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Bis(diphenylphosphino)methane Disulfide

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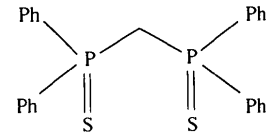
Abstract

The title compound, methylenebis(diphenylphosphine sulfide), $C_{25}H_{22}P_2S_2$, has been structurally characterized and is found to be isostructural with its selenium analog.

Comment

A number of compounds related to the title compound have been characterized previously by X-ray crystallography. Relevant structures include $Ph_2PCH_2PPh_2$ (dppm) [(1); Schmidbaur, Reber, Schier, Wagner & Müller, 1988], $Ph_2P(Se)CH_2P(Se)Ph_2$ (dppmSe$_2$) [(2); Carroll & Titus, 1971] and the related compound $Ph_2PCH_2P(Se)Ph_2$ (dppmSe) [(3); Colton, Hoskins & Panagiotidou, 1987]. The title compound, $Ph_2P(S)CH_2P(S)Ph_2$ (dppmS$_2$), (4), is isostructural with compound (2) and its crystal structure is reported herein.



(4)

The structure of (4) is comprised of discrete monomers with no short intermolecular interactions. A view of the molecular structure of (4) is shown in Fig. 1, with a packing view shown in Fig. 2. The P—S bond lengths [P(1)—S(1) 1.948 (1) and P(2)—S(2) 1.909 (1) Å] in (4) are slightly shorter than the corresponding P—Se bond distances found in compounds (2) [average P—Se 2.100 (4) Å] and (3) [P—Se 2.103 (1) Å]. All other bond lengths are similar to those observed in compounds (1)–(3) and deserve no special comment.

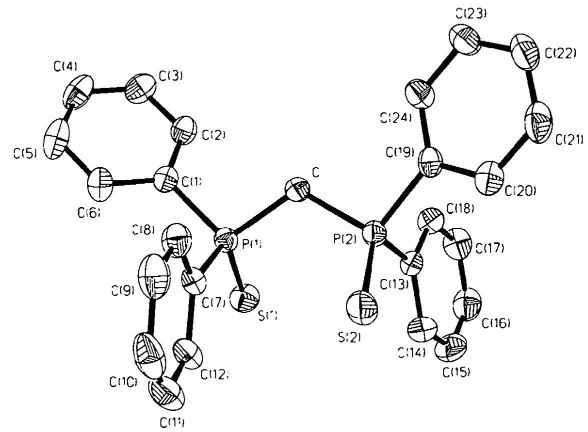


Fig. 1. The structure of compound (4) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

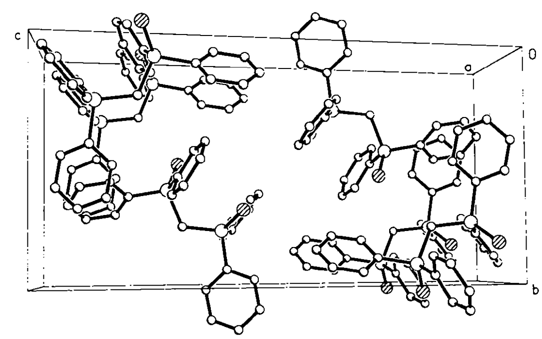


Fig. 2. A view of the packing in compound (4).

The coordination geometry around each P atom in (4) is distorted tetrahedral, with all bond angles similar to the corresponding angles in compound (2). The only significant difference between the dppm moiety of (4) and dppm, (1), itself is the P—C—P bond angle. In (1), the P—C—P angle is 106.2 (3)°, whereas in (4), the angle is several degrees larger with a value of 118.4 (2)° [P(1)—C—P(2)]. In compound (2), the P—C—P angle has a value of 117.9 (6)°, similar to (4), whereas in compound (3), the angle has an intermediate value of 110.6 (2)°. The structures of compounds (2) and (4) are also similar with regard to the Se—P···P—Se and S—P···P—S torsion angles, which are 95.4 and 95.64 (5)°, respectively.

Experimental

A sample of sulfur (0.143 g, 4.46 mmol) was added to a solution of dppm (0.858 g, 2.23 mmol) in toluene (10 ml) at room temperature resulting in a color change from colorless to pale yellow. The mixture was then heated and stirred for about 30 min. On cooling to 243 K, a crystalline pale-cream solid was obtained after a few days (0.790 g, 80% yield). X-ray quality crystals of (4) were subsequently obtained in near quantitative yield from the reaction between bis(biphenylylene)Br (Carmalt, Cowley, Decken, Lawson & Norman, 1996) and dppmS_2 in CH_2Cl_2, after solvent diffusion of hexane. Elemental analysis: found C 66.55, H 4.67%; calculated for $C_{25}H_{22}P_2S_2$ C 66.95, H 4.95%.

Crystal data

$C_{25}H_{22}P_2S_2$	Mo $K\alpha$ radiation
$M_r = 448.49$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	$\theta = 9–12°$
$a = 9.527$ (1) Å	$\mu = 0.385$ mm^{-1}
$b = 10.731$ (1) Å	$T = 293$ (2) K
$c = 22.525$ (2) Å	Irregular
$\beta = 99.63$ (1)°	0.60 × 0.54 × 0.35 mm
$V = 2270.4$ (4) Å^3	Colorless
$Z = 4$	
$D_x = 1.312$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.024$
$2\theta/\omega$ scans	$\theta_{max} = 24.97°$
Absorption correction: none	$h = -1 \rightarrow 11$
5331 measured reflections	$k = -1 \rightarrow 12$
3976 independent reflections	$l = -26 \rightarrow 26$
3052 observed reflections [$I > 2\sigma(I)$]	3 standard reflections frequency: 60 min intensity decay: 5%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$\Delta\rho_{max} = 0.409$ e Å^{-3}
$wR(F^2) = 0.108$	$\Delta\rho_{min} = -0.168$ e Å^{-3}
$S = 1.124$	Extinction correction: none
3974 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
329 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 1.00P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P(1)	0.0083 (1)	0.9115 (1)	0.2358 (1)	0.041 (1)
P(2)	−0.0180 (1)	0.7375 (1)	0.1222 (1)	0.044 (1)
S(1)	0.1454 (1)	1.0281 (1)	0.2120 (1)	0.060 (1)
S(2)	−0.1863 (1)	0.8229 (1)	0.0812 (1)	0.071 (1)
C	0.0171 (3)	0.7554 (3)	0.2042 (1)	0.043 (1)
C(1)	0.0350 (3)	0.8840 (2)	0.3164 (1)	0.045 (1)
C(2)	0.1452 (3)	0.8092 (3)	0.3432 (1)	0.056 (1)
C(3)	0.1691 (4)	0.7908 (4)	0.4048 (1)	0.070 (1)
C(4)	0.0857 (4)	0.8476 (4)	0.4400 (2)	0.076 (1)
C(5)	−0.0233 (4)	0.9221 (4)	0.4143 (2)	0.079 (1)
C(6)	−0.0490 (4)	0.9417 (3)	0.3525 (2)	0.064 (1)
C(7)	−0.1759 (3)	0.9570 (2)	0.2154 (1)	0.045 (1)
C(8)	−0.2833 (3)	0.8794 (3)	0.2285 (1)	0.058 (1)
C(9)	−0.4241 (3)	0.9100 (4)	0.2073 (2)	0.070 (1)
C(10)	−0.4567 (4)	1.0162 (4)	0.1745 (2)	0.079 (1)
C(11)	−0.3523 (4)	1.0932 (4)	0.1625 (2)	0.076 (1)
C(12)	−0.2110 (4)	1.0643 (3)	0.1833 (1)	0.059 (1)
C(13)	0.1439 (3)	0.7815 (2)	0.0956 (1)	0.047 (1)
C(14)	0.1431 (4)	0.8785 (3)	0.0553 (1)	0.065 (1)
C(15)	0.2635 (5)	0.9086 (4)	0.0323 (2)	0.083 (1)
C(16)	0.3861 (5)	0.8432 (4)	0.0497 (2)	0.079 (1)
C(17)	0.3898 (4)	0.7484 (4)	0.0897 (2)	0.070 (1)
C(18)	0.2704 (3)	0.7160 (3)	0.1129 (1)	0.055 (1)
C(19)	−0.0338 (3)	0.5697 (3)	0.1118 (1)	0.044 (1)
C(20)	−0.1043 (3)	0.5269 (3)	0.0567 (1)	0.060 (1)
C(21)	−0.1212 (4)	0.4011 (4)	0.0460 (2)	0.072 (1)
C(22)	−0.0712 (4)	0.3173 (3)	0.0897 (2)	0.070 (1)
C(23)	−0.0011 (4)	0.3576 (3)	0.1441 (2)	0.067 (1)
C(24)	0.0188 (3)	0.4837 (3)	0.1555 (1)	0.056 (1)

Table 2. *Selected geometric parameters (Å, °)*

P(1)—C(7)	1.806 (3)	P(2)—C(13)	1.808 (3)
P(1)—C(1)	1.814 (3)	P(2)—C(19)	1.819 (3)
P(1)—C	1.827 (3)	P(2)—C	1.831 (3)
P(1)—S(1)	1.948 (1)	P(2)—S(2)	1.941 (1)
C—C bond distances: 1.354 (4)–1.393 (6), average 1.374 (12)			
C(7)—P(1)—C(1)	105.4 (1)	C—P(2)—S(2)	115.3 (1)
C(7)—P(1)—C	104.8 (1)	P(1)—C—P(2)	118.4 (2)
C(1)—P(1)—C	103.5 (1)	C(2)—C(1)—P(1)	120.1 (2)
C(7)—P(1)—S(1)	115.1 (1)	C(6)—C(1)—P(1)	121.3 (2)
C(1)—P(1)—S(1)	113.09 (9)	C(12)—C(7)—P(1)	120.1 (2)
C—P(1)—S(1)	113.9 (1)	C(8)—C(7)—P(1)	120.2 (2)
C(13)—P(2)—C(19)	105.8 (1)	C(14)—C(13)—P(2)	120.2 (2)
C(13)—P(2)—C	106.5 (1)	C(18)—C(13)—P(2)	121.5 (2)
C(19)—P(2)—C	103.4 (1)	C(24)—C(19)—P(2)	123.9 (2)
C(13)—P(2)—S(2)	113.7 (1)	C(20)—C(19)—P(2)	117.4 (2)
C(19)—P(2)—S(2)	111.22 (9)		

H atoms were located in the difference synthesis map and their coordinates refined with common isotropic displacement parameters. C—H bond distances range from 0.85 to 0.96 (3) Å, with an average value of 0.91 (3) Å.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 *Software* (Siemens, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Absolute Configuration of 6-*O*-*p*-Bromobenzoylsalvileucolide Methyl Ester

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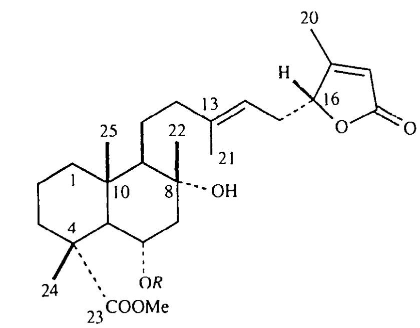
Abstract

The absolute configuration of the title compound, methyl 8-(4-bromobenzoyloxy)-5-[5-(2,5-dihydro-3-methyl-5-oxo-2-furanyl)-3-methyl-3-pentenyl]-6-hydroxy-1,4a,6-trimethyldecahydronaphthalene-1-carboxylate, $C_{33}H_{43}BrO_7$, a derivative of the sesterterpenoid salvileucolide methyl ester isolated from the aerial parts of two Iranian Salvia species, has been determined at 173 K. The compound belongs to the normal (10*R*) series and the configuration at C(16) is also *R*.

Comment

Salvileucolide methyl ester, (I), has been isolated as the major constituent from the aerial parts of *Salvia hypoleuca* (Rustaiyan, Niknejad, Nazarians, Jakupovic & Bohlmann, 1982) and *S. sahendica* (Matloubi Moghaddam, Zaynizadeh & Rüedi, 1995), both species being endemic to Iran. In the previous studies, the conformation of (I) was assigned by spectroscopic methods, especially by extensive ^{1}H and ^{13}C NMR experiments. The relative configuration at C(16) and the absolute configuration of the molecule, however, remained undetermined. Chemical transformation of (I) to an established reference compound (*e.g.* a suitable labdane derivative) and comparison of the chiroptical data would quite easily provide the absolute configuration of the skeleton. The determination of the stereochemistry at C(16) [*e.g.* by degradation of (I) to a 3-hydroxypentanoic acid derivative], however, is not expected to be unambiguously feasible without difficulties, probably due to racemization. This fact prompted us to undertake the X-ray analysis of the 6-O-*p*-bromobenzoyl ester, (II), where the Br atom greatly facilitates the direct determination of the absolute configuration. We now report the crystal structure of (II), which thereby establishes the structure of (I).



(I) $R = H$
(II) $R = p$-Br-benzoyl

The correct absolute configuration of (II), determined by refinement of the structure and the enantiopole parameter according to the method of Flack (1983), is depicted in Fig. 1. The compound has the 4*R*,6*S*,8*R*,9*R*,10*R*,13*E*,16*R* configuration. Therefore, as previously assumed (Rustaiyan *et al.*, 1982; Matloubi Moghaddam *et al.*, 1995), the natural product (I) belongs to the normal cyclic sesterterpenoid (10*R*) series and has an *R* configuration at C(16).

The bond lengths and angles generally have normal values. The two most significant exceptions are the values of 101.2 (4) and 130.3 (6)° for C(3)—C(4)—C(23) and C(18)—C(17)—C(20), respectively. These angles probably result from steric interactions between the two neighbouring ester groups in the first case and between the coplanar methyl group, C(20), and