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Structure of 5,5-Dimethyl-2-phenylamino-1,3,2-dioxaphosphorinane 2-Selenide, $C_{11}H_{16}NO_2PSe$

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Abstract. M_r = 304·2, monoclinic, $P2_1$, a = 7·832 (3), b = 5·687 (2), c = 14·396 (5) Å, β = 93·49 (3)°, Z = 2, V = 639·9 (4) Å^3, D_m = 1·54 (by flotation in aqueous KI solution), D_x = 1·58 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 5·06 mm^{-1}, F(000) = 308, R = 0·039 for 976 independent reflections. The dioxaphosphorinane ring adopts a flattened, slightly distorted chair conformation. The P—Se bond lies in an equatorial position and is 2·068 (1) Å. The P—N bond is 1·649 (5) Å.

Introduction. The structure of the title compound has been determined to elucidate the influence of substituents having different electronegativities and dimensions on the conformation of the dioxaphosphorinane ring and on the P coordination sphere.

Experimental. Prepared by reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane with aniline and subsequent addition of elemental selenium (Lesiak, Leśnikowski, Stec & Zielińska, 1979), crystals suitable for X-ray analysis obtained by slow evaporation from ethanol; preliminary Weissenberg photographs indicated that the crystal system is monoclinic with systematic extinctions consistent with space group $P2_1$ or $P2_1/m$; colourless prism cut to an approximate cube (edge 0·5 mm), Syntex $P2_1$ four-circle diffractometer, cell parameters refined by least-squares method from the setting angles of 15 reflections, intensities collected with Cu $K\alpha$ radiation to $2\theta \leq 115°$, ω–2θ scan, empirical absorption corrections applied to the 1026 observed reflections, equivalent reflections merged and structure amplitudes derived for 980 with $F_o \geq 3\sigma(F_o)$; application of *MULTAN* 78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978) gave solution with the best FOM containing a promising fragment comprising Se, O and four C atoms; a subsequent difference Fourier synthesis revealed all other nonhydrogen atoms; structure refined by full-matrix least-squares method to a conventional R = 0·059 with anisotropic temperature factors; H(1), H(61), H(82), H(83), H(13) and H(14) were then found, remaining H atoms assigned geometrically, all H atoms refined riding on their parent C or N atoms; as our computer storage appeared to be too small, last cycles of refinement performed using a blocked-full-matrix technique; final conventional R = 0·039, R_w = 0·045 and $R_g = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$ = 0·058 for observed reflections;† four further low-angle reflections having F_c much greater than F_o were excluded in the final cycles of refinement; $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 1·871 and 0·00097 respectively; in the final cycle all shifts of parameters were less than 0·3 of their e.s.d.'s, complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations, except *MULTAN* and the *BONDLA* subroutine taken from XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), performed using programs written by Professor G. M. Sheldrick.

Discussion. Final positional and equivalent isotropic thermal parameters are given in Table 1. The bond lengths and bond angles are summarized in Table 2. A view of the molecule is shown in Fig. 1. The dioxaphosphorinane ring adopts a flattened, slightly distorted chair conformation with the P—Se bond lying in an equatorial position. The P—N bond points in an axial direction. The P—Se bond length of 2·068 (1) Å agrees very well with values found for 2-[(3,5-dichlorophenyl)amino]-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-selenide and other similar compounds cited in the literature (Bartczak & Wolf, 1983). The sum of the angles around the N atom is 358·5°, *i.e.* the coordination is practically planar. The P—N bond of 1·649 (5) Å is slightly shorter than in the above-cited compound [1·662 (4) Å]; this may be caused by the difference in electronegativities between phenyl and 3,5-dichlorophenyl substituents (Gałdecki, 1980). The flattening of the dioxaphosphorinane ring is illustrated by the dihedral angles between planes defined by [O(1), O(3), C(4), C(6)] and [P, O(1), O(3)] and [C(4), C(5), C(6)] respectively (Fig. 2). The torsion angles and asymmetry parameters (Duax & Norton, 1975) are given in Fig. 3.

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† Lists of structure factors, anisotropic thermal parameters H-atom parameters and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38161 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* U_{eq} *values* (Å^2 $\times 10^3$) *for the nonhydrogen atoms, with e.s.d.'s in parentheses*

$$U_{eq} = \frac{(U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)}{3(1-\cos^2\beta)}.$$

	x	y	z	U_{eq}
Se	1964 (1)	2154	2960·8 (3)	49·1 (4)
P	3826 (1)	−384 (3)	2833 (1)	35·2 (6)
O(1)	4172 (4)	−1816 (9)	3751 (2)	41 (1)
O(3)	5604 (4)	849 (8)	2629 (2)	37 (1)
N	3459 (6)	−2414 (10)	2028 (3)	43 (1)
C(4)	7097 (6)	−670 (14)	2688 (3)	44 (2)
C(5)	7320 (7)	−1807 (12)	3664 (3)	41 (2)
C(6)	5733 (7)	−3223 (14)	3863 (4)	49 (2)
C(7)	8843 (9)	−3461 (15)	3690 (5)	67 (3)
C(8)	7618 (8)	70 (15)	4435 (4)	60 (2)
C(10)	3013 (5)	−1294 (10)	1070 (3)	37 (2)
C(11)	3558 (6)	−70 (12)	617 (3)	46 (2)
C(12)	3104 (8)	262 (15)	−331 (4)	56 (2)
C(13)	2075 (7)	−1417 (16)	−804 (3)	55 (2)
C(14)	1539 (8)	−3358 (14)	−327 (4)	57 (2)
C(15)	2017 (7)	−3658 (12)	639 (4)	48 (2)

Table 2. *Bond lengths* (Å) *and angles* (°)

P—Se	2·068 (1)	O(1)—P	1·561 (4)
O(3)—P	1·602 (4)	N—P	1·649 (5)
O(6)—O(1)	1·462 (7)	C(4)—O(3)	1·452 (7)
C(10)—N	1·422 (6)	C(5)—C(4)	1·546 (7)
C(6)—C(5)	1·523 (8)	C(7)—C(5)	1·517 (10)
C(8)—C(5)	1·547 (9)	C(11)—C(10)	1·356 (8)
C(15)—C(10)	1·353 (8)	C(12)—C(11)	1·401 (7)
C(13)—C(12)	1·399 (10)	C(14)—C(13)	1·3979 (11)
C(15)—C(14)	1·427 (8)		

O(1)—P—Se	112·1 (2)	O(3)—P—Se	109·7 (2)
O(3)—P—O(1)	106·0 (2)	N—P—Se	117·2 (2)
N—P—O(1)	104·1 (3)	N—P—O(3)	107·1 (2)
C(6)—C(1)—P	118·7 (3)	C(4)—O(3)—P	115·7 (4)
C(10)—N—P	125·9 (4)	C(5)—C(4)—O(3)	110·4 (4)
C(6)—C(5)—C(4)	110·1 (4)	C(7)—C(5)—C(4)	109·1 (5)
C(7)—C(5)—C(6)	108·5 (6)	C(8)—C(5)—C(4)	111·5 (6)
C(8)—C(5)—C(6)	108·6 (5)	C(8)—C(5)—C(7)	109·0 (5)
C(5)—C(6)—O(1)	112·1 (6)	C(11)—C(10)—N	122·4 (5)
C(15)—C(10)—N	115·4 (5)	C(15)—C(10)—C(11)	122·2 (4)
C(12)—C(11)—C(10)	120·6 (6)	C(13)—C(12)—C(11)	119·1 (7)
C(14)—C(13)—C(12)	119·2 (5)	C(15)—C(14)—C(13)	120·3 (6)
C(14)—C(15)—C(10)	118·2 (6)		

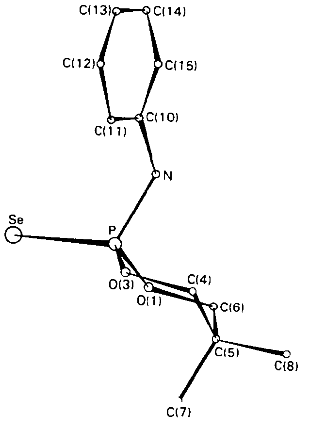

Fig. 1. View of the molecule with the atom numbering.

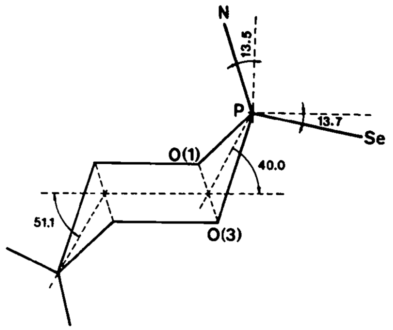

Fig. 2. Flattening of the 1,3,2-dioxaphosphorinane ring illustrated by the dihedral angles (°) (e.s.d.'s *ca* 1·0°).

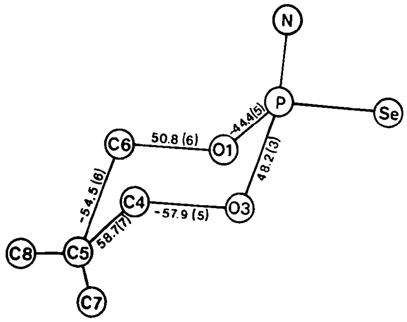

Fig. 3. The torsion angles (°) with e.s.d.'s in parentheses. Asymmetry parameters are: $C_2^{C(4),C(5)} = 3°$, $C_s^{O(3)} = 10°$, $C_s^{P} = 5°$, $C_2^{O(3),C(4)} = 10°$, $C_s^{O(1)} = 5°$, $C_2^{P,O(3)} = 11°$, $\varphi_{av} = 52°$ (e.s.d.'s *ca* 1°).

The dihedral angle between the mean plane through the phenyl ring and the plane fitted by atoms [O(1), O(3), C(4), C(6)] is 79°.

Intermolecular distances do not indicate any interactions stronger than normal van der Waals forces.

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