organic papers

Pyridinium 2-thioxo-2,3-dihydro-1*H*-naphtho[2,3-*d*]-1,3,2λ⁵-diazaphosphole-2-thiolate

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.079
Data-to-parameter ratio = 13.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The reaction of chlorodithiophoshoric acid pyridinium betaine, PyPS$_2$Cl, with 2,3-diaminonaphthalene yields the title compound, (PyH)(C$_{10}$H$_8$N$_2$)PS$_2$ or C$_5$H$_6$N$^+$·C$_{10}$H$_8$N$_2$PS$_2^-$. The P atom is coordinated by both N atoms of 2,3-diamino-naphthalene with the formation of a five-membered ring.

Comment

The betaine-type compound PyPS$_2$Cl is often used as a precursor for the syntheses of dithiophosphoric acid derivatives. It is possible to prepare a large number of derivatives due to the nucleophilicity of the P atom. These compounds are formed from PyPS$_2$Cl by a substitution of the Cl atom and/or the pyridine molecule. The case where both the Cl atom and the pyridine molecule were substituted was exploited for syntheses of cyclic dithiophosphates from the betaine and various bifunctional nucleophiles (Meisel & Donath, 1983; Donath & Meisel, 1987). Though most of the prepared compounds are crystalline, we have not found any published structure of the cyclic dithiophosphate type. We report here the reaction of PyPS$_2$Cl with 2,3-diaminonaphthalene in acetonitrile in the presence of pyridine as the HCl acceptor. This reaction leads to the formation of the title compound, (I).

(I)
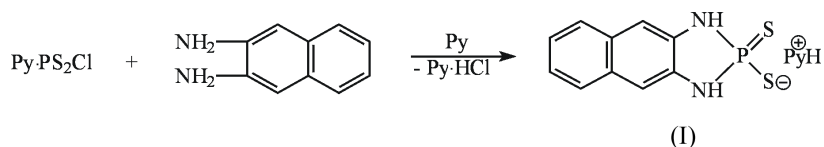
Bond angles around the phosphorus atom confirm the proposed slightly deformed tetrahedral arrangement of the P atom. The P—S1 bond is significantly longer than the P—S2 bond (Table 1). According to published data, the single P—S bond is approximately 2.02–2.03 Å long (Gastaldi *et al.*, 1974); the length of the exocyclic P=S bond in a compound that can be compared with our product is 1.9272 (14) Å (Prevote *et al.*, 1999) or 1.901 (3) Å (Light *et al.*, 1978). Therefore, it can be said that the P=S bond in (I) is delocalized and both P—S bonds have partial double-bond character. The lengthening of the P—S1 bond is probably the result of weak intermolecular interactions (Table 2). The plane formed by S1—P—S2 is oriented almost perpendicular to the plane of the phosphole ring [86.57 (3)°]. The values of the P—N bond distances (Table 1) are comparable with those found in other five-membered P—N—C—C—N rings (Bélanger-Gariépy *et al.*, 1986; Wyatt *et al.*, 1999; Hanessian *et al.*, 1995; Prevote *et al.*, 1999). The approximately planar phosphole ring forms a dihedral angle of 16.81 (8)° with the pyridinium ring. Selected
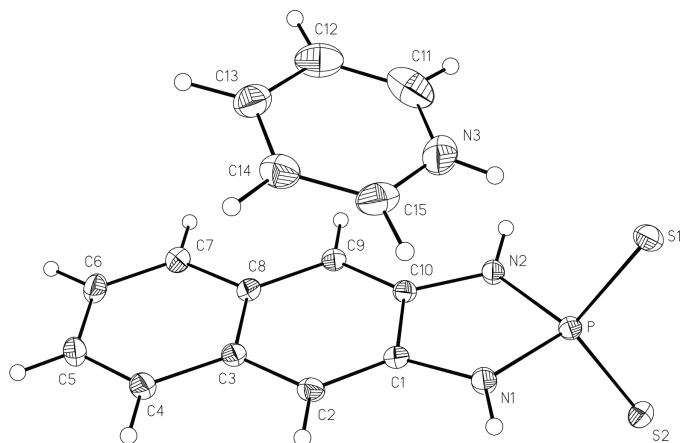
Figure 1
The structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

bond distances and angles of (I) are given in Table 1, its molecular structure is shown in Fig. 1, and Table 2 records the weak intermolecular interactions.

Experimental

The title compound was prepared by the reaction of $PyPS_2Cl$ (0.05 mol) and 2,3-diaminonaphthalene (0.05 mol) in the presence of pyridine (0.05 mol). Acetonitrile (120 ml) was added as the reaction solvent. All operations were performed at laboratory temperature in a dry nitrogen atmosphere. A light-yellow powder was formed in the course of the reaction (yield 1.4 g). The powder is soluble in pyridine and this solvent was used also for growing the single crystals. A yellow plate-like crystal was chosen for the X-ray structure determination.

Crystal data

$C_5H_6N^+ \cdot C_{10}H_8N_2PS_2^-$
$M_r = 331.38$
Monoclinic, $P2_1/c$
$a = 11.6700 (18)$ Å
$b = 11.930 (3)$ Å
$c = 11.108 (3)$ Å
$\beta = 98.005 (18)°$
$V = 1531.4 (5)$ Å^3
$Z = 4$

$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7150 reflections
$\theta = 2.4–27.0°$
$\mu = 0.45$ mm^{-1}
$T = 183 (2)$ K
Plate, yellow
$0.40 \times 0.30 \times 0.10$ mm

Data collection

Bruker SMART three-circle diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.646$, $T_{max} = 0.862$
24 788 measured reflections

3331 independent reflections
2764 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.0°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.05$
3331 reflections
246 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.2P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P—N1	1.6870 (13)	N1—C1	1.3874 (19)
P—N2	1.6966 (13)	N1—H1N	0.82 (2)
P—S2	1.9703 (6)	N2—C10	1.4012 (18)
P—S1	1.9960 (6)	N2—H2N	0.79 (2)
N1—P—N2	90.41 (6)	C1—N1—H1N	122.6 (14)
N1—P—S2	111.72 (5)	P—N1—H1N	121.4 (14)
N2—P—S2	114.77 (5)	C10—N2—P	113.98 (10)
N1—P—S1	112.89 (5)	C10—N2—H2N	120.8 (13)
N2—P—S1	110.27 (5)	P—N2—H2N	120.3 (13)
S2—P—S1	114.49 (3)	C2—C1—N1	128.61 (13)
C1—N1—P	114.85 (10)	N1—C1—C10	110.36 (12)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$S1^i	0.82 (2)	2.55 (2)	3.3632 (15)	172.3 (18)
N3—H3N$\cdots$S1	0.80 (3)	2.44 (3)	3.2127 (19)	163 (2)

Symmetry code: (i) $-x, 1 - y, -z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bélanger-Gariépy, F., Delorme, D., Hanessian, S. & Brisse, F. (1986). *Acta Cryst.* C**42**, 856–860.
Bruker (1997). *SHELXTL.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SMART* (Version 5.059) and *SAINT* (Version 6.06). Bruker AXS Inc., Madison, Wisconsin, USA.
Donath, C. & Meisel, M. (1987). *Z. Anorg. Allg. Chem.* **549**, 46–58.
Gastaldi, L., Porta, P. & Tomlinson, A. A. G. (1974). *J. Chem. Soc. Dalton Trans.* **13**, 1424–1429.
Hanessian, S., Androtti, D. & Gomtsyan, A. (1995). *J. Am. Chem. Soc.* **117**, 10393–10394.
Light, R. W., Campana, C. F., Paine, R. T. & Morosin, B. (1978). *Acta Cryst.* B**34**, 3671–3674.
Meisel, M. & Donath, C. (1983). *Phosphorus Sulfur*, **18**, 159–162.
Prevote, D., Donnadieu, B., Moreno-Manas, M., Caminade, A. M. & Majoral, J. P. (1999). *Eur. J. Org. Chem.* pp. 1701–1708.
Sheldrick, G. M. (1999). *SADABS.* University of Göttingen, Germany.
Wyatt, P. B., Villalonga-Barber, C. & Motevalli, M. (1999). *Tetrahedron Lett.* **40**, 149–152.