

Synthesis and X-Ray Crystal Structures of 2,3-Dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1H)-thione 2-Sulphide Derivatives †

R. Morrin Acheson* and Claire T. Lines

Department of Biochemistry, South Parks Road, Oxford OX1 3QU

Martin R. Bryce

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE

Zbigniew Dauter and Colin D. Reynolds

Department of Chemistry, University of York, Heslington, York YO1 5DD

Alfred Schmidpeter

Institut für Inorganische Chemie der Universität München, 8000 München 2, West Germany

2-Amino-benzamide or -thiobenzamide, with phosphorus pentasulphide in pyridine, gave the pyridine complex (1) of 2,3-dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1H)-thione 2-sulphide (2), which with alkali and dimethyl sulphate yielded 1,2-dihydro-1-methyl-2,4-bismethylthio-2,1,3-benzophosphadiazine 2-sulphide (3). The ^{31}P , ^{13}C , and ^1H n.m.r. and mass spectra and some reactions of (1) and (3) were investigated, and their crystal structures were determined by direct methods.

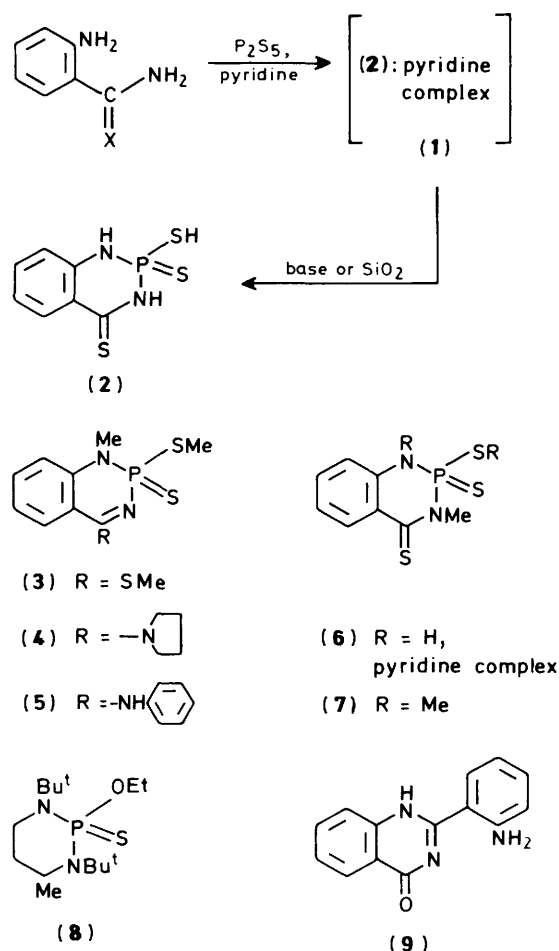
From attempts to prepare 3-amino-2,1-benzisothiazole (obtainable from 2-aminothiobenzamide with hydrogen peroxide¹) by treating 2-aminobenzamide with phosphorus pentasulphide in refluxing pyridine, another compound was obtained. Analysis (C, H, N, S) gave data corresponding to the empirical formula $\text{C}_{12}\text{H}_{11}\text{N}_3\text{S}_4$, and a subsequent X-ray crystal structure analysis suggested that it was a 1:1 molar complex of pyridine with 2,3-dihydro-2,1,3-benzothiadiazine-4(1H)-thione 2,2-disulphide.²

Suspicious were aroused that this structure was not correct when attempted methylation appeared to give a trimethyl derivative, the ^1H n.m.r. spectrum of which showed two of the methyl signals as doublets and the third as a singlet. It is now established that the substance is in fact the pyridine complex (1) of 2,3-dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1H)-thione 2-sulphide (2) which differs from the original structure proposed in that one sulphur atom has been replaced by one phosphorous and one hydrogen atom.

The compound has now been synthesised in high yield by refluxing either 2-amino-benzamide or -thiobenzamide with phosphorus pentasulphide in pyridine. It is not as stable as previously thought² and partially decomposes to 2-aminothiobenzamide on recrystallisation from aqueous dimethylformamide. It gives the expected analytical data for all the elements present and the presence of phosphorus was confirmed by ^{31}P n.m.r. The phosphadiazine itself (2) was obtained as a hygroscopic solid from the pyridine complex by coating it on silica, and eluting with appropriate solvents. The use of 2-amino-N-methylbenzamide similarly gave the analogue (6).

Refluxing 2-aminobenzamide in toluene (instead of pyridine) with phosphorus pentasulphide gave 2-(2-aminophenyl)-4(1H)-quinazolone (9) and no trace of the phosphadiazine (2); adding 2 moles of pyridine before refluxing gave only the quinazolone and none of the phosphadiazine (1). The synthesis failed when the pyridine was replaced by 3-bromo- or 3-chloro-pyridine, or triethylamine, but was successful when 2,6-dimethylpyridine was employed; heating the resulting complex with pyridine gave (1).

Oxidation of the complex (1) by acidified potassium permanganate, or of the phosphadiazine (2) by alkaline permanganate, gave 2-aminothiobenzamide, and attempted



desulphurisation by Raney nickel yielded a mixture of the same thioamide and 2-aminobenzamide. The complex (1) with dimethyl acetylenedicarboxylate in dimethylformamide gave tetramethyl 4H-quinolizine-1,2,3,4-tetracarboxylate³ and the phosphadiazine (2), identified by chromatographic comparison with authentic materials.

Treatment of the complex (1) with cold aqueous alkali, removal of the pyridine in ether, and methylation of the aqueous

† Supplementary data available (No. SUP 56335, 10 pp.): thermal parameters, bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1. Structure factors are available from the editorial office.

Table 3. Atomic co-ordinates ($\times 10^4$) for (3) (e.s.d.s in parentheses)

Atom	x	y	z
C(1)	5 392(6)	5 432(8)	7 711(15)
C(2)	5 986(6)	6 315(8)	8 305(15)
C(3)	5 689(6)	7 516(8)	8 290(16)
C(4)	4 870(8)	7 796(11)	7 699(19)
C(5)	4 290(7)	6 921(9)	7 077(18)
C(6)	4 555(7)	5 734(10)	7 141(15)
C(7)	5 685(7)	4 145(8)	7 762(14)
N(8)	6 497(5)	3 790(6)	7 946(11)
P(9)	7 320(2)	4 723(2)	8 341(1)
N(10)	6 820(5)	6 013(7)	8 915(14)
S(11)	4 827(2)	3 094(2)	7 572(6)
S(12)	8 047(2)	5 001(2)	6 124(6)
S(13)	8 143(2)	4 138(8)	10 223(6)
C(14)	7 365(7)	6 965(9)	9 707(21)
C(15)	5 400(8)	1 674(10)	7 704(21)
C(16)	7 210(8)	5 550(11)	4 655(19)

other atoms in the heterocyclic ring. The geometry at the phosphorus atom is approximately tetrahedral in (3) with a P-S single-bond distance of 2.073(4) Å and a P=S double-bond distance of 1.923(4) Å. The bond angles around the P atom range from 104.4(4) to 113.8(3)°, with a S-P-S angle of 106.4(2)°. The complex (1) shows a greater distortion from tetrahedral geometry at the P atom, with P-S bond distances of 1.946(2) and 1.971(2) Å, and bond angles varying from 96.4(3) to 117.7(1)°, the S-P-S angle having increased to 117.7(1)°. The endocyclic P-N distances in (1) and (3) vary from 1.640(8) to 1.716(4) Å and are all shorter than the expected P-N single-bond distance of 1.77 Å.⁵ The N-P-N bond angles are 96.4(3) and 104.4(4)° in (1) and (3) respectively. The S-P-N angles are in the range 107.8(2) to 113.8(3)°, in good agreement with reported values.⁵ The only other compound closely analogous to (1) and for which structural data are available is (8).⁶ The P-S and P-N distances [1.949(3), 1.668(5), and 1.645(6), respectively] are very similar to those of (1) (Figure 2). The sulphur-containing part of (1) is linked to the pyridine molecule *via* a hydrogen bond between S(13) and N(14), with a S(13) . . . N(14) distance of 3.32 Å. Hydrogen bonds of this type do not seem to be common.⁷

Experimental

N.m.r. spectra are for (CD₃)₂SO solutions [δ_{H} (J/Hz) from Me₄Si at 60 MHz; δ_{P} from H₃PO₄ at 101.23 MHz] unless otherwise stated. Phosphorus pentasulphide was purified by Soxhlet extraction with carbon disulphide.

Preparation of the Pyridine Complex (1) of 2,3-Dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1H)-thione 2-Sulphide.—

(i) Phosphorus pentasulphide (3 g) was added to 2-aminothiobenzamide (2 g) in pyridine (15 ml). The mixture was refluxed for 1.5 h, then allowed to cool and poured into ice-water (50 ml). The yellow precipitate was filtered off and dried giving the *pyridine complex* (1) (3.6 g, 85%), yellow crystals (rapidly from dimethylformamide-water), m.p. 213–215 °C (Found: C, 44.3; H, 3.9; N, 12.8; P, 9.3; S, 29.6. C₁₂H₁₂N₃PS₃ requires C, 44.3; H, 3.7; N, 12.9; P, 9.5; S, 29.5%); ν_{max} (Nujol) 1 607, 1 570, 1 190–1 179br, 1 158, 1 132, 992, 899, 747, 681, and 663 cm⁻¹; δ_{H} (300 MHz) (pyridine moiety) 8.94 (2 H, q, *J* 6.5 and 1.4, 2-H), 8.60 (1 H, m, 4-H), and 8.07 (2 H, q, *J* ca. 6.4 and 6.7, 3-H); (benzophosphadiazine moiety) 11.5 [1 H, br, 3- (or 1-) H], 10.44 [1 H, br d, *J*_{P-C} 10.8, 1- (or 3-) H] (1-H and 3-H are deuterium-exchangeable, positions vary a little with concentra-

tion, and these protons have been observed at 60 MHz to give a single broad peak centred on δ 10.7), 8.27 (1 H, q, *J* 8.1 and 1.4, 5-H), 7.27 (1 H, t, *J* ca. 7.5, 7-H), 6.84 (1 H, d, *J* 7.8, 8-H), and 6.74 (1 H, t, *J* ca. 7.4, 6-H). Irradiation at δ 6.74 caused the quartet at δ 8.27 to collapse to a singlet, and irradiation at δ 8.27 caused the expected change to the triplet at δ 6.74. For the phosphadiazine system, δ_{C} 191.0 (s, 4-C), 141.5 (s, 4a-C), 133.9 (d, 8-C), 133.0 (d), 121.2 (s, 8a-C), 118.1 (d), and 117.6 (d) (all resonances show some coupling with P); for the pyridine system 143.7 (d, 2-C), 133.0 (d, 4-C), and 126.3 (d, 3-C); δ_{P} 63.3 (s, 2-P).

(ii) Phosphorus pentasulphide (5.9 g) was refluxed with 2-aminobenzamide (3.6 g) in pyridine (15 ml) for 1.5 h. The product was worked up as in (i) to give (1) (7.72 g, 90%) with the properties already described.

(iii) Phosphorus pentasulphide (2.0 g), 2-aminobenzamide (1.0 g), and 2,6-dimethylpyridine (15 ml) were refluxed for 1.5 h, cooled, and poured into ice-water (100 ml). Basification with *m*-sodium hydroxide (200 ml) and just acidifying with aqueous *m*-hydrochloric acid precipitated 2,3-dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1H)-thione 2-sulphide 2,6-dimethylpyridine complex (0.5 g), m.p. 222–223 °C, which could not be recrystallised; δ_{H} (90 MHz) (benzophosphadiazine part) 10.35 (1 H, br d, NH), 8.40 (1 H, br s, NH), 7.97 (1 H, d, *J* ca. 7, 5-H), 7.01 (1 H, t, *J* ca. 7 + 7, 7-H), 6.42–6.65 (2 H, m, 6- and 8-H); pyridine part: 7.90 (1 H, t, *J* ca. 7, 4-H), 7.34 (2 H, d, *J* 7, 3- and 5-H), and 2.34 (6 H, s, 2,6-Me₂).

Heating this compound in pyridine and pouring into water precipitated mainly (1), identified from its ¹H n.m.r. spectrum, and methylation (0.5 g) as for (1) using aqueous sodium hydroxide and dimethyl sulphate gave (3) (0.2 g), identical with the analysed specimen.

2,3-Dihydro-2-mercapto-2,1,3-benzophosphadiazine-4(1H)-thione 2-Sulphide (2).—(i) The pyridine complex (1) (500 mg) was refluxed in acetone (100 ml) for 5 min; silica (10 g) was added, the acetone removed *in vacuo*, and the residue placed on top of a six-inch silica column previously washed with methanol (10%) in ethyl acetate. Elution with this solvent gave first 2-aminothiobenzamide, identified from its ¹H n.m.r. spectrum, followed by the phosphadiazine (2) (200 mg, 40%; elution was completed by a 1:1 solvent mixture), a hygroscopic yellow solid, m.p. 170–172 °C, δ_{H} (470 MHz) (COSY) 10.55 (1 H, d, *J*_{P-H} 13.2, NH), 8.76 (1 H, d, *J*_{P-H} 11.8, NH), 8.56 (1 H, d, 5-H), 7.53 (1 H, t, 7-H), 7.10 (1 H, t, 8-H), and 6.98 (1 H, d, 6-H); δ_{C} 191.2 (s, 4-C), 142.0 (s, 4a-C), 133.5 (2 C, d), 121.7 (s, 8a-C), 118.3 (d), and 117.8 (d) (all resonances show small coupling with P).

(ii) The pyridine complex (3.0 g) was dissolved in aqueous *m*-sodium hydroxide (100 ml) and the solution was extracted three times with ether. The dissolved ether was removed from the aqueous layer *in vacuo* and acidification effected with aqueous *m*-hydrochloric acid. The sulphide (2) (0.3 g) precipitated.

Oxidation of the Complex (1).—The complex (1) (2 g) was refluxed for 1 h with acidified potassium permanganate (1 g). The solution was allowed to cool and then decolourised (to yellow) with aqueous sodium hydrogen sulphite. It was then extracted 3 times with dichloromethane and the dichloromethane was removed *in vacuo* yielding 2-aminothiobenzamide (400 mg, 55%), identified by t.l.c. and ¹H n.m.r. comparisons with authentic material.

(ii) The pyridine complex (1) (4 g) was dissolved in aqueous *m*-sodium hydroxide (100 ml) and extracted three times with ether, the extract being discarded. The ether in the aqueous layer was removed *in vacuo* and potassium permanganate (2 g) added, resulting in an exothermic reaction. The mixture was stirred for 1 h, decolourised with aqueous sodium hydrogen sulphite, and extracted with dichloromethane. Evaporation of the extract yielded 2-aminothiobenzamide, identified as before.

Disulphurisation of the Complex (1).—The complex (1) (1 g) was refluxed for 1 h with W-10 Raney nickel (three spatulas full) in ethanol (30 ml); the mixture was filtered hot, then left to cool, and water (30 ml) was added. Extraction with ether yielded a mixture of 2-aminothiobenzamide and 2-aminobenzamide, identified from its ^1H n.m.r. spectrum and t.l.c. comparisons with authentic materials.

Reaction of the Complex (1) with Dimethyl Acetylenedicarboxylate.—The complex (1) (2.0 g) was stirred with the ester (3.0 g) in *N,N*-dimethylformamide (10 ml) or acetonitrile for ca. 15 h. T.l.c. of the resulting solutions showed only the presence of the sulphide (2) and tetramethyl 4*H*-quinolizine-1,2,3,4-tetracarboxylate (by comparison and co-chromatography with authentic materials).

Reaction of 2-Aminobenzamide with Phosphorus Pentasulphide in Toluene.—Phosphorus pentasulphide (3 g) was refluxed with 2-aminobenzamide (2 g) in toluene (15 ml) for 1.5 h. The solution was allowed to cool, poured into ice-water, and basified. It was then made weakly acidic to yield a yellow precipitate of 2-(2-aminophenyl)-4(1*H*)-quinazolone (9) (0.6 g, 16.9%), m.p. 247–250 °C (from dimethylformamide-water) (Found: C, 70.7; H, 4.7; N, 17.6. Calc. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}$: C, 70.9; H, 4.6; N, 17.7%), m/z (in beam electron ionisation) 237 (100, M^+), 119 (75, $M^+ - 2$ -aminobenzonitrile), and 92 (24). Mixed m.p. and spectral comparisons showed the compound to be identical with authentic material, prepared as described⁸ and of m.p. 245–246 °C (lit., 241 °C). The procedure was repeated with the addition of pyridine (2.3 g), and only gave 0.2 g (5.6%) of the same quinazolone.

1,2-Dihydro-1-methyl-2,4-bismethylthio-2,1,3-benzophosphadiazine 2-Sulphide (3).—The pyridine complex (1) (12 g) was dissolved in aqueous *M*-sodium hydroxide (200 ml) and the resulting solution was extracted three times with ether. The aqueous solution, cooled to 0 °C, was stirred for 0.5 h with dimethyl sulphate (20 ml), giving a yellow precipitate which was filtered off, dried and recrystallised (from ca. 20 ml of nitromethane) to yield the trimethyl derivative (3) (4.8 g, 45%), m.p. 140–142 °C (Found: C, 41.9; H, 4.7; N, 9.9; S, 33.0; P, 11.1. $\text{C}_{10}\text{H}_{13}\text{N}_2\text{PS}_3$ requires C, 41.7; H, 4.2; N, 9.7; S, 33.3; P, 11.0%), m/z 288 (46, M^+), 241 (100, $M^+ - \text{SMe}$), 209 (45, $M^+ - \text{SMe} - \text{S}$) [for $M^+ 100\%$, $M + 1$ is 14.52 and $M + 2$ 14.11%; $\text{C}_{10}\text{H}_{13}\text{N}_2\text{S}_3\text{P}$ requires $M + 1$ 14.50, $M + 2$ 14.29%]; δ_{H} (300 MHz) 7.90 (1 H, q, J 8.0 + 1.4, 5-H), 7.55 (1 H, t, J 2 × ca. 8 + 2 × 1.4, 7-H), 7.07 (1 H, d, J 8.7, 8-H), 6.99 (1 H, t, 6-H), 3.37 (3 H, d, $J_{\text{P,H}}$ 10, 4-Me), 2.60 (3 H, s, 4-Me), and 2.08 (3 H, d, $J_{\text{P,H}}$ 16); δ_{C} 177.6 (s, $J_{\text{P,C}}$ 14.7, 4-C), 143.4 (s, 4a-C), 135.9 (d, Ar-C), 127.2 (d, Ar-C), 120.8 (d, Ar-C), 116.9 (s, $J_{\text{P,C}}$ 22, 8a-C), 115.3 (d, $J_{\text{P,C}}$ 5, 8-C?), 31.8 (q, $J_{\text{P,C}}$ 3, 1- CH_3), 15.3 (q, $J_{\text{P,C}}$ 5, 2- SCH_3), and 13.2 (q, $J_{\text{P,C}}$ 0, 4- SCH_3).

1,2-Dihydro-1-methyl-2-methylthio-4-pyrrolidino-2,1,3-benzophosphadiazine 2-Sulphide (4).—The trimethyl derivative (3) (0.5 g) was refluxed for 1 h with pyrrolidine (2 ml). On cooling, the amine (4) (0.4 g, 76%) precipitated; recrystallisation (from nitromethane) gave colourless plates, m.p. 157–158 °C (Found: C, 50.6; H, 5.6; N, 13.2. $\text{C}_{13}\text{H}_{18}\text{N}_3\text{PS}_3$ requires C, 50.2; H, 5.8; N, 13.5%); δ_{H} 6.71–7.33 (4 H, m, 5-, 6-, 7-, and 8-H), 3.3–3.7 (4 H, m, $[\text{CH}_2]_2$), 3.02 (3 H, d, $J_{\text{P,C}}$ 11, 1-Me), 1.78 (3 H, d, $J_{\text{P,C}}$ 16, 2-SMe), and 1.4–1.9 (4 H, br m, $[\text{CH}_2]_2$); m/z (chemical ionisation NH_3) 312 (100, $M^+ + 1$).

4-Anilino-1,2-dihydro-1-methyl-2-methylthio-2,1,3-benzophosphadiazine 2-Sulphide (5).—The trimethyl derivative (3) (0.5 g) was refluxed for 1 h with aniline (15 ml). The solution was allowed to cool and the aniline distilled off under vacuum. The

residue was shaken with ethanol (30 ml) and left for 48 h. The precipitate of the amine (5) was filtered off (0.2 g, 35%), dried, and recrystallised (from nitromethane) to give pale yellow needles, m.p. 177–178 °C (Found C, 54.5; H, 4.9; N, 12.3. $\text{C}_{15}\text{H}_{16}\text{N}_3\text{PS}_2$ requires C, 54.1; H, 4.8; N, 12.6%); δ_{H} 8.11 (1 H, d, J 8, 5-H), 6.95–7.85 (9 H, m, Ar-H and N-H; N-H exchanges with D_2O), 3.22 (3 H, d, $J_{\text{P,H}}$ 10.5, 1-Me), and 1.95 (3 H, d, $J_{\text{P,H}}$ 14.5, 2-SMe); m/z (chemical ionisation, NH_3) 334 (100%, $M + 1$) and 250 (25).

The Pyridine Complex (6) of 2,3-Dihydro-2-mercapto-3-methyl-2,1,3-benzophosphadiazine-4(1H)-thione 2-Sulphide.—This was prepared as for (1), but replacing 2-aminobenzamide by 2-amino-*N*-methylbenzamide (obtained as and with the properties described⁹) as a yellow substance (1.2 g), m.p. 168–169 °C, which decomposed on attempted purification; δ_{H} (90 MHz) (phosphadiazine part) 9.08 (1 H, br s, 1-H, exchanges with D_2O), 8.09 (1 H, d, J 7.5, 5-H), 7.15 (1 H, t, J 7.5 + 7.5, 7-H), 6.78 (1 H, d, J 7.5, 8-H), 6.64 (1 H, t, J 7.5 + 7.5, 6-H), and 3.53 (3 H, d, $J_{\text{C,P}}$ 9, 3-Me); (pyridine part) 8.61 (2 H, d, J ca. 6, 2- H_2), 8.19 (1 H, t, J ca. 7, 4-H), and 7.66 (2 H, t, J ca. 6, 3- H_2); m/z 260 (3, M^+), 227 (2, $M^+ - \text{SH}$), and 79 (100, pyridine).

2,3-Dihydro-1,3-dimethyl-2-methylthio-2,1,3-benzophosphadiazine-4(1H)-thione 2-Sulphide (7).—The complex (6) (1.0 g) was methylated as for (1) using sodium hydroxide and dimethyl sulphate to give the trimethyl compound (7) as a very hygroscopic yellow solid (0.6 g), m.p. ca. 50 °C, δ_{H} (90 MHz) 8.47 (1 H, d, J 7.5, 5-H), 7.58 (1 H, t, J 7.5 + 7.5, 7-H), 6.95–7.30 (2 H, m, 6- and 8-H), 3.72 [3 H, d, $J_{\text{P,H}}$ 9, 3- (or 1-) CH_3], 3.42 [3 H, d, $J_{\text{P,H}}$ 12, 1- (or 3-) CH_3], and 2.12 (3 H, d, $J_{\text{P,C}}$ 17.5, 2- CH_3); m/z 290 (4, $M^+ + 2$), 289 (4, $M^+ + 1$), 288 (25, M^+), 273 (11, $M^+ - \text{Me}$), 241 (48, $M^+ - \text{SCH}_3$), 209 (15, $M^+ - \text{SMe} - \text{S}$), and 168 (100%).

X-Ray Crystal-structure Determinations.—Crystal data of (1): $\text{C}_7\text{H}_7\text{N}_2\text{PS}_3 \cdot \text{C}_5\text{H}_5\text{N}$, $M_r = 325.43$, triclinic, space group $P\bar{1}$, $a = 12.391(3)$, $b = 7.422(2)$, $c = 10.001(2)$ Å, $\alpha = 64.11(2)$, $\beta = 117.21(2)$, $\gamma = 111.79(2)^\circ$, $U = 719.5$ Å³, $Z = 2$, $F(000) = 335$, $D_c = 1.50$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 54.7$ cm⁻¹. Bright yellow crystal (from ethanol) of dimensions 0.30 × 0.20 × 0.15 mm. Crystal data of (3): $\text{C}_{10}\text{H}_{14}\text{N}_2\text{PS}_3$, $M_r = 289.4$, orthorhombic, space group $Pna2_1$, $a = 15.037(4)$, $b = 11.118(2)$, $c = 7.818(2)$ Å, $U = 1307.8$ Å³, $Z = 4$, $D_c = 1.47$ g cm⁻³, $F(000) = 604$, $\mu(\text{Cu-K}\alpha) = 59.2$ cm⁻¹. Pale yellow crystal (from nitromethane) of size 0.25 × 0.20 × 0.50 mm.

Intensity data for both (1) and (3) were collected with a Hilger and Watts Y290 four-circle diffractometer controlled by a microcomputer. Space group and initial cell parameters were determined from Weissenberg photographs. Accurate unit-cell dimensions were obtained by a least-squares refinement of the θ -values of twenty reflections measured with the four-circle diffractometer. The $w-2\theta$ scanning mode was used. For (1) 1713 reflections with $\theta \leq 60^\circ$ and $I \geq 2\sigma(I)$ and for (3) 665 reflections with $\theta \leq 51^\circ$ and $I \geq 2\sigma(I)$ were considered as observed. For both data sets corrections for Lorentz and polarization effects and absorption were made.¹⁰

Structure Solution and Refinement.—Structures (1) and (3) were determined by direct methods using the program MULTAN 80.¹¹ The structures were refined by full-matrix least-squares methods (SHELX 76).¹² Atomic scattering factors and anomalous dispersion corrections were taken from International Tables.¹³ Anisotropic thermal parameters were included in the final cycles for all non-hydrogen atoms. The bond lengths within the pyridine molecule of (1) were kept fixed during the refinement because of high thermal vibrations. All hydrogen atoms were included at calculated positions and methyls were

treated as rigid groups. The refinement for (1) converged at $R = 0.066$, $R_w = 0.076$ for 1 710 observed reflections, and for (3) at $R = 0.048$, $R_w = 0.051$ for 663 observed reflections.

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