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2-Methyl-5,5-diphenyl-1,3,2λ^5-dioxaphosphorinane 2-Sulfide, $C_{16}H_{17}O_2PS$

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Abstract. $M_r = 304\cdot4$, monoclinic, $P2_1/c$, $a = 11\cdot171\ (6)$, $b = 11\cdot174\ (7)$, $c = 12\cdot604\ (8)$ Å, $\beta = 105\cdot24\ (5)°$, $V = 1518\cdot0$ Å^3, $Z = 4$, $D_x = 1\cdot332$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot315$ mm^{-1}, $F(000) = 640$, $T = 150$ K. Final $R = 0\cdot060$ for 2857 observed reflections. As predicted by the anomeric effect, the thiophosphate ring adopts a chair conformation with P=S [1·926 (1) Å] in an axial position and P—CH_3 [1·778 (2) Å] in an equatorial position; the geometrical features compare well with those of other 1,3,2-dioxaphosphorinane 2-sulfides with an axial P=S.

Introduction. In continuation of our conformational studies on 1,3,2-dioxaphosphorinane 2-sulfides and 2-oxides (Van Nuffel, Geise & Lenstra, 1981; Van Nuffel, Lenstra & Geise, 1982) the X-ray determination of 2-methyl-5,5-diphenyl-1,3,2-dioxaphosphorinane 2-sulfide (Fig. 1; abbreviated as MDPPS) was undertaken. The compound was synthesized from 2,2-diphenyl-1,3-propanediol and $CH_3P(=S)Cl_2$ following a route described by Wieber & Werther (1968). Suitable single crystals, m.p. = 371–372 K, were obtained by slow evaporation from a 96% ethanol/water solution.

Experimental. Crystal 0·2 × 0·2 × 0·3 mm. Cell dimensions determined from setting angles of 25 high-order reflections. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo radiation, pure ω-scan, range $0 < \theta \leq 27°$, $0 \leq h \leq 14$, $0 \leq k \leq 14$, $-15 \leq l \leq 15$. Three intensity- and orientation-control reflections measured every 120 min and 200 reflections respectively, no significant drift noted. Intensities not corrected for absorption because of small crystal size and low linear absorption coefficient. 3267 independent reflections measured, 2857 observed with $I > 2\cdot5\sigma(I)$. Structure solved with *MULTAN* (Germain, Main & Woolfson, 1971). An E map using terms with $E > 1\cdot6$ revealed all non-H atoms, H positions found from a difference Fourier map. Least-squares refinement on F's by Gauss–Seidel block method (Sparks, 1974) in which each individual reflection was given a weight based on counting statistics. All atom positions including H were refined, isotropic temperature factors of H atoms fixed to 3 Å^2; $R = 0\cdot060$, $R_w = 0\cdot070$. Extinction parameter refined as $0\cdot38\ (4) \times 10^{-6}$ mm. Max. peak in final difference Fourier map 0·3 e Å^{-3}. Max. least-squares parameter shift $0\cdot04\sigma$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer calculations all with Enraf–Nonius CAD-4 *SDP* (Frenz, 1978).

Discussion. Relevant parameters† are listed in Table 1; the numbering of the atoms is given in Fig. 1 and the packing in Fig. 2.

The anomeric effect – maximization of overlap between the n_π lone pairs of O(1) and O(3) with the energetically lowest σ^* orbital – predicts the chair conformation for the 1,3,2-dioxaphosphorinane ring with P=S in axial and P—CH_3 in equatorial position. This form is indeed observed. Bonded distances, valence and endocyclic torsion angles are given in Table 2. An excellent agreement is observed between the geometrical features of the title compound and those of structurally related 1,3,2-dioxaphosphorinane 2-sulfides with an axial P=S, *e.g.* with 2,5,5-trimethyl-1,3,2-dioxaphosphorinane 2-sulfide (Grand & Robert, 1978) and *cis*-2,5-di-*tert*-butyl-1,3,2-dioxaphosphorinane 2-sulfide (Warrent, Caughlan, Hargis, Yee & Bentrude, 1978).

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† Lists of structure factors, H-atom positions and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39345 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters of the molecule in fractions of the cell edges, with e.s.d.'s in parentheses, and isotropic thermal parameters*

Isotropic temperature parameters (Å^2) are calculated from anisotropic temperature parameters assuming equal volume of the 50% probability region according to Lipson & Cochran (1968): $B_{\rm iso} = 8\pi^2(U^\circ_{11}U^\circ_{22}U^\circ_{33})^{1/3}$. All anisotropic parameters were physically acceptable.

	x	y	z	$B_{\rm iso}$
O(1)	0·9249 (2)	0·0884 (2)	0·1487 (2)	1·92
P(2)	0·87380 (7)	0·18993 (8)	0·05822 (7)	1·95
O(3)	0·7357 (2)	0·1458 (2)	0·0001 (2)	1·80
C(4)	0·6602 (3)	0·1159 (3)	0·0752 (2)	1·77
C(5)	0·7201 (3)	0·0191 (3)	0·1598 (2)	1·52
C(6)	0·8490 (3)	0·0636 (3)	0·2248 (2)	1·83
C(7)	0·7353 (2)	−0·1016 (3)	0·1058 (2)	1·46
C(8)	0·7924 (3)	−0·1960 (3)	0·1725 (2)	1·89
C(9)	0·8054 (3)	−0·3073 (3)	0·1275 (3)	2·26
C(10)	0·7596 (3)	−0·3275 (3)	0·0157 (3)	2·49
C(11)	0·7032 (3)	−0·2350 (3)	−0·0517 (3)	2·23
C(12)	0·6914 (3)	−0·1212 (3)	−0·0080 (2)	1·76
C(13)	0·6303 (3)	0·0075 (3)	0·2336 (2)	1·72
C(14)	0·5379 (3)	−0·0793 (3)	0·2114 (2)	1·86
C(15)	0·4467 (3)	−0·0821 (3)	0·2671 (3)	2·39
C(16)	0·4472 (3)	0·0014 (3)	0·3498 (3)	2·67
C(17)	0·5400 (3)	0·0881 (3)	0·3727 (3)	2·88
C(18)	0·6306 (3)	0·0914 (3)	0·3158 (3)	2·48
S(19)	0·88162 (9)	0·34970 (8)	0·11699 (9)	3·08
C(20)	0·9528 (3)	0·1593 (3)	−0·0442 (3)	2·91

Table 2. *Molecular geometry of MDPPS with e.s.d.'s in parentheses*

(*a*) Bond lengths (Å)

P(2)—O(1)	1·604 (1)	P(2)—O(3)	1·601 (1)
O(1)—C(6)	1·465 (2)	O(3)—C(4)	1·463 (2)
C(6)—C(5)	1·540 (2)	C(4)—C(5)	1·543 (2)
C(5)—C(7)	1·540 (3)	C(5)—C(13)	1·544 (3)
C(7)—C(8)	1·395 (3)	C(13)—C(14)	1·390 (3)
C(8)—C(9)	1·390 (3)	C(14)—C(15)	1·382 (3)
C(9)—C(10)	1·385 (3)	C(15)—C(16)	1·397 (3)
C(10)—C(11)	1·381 (3)	C(16)—C(17)	1·392 (3)
C(11)—C(12)	1·406 (3)	C(17)—C(18)	1·387 (3)
C(12)—C(7)	1·405 (3)	C(18)—C(13)	1·397 (3)
P(2)=S(19)	1·926 (1)	P(2)—C(20)	1·778 (2)

$\langle \text{C—H} \rangle = 0{\cdot}96\ (2)$

(*b*) Bond angles (°)

P(2)—O(1)—C(6)	116·1 (1)	P(2)—O(3)—C(4)	115·1 (1)
O(1)—P(2)—O(3)	103·2 (1)	C(4)—C(5)—C(6)	108·5 (2)
O(1)—P(2)=S(19)	114·3 (1)	C(4)—C(5)—C(7)	112·8 (2)
O(1)—P(2)—C(20)	103·2 (1)	C(4)—C(5)—C(13)	104·1 (2)
O(3)—P(2)=S(19)	113·7 (1)	C(6)—C(5)—C(7)	108·8 (2)
O(3)—P(2)—C(20)	102·2 (1)	C(6)—C(5)—C(13)	111·8 (2)
S(19)=P(2)—C(20)	118·5 (1)	C(7)—C(5)—C(13)	111·0 (2)
O(3)—C(4)—C(5)	112·9 (1)	O(1)—C(6)—C(5)	109·5 (2)
C(5)—C(7)—C(8)	118·8 (2)	C(5)—C(13)—C(14)	120·2 (2)
C(5)—C(7)—C(12)	122·6 (2)	C(5)—C(13)—C(18)	121·0 (2)
C(8)—C(7)—C(12)	118·6 (2)	C(14)—C(13)—C(18)	118·4 (2)
C(7)—C(8)—C(9)	120·7 (2)	C(13)—C(14)—C(15)	121·4 (2)
C(8)—C(9)—C(10)	120·8 (2)	C(14)—C(15)—C(16)	120·4 (2)
C(9)—C(10)—C(11)	119·4 (2)	C(15)—C(16)—C(17)	118·4 (2)
C(10)—C(11)—C(12)	120·7 (2)	C(16)—C(17)—C(18)	121·1 (2)
C(11)—C(12)—C(7)	119·8 (2)	C(17)—C(18)—C(13)	120·4 (2)

(*c*) Torsion angles (°) of the 1,3,2-dioxaphosphorinane ring

C(6)—O(1)—P(2)—O(3)	−54·1 (5)	O(3)—C(4)—C(5)—C(6)	57·5 (5)
O(1)—P(2)—O(3)—C(4)	50·6 (5)	C(4)—C(5)—C(6)—O(1)	−58·3 (5)
P(2)—O(3)—C(4)—C(5)	−56·9 (5)	C(5)—C(6)—O(1)—P(2)	61·4 (5)

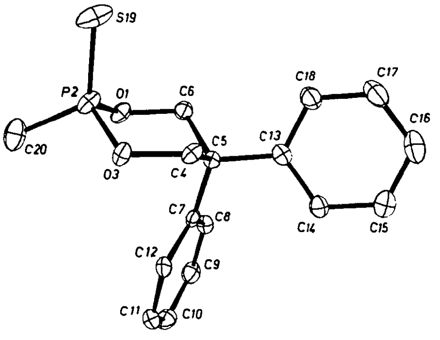

Fig. 1. Conformation of the molecule and numbering of the atoms.

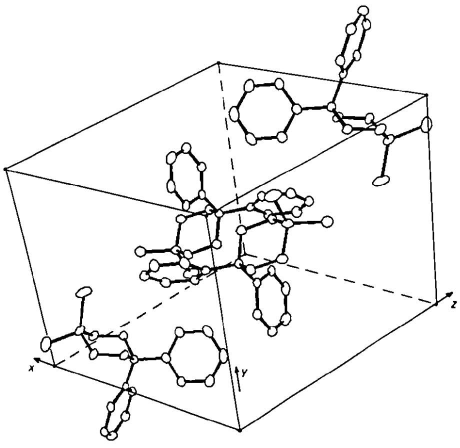

Fig. 2. The contents of a unit cell.

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