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6-(2,4-Dichlorophenoxy)dibenzo[*d*,*f*][1,3,2]dioxaphosphepine-6-sulfide

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.112
Data-to-parameter ratio = 11.5

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

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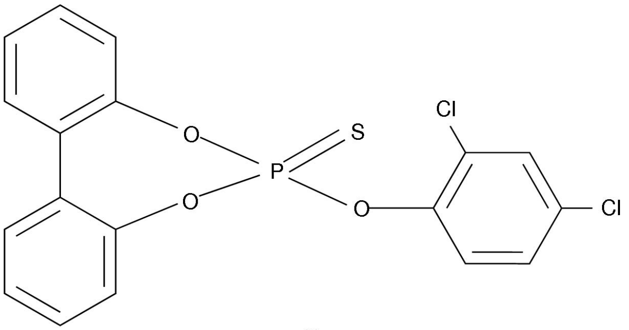
In the title compound, $C_{18}H_{11}Cl_2O_3PS$, the seven-membered phosphepine ring exhibits a distorted-boat conformation, with the phosphoryl sulfide group axial and the dichlorophenoxy group equatorial. Fusion of the phosphepine ring to the biphenyl system causes strain, as evidenced by both widening and compression of the endocyclic angles in the heterocyclic ring. The P═S bond length is 1.8939 (12) Å and the planar dichlorophenyl ring is oriented at an angle of 28.70 (6)° to the phosphepine ring.

Comment

The structure analysis and conformation of organophosphorus compounds have become the subject of study due to their vital importance as insecticides, bactericides, flame retardants and lubricants (Ismail, 1975), and as antioxidants and stabilizers in polymers and oils (Spivack, 1982). These compounds are also useful as pesticides against worms which damage the stems and roots of plants (Emsley & Hall, 1976). The title compound, (I), has both antifungal and antibacterial activity (Ananda Kumar *et al.*, 2001), which prompted us to undertake the present crystal structure determination to examine the influence of the substituents on the conformation of the heterocyclic ring.



(I)

The endocyclic bond lengths (Table 1) in the two P—O—C—C fragments of the seven-membered ring of (I) are equal within the limits of error. However, significant variation is observed in the endocyclic P—O—C bond angles when compared with the corresponding values found in similar structures (Coulter, 1975; Grand & Robert, 1978; Siva Kumar *et al.*, 1989). This may be attributed to the steric effect of the bulky groups attached to the heterocyclic ring. The dihedral angles, and the deviations of atoms P, O1, C7 and C12 [0.006 (1), 0.330 (1), 0.449 (2) and 0.425 (2) Å, respectively] above the best-fit plane through the atoms of the phosphepine ring and of atoms O2, C6 and C1 below [−0.432 (2), −0.375 (2) and −0.457 (2) Å, respectively], indicate that the heterocyclic ring exhibits a distorted-boat conformation. The planes of the benzene rings of the biphenyl system subtend dihedral angles of 39.11 (7)° and 39.32 (6)°, respectively, with the heterocyclic ring plane. This imparts strain on the adjacent heterocyclic ring in order to minimize steric interactions. This is evident from the widening of the angles C11—C12—C7 [122.92 (19)°] and C2—C1—C6 [122.6 (2)°], and compression of the angles C12—C7—C8 [116.7 (2)°] and C5—C6—C1 [116.6 (2)°]. The planar dichlorophenyl group is oriented at 28.70 (6)° to the heterocyclic ring plane, with the benzene rings of the biphenyl fragment inclined at 45.17 (7)° to one another.

Experimental

A solution of thiophosphoryl chloride (0.51 g, 0.003 mol) in dry toluene (20 ml) was added dropwise over a period of 20 min to a cooled (273 K) and stirred solution of 22-dihydroxybiphenyl (0.56 g, 0.003 mol) in dry toluene (25 ml). The reaction mixture was slowly warmed to room temperature, left for 2 h and then stirred at 313–318 K for 3 h, to give a solution of 6-chlorodibenzo[*d*,*f*]-[1,3,2]dioxaphosphepine-6-sulfide. This solution was cooled (273 K) and then added dropwise to a solution of 2,4-dichlorophenol (0.49 g, 0.003 mol) and triethylamine(0.3 g, 0.003 mol) in dry toluene (20 ml). After the addition, the reaction mixture was stirred at room temperature for 2 h and then at 323–328 K for another 5 h. Solid triethylamine hydrochloride was filtered off and the solvent evaporated under reduced pressure. Recrystallization from 2-propanal by slow evaporation gave yellowish transparent single crystals of (I) suitable for X-ray diffraction.

Crystal data

$C_{18}H_{11}Cl_2O_3PS$
$M_r = 409.20$
Monoclinic, $P2_1/n$
$a = 10.816$ (6) Å
$b = 13.615$ (8) Å
$c = 12.321$ (7) Å
$\beta = 99.583$ (9)°
$V = 1789.0$ (18) Å^3
$Z = 4$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 988 reflections
$\theta = 2.3$–25.0°
$\mu = 0.58$ mm^{-1}
$T = 293$ (2) K
Rectangular, block yellow
0.48 × 0.25 × 0.25 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.753$, $T_{max} = 0.864$
8553 measured reflections
3119 independent reflections
2831 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25.0°$
$h = -12 \rightarrow 12$
$k = -16 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.112$
$S = 1.13$
3119 reflections
271 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.5542P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.046 (3)

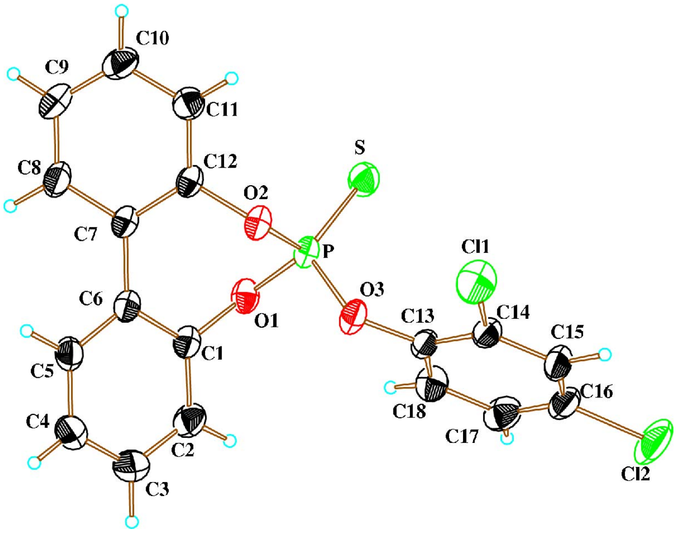


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Table 1
Selected geometric parameters (Å, °).

P—O2	1.5799 (15)	O1—C1	1.410 (3)
P—O3	1.5812 (16)	O3—C13	1.391 (2)
P—O1	1.5842 (16)	C12—C7	1.387 (3)
P—S	1.8939 (12)	C7—C6	1.470 (3)
O2—C12	1.410 (2)	C6—C1	1.388 (3)
O2—P—O1	104.14 (8)	C12—C7—C8	116.7 (2)
O3—P—O1	105.94 (9)	C12—C7—C6	121.58 (17)
O2—P—S	119.06 (7)	C8—C7—C6	121.72 (19)
O3—P—S	117.54 (7)	C1—C6—C5	116.6 (2)
O1—P—S	111.51 (6)	C1—C6—C7	121.85 (19)
C12—O2—P	117.68 (12)	C5—C6—C7	121.59 (18)
C1—O1—P	121.10 (12)	C18—C13—O3	121.33 (19)
C13—O3—P	122.75 (13)	C14—C13—O3	118.03 (18)
C11—C12—C7	122.92 (19)	C2—C1—C6	122.6 (2)
C11—C12—O2	118.53 (18)	C2—C1—O1	118.30 (18)
C7—C12—O2	118.41 (18)	C6—C1—O1	119.01 (18)
O3—P—O2—C12	−159.88 (14)	P—O3—C13—C18	−65.9 (3)
O1—P—O2—C12	−51.53 (16)	P—O3—C13—C14	117.23 (19)
O2—P—O1—C1	−38.57 (16)	C5—C6—C1—O1	176.86 (18)
O3—P—O1—C1	62.80 (16)	C7—C6—C1—O1	−3.7 (3)
P—O2—C12—C7	75.7 (2)	P—O1—C1—C6	71.0 (2)

All H atoms were clearly located in difference Fourier syntheses and refined isotropically.

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: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *enCIFer* (Version 1.0; Allen *et al.*, 2004) and *PARST* (Nardelli, 1995).

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