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Cyclic Sulfur Nitrogen Compounds and Phosphorus Reagents: Part XII. Reactions of S_4N_4 with (2-Pyridylamino) Phosphines [1]

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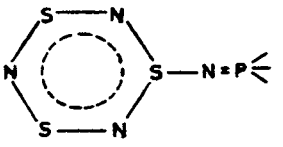
ABSTRACT

*Tetrasulfurtetranitride, S_4N_4 reacts with (2-pyridylamino)-diphenylphosphine in MeCN at room temperature to form the cyclotrithiazene (NC_5H_4NH)-Ph_2PN–S_3N_3 (**1**) in good yield. By contrast, the cyclophosphathiazenes $Ph_2PS_2N_3$ (**2**) and $1,5(Ph_2P)_2S_2N_4$ (**3**) are isolated from the same reaction mixture under reflux conditions. In solution, compound **1** is found to be transformed into **2**. The reaction of S_4N_4 with (2-pyridylamino)phenyl(dicyclohexylamino)phosphine in MeCN at room temperature affords $Ph(DCA)PS_2N_3$ (**4**) (DCA = dicylohexylamino) as the only reaction product. This on treatment with norbornadiene produces the addition product $Ph(DCA)PS_2N_3 \cdot C_7H_8$ (**5**).*

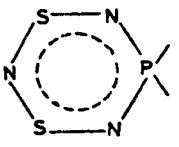
*The structure of **4** has been established by X-ray diffraction. Its PSN ring adopts a skew boat conformation with S–N bond lengths varying from 1.574(4) to 1.606(4) Å. The mean value of the endocyclic P–N bonds amounts to 1.618(3) Å.*

INTRODUCTION

Reactions of phosphines with S_4N_4 studied so far have resulted in the formation of either the (phosphinimino)cyclothiazenes [2–5] or cyclophosphathiazenes [6,7] as heterocyclic products. No example of a phosphine giving both types of ring systems has been observed. In continuation of our work on the reactions of S_4N_4 and phosphines [3–5,8], we have found that the phosphines $Ph_2(AP)P$ and Ph(DCA)(AP)P (AP = 2-pyridylamino) in their reactions with S_4N_4 produce both $\rightarrow P{=}N{-}S_3N_3$ (**A**) and $>PS_2N_3$ (**B**) ring systems. Besides, the ring conversion of **A** → **B** has been observed for the first time.



A



B

We describe here the details of this study as well as the crystal and molecular structures of $Ph(DCA)PS_2N_3$, the first example of a $p^VS_2^{IV}N_3$ heterocycle bearing different substituents on phosphorus.

RESULTS AND DISCUSSION

Reactions of S_4N_4 and $Ph_2(AP)P$

(2-Pyridylamino)diphenylphosphine reacts with S_4N_4 at room temperature to afford the corre-

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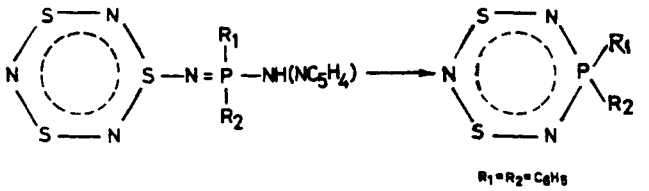
sponding cyclotrithiazene **1** and the phosphine sulfide shown below [2–5]:

$$2(AP)Ph_2P + S_4N_4 \rightarrow$$

$$(AP)Ph_2PN{-}S_3N_3 + (AP)Ph_2P(S)$$

However, in contrast to the behavior of other phosphines [5,9], this reaction gave a deep purple solution in refluxing MeCN, from which the known cyclophosphathiazenes $Ph_2PS_2N_3$ [10] and 1,5-$(Ph_2PN)_2S_2N_2$ were isolated in modest yield.

The following observations were made: (a) mutual exclusion of compounds **1** and **2** in the reactions carried out under reflux and at room temperature, respectively; (b) a gradual color change from orange-red to purple in a $CDCl_3$ solution of **1**; and (c) the formation of a purple melt on heating **1** suggested a ring transformation of **1** to **2** as given below.



In addition to the isolation of **2** in the above reaction, supportive evidence for the ring transformation has been obtained from both UV-Visible and ^{31}P NMR spectroscopy. The slow nature of this ring conversion was revealed on monitoring the changes occurring with time. Though the form in which the 2-pyridylamino group is eliminated in this process is not known, the possibility of an NSR-type fragment [8,11] cannot be ruled out.

Reactions of S_4N_4 and Ph(DCA)(AP)P

The reaction of Ph(DCA)(AP)P with S_4N_4 proceeds much faster than the one with $Ph_2(AP)P$. At room temperature there was formed a bluish purple solution in 30 hours, from which the dark blue needle-like crystals of the Ph(DCA)PS_2N_3 heterocycle **4** were isolated. Complete removal of the by-product, Ph(DCA)(AP)P(S), was essential for the isolation of the cyclic compound. This was achieved by exploiting its poor solubility in MeCN and hexane. The formation of **4** also results from a similar ring transformation to the one described previously. Although the precursor Ph(DCA)(AP)PNS_3N_3 could not be isolated, indications of its formation have been obtained by observing a distinct red color and a characteristic visible absorption at ca. 475 nm [12] during the initial stages of the reaction. The progressive disappearance of this absorption and the appearance of a new absorption at ca. 560 nm (visually red changing to bluish purple), due to the formation of the analogous cyclophosphathiazene, was observed (vide supra). In this case, ring transformation was found to occur in the very early stages of the reaction itself, which is presumably due to a steric effect of the bulky dicyclohexylamino group.

The presence of both phenyl and dicyclohexylamino groups in **4**, which has a distinctly deeper blue color than **2**, was clearly revealed by its ^1H NMR spectrum. The phosphorus chemical shift of **4** (δ = −8.9) lies between that of **2** (δ = −21.1) [7] and $(Me_3SiNH)_2PS_2N_3$ (δ = 1.5) [13] which is suggestive of the deshielding role of alkylamino groups on phosphorus. The electron impact mass spectrum of **4** shows the molecular ion in over 50% intensity as in the case of **2** and $(Me_3SiNH)_2PS_2N_3$. Treatment of compound **4** with norbornadiene produces an addition product, (Ph)(DCA)-$PS_2N_3 \cdot C_7H_8$, as a colorless crystalline compound which slowly regenerates the blue color in solution. It is interesting to note that the addition of norbornadiene to **4** exerts a shielding effect on phosphorus (δ = −8.9 to −13.1), while the reverse is observed in the case of **2** (δ = −22.1 to −18.2) [7].

Crystal and Molecular Structure of **4**

Among the $R_2PS_2N_3$ heterocycles known (R = F [14], CF_3 [15], C_2F_5 [15], Ph [7], OPh [7], and $NHSiMe_3$ [13]), in only two cases (R = Ph [16] and $NHSiMe_3$ [17]) has the X-ray structure been determined. The structure shown in Figure 1 is the first example of this type of heterocycle, possessing different substituents on phosphorus. Molecular geometry data are given in Table 1. The triclinic unit cell contains two discrete molecules of **4** separated by normal Van der Waals distances. The observed conformation of the PSN ring approaches that of a skew boat. The nonplanar nature of the PSN ring was also observed in the case of $(Me_3SiNH)_2PS_2N_3$ [17]. The S–N and P–N bond lengths are not equal. The double bond character of the endocyclic bonds seem to be more pronounced in the segment N(1)–S(1)–N(2) than in the remaining part of the ring. The exocyclic P(1)–N(4) bond length of 1.629(3) Å and a nearly planar geometry at N(4) are suggestive of exocyclic π-bonding.

The phenyl and hexyl rings display normal geometry with mean C–C bond lengths of 1.382(5) and 1.522(2) Å, respectively. The phenyl ring [C(1)–C(6)] and least-squares plane of the cyclohexyl ring [C(7)–C(13)] are nearly parallel, the two planes subtending an angle of only 8.4(2).

CONCLUSION

The ring transformations observed in this study highlight the possible precursor role of $(RNH)R'_2PN{-}S_3N_3$ heterocycles for the formation of cyclophosphadithiatriazenes, illustrated by the isolation of **4**. Studies to demonstrate the further implications of this synthetic approach, as well as

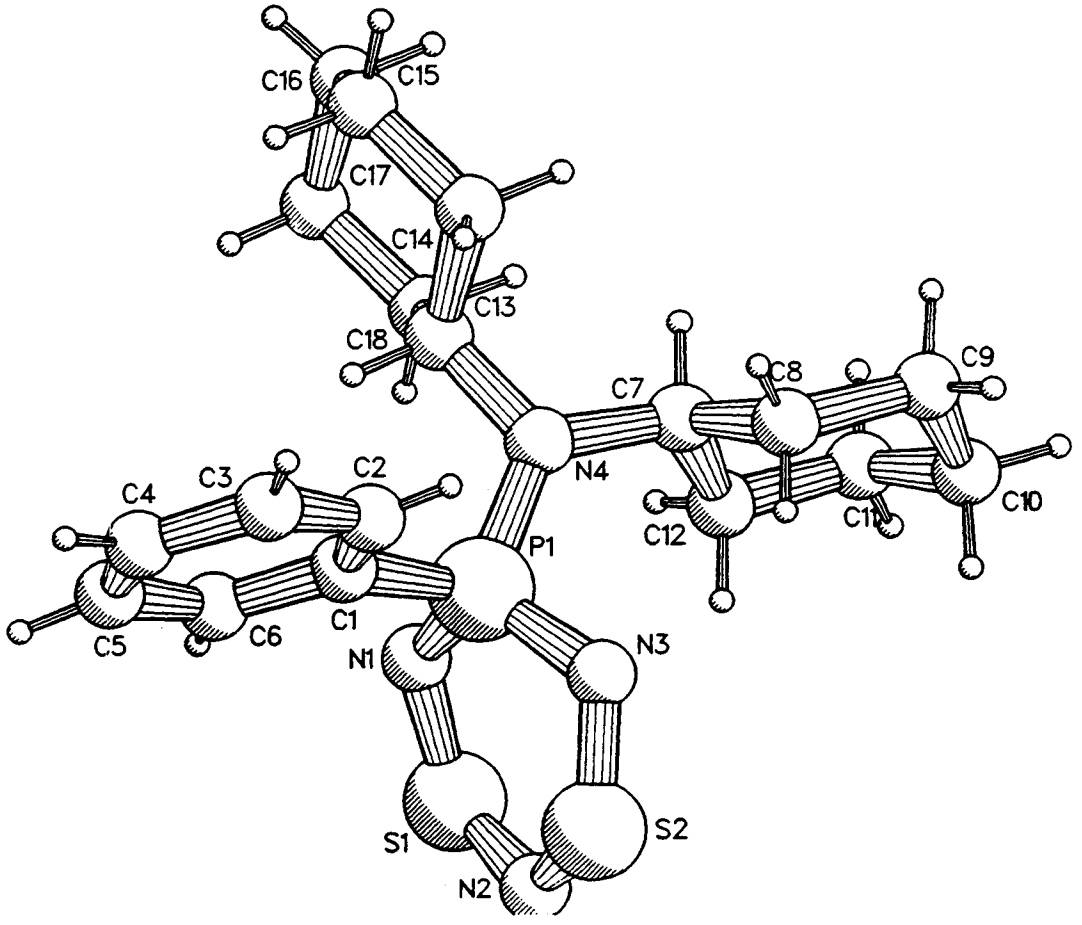


FIGURE 1 PLUTO drawing of the molecule of **4** illustrating the conformation and the adopted numbering scheme.

TABLE 1 Selected Data on the Geometry of Compound **4**[a]

Bond distances (Å)				
S(1)	-N(1)	1.578(4)		average values
S(1)	-N(2)	1.574(4)		(C -C)cyclohexyl 1.522(2)
S(2)	-N(2)	1.606(4)		(C -C)phenyl 1.382(5)
S(2)	-N(3)	1.594(3)		
P(1)	-N(1)	1.628(3)		
P(1)	-N(3)	1.607(3)		
P(1)	-N(4)	1.629(3)		
P(1)	-C(1)	1.798(4)		
N(4)	-C(7)	1.491(5)		
N(4)	-C(13)	1.488(4)		
Bond angles (°)				
N(1)	-S(1)	-N(2)	116.4(2)	average values
N(2)	-S(2)	-N(3)	114.4(2)	(C -C -C)cyclohexyl 111.0(1)
N(1)	-P(1)	-N(3)	113.2(2)	(C -C -C)phenyl 120.0(5)
N(1)	-P(1)	-N(4)	112.9(2)	
S(1)	-N(1)	-P(1)	123.2(2)	
S(1)	-N(2)	-S(2)	122.3(2)	
S(2)	-N(3)	-P(1)	119.2(2)	

[a]Standard deviations in the last decimal place are given in parentheses.

to verify the influence of group R′ on this ring conversion, are currently underway.

EXPERIMENTAL

General

The starting materials S_4N_4 [18], $Ph_2(AP)P$ [19], and Ph(DCA)(AP)P [20] were prepared and purified by literature methods. Solvents (MeCN, CH_2Cl_2, $CHCl_3$, n-C_6H_{14}, C_6H_6, and $C_6H_5CH_3$) were distilled and dried by standard methods [21] before use. All manipulations were done under an oxygen-free dry nitrogen atmosphere.

Instrumental facilities used for the characterization of compounds are as described in Ref. [5]. Only strong absorptions from the IR spectra and a few representative fragments from mass spectra of new compounds have been given.

The identities of the compounds $Ph_2PS_2N_3$ (**2**), 1,5-$(Ph_2P)_2S_2N_4$ (**3**), and $Ph_2PS_2N_3 \cdot C_7H_8$ obtained in this study were established by comparing their physical and spectral (IR, UV-Visible, ^1H and ^{31}P NMR) data with those of authentic samples [6,7].

Reactions of S_4N_4 with $(NC_5H_4NH)Ph_2P$

1:2 Molar Ratio in MeCN. To a stirred suspension of the phosphine (0.55 g, 2.0 mmol) in MeCN (20 mL) at room temperature, S_4N_4 (0.18 g, 1.0 mmol) was added in 15 minutes and the mixture was stirred for 24 hours. Filtration followed by washing with MeCN (2 × 5 mL) gave an orange-red precipitate, $(NC_5H_4NH)Ph_2PN{-}S_3N_3$ (**1**), mp 140°C (dec); yield: 0.30 g, 70%. IR (1600–600 cm^{-1}): 1630, 1600, 1530, 1392, 1118, 1042, 1020, 980, 780, 740, 720, 700. MS (*m/e*): 293 [$(NC_5N_4NH)Ph_2PNH$, 4%]; 291 ($Ph_2PS_2N_3$, 1%); 277 ($Ph_2PS_2N_2$, 8%); 256 (S_8, 11%); 199 (Ph_2PN, 100%); 140 ($NC_5H_4NSNH_2$, 40%); 139 (NC_5H_4NSNH, 5%); 138 (S_3N_3, 2%); 94 ($NC_5H_4NH_2$, 57%). ^1H NMR δ: 5.10 (b, 1H); 6.63 (m, 1H); 6.80 (d, 1H); 7.16 (d, 1H); 7.22 (m, 6H); 7.75 (m, 1H); 7.9 (m, 4H). ^{31}P NMR δ: 22.2 (s, 1P); UV-Visible (in CH_2Cl_2): 478 (2.38×10^3) and 328 (3.7×10^3); CHN Anal. calcd for $C_{17}H_{15}N_6PS_3$(%): C, 47.43; H, 3.51; N, 19.53. Found: C, 48.33; H, 3.67; N, 19.58.

The concentrated red filtrate when cooled at −10°C for 3 days gave $(NC_5H_4NH)Ph_2P(S)$ [19] (mp 139°C; yield: 0.26 g, 85%). IR (1600–600 cm^{-1}): 1600, 1580, 1500, 1470, 1450, 1440, 1420, 1300, 1110, 1000, 950, 940, 780, 710, 693, 640, 630. ^1H NMR δ: 5.60 (b, 1H); 6.40 (t, 1H); 6.70 (t, 1H); 7.0–7.30 (m, 7H); 7.40 (b, 1H); 7.60 (b, 1H); 7.60–7.80 (m, 4H). ^{31}P NMR δ: 51.4 (s, 1P). A hot hexane extract (10 × 5 mL) of the residue gave a deep purple solution which, on treatment with norbornadiene (0.5 mL), gave the known $Ph_2PS_2N_3 \cdot C_7H_8$ (65 mg) [7].

1:2 Molar Ratio in MeCN (under Reflux Condition). S_4N_4 (0.36 g, 2.0 mmol) and the phosphine (1.08 g, 3.9 mmol) were reacted in MeCN (20 mL) under reflux for 6 hours. A small amount of sulfur (25 mg) was isolated from the reaction mixture on cooling. The solution was concentrated and cooled at −10°C for 2 days to produce a violet solid (0.25 g). This was extracted with Et_2O (8 × 5 mL) and the volume of the extract was reduced to ca. 5 mL. MeCN (5 mL) was added and the solution cooled in the freezer (3 hours) to give shiny violet crystals of $Ph_2PS_2N_3$ (**2**) [6] (0.13 g, 23%). The ether insoluble residue was recrystallised from hot MeCN-CH_2Cl_2 (4:1, 10 mL) at room temperature to obtain 1,5-$(Ph_2P)_2S_2N_4$ (**3**) [6] (0.10 g, 11%). A further quantity of $Ph_2PS_2N_3$ (0.10 g, 18%) that was isolated from the hexane extract (12 × 5 mL) of the residual reaction mixture $(NC_5H_4NH)Ph_2P(S)$ (0.18 g) was hexane insoluble.

Ring Transformation of 1 to 2 in Solution. Compound **1** (0.40 g) was stirred in CH_2Cl_2 (8.0 mL) at ca. 30°C. In 4 days, it had become transformed into a clear purple solution. CH_2Cl_2 was removed after 8 days, and the residue was extracted with MeCN (10 mL) which gave a small amount of S_4N_4 (20 mg). The MeCN solution was passed quickly through a silica gel column (30 × 2 cm pack) using C_6H_6–CH_2Cl_2 (1:3) as eluant. The violet fraction (100 mL) collected was evaporated to dryness, and the residue was recrystallised from MeCN-Et_2O (1:1, 20 mL) to give crystalline $Ph_2PS_2N_3$ (0.21 g, 78%).

Reactions of (Ph)(DCA)(AP)P with S_4N_4

1:2 Molar Ratio in MeCN. To a stirred suspension of (Ph)(DCA)(AP)P (2.07 g, 5.4 mmol) in MeCN (20 mL), S_4N_4 (0.5 g, 2.7 mmol) was added as the solid at room temperature. The color of the reaction mixture changed to clear red in ca. 2 hours. Gradually, the color changed to purple and a precipitate was observed. The precipitate after 30 hours was separated by filtration, washed with MeCN (3 × 10 mL), and identified as (Ph)(DCA)(AP)P(S) [mp 142°C, yield 1.02 g). IR (1600–600 cm^{-1}): 1597, 1570, 1487, 1482, 1302, 1295, 1164, 1156, 1105, 1097, 1045, 1035, 991, 983, 920, 915, 865, 775, 742, 715, 679, 642, 616. MS (*m/e*): 413 (M, 1%); 234 (M-DCAH, 12%); 201 [(Ph)(AP)P, 11%]; 180 [(DCA), 100%]. ^1H NMR δ: 1.07 (m, 8H); 1.61 (m, 12H); 3.12 (m, 2H); 6.92 (m, 2H); 7.42 (m, 4H); 7.96 (m, 3H). ^{31}P NMR δ: 58.2 (s, 1P). CHN Anal. calcd for $C_{23}H_{32}N_3PS$(%): C, 66.78; H, 7.81; N, 10.16; Found: C, 66.24, H, 7.45; N, 9.96.

The reddish purple filtrate together with MeCN washings was evaporated to dryness, and the residue was extracted with n-hexane (10 × 2 mL) until a colorless extract resulted. This procedure was repeated four times to remove all of the phosphine sulfide (0.1 g) as a hexane insoluble solid. The blue-

violet extract was then dissolved in CH_2Cl_2-MeCN (1:1, 2 mL) and cooled to −20°C for 1 day to obtain dark blue-violet needle-shaped crystals of $(Ph)(DCA)PS_2N_3$ (0.2 g, 20%) (**4**), mp 93°C. IR (1600–600 cm^{-1}): 1432, 1163, 1150, 1110, 1090, 1048, 1024, 980, 888, 758, 735, 690. MS (*m/e*): 394 (M, 54%); 348 (M-SN, 60%); 316 [(Ph)(DCA)PN, 10%]; 311 (M-C_6H_{11}, 10%); 180 [(DCA), 100%]; 122 (PhPN, 44%); 98 ($C_6H_{11}NH$, 88%). ^1H NMR δ: 1.13 (m, 8H); 1.70 (m, 12H); 2.95 (m, 2H); 7.52 (m, 2H); 7.95 (m, 2H). ^{13}C NMR δ: 132.6, 132.4, 128.7, 128.4 (all due to phenyl); 56.2, 33.2, 26.6, 25.4 (all due to DCA). ^{31}P NMR δ: −8.9 (s, 1P). UV-Visible (in CH_2Cl_2): 558 (1.1×10^4); 315 (3.0×10^3). CHN Anal. calcd for $C_{18}H_{27}PS_2N_4$(%): C, 54.79; H, 6.91; N, 14.20. Found: C, 54.20; H, 7.02: N, 14.82.

Reaction of (Ph)(DCA)PS_2N_3 with Norbornadiene

Norbornadiene (0.86 g, 9.2 mmol) was added to a stirred solution of **4** (0.2 g, 0.5 mmol) in hexane (15 mL) at room temperature in 15 minutes. The blue color was discharged almost instantaneously, and in ca. 30 minutes, the formation of a white precipitate was observed. After 3 hours, the precipitate was collected by filtration and crystallized from CH_2Cl_2–MeCN (1:1, 6 mL) to give colorless needle-shaped crystals of $Ph(DCA)PS_2N_3 \cdot C_7H_8$ (**5**) (0.18 g, 75%), mp 142°C (dec). IR (1600–600 cm^{-1}): 1460, 1437, 1430, 1163, 1103, 1058, 1045, 1035, 1023, 993, 743, 712, 698, 625, 617. MS (*m/e*): 394 (M-C_7H_8, 27%); 348 [M − (SNC_7H_8), 28%]; 180 [(DCA), 100%]; 91 (C_7H_7, 40%). ^1H NMR δ: 1.39 (m, 9H); 1.60 (m, 13H); 2.66 (m, 2H); 2.76 (d, 2H); 3.76 (d, 2H); 5.90 (d, 2H); 7.17 (m, 2H); 7.46 (m, 8H). ^{31}P NMR δ: −13.1 (s, 1P). CHN Anal. calcd for $C_{25}H_{35}P\ S_2N_4$(%): C, 61.69; H, 7.23; N, 11.51. Found: C, 60.81; H, 7.35; N, 10.96.

X-Ray Structure Analysis of **4**

A violet colored crystal of **4** obtained by recrystallization from CH_2Cl_2–MeCN was glued to the top of a glass fiber and mounted on an Enraf-Nonius CAD-4F diffractometer. Precise lattice parameters

TABLE 2 Crystal Data and Details of the Structure Determination of Compound **4**[a]

Chemical formula, mol wt	$C_{18}H_{27}S_2PN_4$, 394.53
Approximate crystal dimension, mm	0.037 × 0.040 × 0.50
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 6.593(1) Å, b = 12.127(1) Å c = 12.531(1) Å, α = 91.817(8)° β = 90.433(7)°, γ = 91.068(8)°
Volume	1001.2(2) Å^3
Z	2
D_{calc}, g · cm^{-3}	1.309
F(000), electrons	420
μ(Cu $K\bar{\alpha}$), cm^{-1}	32.0
Radiation	Cu $K\bar{\alpha}$, 1.54184 Å
Monochromator	graphite
Temperature	295 K
θ range; minimum, maximum	3.53, 72.0°
$\omega/2\theta$ scan	$\Delta\omega$ = (0.90 + 0.14 tg θ)°
Data set	h: 0 → 8; k: −14 → 14; l: −15 → 15
Reference reflections (measured every 3 h)	112, 121, 123
Total data, unique data	4268, 3925
Observed data ($I \geq 2.5\ \sigma(I)$)	2888
Solution	direct methods
Refinement:	full-matrix least squares
nonhydrogen atoms	anisotropic thermal parameters
hydrogen atoms	isotropic thermal parameters
Number of refined parameters	333
Final agreement factors:	
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.053
$wR = [\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma w\|F_o\|^2]^{1/2}$	0.052
Goodness of fit	0.836
Residual electron density in final difference Fourier map, e/Å^3	−0.53, 0.42
Maximum (shift/σ) final cycle	0.357
Average (shift/σ) final cycle	0.064

[a]Numbers in parentheses are standard deviations.

TABLE 3 Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms with ESDs in Parentheses for Compound 4 (Atoms of the Asymmetric Unit)

	x	y	z	$U_{eq}(Å^2)^a$
S(1)	−0.1501(2)	0.0486(1)	0.6789(1)	0.0683(4)
S(2)	0.2327(2)	−0.0430(1)	0.6598(1)	0.0788(5)
P(1)	0.2009(1)	0.16710(8)	0.74875(8)	0.0401(3)
N(1)	−0.0442(5)	0.1499(3)	0.7404(3)	0.053(1)
N(2)	−0.0097(6)	−0.0503(3)	0.6466(3)	0.079(2)
N(3)	0.3227(5)	0.0793(2)	0.6763(3)	0.049(1)
N(4)	0.2769(4)	0.2900(2)	0.7162(2)	0.0390(9)
C(1)	0.2646(6)	0.1561(3)	0.8877(3)	0.043(1)
C(2)	0.4691(7)	0.1608(4)	0.9183(3)	0.055(2)
C(3)	0.5229(8)	0.1479(4)	1.0238(4)	0.065(2)
C(4)	0.3781(9)	0.1299(4)	1.0985(4)	0.068(2)
C(5)	0.1758(9)	0.1252(5)	1.0705(4)	0.077(2)
C(6)	0.1212(7)	0.1377(4)	0.9645(4)	0.065(2)
C(7)	0.3186(5)	0.3183(3)	0.6034(3)	0.040(1)
C(8)	0.5285(6)	0.2816(4)	0.5668(3)	0.050(1)
C(9)	0.5716(7)	0.3212(4)	0.4552(3)	0.054(1)
C(10)	0.4066(7)	0.2838(4)	0.3763(3)	0.054(2)
C(11)	0.1991(7)	0.3214(4)	0.4135(3)	0.055(2)
C(12)	0.1547(6)	0.2800(4)	0.5242(3)	0.048(1)
C(13)	0.2219(5)	0.3835(3)	0.7894(3)	0.038(1)
C(14)	0.4014(6)	0.4626(3)	0.8099(3)	0.046(1)
C(15)	0.3481(7)	0.5542(4)	0.8894(4)	0.057(2)
C(16)	0.1598(8)	0.6148(4)	0.8538(4)	0.062(2)
C(17)	−0.0175(7)	0.5366(4)	0.8337(4)	0.055(2)
C(18)	0.0345(6)	0.4455(3)	0.7523(3)	0.048(1)

$^aU_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

and their standard deviations were derived at 295 K from the angular settings of 22 reflections in the range of $8.56° < \theta < 36.51°$. The intensities were corrected for scale variation and Lorentz and polarization effects, but not for absorption. An overview of the structure determination and refinement is given in Table 2. Scattering factors were taken from Cromer and Mann [22]. Anomalous dispersion factors (from Cromer and Liberman [23]) were included in Fc. The final fractional atomic coordinates and the equivalent isotropic thermal parameters are given in Table 3. All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with program packages XTAL [24], EUCLID [25] (calculation of geometric data), and a locally modified version of the program PLUTO [26] (preparation of illustrations).

SUPPLEMENTARY MATERIAL

Lists of final fractional atomic coordinates, anisotropic thermal parameters for the nonhydrogen atoms, H atom parameters, bond lengths, and angles and an Ortep plot have been deposited with the Cambridge Crystallographic Data Centre.

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