6-(4-Chlorophenoxy)dibenzo[d,f][1,3,2]dioxaphosphepin 6-Sulfide

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Abstract. $C_{18}H_{12}ClO_3PS$, $M_r = 374\cdot76$, triclinic, $P\bar{1}$, $a = 7\cdot180$ (2), $b = 9\cdot647$ (2), $c = 13\cdot296$ (3) Å, $\alpha = 98\cdot11$ (2), $\beta = 92\cdot98$ (2), $\gamma = 110\cdot73$ (2)°, $V = 847\cdot5$ (4) Å^3, $Z = 2$, $D_m = 1\cdot47$ (1), $D_x = 1\cdot468$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1\cdot5418$ Å, $\mu = 41\cdot85$ cm^{-1}, $F(000) = 384$, $T = 298$ K, final $R = 0\cdot051$ for 2802 observed reflections. The seven-membered heterocyclic ring is in a twist-boat conformation and exhibits valence-angle strain owing to the dibenzo fusion. The P=S bond length is $1\cdot894$ (2) Å.

Introduction. Organophosphorus compounds find wide application as insecticides, bactericides, fungicides, flame retardants, lubricants *etc.* (Ismail, 1975). Recently, substituted dibenzo[d,f][1,3,2]dioxaphosphepins have been claimed to be stabilizers to prevent polymer degradation (Pastor, Spivack, Steinhuebel & Matzura, 1983). Crystal structure analysis of the title compound was undertaken to study the conformation of the seven-membered heterocyclic ring.

Experimental. Transparent needle-shaped crystals from benzene, D_m by flotation, crystal size $0\cdot4 \times 0\cdot2 \times 0\cdot2$ mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation; cell parameters from least-squares treatment of setting angles of 20 reflections with $25 < \theta < 35°$; $\omega/2\theta$ scan technique; intensity variation of two standard reflections monitored every 100 reflections less than 2%; total number of reflections measured 3203 with $2\theta \leq 120°$, 2802 observed reflections $[I \geq 3\sigma(I)]$; range of hkl: $h\,0{\to}8$, $k\,-10{\to}10$, $l\,-14{\to}14$; Lp and absorption corrections (azimuthal scan data) applied. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement on F by full-matrix least-squares method; H atoms from difference Fourier map; anisotropic thermal parameters for non-H atoms and isotropic for H atoms; final $R = 0\cdot051$, $wR = 0\cdot066$, $w = [\sigma^2 F_o + 0\cdot00309 F_o^2]^{-1}$, $S = 1\cdot78$; $(\Delta/\sigma)_{max} = 0\cdot002$; max. and min. height in final difference map $0\cdot4$ and $-0\cdot25$ e Å^{-3}; no correction for secondary extinction; atomic scattering factors for all atoms as in *SHELX* (Sheldrick, 1976); other geometrical calculations using *PARST* (Nardelli, 1983); IBM 360/44 computer was used.*

Discussion. Table 1 lists the final atomic coordinates and equivalent isotropic temperature factors. The bond lengths, valence angles and selected torsion angles are listed in Table 2. A perspective view of the molecule is given in Fig. 1 and a packing diagram in Fig. 2.

The seven-membered heterocyclic ring assumes a twist-boat conformation (Table 2). The twist is confirmed by P–O(2) and C(13)–C(18) bonds, which cross the best plane through the four atoms in opposite directions; atoms O(3), C(7) and C(12) pucker to the same side of this plane. In comparison, a twist-chair conformation has been found in the structure of tetramethylene hydrogen phosphate (Coulter, 1975) and a pseudo-chair form in the structure of 1,5-dihydro-7,8-dimethyl-2,4,3-benzodithiaphosphepin 3-oxide (Reddy, Rao, Reddy, Daniel, Jasinsky, Holt & Darell, 1985). The chlorophenyl ring and the two benzene rings fused to the seven-membered ring are planar.

The Cl–C(4) bond length, $1\cdot739$ (3) Å, and its associated endocyclic C(3)–C(4)–C(5) angle of $121\cdot1$ (2)° agree well with values of $1\cdot740$ (1) Å and $121\cdot37$ (9)°, respectively, deduced from *p*-substituted chlorobenzenes (Domenicano, Vaciago & Coulson, 1975), but are slightly different from the corresponding values of $1\cdot69$ (3) Å and $118\cdot2$ (3)° in the dithiaphosphepin (Reddy, Rao, Reddy, Daniel, Jasinsky, Holt & Darell, 1985). The average bond distances for C–O [$1\cdot406$ Å] and P–O [$1\cdot587$ Å] are in agreement with those found in similar structures (Jones, Edwards

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Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}{}^*(Å^2)$
P	0·5757 (1)	0·4689 (1)	0·2362 (1)	3·4 (1)
S	0·5974 (1)	0·6298 (1)	0·1651 (1)	5·2 (1)
Cl	0·1274 (1)	0·8599 (1)	0·5549 (1)	5·7 (1)
O(1)	0·5466 (3)	0·4935 (2)	0·3540 (1)	4·2 (1)
O(2)	0·4010 (3)	0·3185 (2)	0·1816 (1)	3·7 (1)
O(3)	0·7626 (3)	0·4200 (2)	0·2507 (1)	3·8 (1)
C(1)	0·4431 (4)	0·5825 (3)	0·3971 (2)	3·6 (1)
C(2)	0·5535 (4)	0·7146 (3)	0·4609 (2)	4·0 (1)
C(3)	0·4570 (4)	0·7996 (3)	0·5102 (2)	4·1 (1)
C(4)	0·2508 (4)	0·7517 (3)	0·4938 (2)	3·6 (1)
C(5)	0·1399 (4)	0·6192 (3)	0·4289 (2)	4·1 (1)
C(6)	0·2356 (4)	0·5321 (3)	0·3807 (2)	4·0 (1)
C(7)	0·3722 (4)	0·1775 (3)	0·2099 (2)	3·5 (1)
C(8)	0·1955 (4)	0·1067 (3)	0·2480 (2)	4·4 (1)
C(9)	0·1534 (6)	−0·0366 (4)	0·2695 (2)	5·5 (1)
C(10)	0·2928 (7)	−0·1058 (3)	0·2526 (3)	5·8 (1)
C(11)	0·4693 (6)	−0·0321 (3)	0·2132 (2)	4·9 (1)
C(12)	0·5139 (4)	0·1116 (3)	0·1890 (2)	3·7 (1)
C(13)	0·6941 (4)	0·1843 (3)	0·1411 (2)	3·8 (1)
C(14)	0·7587 (5)	0·1035 (4)	0·0635 (2)	4·7 (1)
C(15)	0·9271 (5)	0·1737 (5)	0·0155 (2)	5·4 (1)
C(16)	1·0355 (5)	0·3244 (5)	0·0445 (2)	5·2 (1)
C(17)	0·9768 (4)	0·4088 (4)	0·1226 (2)	4·5 (1)
C(18)	0·8110 (4)	0·3366 (3)	0·1679 (2)	3·6 (1)

$$* B_{eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

Table 2. *Bond lengths (Å), valence angles (°) and selected torsion angles (°)*

P–S	1·894 (2)	C(7)–C(8)	1·372 (3)
P–O(1)	1·587 (2)	C(7)–C(12)	1·397 (4)
P–O(2)	1·589 (2)	C(8)–C(9)	1·381 (4)
P–O(3)	1·583 (2)	C(9)–C(10)	1·397 (6)
Cl–C(4)	1·739 (3)	C(10)–C(11)	1·386 (5)
O(1)–C(1)	1·405 (3)	C(11)–C(12)	1·396 (4)
O(2)–C(7)	1·409 (3)	C(12)–C(13)	1·463 (3)
O(3)–C(18)	1·402 (3)	C(13)–C(14)	1·402 (4)
C(1)–C(2)	1·371 (3)	C(13)–C(18)	1·392 (3)
C(1)–C(6)	1·388 (3)	C(14)–C(15)	1·396 (4)
C(2)–C(3)	1·371 (4)	C(15)–C(16)	1·370 (5)
C(3)–C(4)	1·380 (3)	C(16)–C(17)	1·403 (5)
C(4)–C(5)	1·381 (3)	C(17)–C(18)	1·367 (3)
C(5)–C(6)	1·375 (4)		

O(2)–P–O(3)	103·9 (1)	O(2)–C(7)–C(8)	117·2 (2)
O(1)–P–O(3)	95·6 (1)	C(8)–C(7)–C(12)	123·6 (2)
O(1)–P–O(2)	108·0 (1)	C(7)–C(8)–C(9)	119·4 (3)
S–P–O(3)	119·0 (1)	C(8)–C(9)–C(10)	119·1 (3)
S–P–O(2)	111·0 (1)	C(9)–C(10)–C(11)	120·2 (2)
S–P–O(1)	117·2 (1)	C(10)–C(11)–C(12)	121·8 (3)
P–O(1)–C(1)	123·8 (1)	C(7)–C(12)–C(11)	115·7 (2)
P–O(2)–C(7)	122·5 (1)	C(11)–C(12)–C(13)	121·4 (2)
P–O(3)–C(18)	119·5 (1)	C(7)–C(12)–C(13)	122·8 (2)
O(1)–C(1)–C(6)	120·5 (2)	C(12)–C(13)–C(18)	122·9 (2)
O(1)–C(1)–C(2)	117·4 (2)	C(12)–C(13)–C(14)	121·4 (2)
C(1)–C(2)–C(3)	119·3 (2)	C(14)–C(13)–C(18)	115·6 (2)
C(2)–C(3)–C(4)	119·4 (2)	C(13)–C(14)–C(15)	121·4 (3)
Cl–C(4)–C(3)	119·7 (2)	C(14)–C(15)–C(16)	120·3 (3)
C(3)–C(4)–C(5)	121·1 (2)	C(15)–C(16)–C(17)	119·8 (3)
Cl–C(4)–C(5)	119·1 (2)	C(16)–C(17)–C(18)	118·2 (3)
C(4)–C(5)–C(6)	119·6 (2)	C(13)–C(18)–C(17)	124·4 (2)
C(1)–C(6)–C(5)	118·5 (2)	O(3)–C(18)–C(17)	117·5 (2)
O(2)–C(7)–C(12)	118·8 (2)	O(3)–C(18)–C(13)	117·9 (2)

C(7)–C(12)–C(13)–C(18)	42·5 (3)	O(3)–C(18)–C(13)–C(12)	5·8 (3)
P–O(2)–C(7)–C(12)	−68·9 (2)	O(2)–C(7)–C(12)–C(13)	1·5 (3)
P–O(3)–C(18)–C(13)	−76·2 (2)	O(2)–P–O(3)–C(18)	48·4 (2)
		C(7)–O(2)–P–O(3)	41·2 (2)

& Kirby, 1986; Nuffel, Lenstra & Geise, 1981). The bond angle O(2)–P–O(3) [103·9 (1)°] is normal for six- and seven-membered-ring organophosphorus compounds (Grand & Robert, 1978). The P=S bond length, 1·894 (2) Å, is shorter than expected [1·93 Å: Wieczorek, Sheldrick, Karolak-Wojciechowska, Mikołajczyk & Ziemnicka (1979)]. This increased *s* character is due to the presence of electronegative O atoms. The dibenzo fusions at C(7)–C(12) and C(13)–C(18) cause strain in the seven-membered ring. This is evident from the widening of the angles C(8)–C(7)–C(12) [123·6 (2)°] and C(13)–C(18)–C(17) [124·4 (2)°] and compression of the angles C(7)–C(12)–C(11) [115·7 (2)°] and C(14)–C(13)–C(18) [115·6 (2)°]. The dihedral angle between the least-squares plane of the two benzene rings is 42·0 (1)°.

The molecular packing viewed down **a** is shown in Fig. 2. The crystal structure is stabilized by van der Waals interactions.
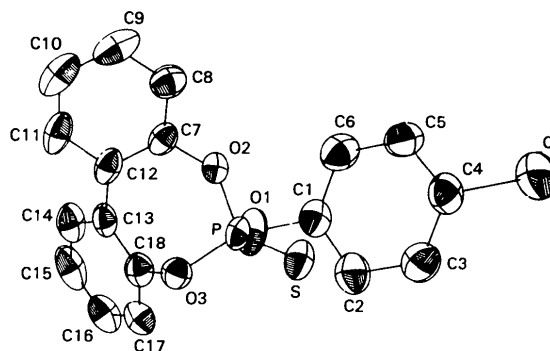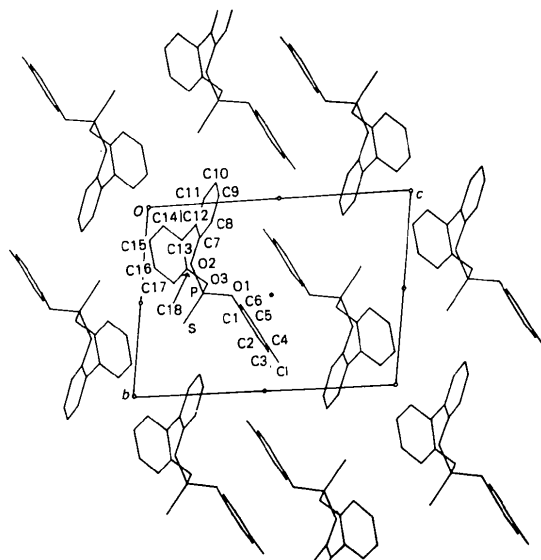

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the title compound. Thermal ellipsoids are at the 50% probability level.

Fig. 2. Molecular packing of the title compound viewed along the *a* axis.

$C_{18}H_{12}ClO_3PS$

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7-Benzyloxy-1,4-dihydro-6-methoxyisocoumarin*

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Abstract. $C_{17}H_{16}O_4$, $M_r = 284.3$, monoclinic, $P2_1/c$, $a = 10.822$ (1), $b = 13.961$ (1), $c = 10.047$ (1) Å, $\beta = 109.57$ (1)°, $V = 1430.3$ (2) Å^3, $Z = 4$, $D_m = 1.33$ (2), $D_x = 1.32$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu = 7.3$ cm^{-1}, $F(000) = 600$, $T = 294$ K, $R = 0.056$ for 2034 observed reflections. The dihydropyran ring is in the boat conformation. The phenyl ring is planar and perpendicular to the plane of the isocoumarin skeleton. The crystal packing is stabilized by van der Waals interactions.

Introduction. Many coumarin and isocoumarin derivatives are of biological importance (Michel & Durant, 1976; Schmalle, Jarchow, Hausen & Schulz, 1982). The crystal structure of the title compound has been determined as part of our program on the crystal-structure analysis of these derivatives.

Experimental. Crystals from methanol–chloroform mixture, density measured by flotation. CAD-4 diffractometer, crystal dimensions $0.20 \times 0.20 \times 0.15$ mm, monochromatized Cu$K\alpha$ radiation, cell parameters by least squares for 21 reflections with $25 \le \theta \le 35°$, intensity data for $0 < \theta < 60°$, $\omega/2\theta$ scan, two standard reflections for every 100 observations, Lp but not absorption, correction; 2242 reflec-

tions ($h\ 0\rightarrow11$, $k\ 0\rightarrow14$, $l\ -11\rightarrow11$), 2034 with $I > 3\sigma(I)$. Direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). An E map, computed from the set of phases with the largest combined figure of merit, revealed the structure. Full-matrix least-squares refinement on F; anisotropic temperature factors for C and O atoms, isotropic for H atoms. H-atom positions from difference map. $w = [\sigma^2(F_o) + 0.0315F_o^2]^{-1}$, final $R = 0.056$, $wR = 0.064$ for 2034 observed reflections; $S = 1.39$, $(\Delta/\sigma)_{max} = 0.047$, final F map featureless; excursions -0.27, 0.25 e Å^{-3}, no corrections for secondary extinction; scattering factors as in *SHELX*76 (Sheldrick, 1976). The geometrical and crystal packing were computed by the program *PARST* (Nardelli, 1983). Calculations were performed on an IBM 360/44 computer.

Discussion. Final atomic parameters are given in Table 1.† Bond distances and angles are given in Figs. 1(*a*) and 1(*b*) respectively. A thermal-ellipsoid plot of the molecule is shown in Fig. 2.

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* 7-Benzyloxy-6-methoxy-3-isochromanone.

† Lists of the structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving H atoms, torsion angles, least-squares planes and intermolecular distances less than 3.5 Å have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51625 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.