of the α protons with an exchange rate between those of LuENTMP and LuHENTMP, which results in the observed line broadening. From Figure 4, we also see that the δ_β at $\bar{n}_H \sim 1$ is ca. 3.2 so the insensitivity of the β-proton shifts in LuENTMP with pH is further evidence that protonation of the complex does not occur at the nitrogen sites. Martell et al.[3] also proposed that protonation occurs on the phosphonate groups and leaves the M–N bonds intact.

A difference in LnEDTA and LnENTMP complexes is found in the temperature dependence of their ^{1}H NMR spectra. As the EDTA solutions are heated, their spectra lose resolution whereas the reverse is true for the spectra of ENTMP complexes. The loss of resolution with increasing temperature for EDTA complexes is explained by the decreased lifetime of the Ln–N bond. Such an effect would be expected to be present also in ENTMP complexes so the increased resolution with temperature must be due to another, larger effect. A probable explanation involves equilibrium between different conformers wherein the rate of transition between these conformers increases with temperature. Support for a model in which conformers have different δ values is found in ref 9a, where the α protons of LuMEDTA (*N*-methylethylenediaminetriacetate) have three separate AB quartets with baricenters of 3.25, 3.50, and 3.55 ppm (δ(LuEDTA) = 3.40). Such different shift values for the three sets of α protons were also observed in HEDTA. The fact that the four sets of α protons in the LnEDTA complexes had identical δ (AB baricenters) values was related to an averaged symmetrical conformation while the presence of different δ values in the HEDTA and MEDTA complexes results from an averaged asymmetry in the conformation. The large residual charge in LnENTMP^{5-} could lead to conformers that minimize the electrostatic repulsions. Such conformers would most likely have relatively small activation barriers to interchange so even modest increases in the temperature would increase the exchange rate. Since the values of such conformers are unlikely to be very different, exchange would lead, in the proper time domain, to line broadening and loss of resolution, as observed.

These studies have demonstrated that the metal–nitrogen bonding in the ENTMP complexes plays a significant role, comparable to that of the metal–nitrogen bond in EDTA complexes. Protonation of the complexes occurs on the phosphonate groups and does not weaken the metal–nitrogen bonding. Decreased spectral resolution with increasing temperature is interpreted to reflect the effect of exchange between different conformers in LnENTMP^{5-}.

Acknowledgment. This research was supported by a contract with the Office of Basic Energy Sciences of the USDOE.

Registry No. ENTMP, 1429-50-1; H_4EDTA, 60-00-4; NaENTMP, 84961-32-0; CaENTMP, 84986-98-1; Y(ENTMP), 84986-99-2; LaENTMP, 84987-00-8; LuENTMP, 84987-01-9; phosphorous acid, 13598-36-2.

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

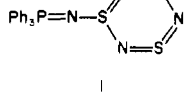
^{31}P NMR Investigation of the Reactions of Tetraphenyl- and Tetramethyldiphosphine and Diphenylphosphine with S_4N_4: Preparation and the Molecular and Electronic Structures of Two Structural Isomers of the Eight-Membered Ring $Ph_4P_2S_2N_4$

N. BURFORD, T. CHIVERS,* and J. F. RICHARDSON

Received July 9, 1982

The reactions of R_2PPR_2 (R = Me, Ph) and Ph_2PH with S_4N_4 in toluene at reflux have been monitored by ^{31}P NMR spectroscopy, and the major products have been isolated and identified. In addition to the six-membered ring $R_2PS_2N_3$ reported previously and the cyclophosphazenes $(R_2PN)_{3,4}$, two structural isomers of the eight-membered ring $R_4P_2S_2N_4$ are formed and the crystal and molecular structures of the phenyl derivatives have been determined. 1,5-$Ph_2P(NSN)_2PPh_2$ crystallizes in the monoclinic space group *C*2/*c* with a = 10.045 (3) Å, b = 15.930 (2) Å, c = 14.130 (4) Å, β = 93.98 (1)°, and Z = 4. The structure was solved by direct methods and refined by full-matrix least-squares techniques to give a final R = 0.045 and R_w = 0.059 for 2193 reflections with $I \geq 3\sigma(I)$. The structure consists of a folded eight-membered ring with a cross-ring S–S contact of 2.527 (1) Å. The angle between the two intersecting planes of the eight-membered ring is 117.3°. The mean endocyclic P–N and S–N bond lengths are 1.622 (3) and 1.590 (3) Å, respectively. 1,3-$(Ph_2PNPPh_2)S_2N_3$ also crystallizes in the monoclinic space group *C*2/*c* with a = 15.200 (11) Å, b = 9.307 (3) Å, c = 17.675 (13) Å, β = 113.24 (3)°, and Z = 4. The structure was solved by direct methods and refined by full-matrix least-squares techniques to give a final R = 0.054 and R_w = 0.063 for 2868 reflections with $I \geq 3\sigma(I)$. The structure consists of an eight-membered ring with phosphorus atoms in the 1,3-positions. The NSNSN unit is essentially planar, and the P atoms lie out and on opposite sides of this plane by 0.697 Å. The mean endocyclic P–N and S–N bond lengths are 1.600 (3) and 1.577 (3) Å, respectively. The electronic structure of 1,3-$(Ph_2PNPPh_2)S_2N_3$ is compared with that of $Ph_2PS_2N_3$ with use of the HMO approach. The strong visible absorption band at ca. 460 nm is tentatively assigned to the HOMO (π^*) → LUMO (π^*) transition of a 10π-electron manifold.

Introduction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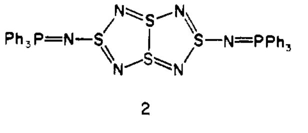
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It was evident from our earlier studies that the nucleophilic degradation of S_4N_4 by phosphines produces a wider range of products than the corresponding reaction with other nucleophiles.[1] For example, the reaction of Ph_3P with S_4N_4 resulted in the formation of the $Ph_3P{=}N$ substituted sulfur-nitrogen rings **1** and **2**, in addition to the anion $S_4N_5^-$ (as its $(Ph_3P{=}N)_3S^+$ salt),[2] which is a frequent product of nucleophilic attack on S_4N_4.[1] In contrast, the reaction of diphosphines, R_2PPR_2 (R = Me, Ph), with S_4N_4 produces the six-membered 8π-electron heterocycles $R_2PS_2N_3$ (**3**). These

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(1) (a) Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* **1978**, *17*, 3668. (b) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1977**, 453. (c) Bojes, J.; Chivers, T. *Inorg. Chem.* **1978**, *17*, 318. (d) Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1978**, 391.

(2) Bojes, J.; Chivers, T.; Cordes, A. W.; MacLean, G.; Oakley, R. T. *Inorg. Chem.* **1981**, *20*, 16.

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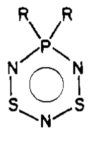

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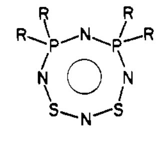

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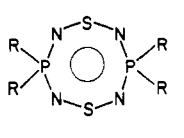

5

intensely purple compounds (λ_{max} 550 nm, R = Ph) were isolated in ca. 20% yield by gel permeation chromatography, which revealed the presence of three other colored fractions, presumably containing additional products.[3]

We have now completed a detailed investigation of the reactions of S_4N_4 with R_2PPR_2 by ^{31}P NMR spectroscopy and have isolated and characterized the major phosphorus-containing products, which include structural isomers of an eight-membered $P_2S_2N_4$ ring, cyclo-1,3-diphospha-5,7-dithia-2,4,6,8-tetrazene (**4**) and cyclo-1,5-diphospha-3,7-dithia-2,4,6,8-tetrazene (**5**). The latter compounds are also formed, in addition to $Ph_2PS_2N_3$, in the reaction of Ph_2PH with S_4N_4 in toluene at reflux.

We have previously reported the formation of the methyl derivative of **5** from the decomposition of **3** (R = Me). An X-ray structural determination of **5** (R = Me) showed it to consist of a folded eight-membered ring with a cross-ring S–S contact of 2.551 (2) Å.[4] In this paper we describe the details of the ^{31}P NMR investigation of the R_2PPR_2/S_4N_4 and Ph_2PH/S_4N_4 reaction mixtures, the spectroscopic characterization of the new heterocycles **4** (R = Me, Ph) and **5** (R = Ph), and the X-ray structural determination of **4** and **5** (R = Ph). We have also carried out extended Hückel calculations for the 1,3-isomer **4**, in order to compare its ground-state electronic structure with that of the closely related six-membered ring **3** and to assign the strong visible absorption at ca. 460 nm to the appropriate electronic transition.

Experimental Section

Reagents and General Procedures. Tetrasulfur tetranitride,[5] tetramethyldiphosphine,[6] and tetraphenyldiphosphine[7] were prepared by the literature methods. Tetramethyldiphosphine disulfide (Alfa), iron powder (Ventron), chlorodiphenylphosphine (Alfa), and lithium aluminum hydride (Alfa) were all commercial products used as received. All the solvents employed were of reagent grade and most were dried before use: toluene and heptane by distillation from sodium, acetonitrile by double distillation from phosphorus pentoxide and calcium hydride. Anhydrous diethyl ether (Amminckrodt) was used as received. All distillations of solvents 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. UV–visible spectra were obtained with a Cary 15 or a Unicam SP1800 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded with a Varian XL 200-MHz spectrometer. Raman spectra were mesured on samples in glass capillaries with a Jarrell-Ash Model 25-100 double-grating spectrometer equipped with a photon-counting detection system, using a coherent radiation dye laser pumped by a CR-4 argon ion laser. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary.

Reaction of Tetraphenyldiphosphine with S_4N_4. Tetrasulfur tetranitride (1.32 g, 7.2 mmol) was added to a solution of tetraphenyldiphosphine (2.65 g, 7.2 mmol) in 50 mL of toluene, and the mixture was stirred and heated to reflux. After 16 h the mixture was cooled to room temperature and reduced in volume to about 20mL by removal of the solvent in vacuo. The solution was then filtered and eluted down a 30 × 500 mm BioBeads S-X8 chromatography column. Four fractions were collected, distinguished by their color: pink, yellow, orange, and purple, respectively. The ^{31}P NMR spectrum of the first fraction showed it to consist of a complex mixture of phosphorus-containing compounds, but no pure components could be isolated. Fractional crystallization of the other three fractions from acetonitrile resulted in the isolation of $(Ph_2PN)_3$ and $(Ph_2PN)_4$ (0.15 g, combined weight) from fraction 2, 1,5-$Ph_2P(NSN)_2PPh_2$ (0.07 g, 0.15 mmol), 1,3-$(Ph_2PNPPh_2)S_2N_3$ (0.28 g, 0.60 mmol), and $(Ph_2PS)_2$ from fraction 3, and $Ph_2PS_2N_3$ (0.35 g, 1.2 mmol) and $(Ph_2PS)_2$ and S_8 (0.08 g, 0.3 mmol) from fraction 4. S_4N_4 (0.36 g, 1.9 mmol) was recovered from the fifth fraction. Due to the difficulties involved in separation, the weights of products reported should be regarded as isolated rather than optimum yields. A ^{31}P NMR spectrum of the reaction mixture shows a number of high-intensity signals, most of which can be attributed to the compounds described above (see Figure 1). 1,3-$(Ph_2PNPPh_2)S_2N_3$ (**4**, R = Ph) was recrystallized from warm acetonitrile; mp 135–136 °C. Anal. Calcd for $C_{24}H_{20}N_4P_2S_2$: C, 58.76; H, 4.11; N, 11.41. Found: C, 58.95; H, 4.01; N, 11.31. The infrared spectrum of 1,3-$(Ph_2PNPPh_2)S_2N_3$ (1600–250-cm^{-1} region) shows bands at 1585 (vw), 1479 (w), 1440 (s), 1332 (vw), 1309 (vw), 1196 (vs), 1179 (vs), 1161 (s), 1127 (m), 1108 (m), 1070 (vw), 1034 (vw), 1030 (vw), 1002 (vw), 976 (vw), 928 (m), 849 (vw), 782 (vw), 762 (vw), 755 (vw), 741 (m), 732 (s), 725 (s), 702 (s), 696 (s), 672 (vw), 623 (vw), 597 (vw), 544 (vs), 534 (s), 513 (vs), 435 (vw), 395 (vw), 348 (vw), and 337 (vw) cm^{-1}. The ^{31}P NMR spectrum of 1,3-$(Ph_2PNPPh_2)S_2N_3$ in $CDCl_3$ shows a singlet at 18.7 ppm (referenced to external 85% H_3PO_4). The UV–visible spectrum of 1,3-$(Ph_2PNPPh_2)S_2N_3$ shows absorption maxima at 460 ($\epsilon \approx 8 \times 10^3$ L M^{-1}) and 342 nm in CH_2Cl_2. 1,5-$Ph_2P(NSN)_2PPh_2$ (**5**, R = Ph) was recrystallized from acetonitrile/methylene chloride; mp 210–215 °C dec. Anal. Calcd for $C_{24}H_{20}N_4P_2S_2$: C, 58.76; H, 4.11; N, 11.42. Found: C, 58.83; H, 4.05; N, 11.75. The infrared spectrum of 1,5-$Ph_2P(NSN)_2PPh_2$ (1600–250-cm^{-1} region) shows bands at 1587 (s), 1574 (vw), 1437 (s), 1332 (vw), 1308 (w), 1166 (w), 1125 (vs), 1086 (s), 1053 (vs), 1027 (vs), 998 (s), 766 (s), 749 (m), 740 (s), 725 (s), 691 (s), 676 (m), 535 (vs), 469 (w), 445 (w), 407 (w), 362 (vw), and 270 (vw) cm^{-1}. The Raman spectrum of 1,5-$Ph_2P(NSN)_2PPh_2$ shows two strong bands at 268 and 233 cm^{-1}, and the ^{31}P NMR spectrum ($CDCl_3$) shows a singlet at 113.9 ppm (referenced to external 85% H_3PO_4).

Reaction of Diphenylphosphine with S_4N_4. Tetrasulfur tetranitride (1.42 g, 7.7 mmol) was added to a solution of diphenylphosphine (2.87 g, 15.4 mmol) in 50 mL of toluene, and the mixture was stirred and heated to reflux. After 16 h the mixture was cooled to room temperature and reduced in volume to about 20 mL by removal of the solvent in vacuo. The solution was filtered and eluted down a 30 × 500 mm BioBeads S-X8 chromatography column. Three fractions were collected, yellow, orange, and purple, and fractional crystallization of each of these from acetonitrile resulted in the isolation of $(Ph_2PN)_3$ from fraction 1, 1,3-$(Ph_2PNPPh_2)S_2N_3$ (1.09 g, 2.2 mmol) and 1,5-$Ph_2P(NSN)_2PPh_2$ (0.02 g, 0.05 mmol) from fraction 2, and $Ph_2PS_2N_3$ (0.51 g, 1.8 mmol) and S_8 (0.10 g, 0.40 mmol) from fraction 3. The ^{31}P NMR spectrum of the reaction mixture showed these to be the major products in addition to $Ph_2P(S)H$.

Reaction of Tetramethyldiphosphine with S_4N_4. Tetrasulfur tetranitride (1.66 g, 9.0 mmol) was added to a frozen solution of tetramethyldiphosphine (1.10 g, 9.0 mmol) in 40 mL of toluene, and the mixture was allowed to warm, with care,[3] to room temperature over a period of 30 min. The mixture was then set to reflux and after 2 h was cooled to room temperature. The volume was reduced to about 20 mL by removal of solvent in vacuo, and then the mixture was filtered and eluted down a 30 × 500 mm BioBeads S-X8 chromatography column. Four fractions were collected: pink, yellow, orange, and purple. The first fraction was shown by ^{31}P NMR to contain a complex mixture of products, but no pure components could be isolated. Fractional crystallization of the other fractions resulted in isolation of $(Me_2PN)_3$ and $(Me_2PN)_4$ from fraction 2, 1,3-$(Me_2PNPMe_2)S_2N_3$, 1,5-$Me_2P(NSN)_2PMe_2$, and $(Me_2PS)_2$ from fraction 3, and $Me_2PS_2N_3$ from fraction 4. Due to the difficulty in separating the products and the relative instability of the methylphosphathiazenes, no yields were recorded. The ^{31}P NMR spectrum of the reaction mixture showed the isolated compounds to be the major products. 1,3-$(Me_2PNPMe_2)S_2N_3$ was recrystallized from acetonitrile; mp 81–82 °C. Anal. Calcd for $C_4H_{12}N_4P_2S_2$: C, 19.83; H, 4.99;

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[3] (a) Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282. (b) Burford, N.; Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1980**, 1204.

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[6] Butter, S. A.; Chatt, J. *Inorg. Synth.* **1974**, *15*, 187.

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Table I. Crystal Data

	$C_{24}H_{20}N_4P_2S_2$ isomer	
	$1,3-(Ph_2PNPPh_2)S_2N_3$	$1,5-Ph_2P(NSN)_2PPh_2$
mol wt	500.1	500.1
space group	*C*2/*c*	*C*2/*c*
a, Å	15.200 (11)	10.045 (3)
b, Å	9.307 (3)	15.930 (2)
c, Å	17.675 (13)	14.130 (4)
β, deg	113.24 (3)	93.98 (1)
V, Å^3	2298 (3)	2256 (1)
Z	4	4
D, g cm^{-3}	1.45	1.47
radiation, Å	Mo Kα (λ = 0.71069)	Cu Kα (λ = 1.5418)
monochromator, filter	graphite monochromator	Ni prefilter
temp, °C	−100 (5)	−100 (5)
max θ, deg	30	75
scan range $\Delta\omega$, deg	1.5(0.8 + 0.347 tan θ)	1.5(0.9 + 0.142 tan θ)
std. reflctns, measd every 1000 s of X-ray exposure time	(0,0,12), (10,2,2), (331)	(080), (087), (404)
reflctns scanned, obsd ($I > 3\sigma(I)$)	2042, 1529	2327, 1994
abs coeff, cm^{-1}	μ(Mo Kα) = 3.91	μ(Cu Kα) = 24.25
cryst descripn	orange plate	colorless prism
cryst dimens, mm	0.40 × 0.32 × 0.15	0.28 × 0.20 × 0.19
boundary planes	7; $\{11\bar{1}\}$, $\{001\}$, $(1\bar{1}0)$	8; $\{010\}$, $\{001\}$, $(\bar{1}10)$, $(1\bar{1}0)$, $(10\bar{1})$, (111)

N, 23.13. Found: C, 19.88; H, 5.12; N, 22.89. The infrared spectrum of $1,3-(Me_2PNPMe_2)S_2iN_3$ (**4**, R = Me) (1600–250-cm^{-1} region) shows bands at 1418 (m), 1409 (m), 1302 (s), 1292 (m), 1284 (s), 1219 (vs), 1116 (vs), 1032 (m), 972 (m), 952 (s), 942 (vs), 932 (s), 881 (s), 870 (m), 857 (m), 778 (vw), 755 (m), 730 (vw), 637 (m), 590 (w), 464 (w), 434 (m), 425 (m), and 373 (vw) cm^{-1}. The ^{31}P NMR spectrum of $1,3-(Me_2PNPMe_2)S_2N_3$ in $CDCl_3$ shows a singlet at 28.3 ppm (referenced to external 85% H_3PO_4), and the ^1H NMR spectrum shows a doublet at 1.58 ppm, $^2J_{P-H}$ = 13.3 Hz (referenced to Me_4Si). The UV–visible spectrum shows maxima at 455 ($\epsilon = 6 \times 10^3$ L M^{-1}) and 350 nm. The spectroscopic characterization of $1,5-Me_2P(NSN)_2PMe_2$ has been described previously.[4,8]

X-ray Data Collection. The crystal data and experimental conditions are given in Table I. Preliminary photographic examinations and observed extinctions during data collection ((hkl), $h + k = 2n + 1$; $(h0l)$, $l = 2n + 1$) identified the space group as either *Cc* or *C*2/*c* for both isomers. In each ase *C*2/*c* was the final choice based on the centric distribution of *E* values. With 4 formula units per unit cell, site symmetry 2 is imposed on the molecules.

The data were collected on an Enraf-Nonius CAD4F automated diffractometer fitted with a low-temperature attachment. The cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurately centered reflections having $5° \leq \theta \leq 21°$ for $1,3-(Ph_2PNPPh_2)S_2N_3$ and $18° \leq \theta \leq 33°$ for $1,5-Ph_2P(NSN)_2PPh_2$. Intensities were measured with use of the ω–2θ scan mode with the first and last 16 steps of a 96-step scan considered to be background. The intensity was calculated as $I = [P - 2(B1 + B2)]Q$, where *P* is the sum of the central 64 steps, *Q* is the scan rate, and B1 and B2 are the backgrounds. The standard deviation of the intensity $\sigma(I) = [P + 4(B1 + B2)]^{1/2}Q$. The data were corrected for background, Lorentz, and polarization effects, and *E* values were calculated by using a *K* curve.[9]

Solution and Refinement. Atomic scattering factors were those of Cromer and Mann.[10] Real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[11] Initial coordinates for all unique non-hydrogen atoms of each structure were obtained by direct methods (MULTAN 78) and refined by full-matrix least-squares techniques on *F*. A series of isotropic and anisotropic refinement cycles resulted in agreement factors of $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.087$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.090$ for $1,3-(Ph_2PNPPh_2)S_2N_3$ and $R = 0.054$ and $R_w = 0.063$ for $1,5-Ph_2P(NSN)_2PPh_2$. The weighting scheme used was $w = [\sigma^2(F) + nF^2]^{-1}$ ($n = 0.0006$ for $1,5-Ph_2P(NSN)_2PPh_2$ and $n = 0.0003$ for $1,3-(Ph_2PNPPh_2)S_2N_3$), where $\sigma(F)$ was derived from counting statistics. The 10 unique H atoms of each structure were readily located in difference Fourier syntheses and included in idealized positions (C–H = 0.95 Å), with thermal parameters 10% greater than the C atom to which they are attached, but not refined.

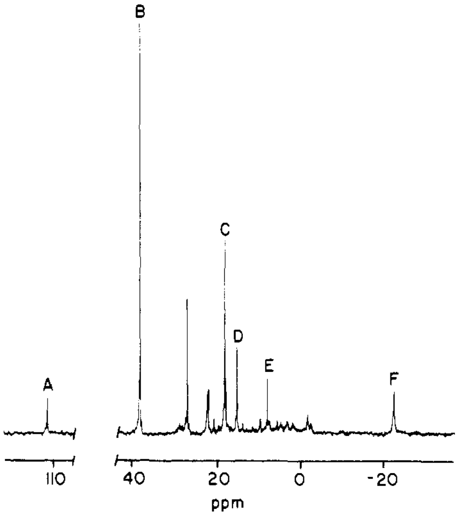

Figure 1. ^{31}P NMR spectrum of the Ph_2PPPh_2/S_4N_4 reaction mixture after 16 h at reflux in toluene showing the identity of the major products: (A) $1,5-Ph_2P(NSN)_2PPh_2$; (B) $(Ph_2PS)_2$; (C) $1,3-(Ph_2PNPPh_2)S_2N_3$; (D) $(Ph_2PN)_3$; (E) $(Ph_2PN)_4$; (F) $Ph_2PS_2N_3$.

After two cycles of refinement including H atom contributions, the model for $1,3-(Ph_2PNPPh_2)S_2N_3$ converged (1529 unique data, 146 variables) with agreement factors of $R = 0.054$ and $R_w = 0.063$. On the final cycle of refinement the maximum shift/error was 0.02, and the error in an observation of unit weight was 2.30. The highest peak in a difference Fourier synthesis was of electron density 1.15 e Å^{-3} at fractional coordinates (0.0049, 0.1429, 0.3275) and is associated with P1. The model for $1,5-Ph_2P(NSN)_2PPh_2$ converged (1994 unique data, 145 variables) with agreement factors of $R = 0.045$ and $R_w = 0.059$. The maximum shift/error on the last cycle was 0.08, and the error in an observation of unit weight was 4.36. The highest peak in a difference Fourier synthesis was of electron density 0.7 e Å^{-3} at fractional coordinates (−0.2124, −0.0576, 0.3075) and is of no chemical significance.

Results and Discussion

Reactions of S_4N_4 with R_2PPR_2 (R = Me, Ph) and Ph_2PH. A ^{31}P NMR spectrum of the Ph_2PPPh_2/S_4N_4 reaction mixture is shown in Figure 1. The major phosphorus-containing products have been isolated by gel permeation chromatogra-

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[8] However, the ^{31}P NMR spectrum was incorrectly reported as −77 ppm in ref 4. The correct value is +110 ppm.

[9] Computing was performed at the University of Calgary with use of the X-RAY 76 package of crystallographic programs: Stewart, J. M., Ed. Technical Report TR-446, Computer Science Center, University of Maryland.

[10] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

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Table II. Positional Parameters (X10^4) of Atoms of the Asymmetric Unit

	$1,3\text{-}(Ph_2PNPPh_2)S_2N_3$			$1,5\text{-}Ph_2P(NSN)_2PPh_2$		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
P1	84.9 (7)	2271.3 (12)	3324.8 (7)	−1646.1 (7)	722.9 (4)	1620.2 (5)
S1	599.2 (9)	771.4 (12)	3415.9 (9)	−708.6 (6)	1658.3 (4)	3205.2 (5)
N1	0[b]	3045 (5)	2500[b]	−1856 (2)	1116 (2)	2659 (2)
N2	755 (3)	868 (4)	3614 (2)	−376 (2)	1150 (2)	1162 (2)
N3	0[b]	−1296 (6)	2500[b]			
C1	−1105 (3)	1843 (4)	3265 (2)	−3095 (3)	952 (2)	851 (2)
C2	−1902 (3)	2436 (4)	2648 (2)	−4363 (3)	741 (2)	1133 (2)
C3	−2820 (3)	2148 (5)	2606 (3)	−5492 (3)	923 (2)	548 (2)
C4	−2941 (3)	1267 (5)	3180 (3)	−5365 (3)	1302 (2)	−316 (3)
C5	−2155 (3)	666 (5)	3800 (3)	−4118 (3)	1506 (2)	−612 (2)
C6	−1231 (3)	954 (5)	3849 (3)	−2976 (3)	1335 (2)	−23 (3)
C7	627 (3)	3526 (4)	4136 (2)	−1531 (2)	−402 (2)	1663 (2)
C8	1354 (3)	3128 (5)	4873 (3)	−1856 (3)	852 (2)	2465 (2)
C9	1793 (3)	4125 (6)	5486 (3)	−1778 (3)	1720 (2)	2465 (3)
C10	1513 (3)	5540 (5)	5364 (3)	−1378 (3)	−214 (2)	1670 (3)
C11	785 (3)	5957 (5)	4646 (3)	−1047 (3)	−1700 (2)	878 (2)
C12	337 (3)	4975 (5)	4026 (2)	−1120 (3)	−829 (2)	866 (2)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. [b] Parameters are restricted by the symmetry of the crystal.

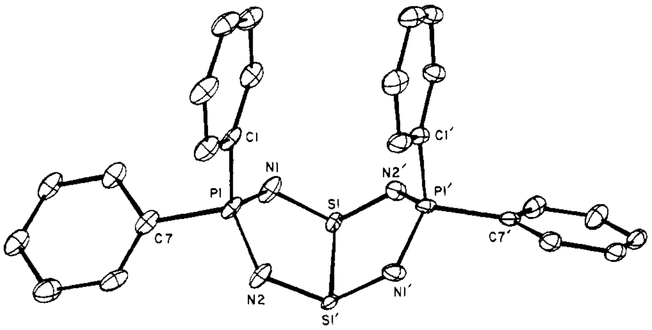

Figure 2. ORTEP drawing (50% probability ellipsoids) of 1,5-$Ph_2P(NSN)_2PPh_2$ showing the atomic numbering scheme.

phy, and the known compounds $(Ph_2PN)_3$, $(Ph_2PN)_4$, $(Ph_2PS)_2$, and $Ph_2PS_2N_3$ have been identified spectroscopically (^{31}P NMR and infrared spectra). In addition, the new compounds 1,3- and 1,5-$Ph_4P_2S_2N_4$ (**4** and **5**, respectively) are formed in significant amounts and have been isolated and structurally characterized (vide infra). The ^{31}P NMR spectrum of the Me_2PPMe_2/S_4N_4 reaction mixture shows a similar distribution of products, and the known compounds $(Me_2PN)_3$, $(Me_2PN)_4$, $(Me_2PS)_2$, and 1,5-$Me_2P(NSN)_2PMe_2$, in addition to the new compound 1,3-$(Me_2PNPMe_2)S_2N_3$, have been identified spectroscopically.

The reaction of Ph_2PH with S_4N_4 gives the same products as the Ph_2PPPh_2/S_4N_4 reaction. However, it is much easier to separate $Ph_2P(S)H$ compared to $(Ph_2PS)_2$ from the products and the former reaction is preferred, particularly for the preparation of 1,3-$(Ph_2PNPPh_2)S_2N_3$.

By comparison with the reaction of Ph_3P with S_4N_4 we propose that nucleophilic attack of the diphosphine at sulfur initiates ring opening. This is followed by migration of the phosphorus substituent from sulfur to nitrogen, which, in the case of Ph_3P, results in the formation of S–N rings bearing exocyclic $Ph_3P{=}N$ substituents, **1** and **2**. By contrast, the reactions with Ph_2PPPh_2 (or Ph_2PH) and Me_2PPMe_2 yield heterocycles in which the R_2P unit is incorporated within the ring (**3**–**5**). This difference is presumably a result of the reactivity of the third valence position due to a P–P bond in $R_2P{-}PR_2$ or a P–H bond in Ph_2PH, but the fate of the hydrogen atom in the reaction of the latter reagent is unknown.

Crystal and Molecular Structures of 1,3-$(Ph_2PNPPh_2)S_2N_3$ and 1,5-$Ph_2P(NSN)_2PPh_2$. The crystal structures of both isomers consist of discrete molecular units with no unusual intermolecular contacts. The final atomic coordinates of the unique non-hydrogen portions of the two molecules are given in Table II. Thermal parameters, parameters for the hydrogen atoms, and the lists of structure factors are available as supplementary material. Selected bond lengths and angles are presented in Table III, and ORTEP drawings of the two molecules, together with atomic numbering schemes, are shown in Figures 2 and 3.

Table III. Selected Interatomic Distances (Å) and Angles (deg)

	$1,3\text{-}(Ph_2PNPPh_2)S_2N_3$		
P1-N1	1.585 (3)	P1-C7	1.779 (4)
P1-N2	1.610 (4)	N2-S1	1.562 (4)
P1-C1	1.814 (5)	S1-N3	1.589 (2)
N1-P1-N2	118.1 (2)	C1-P1-C7	109.0 (2)
N1-P1-C1	109.2 (1)	P1-N1-P1'	126.0 (3)
N1-P1-C7	106.6 (2)	P1-N2-S1	134.5 (2)
N2-P1-C1	109.4 (2)	N2-S1-N3	120.2 (2)
N2-P1-C7	104.1 (2)	S1-N3-S1'	144.1 (4)
	$1,5\text{-}Ph_2P(NSN)_2PPh_2$		
P1-N1	1.623 (3)	N1-S1	1.596 (3)
P1-N2	1.620 (3)	N2-S1'	1.584 (2)
P1-C1	1.792 (3)	S1-S1'	2.528 (1)
P1-C7	1.796 (3)		
N1-P1-N2	110.8 (1)	C1-P1-C7	105.7 (1)
N1-P1-C1	108.6 (1)	P1-N1-S1	120.7 (2)
N1-P1-C7	111.5 (1)	P1-N2-S1'	121.2 (2)
N2-P1-C1	107.5 (1)	N1-S1-N2'	116.1 (1)
N2-P1-C7	112.4 (1)		

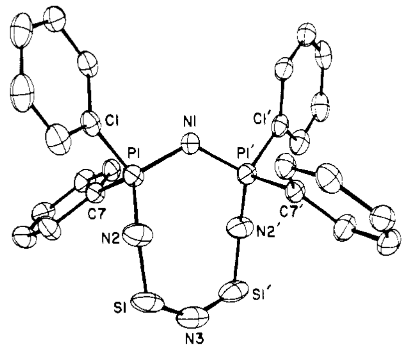

Figure 3. ORTEP drawing (50% probability ellipsoids) of 1,3-$(Ph_2PNPPh_2)S_2N_3$ showing the atomic numbering scheme.

The structure of 1,5-$Ph_2P(NSN)_2PPh_2$ is very similar to that of the corresponding methyl derivative.[4] It can be regarded as a bicyclic molecule in which two 5-membered rings share a common S–S bond. The twofold symmetry axis passes through the center of and is perpendicular to the S–S bond. As a result of the twofold axis the two S and two N atoms form two 4-membered planes (planar to within 0.013 Å), which intersect at an angle of 117.3° (cf. 114.9° in 1,5-$Me_2P(NSN)_2PMe_2$,[4] 144° in $Me_2NC(NSN)_2CNMe_2$,[12] and 120.4° in 1,5-$(Ph_3P{=}N)_2S_4N_4$[2]). The phosphorus atoms lie 0.214 Å below the respective planes.

As in the case of the methyl derivative,[4] the close S1–S1′ transannular interaction imposes angle strain within the PN_2S_2 rings, resulting in significant deviations in the geometry of the $=N{-}PPh_2{=}N-$ unit in 1,5-$Ph_2P(NSN)_2PPh_2$ with respect to that found in phenylcyclophosphazenes; the mean endocyclic bond angles at P (110.7 (1)°) and N (121.0 (3)° are smaller than in $(Ph_2PN)_3$[13] ($\angle P_{endo}$ = 117.8 (3)°, $\angle N$ = 122.1 (7)°) and $(Ph_2PN)_4$[14] ($\angle P_{endo}$ = 119.9 (1)°, $\angle N$ = 127.9 (2)°). The mean P–N distance (1.623 (3) Å; cf. 1.636 Å in 1,5-$Me_2P(NSN)_2PMe_2$)[4] is also significantly longer than in $(Ph_2PN)_n$ (d(P–N) = 1.597 (9) and 1.590 (3) Å for n = 3 and 4, respectively[13,14]). This lengthening of the P–N bond has been ascribed to the relative weakness of the π-bonds of the 4-electron 3-center subunits in $R_2P(NSN)_2PR_2$ compared to the π-bonds in cyclophosphazenes.[4] The mean S–N bond length of 1.590 (3) Å is statistically equivalent to that found for the methyl derivative and slightly longer than those observed for $S_4N_4^{2+}$ (d(S–N) = 1.55 Å).[15] However, the S–S bond is significantly shorter in the phenyl derivative (2.527 (1) Å) than in the methyl compound (2.551 (2) Å).[4]

The crystallographically imposed twofold axis in 1,3-$(Ph_2PNPPh_2)S_2N_3$ passes through atoms N1 and N3. These atoms together with N2, S1, and the symmetry-related atoms of the ring form a plane with the maximum deviation being 0.019 Å for S1. The P atoms lie out and on opposite sides of the plane by 0.697 Å. This displacement is larger than that found in the related molecule containing only one Ph_2PN unit, **3** (0.284 Å). A similar puckering of the ring is found in $(Ph_2PN)_4$.[14]

The heterocyclic ring in 1,3-$(Ph_2PNPPh_2)S_2N_3$ may be considered to consist of two parts, an S_2N_3 unit and a PNP unit. Comparison of the NSNSN unit with that found in $Ph_2PS_2N_3$ (**3**)[3] shows that both are planar and that the respective bond lengths are equivalent within experimental error. The significantly larger bond angles found in the present structure may be attributed to the increase in the size of the ring. The PNP unit shows a remarkable similarity to the corresponding unit in $(Ph_2PN)_4$,[14] having comparable bond lengths and angles. However, the P–N bond length at the junction of the PNP and S_2N_3 units in **4** is significantly longer (1.613 (4) Å) than the mean P–N bond length (1.590 (4) Å) found in the tetrameric phosphazene.[14] It might also be noted that the mean S–N bond length in 1,3-$(Ph_2PNPPh_2)S_2N_3$ (1.577 (4) Å) is significantly longer than the mean bond length in the isoelectronic 10π-electron system $S_4N_4^{2+}$ (1.55 Å).[15-17]

Spectroscopic Properties of 1,3-$(R_2PNPR_2)S_2N_3$ (R = Me, Ph) and 1,5-$Ph_2P(NSN)_2PPh_2$. The major decomposition product of the 6-membered ring $Me_2PS_2N_3$ was suggested to be a dimer $(Me_2PNSN)_2$ on the basis of analytical and mass spectral data.[4] The isomers **4** and **5** were considered to be the most likely structures, but these alternatives could not be distinguished by the NMR spectra ($^1H\{^{31}P\}$, ^{13}C, and ^{31}P). However, the Raman spectrum showed a strong band at 250 cm^{-1} attributable to a transannular S–S bond. This piece of evidence suggested that the decomposition product was the 1,5-isomer, a proposal that was confirmed by an X-ray structural determination (d(S–S) = 2.551 (2) Å).[4] It should be noted here that 1,5-$Ph_2P(NSN)_2PPh_2$ shows a strong Raman band at 268 cm^{-1} consistent with a shorter, and presumably stronger, cross-ring S–S bond (2.527 (1) Å). These data provide further support for the usefulness of Raman spectroscopy in detecting S–S bonding interactions in S–N rings and cages.[4]

In the current investigation we have isolated the 1,3-isomers **4** (R = Me, Ph) and structurally characterized the phenyl derivative. It is significant that the spectroscopic properties of these 1,3-isomers are substantially different from those of the corresponding 1,5-isomers. The most obvious difference is the color. The 1,5-isomers, **5**, are very pale yellow and exhibit no absorption maximum in the visible spectrum, while the 1,3-isomers are an intense orange color due to a strong visible absorption band at 460 nm (R = Ph) and 456 nm (R = Me) attributed to a π^* (HOMO) $\rightarrow$ π^* (LUMO) transition (vide infra).

As expected, both isomers exhibit a singlet in the ^{31}P NMR spectrum; however, there is a surprising chemical shift difference of ca. 100 ppm between them. The signal for the 1,5-isomer (R = Ph) is very deshielded at 114 ppm, whereas the 1,3-isomer has a ^{31}P chemical shift of 19 ppm (cf. ca. 20 ppm in cyclophosphazenes).[18] Cyclophosphazene characteristics are also evident from the P–N infrared stretching vibrations, which occur at ca. 1190 cm^{-1} for the 1,3-isomer (cf. 1213 cm^{-1} in $(Ph_2PN)_4$)[18] compared to ca. 1050 cm^{-1} in the 1,5-isomer. Thus the NMR and infrared spectral data of the 1,3-isomer show a close similarity to the corresponding data for cyclophosphazenes, presumably due to the presence of an NPNPN sequence in the ring. However, the electron richness of the phosphathiazene **4** (a 10π-electron system) relative to the cyclophosphazene, $(R_2PN)_4$ (an 8π-electron system), gives rise to a distinctive electronic spectrum for the former.

Comparison of Electronic Structure and Bonding in 1,3-$(Ph_2PNPPh_2)S_2N_3$ with Those in $Ph_2PS_2N_3$ and with Those in 1,5-$Ph_2P(NSN)_2PPh_2$. Previous molecular orbital calculations on unsaturated S–N or P–S–N heterocycles have shown good agreement between the general conclusions derived from a simple Hückel approach and those obtained from all electron calculations.[3,4,17,19,20] However, difficulties do arise when the Hückel approximation is used due to the fact that, unlike the case for carbocyclic π-systems, the lower π-levels in S–N systems are buried amongst the σ energy levels and it is only the higher π-levels that can be viewed as truly separate from the σ system of the ring.[17] Nevertheless, useful information may still be obtained about the ordering and composition of frontier orbitals, providing suitable Hückel parameters are chosen.[17]

In the ab initio treatment of the electronic structure of the 8π-electron system, $R_2PS_2N_3$ (**3**, R = H),[3] it was found that most of the π-electron density was located on the S_2N_3 unit, suggesting that the molecule may be described as an internal salt, $R_2P^+S_2N_3^-$, for the qualitative simple Hückel approach. We have now carried out extended Hückel calculations for $H_2PS_2N_3$ and compared the results with those obtained for 1,3-$(H_2PNPH_2)S_2N_3$, in which the S_2N_3 unit is remarkably similar to that in **3**. The 8-membered ring is a 10π-electron system, one electron being donated to the π system by each

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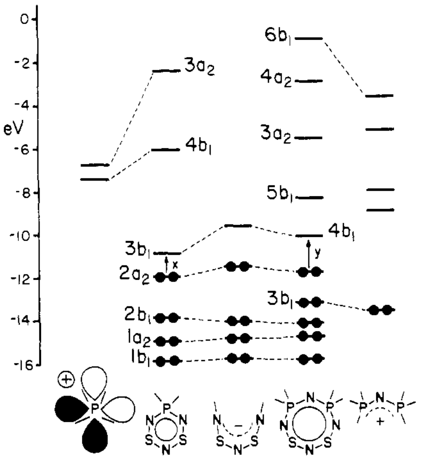

Figure 4. Correlation diagram for the π MO energy levels of $H_2PS_2N_3$, 1,3-$(H_2PNPH_2)S_2N_3$, and the fragments $H_2S_2N_3^-$, $H_3PN^+PH_3$, and H_2P^+. Experimental values of *x* and *y* are 550 and 460 nm, respectively.

phosphorus and nitrogen atom and two by each sulfur. As an internal salt, $(H_2P{=}N^+{=}PH_2)(S_2N_3^-)$, the $S_2N_3^-$ unit will accommodate 8 π-electrons (cf. $H_2PS_2N_3$) and the $H_2P{=}N^+{=}PH_2$ unit possesses 2 π-electrons. The results of these calculations are illustrated in Figure 4. For the six-membered ring the most prominent effect of the interaction of the d orbitals of H_2P^+ having π-symmetry, i.e. d_{xz} (homomorphic interaction)[22] and d_{yz} (heteromorphic interaction),[22] with the π-MOs of the $S_2N_3^-$ unit is the lowering in energy of the HOMO ($2a_2$) and LUMO ($3b_1$), both of which are antibonding orbitals. In a similar manner the interaction of the π MOs of the $H_2P{=}N^+{=}PH_2$ unit with the π MOs of the $S_2N_3^-$ unit also leads to a stabilization of the HOMO ($2a_2$) and LUMO ($4b_1$) levels for the 8-membered ring. In unsaturated P–N heterocycles the extent of dπ–pπ bonding has been a major point of contention because the large energy difference between orbitals of similar symmetry leads to a weak interaction. This is also evident in Figure 4. However, the consequences of such interactions are important. In $R_2PS_2N_3$ the result of dπ–pπ bonding is a narrow HOMO–LUMO gap corresponding to the low-energy absorption (λ_{max} ~550 nm, $\pi^*(2a_2) \rightarrow \pi^*(3b_1)$).

This assignment has been confirmed by ab initio calculations.[3] It therefore seems reasonable to suggest that a similar electronic transition, $\pi^*(2a_2) \rightarrow \pi^*(4b_1)$, is responsible for the strong visible absorption band observed at ca. 460 nm and hence the orange color of 1,3-$(R_2PNPR_2)S_2N_3$.

Finally, it should be noted that, in the absence of a transannular interaction, the 1,5-isomer should also be a 10π-electron system. However, as discussed for the methyl derivative,[4] the π^* HOMO of a planar 8-membered ring transforms into an S–S σ-bonding orbital in the folded ring. Such cross-ring bonding interactions are not possible in the 1,3-isomers and, consequently, the additional pair of π-electrons is accommodated in an antibonding orbital in these 10π-electron 8-center heterocycles.

Summary and Conclusions

Investigations of the reactions of phosphines (R_2PPR_2 (R = Me, Ph) and Ph_2PH) with S_4N_4 by ^{31}P NMR spectroscopy have led to the characterization of structural isomers of the 8-membered ring $R_4P_2S_2N_4$, in addition to the previously characterized 6-membered ring $R_2PS_2N_3$. The transannular S–S interaction observed for the 1,5-isomers $R_2P(NSN)_2PR_2$ is absent in the 1,3-isomers $(R_2PNPR_2)S_2N_3$. The latter represent a novel example of a 10π-electron 8-center system, and as a consequence of their electron richness, they exhibit characteristic electronic spectra. These ring systems can be represented by the general formula $(R_2PN)_n(SN)_2$ (n = 1, 2), suggesting that they are hybrids of cyclophosphazenes and cyclothiazenes. Since larger ring sizes are well-known for both P–N and S–N systems, e.g. $S_5N_5^+$ and $(Ph_2PN)_{5,6}$, it seems reasonable to suggest that an extension of the homologous series to give larger rings should also be possible for the mixed phosphazene–thiazene systems.

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Registry No. **4** (R = Ph), 85028-69-9; **4** (R = Me), 85028-70-2; **5** (R = Ph), 85028-71-3; Ph_2PPPh_2, 1101-41-3; S_4N_4, 28950-34-7; Ph_2PH, 829-85-6; Me_2PPMe_2, 3676-91-3.

Supplementary Material Available: Listings of calculated and observed structure factors, parameters for the hydrogen atoms, and thermal parameters for 1,5-$Ph_2P(NSN)_2PPh_2$ and 1,3-$(Ph_2PNPPh_2)S_2N_3$ (34 pages). Ordering information is given on any current masthead page.

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