Monoclinic
$P2_1/n$
$a = 9.0207\,(6)$ Å
$b = 10.1127\,(8)$ Å
$c = 10.5364\,(10)$ Å
$\beta = 111.809\,(6)^\circ$
$V = 892.38\,(13)$ Å^3
$Z = 4$
$D_x = 1.170$ Mg m^{-3}
D_m not measured

Cell parameters from 65 reflections
$\theta = 5.0$–12.5°
$\mu = 0.083$ mm^{-1}
$T = 173\,(2)$ K
Flattened pyramid
$0.45 \times 0.45 \times 0.30$ mm
Pale yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3733 measured reflections
2048 independent reflections
1648 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

$\theta_{\rm max} = 27.5^\circ$
$h = -11 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.103$
$S = 1.050$
2048 reflections
104 parameters
H atoms: rigid methyls and OH, others riding

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.0536P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.244$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.192$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.3373 (13)	C3—C4	1.5412 (14)
N1—C5	1.4633 (14)	C4—C5	1.5405 (15)
C2—C3	1.5294 (15)		
C2—N1—C5	112.59 (9)	C5—C4—C3	101.10 (8)
N1—C2—C3	108.20 (9)	N1—C5—C4	103.68 (8)
C2—C3—C4	103.49 (8)		
C5—N1—C2—C3	1.69 (12)	C2—N1—C5—C4	−21.76 (12)
N1—C2—C3—C4	19.05 (11)	C3—C4—C5—N1	31.41 (11)
C2—C3—C4—C5	−30.37 (10)		

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1349). Services for accessing these data are described at the back of the journal.

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A New Modification of Bis(diphenylphosphino)methane Diselenide

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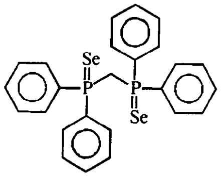
Abstract

In the title compound, $C_{25}H_{22}P_2Se_2$ (dppmSe$_2$), the methylene C atom lies on a crystallographic twofold axis, in contrast to the previously known modification, which had no imposed symmetry. The conformation is expressed by the torsion angle Se—P···P—Se 148.12 (7)°. Bond lengths and angles are similar to those in other dppmX_2 molecules.

Comment

Bis(diphenylphosphino)methane (dppm) and its dichalcogenide derivatives (with O, S, Se) are well known compounds (Grim & Walton, 1980, and references therein). Structures are known for dppm (Schmidbaur *et al.*, 1988), dppmO$_2$ (Antipin *et al.*, 1980), dppmS$_2$ (Carmalt *et al.*, 1996), and dppmSe$_2$ (isostructural with dppmS$_2$) (Carroll & Titus, 1977), and also for the fluorinated derivative $(Ph_2PS)_2CF_2$ (dppfmS$_2$) (Jones & Bembenek, 1996).

We have fortuitously obtained a new modification of dppmSe$_2$, (1), crystallizing in the space group *C*2/*c* with the methylene C atom lying on a twofold axis; the previously known modification crystallized in $P2_1/c$ (Carroll & Titus, 1977) with no imposed symmetry.



(1)

The new modification shows some minor changes in bond lengths with respect to those of the previous form: the P—CH$_2$ bond is slightly shorter [1.828 (3) *cf.* 1.853 (11) and 1.833 (10) Å] and the P···P distance is slightly longer [3.183 (2) *cf.* 3.1567 (4) Å]. The P—Se bond length [2.1029 (12) Å] is, however, closely similar to the previous values [2.103 (3) and 2.097 (4) Å].

The P—C—P bond angle is widened appreciably from 106.2 (3)° in dppm to 121.1 (3)° in the title compound; this is a general feature of all dppmX_2 structures [dppmO$_2$: 119.5 (4) and 121.3 (4)° in two independent molecules; dppmS$_2$: 118.4 (2)°; $P2_1/c$ modification of dppmSe$_2$: 117.9 (6)°; dppfmS$_2$: 116.89 (13)°].

The coordination geometry at the P atom is distorted tetrahedral [angles 102.5–115.9° in the various dppm derivatives; 104.2 (2)–113.06 (6)° in the title compound]. As expected, the narrower angles are C—P—C angles and the widest involve the Se atom; this is a general feature of P═X structural units.

The conformations of the dppmX_2 species show considerably greater variation. The X—P···P—X torsion angles are 148.12 (7)° in the title compound, 95.4 (1)° in the earlier modification, 95.64 (5)° in dppmS$_2$, 90.76 (5)° in dppfmS$_2$, and 169.7 and 177.9° in dppmO$_2$. The orientations of the phenyl rings also differ considerably; values of the relevant torsion angles for the title compound are given in Table 1.

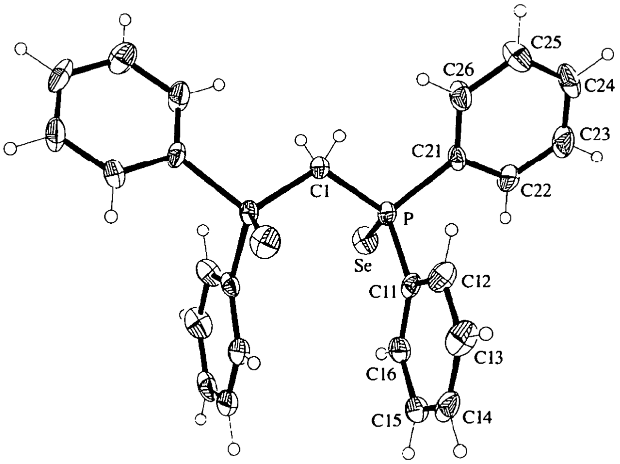


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

Experimental

Crystals of compound (1) were obtained during an attempt to synthesize OdppmSe from dppmSe and H$_2$O$_2$ (Grim & Walton, 1988) in dichloromethane.

Crystal data

$C_{25}H_{22}P_2Se_2$
$M_r = 542.29$
Monoclinic
$C2/c$
$a = 21.903\ (4)$ Å
$b = 10.4490\ (14)$ Å
$c = 10.1168\ (14)$ Å
$\beta = 107.298\ (12)^\circ$
$V = 2210.6\ (6)$ Å^3
$Z = 4$
$D_x = 1.629$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 63 reflections
$\theta = 4$–11.5°
$\mu = 3.500$ mm^{-1}
$T = 173\ (2)$ K
Prism
0.58 × 0.12 × 0.06 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\min} = 0.682$, $T_{\max} = 0.811$
3490 measured reflections
1941 independent reflections
1395 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\max} = 25^\circ$
$h = -26 \rightarrow 26$
$k = -4 \rightarrow 12$
$l = -12 \rightarrow 7$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 0.925$
1941 reflections
132 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.534$ e Å^{-3}
$\Delta\rho_{\min} = -0.522$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Se—P	2.1029 (12)	P—C1	1.828 (3)
P—C11	1.817 (4)	P—C21	1.829 (4)
C11—P—C1	108.65 (18)	C1—P—Se	113.06 (6)
C11—P—C21	104.18 (19)	C21—P—Se	112.27 (14)
C1—P—C21	105.4 (2)	P—C1—P$^{\rm i}$	121.1 (3)
C11—P—Se	112.70 (15)		
Se—P—C11—C12	168.2 (3)	Se—P—C21—C26	130.4 (4)
Se—P—C11—C16	−12.2 (4)	Se—P—P$^{\rm i}$—Se$^{\rm i}$	148.12 (7)
Se—P—C21—C22	−49.2 (4)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1358). Services for accessing these data are described at the back of the journal.

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8-Hydroxy-4-methyl-9-phenylthio-7,8,9,10-tetrahydro-7,8-benzocoumarin

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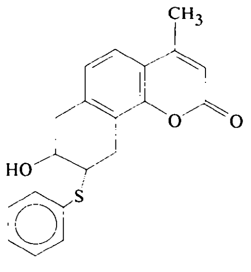
Abstract

In the title molecule (alternative name: 8-hydroxy-4-methyl-9-phenylthio-7,8,9,10-tetrahydro-2*H*-benzo[*f*]chromen-2-one; $C_{20}H_{18}O_3S$), the tetrahydrobenzene ring is in a half-chair conformation. The planes of the coumarin and thiophenyl rings form a dihedral angle of 126.31 (5)°. The crystal structure is stabilized by O—H···O hydrogen bonds involving carbonyl and hydroxy O atoms.

Comment

Coumarin derivatives are found in natural products and exhibit antifungal and anticoagulant properties (Parrish *et al.*, 1974; Barry & Toste, 1996). Amino and hydroxy coumarin derivatives are widely used in laser dyes (Maeda, 1984). The crystal structure determination of the title compound, (I), was undertaken as part of our structural studies on coumarin derivatives.



(I)

The coumarin ring system and tetrahydrobenzene ring have normal bond lengths and angles (Chinnakali, Sivakumar & Natarajan, 1992; Chinnakali *et al.*, 1997). The mean value of the C—C lengths in the phenyl ring is 1.376 (3) Å. The coumarin moiety is planar within ±0.029 (1) Å. Planarity of the coumarin system is usually observed (Gnanaguru *et al.*, 1985). The tetrahydrobenzene ring adopts a half-chair conformation with C13 and C14 deviating from the mean plane by −0.329 (2) and 0.436 (2) Å, respectively. The asymmetry parameter (Nardelli, 1983*a*) ΔC_2(C7—C8) is 0.018 (1). The thiophenyl ring is planar and makes a dihedral angle of 126.31 (5)° with the coumarin plane.

In the crystal, the glide-related molecules are linked by O—H···O hydrogen bonds involving the hy-

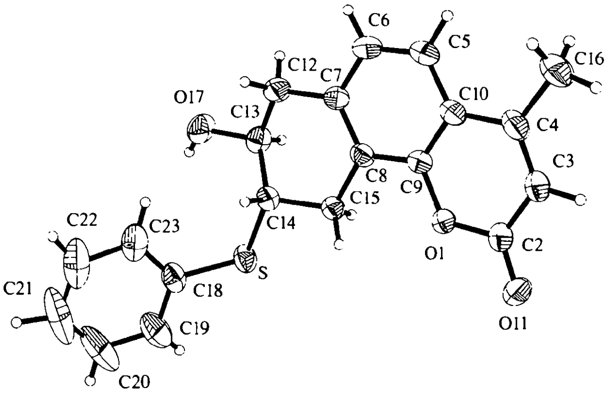


Fig. 1 The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.