

## 5-Phenyldibenzophosphole 5-Selenide\*

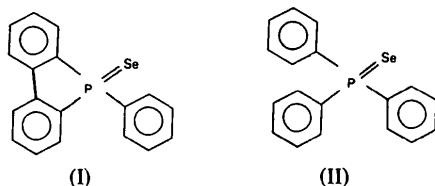
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**Abstract.**  $C_{18}H_{13}PSe$ ,  $M_r = 339.2$ , monoclinic,  $P2_1/n$ ,  $a = 20.080$  (3),  $b = 8.842$  (5),  $c = 17.834$  (2) Å,  $\beta = 105.23$  (1)°,  $V = 3055$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.475$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 25.2$  cm<sup>-1</sup>,  $F(000) = 1360$ ,  $T = 294$  K,  $R = 0.039$  for 1554 observed reflections. The two independent molecules in the asymmetric unit differ mainly in the orientation of the unrestricted phenyl ring with respect to the P=Se bond. Principal bond lengths are P=Se 2.086 (3), 2.110 (2), P–C(aromatic) 1.772 (10)–1.812 (9), mean 1.794 Å. The mean maximum cone angle for 5-phenyldibenzophosphole (in its selenide) is 155°, some 13° smaller than the corresponding value for triphenylphosphine in triphenylphosphine selenide.

**Introduction.** Growing interest in the metal complexes of phospholes (Mathey, Fischer & Nelson, 1983) led us to investigations of the relative coordinating ability of 5-phenyldibenzophosphole (5-PhDBP) and triphenylphosphine (Ph<sub>3</sub>P) (Alyea & Nelson, 1985, unpublished work). To evaluate the steric properties of these two related ligands, we undertook this crystal-structure analysis of 5-phenyldibenzophosphole 5-selenide (I) to allow a direct comparison with the known structure of Ph<sub>3</sub>PSe (II) (Coddling & Kerr, 1979).



**Experimental.** Pale-yellow plates crystallized from 1:3 chloroform: *n*-hexane solution, 0.10 × 0.35 × 0.35 mm. Enraf–Nonius CAD-4 diffractometer, Mo radiation, graphite monochromator,  $\omega$ -2 $\theta$  scans. Unit-cell dimensions and crystal orientation matrix from least-squares refinement of setting angles of 25 reflections with  $10 < \theta < 15^\circ$ . Intensity data collected with

$2 < \theta < 20^\circ$  corresponding to  $h0 \rightarrow 19$ ,  $k0 \rightarrow 8$ ,  $l-17 \rightarrow 17$ . Intensities of three reflections monitored every 50 min of exposure time showed no evidence of decay. 3338 reflections measured of which 2844 unique ( $R_{\text{int}} = 0.024$ ), of these 1554 with  $I > 3\sigma(I)$  labelled observed. Space group determined uniquely from systematic absences ( $h0l$  absent if  $h + l = 2n + 1$ ,  $0k0$  absent if  $k = 2n + 1$ ). Data corrected for Lorentz and polarization effects, no correction for absorption. All calculations performed on a PDP11-73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1984) system of programs. Structure solved by heavy-atom method, P and Se atoms from Patterson synthesis. Refinement by full-matrix least-squares calculations initially with isotropic and finally with anisotropic thermal parameters for non-H atoms. H atoms visible in difference maps and included in idealized positions (C–H 0.95 Å) but not refined in final refinement cycles. At convergence,  $R = 0.0387$ ,  $wR = 0.0422$  for the 1554 observed data,  $R = 0.1077$  for all data. Goodness-of-fit 1.13. 362 variables. Max. shift/e.s.d. ratios 0.02 for  $y$  coordinate of C(135) and 0.02 for  $b_{22}$  parameter of C(134). Final difference map had peaks  $\pm 0.3$  e Å<sup>-3</sup> near Se but no chemically significant features. Weighting scheme  $w = 1/[\sigma^2(F_o) + 0.05F_o^2]$ ,  $\sum w(\Delta F)^2$  minimized. Scattering-factor data and anomalous-dispersion corrections from Cromer (1974) and Cromer & Waber (1974). Atomic coordinates and equivalent  $B$  values are in Table 1.‡ Selected bond distances and angles are in Table 2. *ORTEPII* (Johnson, 1976) views of the two independent molecules are given in Fig. 1.

**Discussion.** The crystal structure contains discrete molecules separated by normal van der Waals distances. The principal difference between the two independent molecules is in the orientation of the pendant phenyl rings [torsion angles Se(1)–P(1)–

‡ Lists of structure factors, anisotropic thermal parameters, calculated H coordinates, complete interatomic distances and angles, torsion angles and mean-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42830 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Alternative name: 5-phenylbenzo[*b*]phosphindole 5-selenide.

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters for  $C_{18}H_{13}PSe$  with *e.s.d.'s* in parentheses

	x	y	z	$B_{eq}(\text{\AA}^2)$
Se(1)	0.58486 (5)	0.30779 (12)	0.08511 (5)	5.33 (3)
Se(2)	0.91773 (6)	-0.26508 (12)	0.00657 (6)	6.35 (3)
P(1)	0.6393 (1)	0.2871 (3)	0.2031 (1)	3.83 (6)
P(2)	0.8658 (1)	-0.1195 (3)	0.0639 (1)	4.01 (6)
C(111)	0.7223 (4)	0.3739 (9)	0.2273 (4)	3.4 (2)
C(112)	0.7617 (4)	0.3639 (11)	0.1756 (5)	5.3 (3)
C(113)	0.8276 (5)	0.4193 (12)	0.1942 (5)	6.4 (3)
C(114)	0.8558 (5)	0.4867 (12)	0.2638 (6)	6.4 (3)
C(115)	0.8157 (5)	0.5029 (11)	0.3154 (5)	6.1 (3)
C(116)	0.7496 (5)	0.4432 (10)	0.2971 (5)	4.7 (2)
C(121)	0.5920 (4)	0.3433 (10)	0.2721 (4)	3.9 (2)
C(122)	0.5840 (4)	0.2259 (10)	0.3185 (4)	4.2 (2)
C(123)	0.5428 (5)	0.2455 (12)	0.3694 (5)	6.7 (3)
C(124)	0.5131 (5)	0.3804 (15)	0.3740 (5)	8.6 (4)
C(125)	0.5242 (5)	0.4989 (13)	0.3302 (5)	7.6 (3)
C(126)	0.5633 (5)	0.4818 (11)	0.2765 (5)	5.5 (3)
C(131)	0.6510 (4)	0.1003 (10)	0.2438 (5)	4.3 (2)
C(132)	0.6196 (5)	0.0902 (9)	0.3037 (4)	4.5 (2)
C(133)	0.6278 (6)	-0.0449 (12)	0.3449 (5)	7.2 (3)
C(134)	0.6630 (7)	-0.1601 (11)	0.3243 (6)	8.8 (4)
C(135)	0.6935 (6)	-0.1516 (11)	0.2639 (6)	7.6 (3)
C(136)	0.6860 (5)	-0.0164 (10)	0.2220 (5)	5.8 (3)
C(211)	0.9029 (4)	-0.1011 (9)	0.1677 (4)	3.8 (2)
C(212)	0.9572 (4)	-0.1878 (10)	0.2047 (5)	5.6 (3)
C(213)	0.9859 (5)	-0.1767 (13)	0.2841 (6)	7.7 (3)
C(214)	0.9585 (5)	-0.0801 (14)	0.3272 (5)	8.9 (4)
C(215)	0.9048 (6)	0.0053 (14)	0.2904 (5)	8.5 (4)
C(216)	0.8751 (5)	-0.0021 (12)	0.2105 (5)	6.1 (3)
C(221)	0.8510 (4)	0.0687 (9)	0.0262 (4)	3.4 (2)
C(222)	0.7811 (4)	0.1030 (9)	0.0061 (4)	3.6 (2)
C(223)	0.7583 (4)	0.2449 (10)	-0.0252 (5)	4.5 (2)
C(224)	0.8074 (5)	0.3449 (10)	-0.0333 (5)	5.7 (3)
C(225)	0.8763 (5)	0.3129 (11)	-0.0144 (5)	6.0 (3)
C(226)	0.8997 (4)	0.1711 (10)	0.0172 (5)	4.6 (2)
C(231)	0.7760 (4)	-0.1489 (9)	0.0485 (4)	3.6 (2)
C(232)	0.7377 (4)	-0.0223 (10)	0.0165 (4)	3.7 (2)
C(233)	0.6663 (4)	-0.0297 (10)	-0.0006 (5)	4.8 (3)
C(234)	0.6335 (4)	-0.1557 (12)	0.0116 (5)	5.8 (3)
C(235)	0.6710 (5)	-0.2832 (11)	0.0434 (5)	6.3 (3)
C(236)	0.7429 (4)	-0.2784 (10)	0.0616 (5)	5.0 (3)

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

C(111)–C(112)  $-38.7(4)$ , Se(2)–P(2)–C(211)–C(212)  $-5.4(4)^\circ$ ]. The molecular dimensions are entirely in accord with those found in related molecules. The mean P=Se distance  $2.098(3)\text{\AA}$  agrees with the values  $2.106(1)\text{\AA}$  found in triphenylphosphine selenide (Coddling & Kerr, 1979),  $2.109(5)\text{\AA}$  in tri-*m*-tolylphosphine selenide (Cameron, Howlett & Miller, 1978) and others ( $1.933$ – $2.123\text{\AA}$ ) listed in Table 5 of Gałdecki, Głowska, Michalski, Okruszek & Stec (1977). The P–C distances (average  $1.794\text{\AA}$ ) are typical of P–C(aromatic) bonds; the C–P–C angles in the five-membered rings average  $90.9(5)^\circ$  and the exocyclic angles average  $107.6(5)^\circ$ . This restricting effect of the dibenzophosphole allows the Se–P–C angles to be  $114.3$  to  $117.5(3)^\circ$  (mean  $116.5^\circ$ ), larger than the corresponding angles in  $Ph_3P=Se$   $113.1(8)^\circ$ . Other dimensions are summarized in Table 2 and are as anticipated.

The bridged benzene rings are twisted away from each other, about the ring-to-ring bond ( $6.7^\circ$  in molecule 1;  $3.6^\circ$  in molecule 2).

Our previous work on bulky phosphine ligands (Ferguson, Roberts, Alyea & Khan, 1978; Alyea, Dias, Ferguson & Siew, 1983, 1984) led us to calculate maximum semi-cone angles ( $\theta/2$ ) and maximum cone angles ( $\theta$ ) for various bulky phosphine ligands. In a manner similar to that described earlier we obtained the  $\theta/2$  and  $\theta$  values shown in Table 3 for (I) and (II). The mean maximum cone angle for 5-PhDBP in (I) is some  $13^\circ$  smaller than the corresponding value for  $Ph_3P$  in (II), entirely in accord with, for example, the ability of 5-phenyldibenzophosphole to form a pentacoordinate complex with  $Co(NCS)_2$ , whereas the bulkier ligand  $Ph_3P$  can only form a tetrahedral complex (Alyea & Nelson, 1985, unpublished work).

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Table 2. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $C_{18}H_{13}PSe$

Se(1)	P(1)	2.110 (2)	P(2)	C(211)	1.812 (9)		
Se(2)	P(2)	2.086 (3)	P(2)	C(221)	1.791 (9)		
P(1)	C(111)	1.782 (9)	P(2)	C(231)	1.772 (10)		
P(1)	C(121)	1.809 (10)	C(122)	C(132)	1.456 (13)		
P(1)	C(131)	1.795 (10)	C(222)	C(232)	1.452 (12)		
C <sub>sp</sub> –C <sub>sp</sub> 1.341 (13)–1.404 (13), mean 1.374 (13)							
Se(1)	P(1)	C(111)	114.3 (4)	C(121)	C(122)	C(132)	112.0 (10)
Se(1)	P(1)	C(121)	115.3 (3)	C(123)	C(122)	C(132)	128.7 (10)
Se(1)	P(1)	C(131)	117.5 (3)	P(1)	C(131)	C(132)	109.6 (9)
C(111)	P(1)	C(121)	110.0 (5)	P(1)	C(131)	C(136)	127.1 (10)
C(111)	P(1)	C(131)	106.5 (4)	C(122)	C(132)	C(131)	115.7 (10)
C(121)	P(1)	C(131)	90.8 (6)	C(122)	C(132)	C(133)	127.5 (10)
Se(2)	P(2)	C(211)	115.6 (4)	P(2)	C(211)	C(212)	120.6 (10)
Se(2)	P(2)	C(221)	116.4 (3)	P(2)	C(211)	C(216)	120.4 (8)
Se(2)	P(2)	C(231)	116.9 (3)	P(2)	C(221)	C(222)	110.9 (8)
C(211)	P(2)	C(221)	106.5 (4)	P(2)	C(221)	C(226)	127.1 (8)
C(211)	P(2)	C(231)	107.4 (5)	C(221)	C(222)	C(232)	113.7 (10)
C(221)	P(2)	C(231)	90.9 (5)	C(223)	C(222)	C(232)	126.2 (10)
P(1)	C(111)	C(112)	118.6 (9)	P(2)	C(231)	C(232)	112.0 (8)
P(1)	C(111)	C(116)	122.7 (9)	P(2)	C(231)	C(236)	127.9 (9)
P(1)	C(121)	C(122)	111.8 (8)	C(222)	C(232)	C(231)	112.4 (10)
P(1)	C(121)	C(126)	126.2 (10)	C(222)	C(232)	C(233)	129.0 (10)

Aromatic C–C–C  $116.8(10)$ – $123.7(10)$ , mean  $120.0(10)$

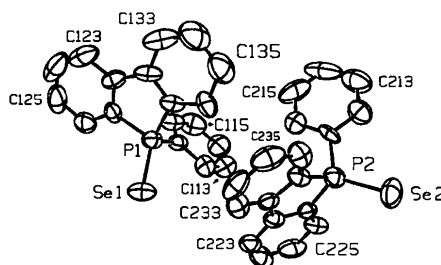


Fig. 1. A view of the two independent molecules of 5-phenyldibenzophosphole 5-selenide. The phenyl rings are numbered C(*nm*1) to C(*nm*6) where *n* represents the molecule number (1 or 2) and *m* represents the ring number (1, 2 or 3).

Table 3. Cone-angle data ( $^{\circ}$ ) for 5-phenyldibenzophosphole 5-selenide (I) and triphenylphosphine selenide (II)

	(I)	(II)
P(1)–Se(1)–H[C(136)]	$\theta/2$	71
P(1)–Se(1)–H[C(126)]		73
P(1)–Se(1)–H[C(112)]		85
	$\theta$	153
P(2)–Se(2)–H[C(236)]	$\theta/2$	73
P(2)–Se(2)–H[C(226)]		73
P(2)–Se(2)–H[C(212)]		85
	$\theta$	158
Average $\theta$		155

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## Structure of Diethyl 2,6-Dimethyl-4-(5-methyl-3-phenylisoxazol-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate, a Calcium Antagonist

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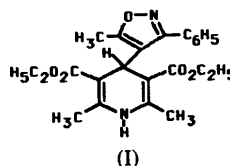
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**Abstract.**  $C_{23}H_{26}N_2O_5$ ,  $M_r = 410.48$ , orthorhombic, *Pbca*,  $a = 8.828$  (3),  $b = 17.181$  (5),  $c = 27.896$  (7) Å,  $V = 4231$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.29$  g cm<sup>-3</sup>, Mo *K* $\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.85$  cm<sup>-1</sup>,  $F(000) = 1744$ ,  $T = 140$  K,  $R = 0.052$  for 2808 observed reflections. In molecules of the title compound, (I), the 1,4-dihydropyridine ring exhibits a boat conformation. The five-membered isoxazolyl heterocyclic ring is held perpendicular to the dihydropyridine ring by interaction with the ester substituents. Both of these structural factors may be important to the calcium antagonist activity of (I).

**Introduction.** Some derivatives of 1,4-dihydropyridine, such as nifedipine, are potent calcium antagonists, or 'slow channel blockers'. The previously delineated structural requirements for biological activity for this class of compound (Janis & Triggle, 1983) include: (a) integrity of the 1,4-dihydropyridine ring, (b) no

substitution on the N atom at the 1 position, (c) 2,6-dialkyl substituents, (d) 3,5-diester substituents, (e) an aryl substituent at the 4 position of the dihydropyridine ring.

Compound (I) bears a substituted isoxazolyl five-membered ring at the 4 position, instead of the aryl substituent characteristic of nifedipine and related compounds. Compound (I) was originally synthesized (Natale & Quincy, 1983) to ascertain whether the presence of the five-membered heterocyclic isoxazolyl ring substituent at the 4 position of the 1,4-dihydropyridine ring would preserve calcium antagonist activity. If so, the isoxazolyl ring would allow ready substitution by a variety of groups, in attempts to discover yet more potent therapeutic agents.



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