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Synthesis and X-Ray Crystal Structure of 1-[Diphenyl(2-pyridyl)phosphoranylideneamino]-1*H*-1,3,5,2,4,6-trithia (5-S^{IV})triazine

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Synopsis. A 1 : 2 mole reaction between S_4N_4 and diphenyl(2-pyridyl)phosphine has given $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$ in 70% yield. Crystals of $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$ are monoclinic, space group $P2_1/n$ with a=11.543(8), b=13.254(9), c=13.636(5) Å, β=104.65(6)°, and Z=4. The structure is refined to a final R value of 0.057 using 2916 reflections $[I>2\sigma(I)]$. The S_3N_3 ring is stacked against one of the phenyl rings with an average SN distance of 1.61 Å.

Although several examples of 1-phosphanylideneamino-1*H*-1,3,5,2,4,6-trithia(5-S^{IV})triazines[1—9] are known today, X-ray crystal structures of symmetrical P–N[4] and P–C[10] bonded $R_3P{=}N{-}S_3N_3$ heterocycles have only been reported so far. Among these two derivatives some important structural differences have been noticed. For example, in the crystal structure of $(C_5H_{10}N)_3P{=}N{-}S_3N_3$, the endocyclic S–N bonds are shorter and have identical lengths in comparison to those ones in the structure of $Ph_3P{=}N{-}S_3N_3$. As the π-bonding characteristics of the S_3N_3 ring seems to be influenced by the nature of phosphine substituents, in this paper we describe the synthesis and X-ray determination of an unsymmetrical phosphanylideneamino derivative, $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$, which is isoelectronic with the reported $Ph_3P{=}N{-}S_3N_3$ compound. The crystal structure of $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$ is compared with the known $R_3P{=}N{-}S_3N_3$ (R=Ph;[10] $C_5H_{10}N$[4]) derivatives.

Experimental

All experimental manipulations were done under dry N_2 atmosphere using standard Schlenk techniques. Acetonitrile (Aldrich) was distilled thrice over P_2O_5 and stored over CaH_2. Thiofene-free benzene (CAUTION! Potential Carcinogen) was purchased from Aldrich, and distilled over Na, and stored over molecular sieves. 2-(Diphenylphosphino)pyridine was obtained from strem Chemicals, Inc., and was used as such. S_4N_4[11] (CAUTION! It may cause explosion. Adequate safety precautions need to be employed[12]) was synthesized by the reported procedure and recrystallized from toluene. Trace amounts of sulfur present in the sample were removed by washing the sample with CS_2. The NMR data were obtained on a G. E. (Nicolet) 300 MHz multinuclear FT-NMR spectrometer operating at 75.5 and 121.5 MHz for ^{13}C and ^{31}P, respectively. Spectral data were obtained as 0.2 M $CDCl_3$ solutions (M=mol dm^{-3}) of the compounds with Me_4Si (internal) and 85% H_3PO_4 (external) as the respective standards. IR spectrum (1600—400 cm^{-1}) was recorded on KBr plates using a Nicolet IR/42 FT spectrophotometer as Nujol mull. Perkin-Elmer Lambda 6 UV-vis spectrophotometer was used to record the UV-visible spectrum. EI-MS data were recorded by directly introducing the sample into the probe on a HP 5986A GC/MS spectrometer operated at 70 eV. CHN analysis was done at E & R Microanalytical Laboratory, Inc., 96-34 Corona Avenue, Corona, N.Y. Melting points were determined in sealed capillaries and are uncorrected.

Preparation of $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$. Tetranitrogen tetrasulfide (0.90 g, 4.9 nmol) was added to a stirred suspension of $(NC_5H_4)Ph_2P$ (2.6 g, 9.9 mmol) in CH_3CN (50 ml) at RT and then stirred for 24 h., at ca. 50 °C. The reaction mixture on cooling in the refrigerator for a day gave a red solid, which was recrystallized from a mixture of $C_6H_6{-}CH_3CN$ (10 ml/10 ml) to isolate red X-ray quality crystals of (NC_5H_4) $Ph_2P{=}N{-}S_3N_3$ (mp 145 °C decomp) in 70% yield. (Found: C, 49.03; H, 3.57; N, 16.89%. Calcd for $C_{17}H_{14}N_5PS_3$: C, 49.14; H, 3.39; N, 16.85%); UV-vis λ_{max}/nm ($CHCl_3$) 479 and 329 (4.51×10^3 and 3.41×10^3); IR (Nujol) 1464s, 1438s, 1425s, 1369sh, 1139m, 1112s, 1077vs, 1043m, 1026m, 990m, 944s, 911m, 850m, 784s, 770s, 744vs, 737vs, 728vs, 690 vs, 616s, 582s, 552vs, 527vs, 508vs, and 466vs cm^{-1}. Filtrate was worked up as reported previously[1] to isolate colorless crystals of $(NC_5H_4)Ph_2PS$ (mp 116 °C) in 75% yield. MS m/z 295 (M^+), 263 (M−S), 218 (M−Ph), 186 (M−Ph+S) and 185 ($M-NC_5H_4+S$). The ^{31}P and ^{13}C NMR data of the S_3N_3, sulfide and the phosphine are compared in Table 1.

X-Ray Determination of $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$. Crystal Data. $C_{17}H_{14}N_5PS_3$ M=415.5, Monoclinic, a=11.543(8), b=13.254(9), c=12.617(9) Å, β=104.65(5)°, Space group, $P2_1/n$, U=1867.5 Å^3, $F(000)$=856, D_c=1.48 g cm^{-3}, Z=4, Cu $K\alpha$ radiation, λ=1.5418 Å, μ=4.63 cm^{-1}.

Data Collection. A rectangular shaped crystal of dimensions 0.42×0.30×0.21 mm was mounted at the end of a glass capillary for three-dimensional intensity data collection. Preliminary examination and data collection were performed on an Enraf–Nonius CAD4 diffractometer equipped with a graphite crystal incident beam monochromator and a sealed tube source of Cu $K\alpha$ radiation (λ=1.5418 Å). Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 reflections in the range of $21°<\theta<27°$.

Intensity data were obtained at room temperature (23 °C) with a $\omega{-}2\theta$ scan technique to a maximum 2θ of 150°.

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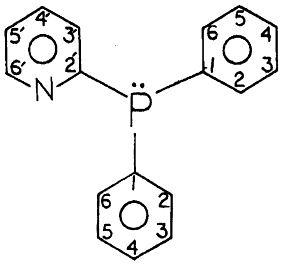
#Demised.

Table 1. ^{13}C and ^{31}P NMR Spectral Data [ppm (JPC)] of $(NC_5H_4)Ph_2P$ (**1**), $(NC_5H_4)Ph_2PS$ (**2**), and $(NC_5H_4)Ph_2PN\ S_3N_3$ (**3**), a Comparison

	^{13}C Chemical shifts with P–C coupling constants in TMS									^{31}P
Compd	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C'_2	C'_3	C'_4	C'_5	C'_6	
1	136.17	134.15	128.58	129.02	163.96	127.78	135.66	122.12	150.29	−3.50
	(10.5)	(19.7)	(4.1)		(1.5)	(15.5)			(12.4)	
2	136.36	132.36	128.16	131.44	156.16	128.66	132.51	124.85	149.56	38.0
	(10.3)	(10.3)	(12.6)		(112.1)	(25.8)	(85.8)		(22.4)	
3	136.54	133.82	128.25	133.15	152.69	130.34	126.41	126.03	150.28	18.5
	(9.4)	(10.6)	(12.8)		(138.9)	(21.2)	(98.7)		(20.8)	



A total of 3,744 unique reflections were measured and 2916 reflections were found to have their intensities greater than $2\sigma(I)$. These reflections were used for structure determination and refinement. Three reflections measured every hours during data collection to monitor the electronic stability and the crystal decay due to radiation, showed no radiation damage. Lorenz and polarization corrections were applied to the data. Absorption corrections were not made.

Structure Determination and Refinement. The structure was solved by the combination of Patterson and by direct methods using SHELEX-86 program.[13] P to P vectors were interpreted from the Patterson map and from the subsequent Fourier map and using the direct methods, the entire molecule was located. The structure was refined by full-matrix least squares procedure for positional parameters, scale factor and isotropic temperature factors to $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.084$. From the difference Fourier map all the hydrogen atoms were located and their positional parameters were included for structure factor calculations, but not refined. Few cycles of refinement of positional parameters and anisotropic temperature factors of all non-hydrogen atoms and the scale factor gave a final R value of 0.057 and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.058$. The total number of parameters varied during the refinement are 236. A final Fourier map showed no electron density greater than 0.37 e Å^{-3}. All computations were performed on a digital VAX6400 computer. Final atomic coordinates of the molecules are listed in the Table 2.

F_o-F_c data, thermal parameters, complete list of bond angles and bond lengths, and positional parameters of hydrogen atoms are deposited as Document No. 66014 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 2. Positional Parameters with Their Estimated Standard Deviations in Parantheses

Atom	x	y	z	U_{eq}/Å^2
P	0.18071(7)	0.56482(7)	0.30849(6)	0.044(2)
N(2)	0.1426(3)	0.6758(2)	0.3418(2)	0.060(8)
S(1)	0.20329(9)	0.72454(7)	0.45718(7)	0.056(2)
N(3)	0.1394(3)	0.6655(3)	0.5424(3)	0.066(8)
S(2)	0.4228(1)	0.6867(1)	0.60899(9)	0.078(3)
N(4)	0.3470(4)	0.6703(3)	0.6970(3)	0.08(1)
S(3)	0.2066(1)	0.6623(1)	0.66955(8)	0.087(3)
N(5)	0.3446(3)	0.6877(3)	0.4848(2)	0.059(7)
C(1)	0.2216(3)	0.4741(2)	0.4174(2)	0.043(7)
C(2)	0.1321(3)	0.4340(3)	0.4599(3)	0.052(8)
C(3)	0.1616(4)	0.3722(3)	0.5508(3)	0.062(9)
C(4)	0.2800(4)	0.3520(3)	0.6002(3)	0.07(1)
C(5)	0.3697(4)	0.3917(4)	0.5578(3)	0.06(1)
C(6)	0.3404(3)	0.4525(3)	0.4664(3)	0.051(7)
C(7)	0.2978(3)	0.5718(3)	0.2372(2)	0.049(7)
C(8)	0.3462(3)	0.4853(3)	0.2068(3)	0.056(8)
C(9)	0.4345(4)	0.4923(4)	0.1509(3)	0.07(1)
C(10)	0.4735(4)	0.5862(4)	0.1266(3)	0.08(1)
C(11)	0.4255(4)	0.6724(4)	0.1566(3)	0.08(1)
C(12)	0.3375(4)	0.6669(3)	0.2138(3)	0.061(9)
C(13)	0.0498(3)	0.5142(3)	0.2123(2)	0.048(7)
C(14)	−0.0594(4)	0.5627(3)	0.1915(3)	0.062(9)
C(15)	−0.1544(4)	0.5185(4)	0.1161(4)	0.08(1)
C(16)	−0.1384(4)	0.4299(4)	0.0657(3)	0.08(1)
C(17)	−0.0279(4)	0.3860(4)	0.0939(4)	0.08(1)
N(1)	0.0677(3)	0.4264(3)	0.1664(3)	0.070(9)

Results and Discussion

The monosubstituted trithiatriazine heterocycle, $Ph_2(NC_5H_4)P{=}N{-}S_3N_3$ was readily synthesized in 70% yield by reacting S_4N_4 with $Ph_2P(NC_5H_4)$ in CH_3CN medium. In its IR spectrum, peak at 944 cm^{-1} is assigned to be due to ν_{SN} of the S_3N_3 ring. The UV-visible and ^{31}P NMR spectrum of this compound is quite identical to the other derivatives reported in the literature.[1,2] The mass spectrum of $Ph_2(NC_5H_4)$-$P{=}N{-}S_3N_3$ by direct insertion probe technique has given molecular ion peak (m/z 415) of intensity 2.5% at 65 °C. Very interestingly, in the ^{13}C NMR spectra of $Ph_2(NC_5H_4)P{=}N{-}S_3N_3$ and $Ph_2(NC_5H_4)PS$, the pyridyl C'_2 and C'_4 coupling constants between the P are significantly larger than those in the parent, phosphine. At the moment, we are not able to provide any explanation for this observation. More detailed NMR study may be needed to clarify this point.

Structure of $Ph_2(NC_5H_4)P{=}N{-}S_3N_3$. The important interatomic distances and bond angles are given in Table 3. The structure of the molecule and the packing are shown in Figs. 1 and 2 respectively.

As shown in Fig. 2, the compound is crystallized in monoclinic space with four molecules in the unit cell. The least intermolecular distance between C and C is around 2.95 Å. There are no intermolecular hydrogen bonding between these molecules and the lattice is completely stabilized by van der Waals interactions. The phosphorus atom in this molecule has a close tetrahedral geometry with two phenyl groups, a pyridyl group and a $=N{-}S_3N_3$ unit.

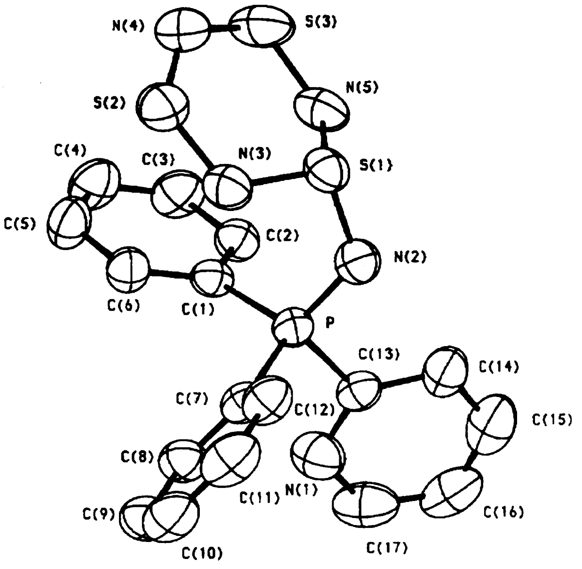


Fig. 1. ORTEP plot (50% probability ellipsoids) of $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$ showing the atomic numbering scheme.

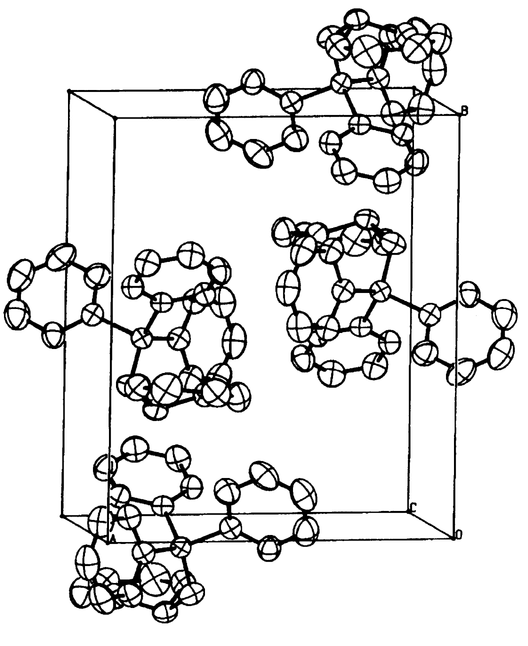


Fig. 2. Packing of the molecule in the unit cell.

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) with Estimated Standard Deviations in Parentheses

	a) Bond Distances		
P-C(1)	1.798(3)	S(1)-N(2)	1.586(3)
P-C(7)	1.806(3)	S(1)-N(3)	1.648(4)
P-C(13)	1.812(3)	S(1)-N(5)	1.654(4)
P-N(2)	1.621(3)	S(2)-N(3)	1.597(4)
C(13)-N(1)	1.339(5)	S(2)-N(4)	1.573(5)
C(17)-N(1)	1.354(6)	S(3)-N(4)	1.593(4)
		S(3)-N(5)	1.599(3)
Av C-C in benzene ring C(1) to C(6)			1.383
Av C-C in benzene ring C(7) to C(12)			1.382
Av C-C in pyridyl ring C(13) to C(17)			1.376
	b) Bond Angles		
N(2)-S(1)-N(3)	103.8(2)	P-N(2)-S(1)	122.5(2)
N(2)-S(1)-N(5)	104.8(2)	N(2)-P-C(1)	116.4(1)
N(3)-S(1)-N(5)	107.6(2)	N(2)-P-C(7)	111.7(2)
S(1)-N(3)-S(2)	119.0(2)	N(2)-P-C(13)	106.9(2)
N(3)-S(2)-N(4)	115.5(2)	C(1)-P-C(7)	109.3(2)
S(2)-N(4)-S(3)	125.9(2)	C(1)-P-C(13)	106.1(1)
N(4)-S(3)-N(5)	114.3(2)	C(7)-P-C(13)	106.8(1)
S(1)-N(5)-S(3)	119.4(2)	C(13)-N(1)-C(17)	116.6(4)
		N(1)-C(13)-C(14)	123.8(3)
		N(1)-C(17)-C(16)	123.7(5)
Av C-C-C in benzene ring C(1) to C(6)			120.1
Av C-C-C in benzene ring C(7) to C(12)			120.0
Av C-C-C in pyridyl ring C(13) to C(17)			118.6

Although, $Ph_2(NC_5H_4)P{=}N{-}S_3N_3$ is isoelectronic with $Ph_3P{=}N{-}S_3N_3$, in its structure there are some noticeable differences and similarities in comparison to the two reported structures, $R_3P{=}N{-}S_3N_3$ (R= Ph[10] and $C_5H_{10}N$[4]). As far as the shape (relative orientation of phenyl rings and S_3N_3 ring) of the molecule is concerned, the structure is identical to $Ph_3P{=}N{-}S_3N_3$, while the bonding is more similar to that in $(C_5H_{10}N)_3P{=}N{-}S_3N_3$. For example, in $(C_5H_{10}N)_3P{=}N{-}S_3N_3$[4] all the four groups are widely separated, while in $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$, the S_3N_3 ring is stacked against one of the phenyl rings as in $Ph_3P{=}S_3N_3$.[10] Whereas, the S-N distances of the S_3N_3 ring in $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$ are more identical and shorter (1.586—1.654 Å: S-N (av) = 1.610 Å) than those ones in $Ph_3P{=}N{-}S_3N_3$ (1.522—1.693 Å: S-N (av) = 1.620 Å). This situation is more similar to the S-N bonding in $(C_5H_{10}N)_3P{=}N{-}S_3N_3$ (1.579—1.640: S-N (av) = 1.607 Å). The exocyclic P-N (1.621 Å) and S-N (1.586 Å) bond distances are shorter than the respective single bond[14,15] distances and the PN/SN distances in $Ph_3P{=}N{-}S_3N_3$,[10] but close to

$(C_5H_{10}N)_3P{=}N{-}S_3N_3$.[4] The crystal structure of the first and the only example of 1-(arsoranylideneamino) trithiatriazine, $Ph_3As{=}N{-}S_3N_3$ was also reported[16] by Holt et al.

In summary, the molecule, $(NC_5H_4)Ph_2P{=}N{-}S_3N_3$ can be considered to have a structure intermediate between $Ph_3P{=}N{-}S_3N_3$ and $(C_5H_{10}N)P{=}N{-}S_3N_3$.

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