

2-(*p*-Methoxyphenyl)-3-[*o*-(methylaminothiocarbonyl)phenyl]-1,3,2-oxazaphospholidine 2-sulfideSheng-Lou Deng,* Dong-Zhi Liu
and Wei LiSchool of Chemical Engineering, Tianjin
University, Tianjin 300071, People's Republic
of ChinaCorrespondence e-mail:
shengloudeng@hotmail.com

Key indicators

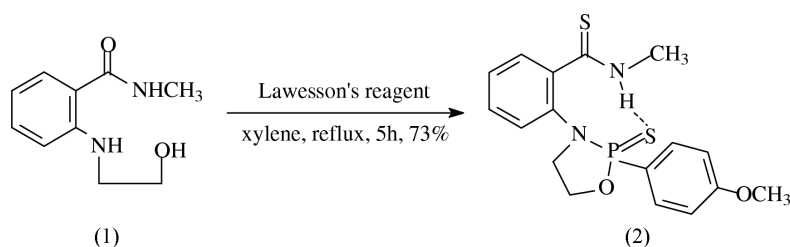
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$
 R factor = 0.045
 wR factor = 0.103
Data-to-parameter ratio = 11.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{PS}_2$, the five-membered phosphorus heterocycle has an envelope conformation. The carbamide moiety is involved in an $\text{N}-\text{H}\cdots\text{S}$ intramolecular hydrogen bond. The existence of a $d-p$ π bond between the P atom and the adjacent N atom is observed.

Received 29 October 2002
Accepted 19 November 2002
Online 30 November 2002

Comment

The title compound, (2), was synthesized through thiation and regioselective cyclization of multifunctional 2-[*N*-(2'-hydroxyethyl)amino]-*N'*-methylbenzamide, (1), with Lawesson's reagent in a one-pot procedure. This compound exhibits moderate herbicidal activity below a concentration of 100 p.p.m. in preliminary bioassays. In spite of a full characterization of the structure by spectroscopic and micro-analytical methods, compound (2) was subjected to X-ray diffraction analysis for the purpose of structure-activity study. The molecule consists of two phenyl rings and one five-membered phosphorus heterocycle bearing an O-P-N moiety, which confers potential bioactivity of this structure in comparison with numerous P-O- or P-N-containing molecules of pharmaceutical or agricultural importance (Brassfield *et al.*, 1975; Gilard *et al.*, 1999; Darrow & Drueckhammer, 1996; Morita *et al.*, 1987; Deng & Chen, 2001).



There are four independent molecules in the asymmetric unit, all having similar shapes and geometries, and the molecular structure of one of these molecules is shown in Fig. 1. The five-membered ring exists in an envelope conformation and atom C10 deviates from the plane defined by atoms P1, N1, O1 and C9. Further investigation of the bond-length data reveals that there exists $d-p$ π -bonding character between the P and N atoms, as shown by the shorter bond length [1.653 (5)–1.668 (5) Å] than that of a single normal P–N bond (1.76 Å) based on Riess's theory (Riess, 1986). In addition, the thiocarbamide N atom interacts with the neighboring S atom of the P=S group, resulting in the formation of an intramolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bond (Fig. 1 and Table 2).

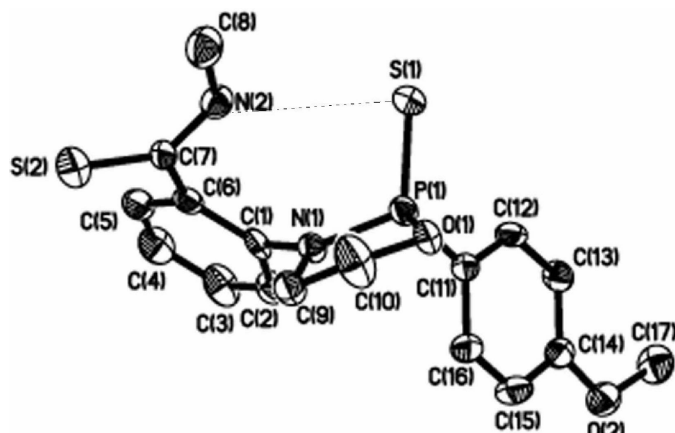


Figure 1
View of the molecule of (2), with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. A dashed line indicates the hydrogen-bonding interaction.

Experimental

A suspension of (1) (2.5 mmol) and an equivalent amount of Lawesson's reagent in anhydrous xylene (50 ml) was refluxed with stirring, under N_2 , for 5 h. The reaction mixture was filtered and the filtrate concentrated on a rotary evaporator at reduced pressure. The residue was chromatographed using a mixture of ethyl acetate and petroleum ether (1/5, v/v) as eluant, yielding a crude product. Further recrystallization of the crude product from a mixture of methylene chloride and light petroleum ether (1/3, v/v) afforded the title compound, (2), as colorless crystals (m.p. 373 K). 1H NMR ($CDCl_3$ as a solvent, TMS as internal reference, δ): 3.35 (*d*, 3H, $3J_{H-H} = 5.15$ Hz, $NHCH_3$), 3.71–4.03 (*m*, 2H, NCH_2CH_2O), 3.91 (*s*, 3H, OCH_3), 4.32–4.65 (*m*, 2H, CH_2CH_2O), 7.03 (*dd*, 2H, $4J_{P-H} = 3.36$ Hz, $3J_{H-H} = 8.50$ Hz, H_{arom}), 7.06–7.85 (*m*, 4H, H_{arom}), 7.91 (*dd*, 2H, $3J_{P-H} = 8.12$ Hz, $3J_{H-H} = 8.50$ Hz, H_{arom}), 9.65 (*br*, 1H, NH). ^{31}P NMR ($CDCl_3$ as a solvent, 85% H_3PO_4 as an external reference, δ): 89.60. FT IR (KBr, cm^{-1}): 3234 (NH), 1595, 1568, 1502, 1452 (Ar), 1259 (C=S), 1113 (P–O–C), 1020 (Ar–O–C). Elemental analysis, found: C 53.62, H 4.89, N 7.78%; calculated: C 53.97, H 5.03, N 7.41%.

Crystal data

$C_{17}H_{19}N_2O_2PS_2$	$D_x = 1.321$ Mg m^{-3}
$M_r = 378.43$	Mo $K\alpha$ radiation
Monoclinic, Pn	Cell parameters from 874 reflections
$a = 9.905$ (3) Å	$\theta = 2.4$ – 22.1°
$b = 19.091$ (5) Å	$\mu = 0.38$ mm $^{-1}$
$c = 20.384$ (5) Å	$T = 293$ (2) K
$\beta = 99.180$ (5) $^\circ$	Prism, colorless
$V = 3805.0$ (17) Å 3	$0.25 \times 0.20 \times 0.20$ mm
$Z = 8$	

Data collection

Bruker SMART CCD area-detector diffractometer	10230 independent reflections
φ and ω scans	6200 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.042$
$T_{min} = 0.912$, $T_{max} = 0.929$	$\theta_{max} = 25.0^\circ$
15649 measured reflections	$h = -11 \rightarrow 9$
	$k = -16 \rightarrow 22$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{max} = 0.028$
$S = 0.97$	$\Delta\rho_{max} = 0.28$ e Å $^{-3}$
10230 reflections	$\Delta\rho_{min} = -0.24$ e Å $^{-3}$
866 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	3497 Friedel pairs
	Flack parameter = 0.00 (7)

Table 1

Selected interatomic distances (Å).

P1–O1	1.646 (5)	P3–O5	1.609 (4)
P1–N1	1.668 (5)	P3–N6	1.657 (5)
P1–C11	1.784 (6)	P3–C45	1.790 (7)
P1–S1	1.938 (2)	P3–S6	1.930 (3)
P2–O3	1.608 (4)	P4–O7	1.640 (5)
P2–N4	1.662 (5)	P4–N8	1.653 (5)
P2–C28	1.779 (6)	P4–C62	1.804 (6)
P2–S4	1.934 (2)	P4–S8	1.933 (2)

Table 2

Hydrogen-bonding geometry (Å, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2B \cdots S1	0.86	2.59	3.420 (6)	162
N3–H3B \cdots S4	0.86	2.64	3.480 (6)	165
N5–H5B \cdots S6	0.86	2.63	3.458 (5)	163
N7–H7A \cdots S8	0.86	2.60	3.426 (6)	163

H atoms were positioned geometrically and refined with riding-model positional parameters and fixed isotropic displacement parameters. There are solvent-accessible voids of 46 Å 3 in the crystal.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT; data reduction: SMART (Bruker, 1997) and SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

We are grateful to Professor Hong-Gen Wang and his assistant Xue-Bing Leng for the X-ray diffraction measurements.

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