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2-Seleno-2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane

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Abstract. Monoclinic, $P2_1/c$, $a=10{\cdot}748$ (1), $b=6{\cdot}643$ (6), $c=13{\cdot}864$ (2) Å, $\beta=93{\cdot}50$ (1)°, $C_6H_{13}O_3PSe$, $Z=4$, F.W. 243·1, $F(000)=488$, $D_c=1{\cdot}63$, $D_x=1{\cdot}59$ (2) g cm^{-3}. The ring adopts a chair conformation with P=Se lying in the equatorial position.

Introduction. The sample of 2-seleno-2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane was obtained by addition of Se to 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane and recrystallized from CCl_4. Systematic absences were $h0l$ with l odd and $0k0$ for k odd. The crystal was enclosed in a thin-walled glass capillary and mounted around **b**. The intensities of 1247 independent reflexions ($3° < \theta < 70°$) were recorded with Ni-filtered Cu $K\alpha$ radiation by the five-points method on the four-circle Siemens diffractometer of the Laue–Langevin Institute of Grenoble. The $\bar{5}12$ reflexion was checked periodically, and showed no fall in intensity. Intensities were corrected for Lorentz and polarization factors, but not for absorption. Scattering factors were taken from *International Tables for X-ray Crystallography.*

The phases of 381 reflexions were determined with *MULTAN* (Germain, Main & Woolfson, 1971). The structure was refined by the full-matrix least-squares program *ORFLS* (Busing & Levy, 1959) with anisotropic temperature factors until $R_w=(\sum w\{F_o-F_c\}^2/\sum F_o^2)^{1/2}$ had converged to 0·060 and $R=(\sum|F_o-F_c|/\sum F_o)$ to 0·049. The final parameters are given in Table 1, the bond distances and angles in Table 2.*

Table 2. *Bond lengths* (Å) *and angles with standard deviations in parentheses*

P——O(1)	1·565 (4)	P——O(3)	1·568 (4)
O(1)–C(6)	1·454 (7)	O(3)–C(4)	1·490 (7)
C(5)–C(4)	1·478 (8)	C(5)–C(6)	1·524 (7)
C(5)–C(7)	1·550 (9)	C(5)–C(8)	1·531 (9)
P——O(9)	1·588 (4)	O(9)–C(10)	1·429 (7)
P=Se	2·055 (2)		
C(6)–O(1)–P	116·1 (3)	C(4)–O(3)–P	117·6
C(5)–C(6)–O(1)	112·0 (5)	C(5)–C(4)–O(3)	112·1 (5)
C(6)–C(5)–C(8)	110·9 (5)	C(4)–C(5)–C(7)	107·7 (5)
C(6)–C(5)–C(7)	108·3 (5)	C(4)–C(5)–C(8)	111·5 (5)
C(4)–C(5)–C(6)	109·4 (5)	C(7)–C(5)–C(8)	108·9 (5)
O(1)–P——Se	112·3 (1)	O(3)–P——O(9)	100·9 (2)
O(1)–P——O(9)	105·9 (2)	O(3)–P——Se	114·2 (2)
O(1)–P——O(3)	106·5 (2)	O(9)–P——Se	116·0 (1)
P——O(7)–C(8)	120·7 (4)		

Discussion. In a stereochemical and n.m.r. study of a series of diastereomeric 2-seleno-1,3,2-dioxaphosphorinanes, the assignment of the P=Se bond orientation (axial or equatorial) has been based on chemical argu-

Table 1. *Final position coordinates* (×10^4) *and thermal parameters* (×10^3)

Standard deviations given in parentheses refer to the last digit. The thermal factors have the form $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
P	2150 (1)	581 (2)	1920 (1)	66 (1)	201 (3)	43 (1)	−2 (1)	1 (1)	3 (1)
O(1)	1612 (4)	928 (6)	2930 (3)	90 (4)	246 (10)	46 (2)	−24 (5)	15 (2)	6 (4)
O(3)	3558 (3)	1205 (6)	2027 (3)	50 (3)	236 (10)	62 (2)	−5 (4)	7 (2)	−26 (4)
C(4)	3880 (5)	3086 (9)	2572 (5)	77 (4)	245 (15)	61 (4)	−15 (6)	1 (3)	−11 (6)
C(5)	3350 (5)	3117 (9)	3530 (4)	87 (5)	245 (14)	49 (3)	−6 (6)	−1 (3)	9 (5)
C(6)	1943 (5)	2823 (9)	3407 (4)	88 (5)	290 (17)	52 (3)	−14 (7)	18 (3)	−15 (6)
C(7)	3606 (7)	5200 (10)	3974 (6)	115 (7)	297 (18)	74 (5)	16 (8)	13 (4)	−30 (8)
C(8)	3957 (7)	1496 (12)	4211 (6)	150 (8)	300 (19)	67 (4)	26 (1)	−21 (5)	16 (8)
O(9)	1594 (4)	2335 (6)	1245 (3)	82 (3)	232 (10)	55 (2)	3 (5)	4 (2)	21 (4)
C(10)	2799 (6)	2504 (1)	1033 (6)	103 (6)	329 (18)	73 (4)	35 (8)	−19 (5)	18 (8)
Se	1850 (7)	2301 (1)	1420 (6)	137 (1)	233 (1)	72 (1)	−10 (1)	−14 (1)	−12 (1)

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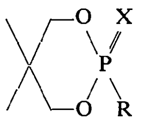
* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31093 (22 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ments (Stec, 1974). It was interesting to determine the structure of a symmetrically substituted 2-seleno-2-*R*-1,3,2-dioxaphosphorinane which does not exhibit diastereoisomerism in order to check the preferred orientation of the P=Se and P–R bonds.

By the same deductive reasoning we used in a previous study on 2-thiono-2-*R*-1,3,2-dioxaphosphorinane (Dutasta, Grand, Robert & Taieb, 1974), the results obtained in the present study can be useful in performing the conformational analysis of different 2-seleno-2-*R*-1,3,2-dioxaphosphorinanes studied in solution. In the seleno compounds, one can use in addition to the ^{1}H chemical shifts and J(PH) n.m.r. coupling constants, the ^1J(PSe) value which has been shown to be highly stereospecific (Stec, 1974).



X = S. 2-Thiono-2-*R*-5,5-dimethyl-1,3,2-dioxaphosphorinane
X = Se. 2-Seleno-2-*R*-5,5-dimethyl-1,3,2-dioxaphosphorinane

The ring adopts a chair conformation with P=Se in the equatorial position (Fig. 1). It is interesting to note that in the various symmetrically ring-substituted 2-*R*-2-oxo-1,3,2-dioxaphosphorinanes which have been studied in the solid state [$R = OC_6H_5$ (Geise, 1967); R = Cl (Silver & Rudman, 1972); $R = C_6H_5$ (Killean, Lawrence & Magennis, 1971); R = OH (Mazhar-ul-Haque, Caughlan & Moats, 1970; Murayama & Kainosho, 1969)], P=O adopts the equatorial orientation. On the other hand, in 2-thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane, P=S is axial (Dutasta, Grand & Robert, 1974).

The angle between the plane formed by C(4), C(5), C(6) and the least-squares plane through C(4), C(6), O(3), O(1) is 51·5°, while that formed between the O(1), P, O(3) plane and the least-squares plane is 38·5°. Such a flattening of the six-membered ring has already been observed in 2-oxo-1,3,2-dioxaphosphorinanes.

A least-squares plane calculation shows that P, Se, O(9), C(5), C(7) and C(8) are almost coplanar (deviation −0·011; −0·012; 0·021; 0·003; −0·021 and 0·020 Å respectively). C(4), C(6), O(1) and O(3) are 1·21 (6), −1·238 (6), −1·255 (4) and 1·253 (4) Å away from this plane. The methoxy group is directed away from the six-membered ring and the P, O(9), C(10) plane is tilted away from the P, Se, O(9), O(3), C(5), C(7), C(8) plane by an angle of 62°.

The endocyclic bond angles and distances agree well with those found in several other dioxaphosphorinanes (Khaikin & Vilkov, 1972). The exocyclic P–O bond is slightly longer than the P–O bonds in the ring. There exist only a few other P=Se distances reported in organophosphorus molecules to which the 2·055 Å bond length reported here can be compared (Van Meerssche & Leonard, 1960; Husebye & Helland-Madsen, 1966; Lepicard, de Saint-Giniez-Liebig, Laurent & Rérat, 1969). The geometrical parameters reported in the present study are also in good agreement with recent X-ray structure determinations of the two diastereoisomers of 2-seleno-2-t-butylamino-4-methyl-1,3,2-dioxaphosphorinane (W. Stec, to be published).

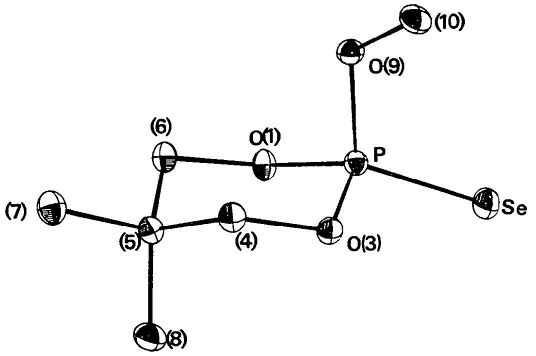


Fig. 1. Structure of 2-seleno-2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane.

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