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6-Bromo-3-(4-chlorophenyl)-2-(4-methoxyphenyl)-3,4-dihydro-1,3,2-benzoxazaphosphinine 2-sulfide

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Key indicators

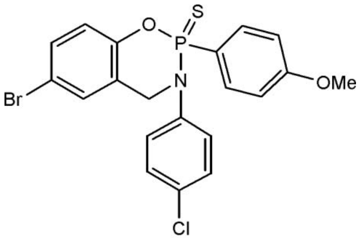
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.047
wR factor = 0.131
Data-to-parameter ratio = 14.5

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

In the title compound, $C_{20}H_{16}BrClNO_2PS$, the six-membered oxazaphosphinine ring exhibits a boat conformation, with the S atom in an axial position. The methoxyphenyl and chlorobenzene groups are *trans* to each othe. The structure is stabilized by intermolecular C—H···S hydrogen bonds, linking the molecules into chains.

Comment

An increasing interest has been shown for the past 20 years in the chemistry of phosphorus heterocycles owing to their unique physicochemical properties (He *et al.*, 2002) and potential biological activities (Rao *et al.*, 2000). Many classes of phosphorus heterocyclic system bearing PO and PN units, such as cyclophosphamide and its derivatives, are antitumor agents (Gilard *et al.*, 1999). The structure determination of the title compound, (I), was undertaken as part of continuing efforts to study the effect of substituents on significant features on the conformation and molecular geometry of the heterocyclic ring (Fig. 1).



(I)

In (I), the endocyclic bond lengths and angles (Table 1) of the oxazaphosphinine unit are in good agreement with the values of other six-membered-ring structures (Krishnaiah *et al.*, 2007; Selladurai & Subramanian, 1990; Nuti *et al.*, 1988). The methoxy group is coplanar with the benzene ring to which it is substituted, with a C8—C9—O4—C25 torsion angle of −0.4 (8)°.

The oxazaphosphinine ring adopts a boat conformation with atoms P1, N5, C17 and C12 coplanar [maximum deviations 0.023 (4) and −0.025 (4) Å for C12 and C17] and with atoms O3 and C18 displaced in the same direction by 0.591 (3) and 0.517 (4) Å, respectively. The least-squares plane of the bromophenyl ring is inclined at an angle of 24.1 (1)° to the mean plane of the heterocyclic ring. The torsion angle P1—N5—C19—C20 [67.8 (4)°] indicates that the chlorobenzene is rotated by 55.24 (11)° with respect to the P1/N5/C17/C12 plane. The distance S2···C20 is 3.746 (4) Å. The above rotation occurs to avoid interaction of the chlorobenzene with

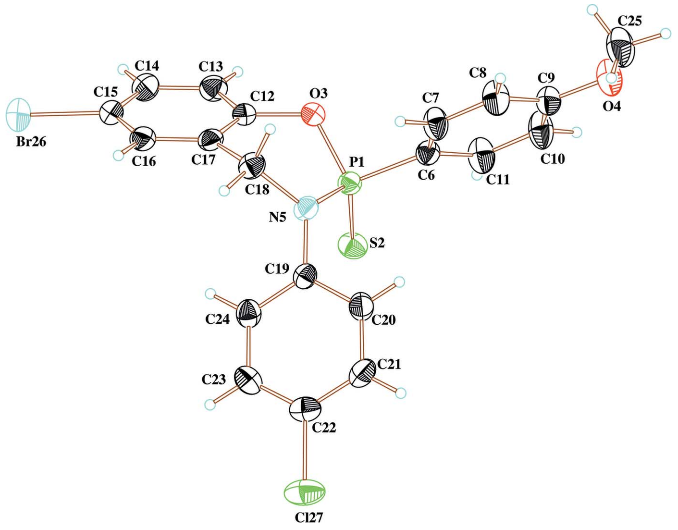


Figure 1
View of the molecular structure, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by circles of arbitrary radius.

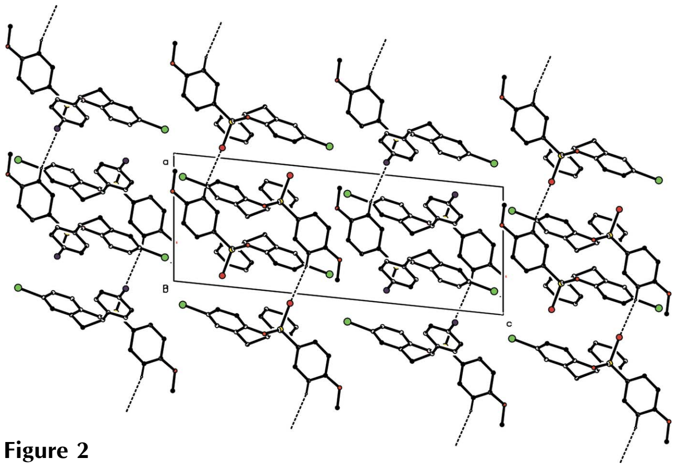


Figure 2
The molecular packing of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines and H atoms not involved in these interactions have been omitted.

atom S2. Hence the conformation of the phosphinine ring is forced to be that of a boat. The methoxyphenyl and chlorobenzene groups are *trans* to each other and are at equatorial positions on the oxazaphosphinine ring. These ring planes are perpendicular to each other [dihedral angle 82.6 (1)°], and the former makes a dihedral angle of 69.6 (2) with the P1/N5/C17/C12 plane.

The crystal packing is stabilized by intermolecular C—H···S hydrogen interactions linking the molecules to form chains running parallel to the *b* axis (Fig. 2, Table 2).

Experimental

A three-necked flask equipped with a dropping funnel, stirrer, dry $CaCl_2$ tube and nitrogen gas inlet was charged with 10 ml of anhydrous toluene and 1 mmol of 4-bromo-2-[(4-chlorophenylamino)-methyl]phenol. 2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (1 mmol) was added to the flask at room temperature and the reaction mixture was refluxed with stirring under dry nitrogen for 6–8 h until no starting materials could be detected with TLC. Evaporation of the solvent followed by column chromatography on silica gel using petroleum ether–ethyl acetate (8:2 *v*/*v*) as eluant afforded a white single crystal of (I) suitable for X-ray diffraction.

Crystal data

$C_{20}H_{16}BrClNO_2PS$
$M_r = 480.73$
Monoclinic, $P2_1/c$
$a = 8.7765\ (10)$ Å
$b = 10.1549\ (12)$ Å
$c = 22.707\ (3)$ Å
$\beta = 95.885\ (2)^\circ$
$V = 2013.1\ (4)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.37$ mm^{-1}
$T = 293\ (2)$ K
0.24 × 0.24 × 0.13 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{\min} = 0.588$, $T_{\max} = 0.731$
18958 measured reflections
3543 independent reflections
2775 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.131$
$S = 1.03$
3543 reflections
244 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.619 (3)	N5—C18	1.489 (5)
P1—N5	1.678 (3)	C12—C17	1.381 (5)
O3—C12	1.404 (4)	C17—C18	1.505 (5)
O3—P1—N5	100.24 (14)	C17—C12—O3	117.0 (3)
C12—O3—P1	118.0 (2)	C12—C17—C18	116.4 (3)
C18—N5—P1	118.4 (2)	N5—C18—C17	111.8 (3)
N5—P1—O3—C12	−49.2 (3)	O3—C12—C17—C18	−1.1 (5)
O3—P1—N5—C18	−0.2 (3)	P1—N5—C18—C17	44.2 (4)
P1—O3—C12—C17	54.0 (4)	C12—C17—C18—N5	−46.4 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···S2$^{\rm i}$	0.93	2.84	3.750 (5)	167

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

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, or $1.5U_{\rm eq}({\rm C})$ for CH_3 groups. The highest residual density peak is located 1.40 Å from atom Br26

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEPII* (Zsolnai, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *PARST* (Nardelli, 1995).

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