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The Stereochemistry of the Phosphorus–Selenium Bond. VII.* Structure of 5,5-Dimethyl-2-(*o*-nitrophenyl)amino-1,3,2-dioxaphosphorinane 2-Selenide

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Abstract. $C_{11}H_{15}N_2O_4PSe$, $M_r = 349{\cdot}2$, monoclinic, $P2_1/c$, $a = 10{\cdot}204$ (3), $b = 19{\cdot}891$ (3), $c = 6{\cdot}823$ (3) Å, $\beta = 94{\cdot}41$ (3)°, $U = 1380{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}66$, $D_x = 1{\cdot}68$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}05$ mm^{-1}, $F(000) = 704$, room temperature, $R = 0{\cdot}026$ for 1755 observed reflections [$I > 3\sigma(I)$]. The dioxaphosphorinane ring adopts a flattened chair conformation with P=Se and P—N bonds in equatorial and axial positions respectively. The properties of the molecule are mainly governed by anomeric interactions between endocyclic oxygen lone pairs and antibonding orbitals of the axial P—N bond.

Introduction. Numerous organothiophosphorus compounds are powerful inhibitors of cholinoesterase. Certain organothiophosphorus compounds are effective and relatively safe pesticides produced industrially.

However, very little is known about toxicity and biological activity of the corresponding seleno compounds. Some organoselenophosphorus compounds as described by Åkerfeldt & Fagerlind (1967) are among the most toxic phosphorus compounds, with LD_{50} values ranging from 0·02 to 0·06 mg kg^{-1} when injected subcutaneously into mice. They are more toxic than corresponding sulfur analogs. Their toxicity is due to the ability to inhibit cholinoesterase, as has been shown in tests with human erythrocyte enzyme (Michalski & Markowska, 1973, and references cited therein). The different biological activities of selenophosphorus and thiophosphorus analogues are presumably caused by very subtle differences between the characters of phosphorus–selenium and phosphorus–sulfur bonds. As has been shown by McFarlane & Rycroft (1972), Grim & Walton (1980) and confirmed recently by Allen & Taylor (1986) these bonds may be described by a resonance hybrid of two canonical forms: —P=*X* and —P$^+$—*X*$^-$ (where *X* = Se or S). The real structure depends on the ability of the substituents at phosphorus to be involved in p_π–d_π interactions with phosphorus orbitals. In 2-amino-1,3,2-dioxaphosphorinanes these interactions are in equilibrium with stereoelectronic effects which outweigh the usual steric interactions and are responsible for the main conformational properties of the molecule (Wolf, 1988). Therefore careful analyses of the whole pattern of conformational deformations in a large group of 2-seleno-2-amino-1,3,2-dioxaphosphorinanes as well as in their thio analogues may give valuable indications to the real nature of the phosphorus–selenium bonds in these compounds. For this reason, the title compound (1) was synthesized and its structure determined. Structural features of this compound are discussed in comparison with those reported for *cis*-2-*tert*-butylamino-4-methyl-1,3,2-dioxaphosphorinane 2-selenide (2) (Bartczak, Christensen, Kinas & Stec, 1975), 5,5-dimethyl-2-ethylamino-1,3,2-dioxaphosphorinane 2-selenide (3) (Bartczak, Gałdecki, Wolf, Lesiak & Stec, 1986), *trans*-2-*tert*-butylamino-4-methyl-1,3,2-dioxaphosphorinane 2-selenide (4) (Bartczak, Christensen, Kinas & Stec, 1976), 2-(3,5-dichloroanilino)-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-selenide (5) (Bartczak & Wolf, 1983) and 2-anilino-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-selenide (6) (Bartczak, Gałdecki, Trzeźwińska & Wolf, 1983). In all the

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above compounds dioxaphosphorinane rings adopt flattened chair conformations. In (2) and (3), P═Se bonds are situated axially but in (4), (5) and (6) these bonds are equatorial.

Experimental. Preparation by reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane with *o*-nitroaniline and subsequent addition of elemental selenium (Lesiak, Leśnikowski, Stec & Zielińska, 1979). Yellow crystals grown by slow evaporation from chloroform–*n*-hexane, 1:1. D_m by flotation in aqueous KI solution. Three specimens cut from the best looking prisms, sealed in Lindemann-glass capillaries, examined using oscillation and Weissenberg photographs, best crystal dimensions 0·4 × 0·4 × 0·6 mm; CAD-4F automated diffractometer; graphite-monochromated Mo $K\alpha$ radiation; accurate cell dimensions by least-squares calculations from angular settings of 25 reflections; $8 < \theta < 15°$, $\theta/2\theta$ scan mode; three orientation controls (checking every 100 measured reflections) and three different intensity controls (checking every 3600 s), no significant variation; 3990 reflections measured; 2101 unique reflections with $\theta \leq 25°$; *hkl*: $-12 \rightarrow 12$, $0 \rightarrow 23$, $0 \rightarrow 8$; R_{int} after merging 0·021; absorption corrections were not applied; 1755 reflections with $I < 3\sigma(I)$ considered as observed and used in further calculations; direct methods; refinement on F by standard full-matrix least squares and difference electron density syntheses; all H atoms located on a difference Fourier map after two cycles of anisotropic refinement, positional parameters included in last stages of refinement, temperature factors assumed to be equal to equivalent isotropic thermal parameters of non-hydrogen atoms with e.s.d.'s 0·001 Å^2 and refined with soft constraints; also N—H distance constrained to be equal to 0·95 Å with e.s.d. 0·03 Å; final weighting scheme based on Chebyshev polynomials (Carruthers & Watkin, 1979) with coefficients 155·7, 218·6 and 75·6; refinement converged with $R = 0{\cdot}026$, $wR = 0{\cdot}028$, $S = 1{\cdot}13$, max. $\Delta/\sigma = 0{\cdot}04$ for U_{33} coefficient of C(7); highest peak in final difference Fourier map 0·4 e Å^{-3} located near selenium atom, min. density $-0{\cdot}2$ e Å^{-3}, scattering factors from Cromer & Mann (1968). Calculations carried out on the University of Oxford Chemical Crystallography Laboratory VAX 11/750 computer using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *CRYSTALS* (Watkin & Carruthers, 1981) and *CHEMGRAF* (Davies, 1981).*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51982 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structure of the title compound (1) and a numbering scheme are shown in Fig. 1. Final positional and equivalent isotropic thermal parameters are listed in Table 1. Bond distances and valency angles are in Table 2. The dioxaphosphorinane ring adopts a flattened slightly distorted chair conformation (Figs. 2 and 3). The P═Se bond points in the equatorial direction and the P—N bond adopts the axial position.

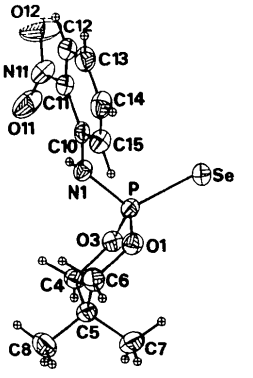

Fig. 1. View of the molecule with atom numbering. Thermal ellipsoids are drawn at 50% probability level.

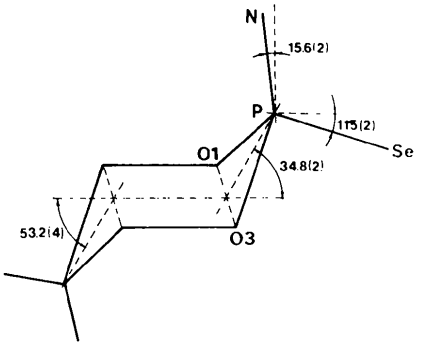

Fig. 2. Flattening of the 1,3,2-dioxaphosphorinane ring illustrated by the dihedral angles (°).

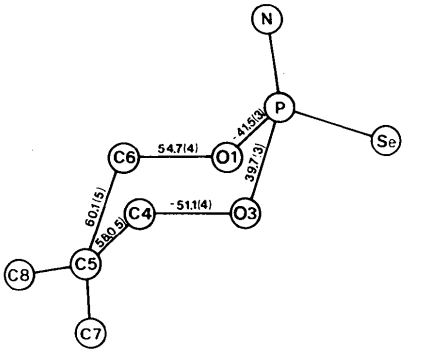

Fig. 3. The torsion angles (°). Asymmetry parameters (°) (Duax & Norton, 1975) are: $\Delta C_s^P = 2{\cdot}6$ (2), $\Delta C_s^{C(6)} = 12{\cdot}0$ (2), $\Delta C_s^{O(1)} = 14{\cdot}6$ (2), $\Delta C_2^{C(5),C(6)} = 7{\cdot}2$ (4), $\Delta C_2^{P,O(1)} = 12{\cdot}4$ (4), $\Delta C_2^{O(1),C(6)} = 18{\cdot}5$ (4).

Table 1. *Fractional atomic coordinates with their e.s.d.'s in parentheses and* U_{eq}

$U_{eq} = (U_1U_2U_3)^{1/3}$.

	x	y	z	U_{eq}(Å^2)
Se	0·068685 (4)	0·04485 (2)	−0·28218 (5)	0·0388 (5)
P	0·7105 (1)	0·01767 (4)	0·0116 (1)	0·0277 (5)
O1	0·8594 (2)	0·0013 (1)	0·0738 (3)	0·035 (1)
O3	0·6301 (2)	−0·0463 (1)	0·0645 (3)	0·032 (1)
C4	0·6671 (3)	−0·0828 (2)	0·2502 (5)	0·036 (1)
C5	0·8133 (3)	−0·0992 (2)	0·2699 (5)	0·036 (1)
C6	0·8911 (3)	−0·0339 (2)	0·2618 (5)	0·038 (1)
C7	0·8482 (5)	−0·1475 (2)	0·1067 (6)	0·049 (2)
C8	0·8455 (5)	−0·1308 (3)	0·4726 (6)	0·053 (2)
N	0·6620 (3)	0·0733 (1)	0·1760 (4)	0·031 (1)
C10	0·7049 (3)	0·1405 (1)	0·1857 (4)	0·029 (1)
C11	0·6225 (3)	0·1958 (2)	0·2097 (4)	0·033 (2)
C12	0·6695 (4)	0·2616 (2)	0·2083 (5)	0·039 (1)
C13	0·7996 (4)	0·2740 (2)	0·1876 (5)	0·042 (1)
C14	0·8833 (4)	0·2207 (2)	0·1688 (5)	0·042 (1)
C15	0·8377 (3)	0·1550 (2)	0·1669 (5)	0·037 (1)
N11	0·4842 (3)	0·1876 (2)	0·2426 (5)	0·046 (3)
O11	0·4464 (3)	0·1337 (1)	0·3030 (5)	0·056 (3)
O12	0·4100 (3)	0·2351 (2)	0·2122 (6)	0·077 (3)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

P—Se	2·072 (1)	C5—C8	1·531 (5)
P—O1	1·580 (2)	C10—C11	1·401 (4)
P—O3	1·570 (2)	C10—C15	1·401 (5)
P—N	1·677 (3)	C11—C12	1·395 (5)
O1—C6	1·475 (4)	C11—N11	1·455 (4)
O3—C4	1·484 (4)	N11—O11	1·221 (4)
N—C10	1·406 (4)	N11—O12	1·218 (4)
C4—C5	1·523 (4)	C12—C13	1·369 (5)
C5—C6	1·526 (5)	C13—C14	1·373 (5)
C5—C7	1·532 (5)	C14—C15	1·387 (5)

Se—P—O1	110·57 (8)	C7—C5—C8	110·8 (3)
Se—P—O3	114·20 (8)	O1—C6—C5	110·9 (2)
Se—P—N	117·1 (1)	N—C10—C11	124·3 (3)
O1—P—O3	106·3 (1)	N—C10—C15	119·4 (3)
O1—P—N	106·4 (1)	C11—C10—C15	116·3 (3)
O3—P—N	101·2 (1)	C10—C11—C12	121·8 (3)
P—O1—C6	118·2 (2)	C10—C11—N11	121·8 (3)
P—O3—C4	119·4 (2)	C12—C11—N11	116·3 (3)
P—N—C10	123·5 (2)	C11—N11—O11	119·0 (3)
O3—C4—C5	111·3 (2)	C11—N11—O12	119·0 (3)
C4—C5—C6	108·8 (2)	O11—N11—O12	122·0 (3)
C4—C5—C7	110·5 (2)	C11—C12—C13	120·4 (3)
C4—C5—C8	107·9 (3)	C12—C13—C14	119·1 (3)
C6—C5—C7	110·9 (3)	C13—C14—C15	121·2 (4)
C6—C5—C8	107·8 (3)	C10—C15—C14	121·3 (3)

The P═Se bond length is 2·072 (1) Å. Practically the same values have been reported for two 2-arylamino-1,3,2-dioxaphosphorinane 2-selenides investigated by X-ray analysis. These are 2·069 (2) and 2·068 (1) Å for (5) and (6) respectively. P═Se bonds in 2-alkylamino-1,3,2-dioxaphosphorinane 2-selenides seem to be slightly longer than in previous groups. Bond lengths are 2·086 (3), 2·081 (1), 2·081 (3) Å for (2), (3) and (4) respectively. As is well demonstrated by comparison of structures (2) and (4), a change in the position of the P═Se bond from axial to equatorial does not significantly change the phosphorus–selenium bond length. Therefore, small differences in P═Se bond length between arylamino and alkylamino derivatives may be attributed to the direct interactions between phosphorus and selenium orbitals rather than anomeric effects. The latter favour transfer of electron density from endocyclic oxygen n_π lone pairs to the axial bond (Van Nuffel, Alsenoy, Lenstra & Geise, 1984). The magnitude of these interactions depends on the ability of the axial substituent to stabilize this additional negative charge. However, because of the polar character of the P═Se bond, the selenium atom bears negative charge and further growth of electron density around this atom destabilizes the molecule. The opposite situation is observed in dioxaphosphorinanes with axially oriented P—N bonds like (1), (4), (5) and (6). In this case the most stabilizing interactions are those between endocyclic oxygen n_π and antibonding σ^* orbitals of exocyclic P—N bonds. They increase electron density around N atoms. Electron-withdrawing substituents bonded to N can stabilize this additional charge, increase anomeric interactions and therefore tend to occupy axial positions in respect to the heterocyclic ring. For this reason in most cases arylamino substituents tend to occupy axial positions, while alkylamino substituents prefer equatorial positions.

Axially oriented P—N bonds in 1,3,2-dioxaphosphorinane selenides are longer than equatorial ones. The average values are 1·658 (11) and 1·609 (8) Å for axial and equatorial bonds respectively.

P$\widehat{O}$C endocyclic valency angles in (1), like those in (4), (5) and (6), are close to 120° indicating that oxygens are sp^2 hybridized. This suggests that in 1,3,2-dioxaphosphorinanes the oxygen lone pairs are non equivalent and an orbital of higher energy, *i.e.* 2*p*, is involved in anomeric interactions (Hudson & Verkade, 1975; Van Nuffel, Lenstra & Geise, 1981). The natural consequence of this phenomenon is a flattening of the heterocyclic ring. In dioxaphosphorinanes with equatorial amino substituents like (2) and (3) this effect is smaller, indicating weaker anomeric interactions.

Like the situation observed in phosphine selenides (Allen, Nowell & Taylor, 1985) the phosphorus atom in the title compound (1) is in the configuration of a distorted tetrahedron. The Se*PX* valency angles, where *X* = O or N, are larger than the corresponding *XPX* angles. Average values are 114·0 (2) and 104·6 (2)°. respectively.

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An Unusual Rearrangement in the Boron-Trifluoride-Promoted Reaction of Tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane-2,7-dione Monoethylene Acetal with Ethyl Diazoacetate

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Abstract. 4,10-Ethylenedioxypentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4-oxyacetic acid, $C_{15}H_{18}O_5$, M_r = 278·31, triclinic, $P\bar{1}$, a = 6·705 (1), b = 7·945 (1), c = 13·087 (2) Å, α = 105·73 (1), β = 101·27 (1), γ = 98·73 (1)°, V = 642·4 (2) Å^3, Z = 2, D_x = 1·439 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 1·01 cm^{-1}, F(000) = 296, T = 295 K, R = 0·0470 for 1968 observed reflections. The cage structure is composed of six fused five-membered rings with three recognizable norbornane moieties, a seven-membered heterocyclic ring in a twist-chair conformation and an extended side chain. The five-membered rings of the norbornane moieties are twisted from the normal envelope conformation toward half-chair. There is an intermolecular hydrogen bond involving the disordered side chain. Molecular-mechanics calculations estimate the angle and torsional strains to be 163·1 and 121·4 kJ mol^{-1}, respectively.

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