bonds; two are of the asymmetric type and one is of the symmetric type according to the classification of Newton, Jeffrey & Takagi (1979), as Table 3 shows. These three configurations are nearly planar, as follows from the sum of angles around the H atoms: for the bifurcated bonds involving the donor O atoms O(3), O(5) and O(15) these sums are 360 (4), 358 (4) and 360 (4)° respectively.

Each molecule is connected to six surrounding molecules by 14 hydrogen bonds, thus constituting a closely knit three-dimensional network.

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Structure of the Pyridine Adduct of Dithiophosphoryl Monochloride

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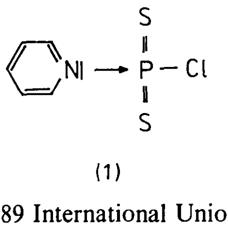
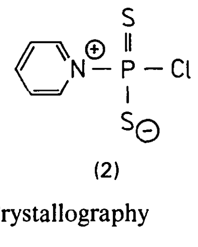
Abstract. $C_5H_5N.PS_2Cl$ (1), $M_r = 209{\cdot}66$, triclinic, $P\bar{1}$, $a = 9{\cdot}105\,(7)$, $b = 7{\cdot}954\,(6)$, $c = 6{\cdot}541\,(5)$ Å, $\alpha = 107{\cdot}89\,(1)$, $\beta = 101{\cdot}85\,(1)$, $\gamma = 78{\cdot}18\,(1)°$, $V = 436\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}597$ Mg m^{-3}, $\lambda(\text{Ag }K\alpha) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}513$ mm^{-1}, $F(000) = 212$, $T = 295$ K, final $R = 0{\cdot}037$ for 1693 unique reflections. The most striking feature of the molecular structure of (1) is the remarkably long P—N bond (1·849 Å) which is, as far as is known, the longest P—N distance found in a compound containing tetrahedrally coordinated phosphorus. This results in the formation of a strongly distorted tetrahedron with the PS_2Cl group forming a relatively flat trigonal pyramid.

Introduction. The compound $C_6H_5N.PS_2Cl$ can be formulated either as a donor stabilized dithiomonometaphosphoryl chloride (1) or as a resonance stabilized zwitterionic pyridinium chlorodithiophosphinate betaine (2) (Meisel & Grunze, 1968; Meisel 1986):



(1)



(2)

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Up to now there have been no structural data for this type of compound. Towards understanding the reaction behaviour of $C_6H_5N.PS_2Cl$ against nucleophiles it seemed interesting to obtain information on the bonding states, especially of the P—Cl and P—N bonds.

Experimental. The title compound was prepared according to:

$$P_4S_{10} + 2PSCl_3 + 6C_6H_5N \rightarrow 6C_6H_5N.PS_2Cl$$

by reacting phosphorus(V) sulfide with thiophosphoryl chloride in an excess of pyridine (Meisel & Grunze, 1968).

Crystals were obtained by recrystallization from pyridine. They appeared as yellow irregular prisms.

Experimental density: 1·556 Mg m^{-3}, by flotation. Prism fragment 0·40 × 0·40 × 0·40 mm. Philips PW 1100 diffractometer, graphite monochromator. 16 reflections ($10 < \theta < 13°$) for refining the unit-cell dimensions. $\omega/2\theta$ scan. Scan width: 1·30°, scan speed: 0·03° s^{-1}, total background measuring time: 10 s. 2447 reflections measured ($3 < \theta < 25°$), 2436 unique; $\pm h, \pm k, l$, $h_{\max} = -13, 13$; $k_{\max}$ $-11, 10$; $l_{\max} = 9$.

Intensity and orientation reflections ($\bar{6}01$ and $60\bar{1}$) every two hours; no significant variation. Lorentz and polarization corrections, no absorption correction. Direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977) used for structure determination. H atoms located by difference-Fourier synthesis. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Unit weights. Final refinement with 1693 independent reflections ($I > 4\sigma_I$). Final $R = 0·036$, $wR = 0·037$, $S = 0·484$, max. $\Delta/\sigma = 0·14$. Max. peak height in the final difference-Fourier map = 0·20 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974).

Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: VAX 780.

Discussion. Table 1 reports the final atomic coordinates.* Fig. 1 shows the centrosymmetric arrangement of the two molecules of $C_6H_5N.PS_2Cl$ in the unit cell (projection along the **c** direction). The N—PS_2Cl unit forms a strongly distorted tetrahedron due to opening of the SPS angle and shortening of the Cl—P—N angle (*cf.* Table 2). In Table 2 the interatomic distances and bond angles are given.

Table 1. *Final atomic coordinates for non-*H *atoms and their B_{eq} values*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	B_{eq}(Å^2)
Cl	0·9598 (1)	0·2474 (1)	0·2062 (2)	4·73 (2)
S(1)	1·1993 (1)	0·6541 (1)	0·2442 (1)	4·75 (2)
S(2)	1·3968 (1)	0·7963 (1)	−0·0398 (2)	4·33 (2)
P	1·24007 (9)	0·6741 (1)	−0·0230 (1)	3·09 (1)
N	0·2675 (3)	0·4454 (3)	0·7925 (4)	2·96 (5)
C(1)	0·3471 (4)	0·4100 (4)	0·6287 (5)	4·06 (7)
C(2)	0·3630 (5)	0·2422 (5)	0·4859 (6)	5·3 (1)
C(3)	0·3000 (4)	0·1113 (5)	0·5125 (6)	5·09 (9)
C(4)	0·2193 (4)	0·1485 (4)	0·6786 (7)	4·93 (9)
C(5)	0·2039 (4)	0·3170 (4)	0·8183 (5)	3·98 (7)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *in* $C_6H_5N.PS_2Cl$

N—P	1·849 (2)	N—P—S(1)	107·1 (1)
P—S(1)	1·919 (1)	N—P—S(2)	108·11 (9)
P—S(2)	1·922 (1)	N—P—Cl	93·94 (8)
P—Cl	2·058 (1)	S(1)—P—S(2)	123·68 (5)
		S(1)—P—Cl	109·83 (6)
		S(2)—P—Cl	109·96 (6)
		C(1)—N—P	119·8 (2)
		C(5)—N—P	120·0 (2)
C(1)—C(2)	1·373 (4)	C(1)—C(2)—C(3)	119·8 (4)
C(2)—C(3)	1·356 (7)	C(2)—C(3)—C(4)	119·6 (3)
C(3)—C(4)	1·360 (6)	C(3)—C(4)—C(5)	119·6 (4)
C(4)—C(5)	1·369 (4)	C(4)—C(5)—N	120·6 (3)
C(1)—N	1·342 (4)	C(5)—N—C(1)	120·2 (2)
C(5)—N	1·339 (5)	N—C(1)—C(2)	120·1 (4)

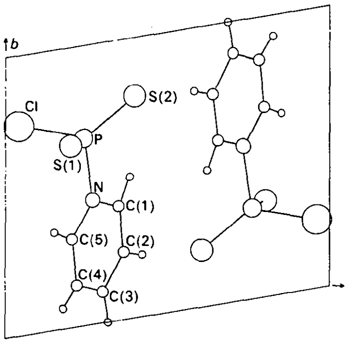

Fig. 1. Projection along the *c* axis of the atomic arrangement of $C_5H_5N.PS_2Cl$.

There are some remarkable features of the molecular structure of $C_6H_5N.PS_2Cl$ compared with other sulfur and nitrogen containing phosphorus compounds.

The P—N bond length differs distinctly from those theoretically calculated by SCF methods (Trinquier, 1986) and the values experimentally found in many phosphorus–nitrogen compounds (*cf.* Corbridge, 1974; Wells, 1984).

The calculated P—N single-bond length (1·69 Å) is in good agreement with experimentally found P—N—P bond lengths in *e.g.* *cyclo*-phosphazanes (1·69–1·75 Å) or the monoamidomonothiophosphate

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52132 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

anion [1·688 (5) Å]. Up to now the longest value found for a P—N bond was that due to the zwitterionic monoamidophosphate anion in the corresponding potassium salt [1·800 (4) Å; Cameron, Chan & Chute, 1980].

In this case the nitrogen lone pair is unable to form donor $p\pi(N)\rightarrow d\pi(P)$ bonding because of the additional bonding of a proton.

The longer P—N distance in $C_6H_5N.PS_2Cl$ of 1·849 (2) Å means that the P—N bond is only relatively weak without any π back donation. The P—N bond length is of the same order as that found in the adduct of ammonia with phosphorus pentafluoride [1·842 (2) Å; Storzer, Schomburg, Röschenthaler & Schmutzler, 1983] and only slightly shorter than in the corresponding pyridine adduct of PF_5 [1·885 (4) Å; Sheldrick, 1974]. This should be expected because bond distances in penta- and hexacoordinated phosphorus adducts are generally longer than in tetracoordinated ones.

The P—S distances ($\overline{\text{P—S}}$ = 1·920 ± 0·002 Å) are typical for P—S double bonds which normally lie within the range 1·90 to 1·95 Å, whereas the P—Cl distance of 2·058 Å is considerably longer than the average value for the P—Cl single-bond length of 2·02 ± 0·01 Å (Corbridge, 1974).

Based on the determined bond lengths one can conclude that the compound $C_6H_5N.PS_2Cl$ is preferably formulated as a donor stabilized dithiophosphoryl monochloride corresponding to form (1). This is supported by the large S—P—S bond angle of 123·68° which is of the same order as that found for the threefold coordinated planar dithioxo(tri-*tert*-butylphenyl)phosphorane, $C_{18}H_{29}PS_2$ (126°; Appel, Knoch & Kunze, 1983). In normal dithiophosphates containing strongly tetrahedrally coordinated P atoms the S—P—S angles vary only between 108 and 118° (Aurivillius & Stålhandske, 1975).

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X-ray Study of 3-*tert*-Butyl-1-methyl-2-phenylindole, the Product of an Unexpected *tert*-Butylation Reaction

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Abstract. $C_{19}H_{21}N$, $M_r = 263·4$, orthorhombic, $Pbca$, $a = 20·152$ (4), $b = 18·267$ (4), $c = 8·488$ (2) Å, $V = 3124·6$ (12) Å^3, $Z = 8$, $D_x = 1·12$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 4·6$ cm^{-1}, $F(000) = 1136$, $T = 293$ K, final $R = 0·052$ for 1755 symmetry-independent observed reflections. The indole nucleus adopts an almost planar conformation with a dihedral angle between the mean planes of the two

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