−N(2)	1.562(4)
S(2)−N(2)	1.572(4)	1.559(5)	S(2)−N(3)	1.570(3)
S(2)−N(3)	1.555(4)	1.552(5)	S(2)−N(4)	1.555(4)
P(1)−N(1)	1.618(4)	1.608(5)	P(1)−N(1)	1.609(4)
P(1)−N(2)	1.616(4)	1.616(5)	P(1)−N(4)	1.621(4)
P(2)−N(3)	1.604(4)	1.621(5)	P(2)−N(2)	1.620(4)
P(2)−N(4)	1.618(4)	1.625(5)	P(2)−N(4)	1.620(4)
S(1)−C(1)	1.782(5)	1.763(8)	S(1)−C(1)	1.765(5)
S(1)−C(7)	1.777(5)		S(2)−C(2)	1.758(5)
S(1)−C(2)		1.757(7)		
			N(1)−S(1)−N(2)	112.5(2)
N(1)−S(1)−N(4)	113.5(2)	113.8(3)	N(3)−S(2)−N(4)	112.7(2)
N(2)−S(2)−N(3)	112.6(2)	113.3(3)	S(1)−N(1)−P(1)	122.5(2)
S(1)−N(1)−P(1)	126.6(3)	128.7(4)	S(1)−N(2)−P(2)	123.8(2)
S(1)−N(4)−P(2)	122.1(3)	123.3(3)	S(2)−N(3)−P(2)	123.2(2)
S(2)−N(2)−P(1)	127.4(2)	124.1(3)	S(2)−N(4)−P(1)	123.4(2)
S(2)−N(3)−P(2)	127.3(3)	126.6(4)	N(1)−P(1)−N(4)	118.8(2)
N(1)−P(1)−N(2)	118.9(2)	119.0(3)	N(2)−P(2)−N(3)	118.4(2)
N(3)−P(2)−N(4)	118.5(2)	119.1(3)		

Table 4. Selected Torsion Angles (deg) for *trans*-**4a**, *trans*-**4b**, and *cis*-**4b**

	trans-**4a**	*trans*-**4b**	*cis*-**4b**
S(1)−N(1)−P(1)−N(2)	−53.0(4)	31.6(6)	−57.5(4)
S(2)−N(3)−P(2)−N(4)	−57.7(4)	34.3(5)	−55.2(3)
S(1)−N(4)−P(2)−N(3)	−38.9(4)	61.5(5)	−32.7(4)
S(2)−N(2)−P(1)−N(1)	−35.6(4)	61.8(5)	−30.9(3)
P(2)−N(4)−S(1)−N(1)	82.0(3)	−22.2(5)	83.6(3)
P(1)−N(2)−S(2)−N(3)	73.1(4)	−19.3(5)	83.9(3)
P(1)−N(1)−S(1)−N(4)	8.9(4)	−69.6(5)	7.1(4)
P(2)−N(3)−S(2)−N(2)	19.8(4)	−73.8(5)	5.2(4)

The SO distances of ca. 1.44 Å are consistent with an $S^{VI}{=}O$ double bond [cf. d(SO) = 1.417(3) Å in 1,5-$(Me_2N)_2C_2N_4[S(O)N(CF_3)_2]_2$[25] and 1.422(3) Å in $Cl_4P_2N_3S(O)Cl$[26]].

The structural parameters for the S(VI) ring systems **4a**,**b** can be compared with those of their S(IV) analogues, $Ph_4P_2N_4(SR)_2$ (R = Ph,[9a] Me[9b]). There is a significant contraction in the mean S−N bond distance from 1.62 Å to ca. 1.56 Å which is accompanied by an increase in the mean NSN bond angle from 109−110° to ca. 113°, upon oxidation of the S(IV) centers. The P−N distances and NPN bond angles are not affected significantly by the change from chair or boat conformations in the S(IV) heterocycles[9] to a twist-boat structure, but there is an increase in the mean SNP bond angle from ca. 119° to ca. 125°.

The torsion angles for *trans*-**4a**, *trans*-**4b**, and *cis*-**4b** are compared in Table 4. All three of these eight-membered rings have a twist-boat conformation. However, the twist-boat conformation of *trans*-**4b** differs significantly from those of *trans*-**4a** and *cis*-**4b** (see Figure 1). This difference is evident in the torsion angles. For example, the torsion angle S(1)−N(1)−P(1)−N(2) is −53.0(4)° for *trans*-**4a** and −57.5(4)° for *cis*-**4b**, but in *trans*-**4b** this torsion angle is 31.6(6)°. A wide variety of conformations exists for the P_4N_4 ring system in cyclotetraphosphazenes, and the particular structure adopted arises from both inter- and intramolecular forces, including the steric and polar character of substituents and crystal packing

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(25) Boeré, R. T.; Cordes, A. W.; Craig, S. L.; Oakley, R. T.; Reed, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 868.

(26) Van Bolhuis, F.; van de Grampel, J. C. *Acta Crystallogr.* **1976**, *B32*, 1192.

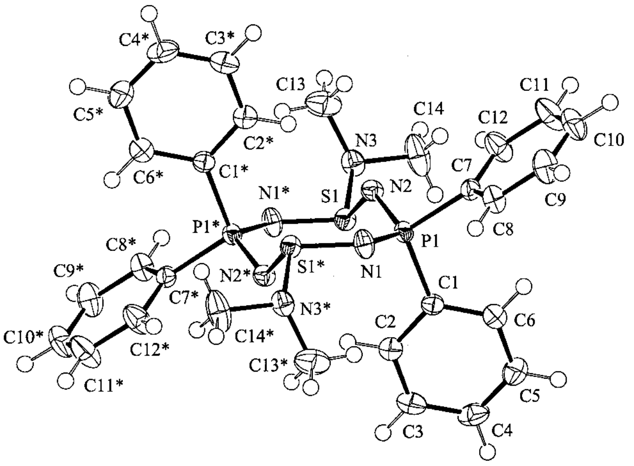

Figure 2. ORTEP drawing of $Ph_4P_2N_4(SNMe_2)_2$ (**5a**).

effects.[27] The different ring conformations of $P_2N_4S_2$ rings found in this and previous[9b] work are likely the result of a combination of these factors.

Synthesis and Spectroscopic Characterization of $R_4P_2N_4(SNMe_2)_2$ (R = Ph, 5a; R = Et, 5b). The *S*,*S*-bis(dimethylamino) derivatives **5a**,**b** were obtained by the reaction of the corresponding *S*,*S*-dichlorides[16,17] with a slight excess of Me_2NSiMe_3 (eq 1).

$$R_4P_2N_4(SCl)_2 + 2Me_2NSiMe_3 \xrightarrow[-78\ °C]{THF} \underset{\substack{\mathbf{5b},\ R = Ph\\ \mathbf{5b},\ R = Et}}{R_4P_2N_4(SNMe_2)_2} \quad (1)$$

The progress of this reaction was readily monitored by ^{31}P NMR spectroscopy through the disappearance of the resonance for the *S*,*S*′-dichloride and the appearance of a new resonance ca. 12 ppm downfield for **5a** or **5b**. In both cases the formation of a small amount of a second species was observed. In the case of **5b** this minor product, $\delta(^{31}P)$ +34.7 ppm (ca. 3% by integration of the ^{31}P NMR resonances), may be the monosubstituted compound $Et_4P_2N_4(SCl)(SNMe_2)$. The derivative **5b** is moisture-sensitive and thermally unstable. Consequently, the workup procedure involved the removal of solvent at −30 °C. In this way yields of 84% were achieved. The product should be stored at −20 °C to avoid decomposition The minor product ($\delta(^{31}P) = +6.0$ ppm, ca. 12%) that accompanies the formation of **5a** has a solubility in a variety of solvents similar to that of **5a**. Thus several recrystallizations were necessary to obtain pure **5a** and the yields were only ca. 25%. The compounds **5a**,**b** were readily identified by ^1H and ^{31}P NMR, IR, and mass spectra, and the ring conformations were determined by X-ray crystallography (vide infra).

X-ray Structures of 5a,b. The structures of **5a**,**b** were determined by X-ray crystallography, and ORTEP diagrams are represented in Figures 2 and 3, respectively. Bond lengths, bond angles, and torsion angles are compared in Table 5. The ring conformation in **5b** is a chair in which the sulfur atoms are 0.91 Å out and on opposite sides of the P_2N_4 plane, for which the maximum deviation is 0.094 Å. By contrast, **5a** adopts a distorted chair conformation in which a pair of antipodal nitrogen atoms are on opposite sides of the $P_2N_2S_2$ plane by 0.73 Å. The maximum deviation for the $P_2N_2S_2$ plane is 0.041 Å. These conformational differences are reflected in the marked disparity between the torsion angles for **5a**,**b** (see Table 5). The structure of **5b** is quite different from that of the related eight-membered ring 1,5-$(Me_2N)_2S_4N_4$, which has a boat conformation involving a significant interaction of a Me_2N group with the antipodal sulfur atom [$d(S\cdots N) = 2.76$ Å].[28] The chair conformation of **5b** does not permit this type of transannular interaction. The replacement of Cl substituents in $Et_4P_2N_4(SCl)_2$ by NMe_2 groups results in an increase in the mean endocyclic S−N bond distances from 1.545(3) Å[17] to 1.603(3) Å; cf. $|d(S-N)| = 1.590(5)$ Å in the 12-membered ring $Ph_8P_4N_6(SNMe_2)_2$.[14a]

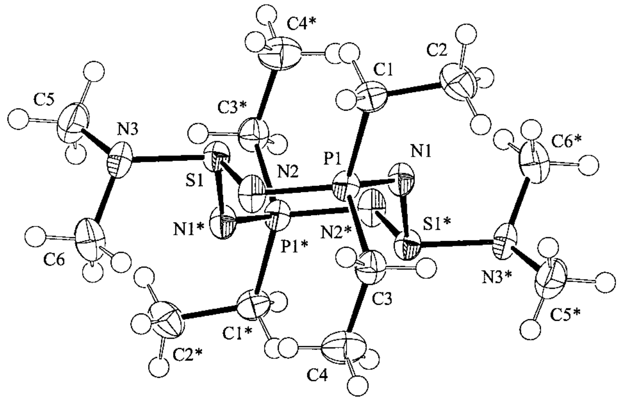

Figure 3. ORTEP drawing of $Et_4P_2N_4(SNMe_2)_2$ (**5b**).

Table 5. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for $R_4P_2N_4(SNMe_2)_2$ (**5a**, R = Ph; **5b**, R = Et)

	5a	**5b**
S(1)−N(1)	1.595(2)	1.599(3)
S(1)−N(2)	1.622(2)	1.607(3)
S(1)−N(3)	1.675(2)	1.704(3)
P(1)−N(1)	1.604(2)	1.617(3)
P(1)−N(2)	1.610(2)	1.620(3)
N(1)−S(1)-N(2)	109.6(1)	107.9(2)
N(2)−S(2)-N(3)	105.2(1)	98.0(2)
S(1)−N(1)-P(1)	125.2(1)	125.7(2)
S(1)−N(2)-P(1)	123.3(1)	117.1(2)
N(1)−P(1)-N(2)	116.6(1)	117.6(2)
S(1)−N(1)-P(1)−N(2)	−28.9(2)	61.1(3)
P(1)−N(1)-S(1)−N(2)	33.2(2)	114.0(2)
P(1)−N(2)-S(1)−N(1)	104.5(1)	85.8(2)
S(1)−N(2)-P(1)−N(1)	−105.9(1)	−26.7(3)
P(1)−N(1)-S(1)−N(3)	143.0(2)	−142.9(2)
P(1)−N(2)-S(1)−N(3)	−150.0(1)	−167.2(2)

The mean exocyclic S−N bond distances in **5a**,**b** (1.675(2) and 1.704(3) Å, respectively) are comparable to those observed for the corresponding bonds in the six-membered ring $Ph_4P_2N_3SNMe_2$ (1.685 Å)[29] and the 12-membered ring $Ph_8P_4N_6(SNMe_2)_2$ (1.703(3) Å).[14a] The small, but significant, difference in the S−N bond lengths in **5a**,**b** and in the sum of the bond angles at the exocyclic nitrogen atom N(3) (340.7° vs 334.7°) may indicate slightly stronger π-donation (from the NMe_2 group to sulfur) in **5a** compared to **5b**. This π-donation may account for the distorted ring conformation and unequal S−N distances (1.595(2) and 1.622(2) Å) in **5a**, although we cannot rule out other contributing factors.

Thermolysis of 5a,b. The thermolysis of **5b** [$\delta(^{31}P)$ 39.4 ppm] at 80 °C under vacuum was monitored by ^{31}P NMR in an

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[27] Allen, C. W. In *The Chemistry of Inorganic Homo- and Heterocycles*; Ed. Haiduc, I., Sowerby, D. B., Eds.; Academic Press: San Diego, CA, 1987; Vol. 2, Chapter 20.

[28] Roesky, H. W.; Rao, M. N. S.; Graf, C.; Gieren, A.; Hädicke, E. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 592.

[29] Burford, N.; Chivers, T.; Hojo, M.; Laidlaw, W. G.; Richardson, J. F.; Trsic, M. *Inorg. Chem.* **1985**, *24*, 709.

attempt to identify the products of ring-opening promoted by the NMe_2 substituents. In the early stages (~30 h) the formation of a red species [$\delta(^{31}P)$ 38.3 ppm] was observed. After prolonged heating (~90 h) this species was replaced by a broad resonance at $\delta(^{31}P)$ 21−23 ppm and a signal at $\delta(^{31}P)$ 134 ppm, assigned to 1,5-$Et_4P_2N_4S_2$.[8d] Thermolysis of **5b** at 120 °C produced 1,5-$Et_4P_2N_4S_2$ more quickly, in addition to the hydrolysis product $Et_2PN_2H_3^+$. Thus it appears that cleavage of the S−NMe_2 bonds is the primary thermolysis pathway for **5b**. Consistently, the EI mass spectrum of **5b** reveals that this fragmentation is facile. No molecular ion is observed, and the parent ion is $Et_4P_2N_4S_2^{\bullet +}$. By contrast, the thermolysis of the tetraphenyl derivative **5a** at 170 °C for 22 h produces a very complex mixture of products, including a broad resonance at $\delta(^{31}P) \sim 0$ ppm, but no $Ph_4P_2N_4S_2$ is formed under these conditions. In view of the bifunctional nature of **5a** and the known tendency of Me_2N groups to promote ring-opening of PNSN heterocycles,[14] the formation of a variety of products from the thermal decomposition of **5a** is not surprising. It should also be noted that the aerial hydrolysis of the related six-membered ring $Ph_4P_2N_3SNMe_2$ produces the S(VI) species $Ph_4P_2N_3SO_2^-$ and $Ph_4P_2N_3S(O)(NPPh_2)_2NH_2$.[30]

Conclusions

Eight-membered ring systems containing alternating phosphazene and sulfanuric units are readily accessible by oxidation of the corresponding sulfur(IV) derivatives with MCPBA. These new heterocycles exhibit high thermal stability. Thus they are unsuitable as precursors, via ring-opening, for hybrid phosphazene−sulfanuric polymers. The desirable polymer precursors containing an −N═S(O)Cl− functionality should be accessible from the dimethylamino-substituted rings $R_4P_2N_4[S(O)NMe_2]_2$ by reaction with HCl or BCl_3. In this work the new sulfur(IV) derivatives $R_4P_2N_4(SNMe_2)_2$ (R = Ph, Et) were prepared, but oxidation to the corresponding sulfur(VI) systems with MCPBA is not feasible in view of the protolytic sensitivity of the S−NMe_2 linkage.

Acknowledgment. Financial support from the Natural Sciences and Engineering Council of Canada is gratefully acknowledged.

Supporting Information Available: Listings of crystal data and data collection and refinement parameters, atomic coordinates and *B* values, bond distances, bond angles, torsion angles, and anisotropic displacement parameters for **4a**, *cis*- and *trans*-**4b**, and **5a**,**b** (51 pages). Ordering information is given on any current masthead page.

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[30] Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1531.