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P-Methyl-*P*-phenylpropylphosphine Selenide

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Abstract. $C_{10}H_{15}PSe$, $M_r = 245 \cdot 15$; orthorhombic, space group $P2_12_12_1$, $a = 9 \cdot 26$ (1), $b = 10 \cdot 94$ (1), $c = 11 \cdot 47$ (1) Å; $V = 1162$ Å^3; $Z = 4$. $D_m = 1 \cdot 38$ g cm^{-3} (by flotation in KI solution), $D_x = 1 \cdot 40$ g cm^{-3}, $F(000) = 496$; $\mu = 57 \cdot 5$ cm^{-1} (Cu $K\alpha$). The structure was determined by Patterson and Fourier methods and refined by full-matrix least-squares calculations to a final R of 0·048 for 969 independent reflexions (Weissenberg camera, Cu $K\alpha$ radiation). The spontaneous resolution of the racemic compound during crystallization has been observed. The mean P–C bond length and C–P–C and Se=P–C angles are 1·83 Å, 106 and 112·5° respectively, while a P=Se distance of 2·12 Å has been found.

Introduction. A few years ago the synthesis and absolute-configuration assignment of the first optically active phosphine selenide (Stec, Okruszek & Michalski, 1971) was reported. The determination of the absolute configuration was based on the knowledge of the configuration of optically active *P*-methyl-*P*-phenylpropylphosphine (Horner, 1964) and the reasonable assumption that the addition of Se to phosphine proceeds with retention of the configuration at the P atom. Since the absolute configurations of optically active phosphines, phosphine oxides, sulphides and selenides have never been determined by X-ray techniques, we thought it worth while to make such a determination. In this paper the preliminary results of our studies on the crystal and molecular structure of the enantiomeric title compound, obtained by spontaneous resolution during crystallization of the racemic compound, are reported. The optical rotation of the enantiomer investigated was not determined, because only very small quantities of separated material were available, but its enantiomeric character is obvious in the light of the crystal parameters (one molecule in the independent part of the unit cell, in a non-centrosymmetric space group).

Crystals in the form of rose-coloured plates elongated along [101], were obtained by slow evaporation of a saturated solution in toluene. The cell-dimensions were calculated from Weissenberg photographs.

Intensities of 969 independent reflexions (70% of total) were collected on a Weissenberg camera (equi-inclination, multiple-film technique) with filtered Cu radiation, and estimated visually by comparison with standard strips. To obtain the best results possible very careful estimation of one half of each of eight photographs from each layer was made. In our opinion, proper scale factors between films of the same layer are the most important factor in increasing accuracy, apart from the estimation of blackening. The reflexions were collected with a spherical crystal, about [100] up to the fifth layer. Interlevel scale factors were initially calculated from $hk0$ reflexions and refined during least-squares calculations. The intensities were corrected for absorption (*International Tables for X-ray Crystallography*, 1959). These data were processed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The scattering factors for Se, P and C were those given by Doyle & Turner (1968) and those from *International Tables for X-ray Crystallography* (1962) were used for H. The illustrations were prepared with *ORTEP* (Johnson, 1965).

The approximate position of the Se atom was found from a three-dimensional Patterson map ($R = 0 \cdot 37$). Successive use of Fourier and difference Fourier

Table 1. *Atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z
Se	5959 (2)	3495 (1)	−852 (1)
P	6516 (4)	4629 (2)	576 (1)
C(1)	5109 (16)	4769 (9)	1651 (7)
C(2)	3814 (17)	4112 (10)	1554 (10)
C(3)	2715 (19)	4245 (12)	2383 (11)
C(4)	2862 (21)	5068 (12)	3316 (10)
C(5)	4169 (20)	5706 (11)	3402 (9)
C(6)	5303 (18)	5622 (11)	2574 (9)
C(7)	8119 (21)	4101 (13)	1349 (11)
C(8)	6944 (19)	6216 (9)	125 (11)
C(9)	5716 (20)	6844 (10)	−495 (12)
C(10)	6159 (21)	8131 (13)	−933 (13)

Table 2. *Hydrogen atom parameters* (×10^3)

	x	y	z	B(Å^2)
H(2)	360 (19)	397 (12)	74 (12)	6·6 (3)
H(3)	214 (20)	378 (14)	245 (12)	8·1 (4)
H(4)	211 (15)	519 (11)	393 (9)	6·0 (3)
H(5)	405 (20)	634 (17)	402 (15)	9·4 (7)
H(6)	602 (22)	619 (16)	252 (14)	5·7 (5)
H(71)	880 (23)	413 (17)	80 (17)	10·0 (5)
H(72)	852 (28)	469 (19)	207 (17)	9·5 (6)
H(73)	800 (24)	320 (18)	154 (15)	7·3 (5)
H(81)	762 (18)	657 (15)	66 (14)	8·0 (4)
H(82)	765 (34)	600 (24)	−40 (20)	12·1 (8)
H(91)	555 (24)	670 (17)	−218 (14)	12·5 (5)
H(92)	557 (19)	692 (15)	−134 (15)	12·0 (5)

Table 3. *Bond lengths* (Å) *and angles* (°)

Mean value of the H–C distances is 0·975 Å.

P–Se	2·119 (5)	C(3)–C(4)	1·405 (11)
P–C(1)	1·800 (22)	C(4)–C(5)	1·399 (14)
P–C(7)	1·823 (25)	C(5)–C(6)	1·421 (31)
P–C(8)	1·854 (18)	C(6)–C(1)	1·423 (25)
C(1)–C(2)	1·403 (13)	C(8)–C(9)	1·508 (36)
C(2)–C(3)	1·400 (17)	C(9)–C(10)	1·550 (20)
Se–P–C(1)	113·8 (1)	C(2)–C(1)–C(6)	120·2 (2)
Se–P–C(7)	112·9 (1)	C(1)–C(2)–C(3)	121·0 (1)
Se–P–C(8)	112·6 (2)	C(2)–C(3)–C(4)	120·9 (1)
C(1)–P–C(7)	106·5 (2)	C(3)–C(4)–C(5)	117·2 (2)
C(1)–P–C(8)	105·4 (1)	C(4)–C(5)–C(6)	124·1 (3)
C(7)–P–C(8)	105·0 (1)	C(5)–C(6)–C(1)	116·5 (3)
P–C(1)–C(2)	121·4 (2)	C(8)–C(9)–C(10)	111·5 (2)
P–C(1)–C(6)	118·3 (2)	P–C(8)–C(9)	113·4 (2)

Table 4. *Intermolecular distances less than* 4·0 Å

The first atom is at x,y,z and the Roman numerals refer to equivalent positions: (i) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}+x, 1-y, z-\frac{1}{2}$; (iv) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$.

C(10)···C(3$^{\text{i}}$)	3·618Å	C(7)···Se$^{\text{ii}}$	3·912Å
C(1)···C(4$^{\text{i}}$)	3·721	Se···C(2$^{\text{ii}}$)	3·970
C(10)···C(2$^{\text{i}}$)	3·956	Se···C(4$^{\text{iii}}$)	3·988
Se···C(3$^{\text{ii}}$)	3·835	C(7)···C(9$^{\text{iv}}$)	3·914

syntheses revealed all the non-hydrogen atoms (R = 0·17). Three cycles of full-matrix least-squares refinement of the positional and isotropic vibrational parameters (R = 0·086) and a further five cycles of anisotropic refinement reduced R to 0·060 (omitting 71 less-than reflexions). Although the positions of all but three H atoms were easily found from a number of difference Fourier maps calculated in alternation with refinement, they refined with difficulty. The best R value for observed reflexions was 0·048. The weighting scheme applied was $w^{-1} = 10 + |F| + 0{\cdot}021|F|^2$.

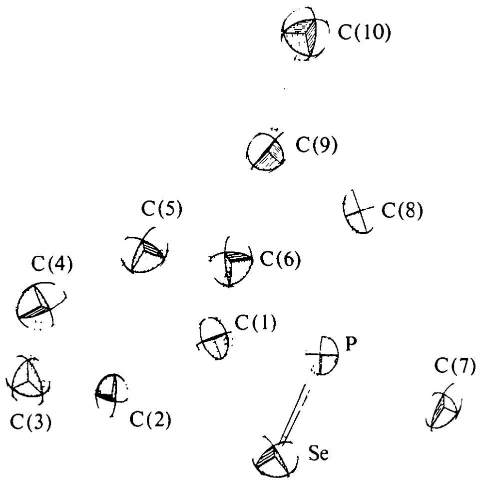

Fig. 1. Computer drawing of *P*-methyl-*P*-phenylpropylphosphine selenide. The thermal ellipsoids have been scaled to include 40% probability. Hydrogen atoms are omitted for clarity.

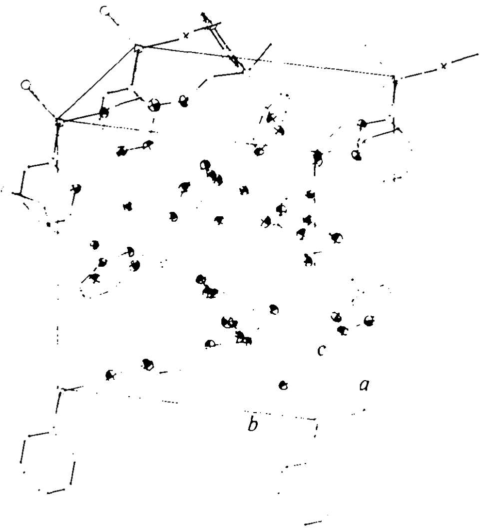

Fig. 2. Projection of the unit-cell contents.

Table 5. *Comparison of bond lengths and angles for known compounds containing the* P=Se *group*

Compound	P=Se	P–C	Se=P–C	C–P–C	References
P-Methyl-*P*-phenylpropylphosphine selenide	2·119	1·800	112·6	105·0	1
		1·823	112·9	105·4	
		1·854	113·8	106·5	
Triethylphosphine selenide	1·963	1·907	114	106	2
Tri-*o*-tolylphosphine selenide	2·13	1·83	112·4	107·1	3
Triphenylphosphine selenide–mercury(II) chloride	2·169	1·83	112·1	107·4	4
		1·82	106·1	111·2	
		1·77	111·8	108·0	
Bis(diphenylphosphinoselenoyl)methane	2·103	1·819 1·811	113·9 115·9	106·3 104·6	5
	2·097	1·816 1·796	112·3 113·6	103·1 107·4	
		1·833 1·853	115·1 111·5	105·1 102·6	
Methyl diphenylselenophosphinite	2·081	1·81	114·9	104·8	6
		1·80	113·8		
Selenium bis(diethyldiselenophosphinate)	2·095				7
Diethylthioselenophosphinatothallium	2·115				8
Tetraphosphorus pentaselenide	2·123				9
2-Seleno-2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane	2·055				10
cis-2-*tert*-Butylamino-2-seleno-4-methyl-1,3,2-dioxaphosphorinane	2·086				11
trans-2-*tert*-Butylamino-2-seleno-4-methyl-1,3,2-dioxaphosphorinane	2·080				
	2·082				12

References: (1) Present work. (2) Van Meerssche & Leonard (1959). (3) Shaw, Woods, Cameron & Dahlén (1971). (4) Dent Glasser, Ingram, King & McQuillan (1969). (5) Carrol & Titus (1976). (6) Lepicard, de Saint-Giniez-Liebig, Laurent & Rérat (1969). (7) Husebye & Helland-Madsen (1969). (8) Esperas & Husebye (1973). (9) Penney & Sheldrick (1971). (10) Grand, Martin, Robert & Tordjman (1975). (11) Bartczak, Christensen, Kinas & Stec (1975). (12) Bartczak, Christensen, Kinas & Stec (1976).

Discussion. Tables 1 and 2 show the final atomic parameters and their estimated standard deviations as obtained from the least-squares refinement.* The bond lengths and angles for non-hydrogen atoms, not corrected for thermal vibration, are summarized in Table 3. The P=Se bond length of 2·12 Å is a little longer than the mean distance reported so far (Table 5). The mean P–C distance, 1·826 Å, C–P–C and Se=P–C angles, 106 and 112·5°, are in good agreement with other reported values within the limits of errors. Figs. 1 and 2 show the molecular conformation and unit-cell contents. Table 4 shows the intermolecular contacts.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32588 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.