C(5)]. The angle between the normals to the [N, C(5), C(4)] and [N, P, O, C(5)] planes is 34·5 (9)°. While in BASTEL the ring formed almost an ideal envelope, here it is rather a combination of a C(4)-envelope and a half-chair as shown by the asymmetry parameters (Fig. 2). The deviation of C(4) from the plane [N, P, O, C(5)] changes the direction of the C(4)—C(6) bond. It forms an angle of 105·6 (9)° with the normal to the above plane, *i.e.* it is almost ideally equatorial to this plane, whereas this bond in BASTEL was practically axial in relation to this plane. The bond N–C(7) is equatorial as in BASTEL {angle with normal to [N, P, O, C(5)] plane is 85·7 (9)° }. The bonds S–P and Cl–P are in a similar disposition in relation to the ring plane [N, P, O, C(5)]. The angle between these bonds is practically the same: 110·4 (1) and 109·2 (1)°, whereas that between the normal to the above plane and the Cl–P bond is 19 (1)° [44·5 (5)°], S–P 129 (1)° [153·4 (5)°], for TELBAS and BASTEL respectively. This means that the Cl–P bond is even more axial and the S–P bond more equatorial in TELBAS than in BASTEL. The angle between the normals to the phenyl ring and [N, P, O, C(5)] planes is 91 (1)°, *i.e.* this ring is almost exactly

perpendicular to the 1,3,2-oxazaphospholidine ring plane. In BASTEL this angle is 121·8 (4)°.

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Structure of 2-[(3,5-Dichlorophenyl)amino]-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-Selenide, C₁₁H₁₄Cl₂NO₂PSe

BY T. J. BARTCZAK* AND W. WOLF

Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90–924 Łódź, Poland

Abstract. $M_r = 373 \cdot 1$, monoclinic, $P2_1/c$, $a = 9 \cdot 958$ (5), $b = 7 \cdot 026$ (3), $c = 21 \cdot 896$ (4) Å, $\beta = 103 \cdot 97$ (3)°, $Z = 4$, $V = 1487$ (1) Å^3, $D_m = 1 \cdot 64$ (by flotation in KI aqueous solution), $D_c = 1 \cdot 67$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, μ(Mo $K\alpha$) = $3 \cdot 113$ mm^{-1}, $F(000) = 744$. The least-squares refinement gave a conventional R of 0·051 for 1736 independent reflections $[F_o \geq 3\sigma(F_o)]$. The dioxaphosphorinane ring adopts a flattened chair conformation with the P=Se bond lying in the equatorial position and the P–N bond in the axial position.

Introduction. The present work continues investigations of the structures of 1,3,2-dioxaphosphorinane 2-selenides (Grand, Martin, Robert & Tordjman, 1975; Bartczak, Christensen, Kinas & Stec, 1975*a,b*, 1976; Kinas, Stec & Krüger, 1978).

Experimental. Preparation by reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane with 3,5-dichloroaniline and subsequent addition of elemental selenium (Lesiak, Leśnikowski, Stec & Zielińska, 1979), recrystallization from chloroform–*n*-hexane, thin colourless plates, 0·3 × 0·5 × 0·7 mm. Syntex $P2_1$ four-circle automatic diffractometer, graphite-monochromatized Mo $K\alpha$, 3420 observed, θ–2θ scan mode, $\theta \leq 2\theta \leq 55°$; 1751 with $F_o \geq 3\sigma$ (F_o), Lp correction, not absorption. First attempts to solve the structure involved application of direct methods. The distribution of E values suggested a noncentrosymmetric space group. Examination of I values showed three reflections of $h0l$ type with $l = 2n + 1$ several times greater than their σ's. This led to the conclusion that the space group of the crystal might be $P2_1$ with two independent molecules in the asymmetric unit. The phases of 400 reflections were determined with *MULTAN* 78 (Main, Lessinger, Woolfson, Germain &

* The author to whom all correspondence should be addressed.

Declercq, 1978). The Se and P atoms were located from an E map with best figure of merit. All other nonhydrogen atoms were found from the subsequent difference Fourier maps. The structure was refined to a conventional $R = 0.047$ in $P2_1$. Although the final bond lengths and angles were generally within the range commonly observed for 1,3,2-dioxaphosphorinane rings, striking differences were observed between the two rings. At this point, we decided to redetermine the structure in the initially chosen space group $P2_1/c$, following the suggestion of a referee and conclusions given by Marsh & Schomaker (1979). The above-mentioned reflections violating the c glide may result from multiple reflections as they are not visible on appropriate Weissenberg photographs taken with Cu $K\alpha$ radiation. The atomic coordinates of respective supposedly independent atoms were related by the following conditions: $x_1 = x_2$, $y_1 + y_2 = 0.36$ and $z_1 = z_2 + 0.5$. This led to the conclusion that the molecules treated independently are related by the c glide crossing the 2_1 axis at $y = 0.18$. The atomic coordinates were transformed to be consistent with the $P2_1/c$ standard setting and then refined using blocked full-matrix least-squares technique. All hydrogen atoms were found from difference Fourier synthesis based on reflections with $\sin \theta/\lambda \leq 0.3$ Å^{-1} and were refined in a riding model on their parent C or N atoms. Final refinement converged with a conventional $R = 0.051$, $R_w = 0.056$ and $R_G = (\sum w \Delta^2 / \sum w |F_o|^2)^{1/2} = 0.068$ for observed reflections. Apart from the reflections rejected according to $F_o \geq 3\sigma (F_o)$, 15 further F_o's showing a large $(F_o - F_c)/\sigma(F_o)$ ratio were excluded in the final stages of refinement. The weights were $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 1.558 and 0.00256 respectively. In the final cycle all shifts in parameters were less than 0.5 of their e.s.d.'s. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations except *MULTAN* and two programs taken from XRAY 76, *BONDLA* and *LSQPL* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), were performed using the *SHELX* 76 system of crystallographic programs (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975).

Discussion. The atom numbering is shown in Fig. 1. Final positional and equivalent isotropic thermal parameters are given in Table 1.* The bond lengths and angles are given in Table 2. The dioxaphosphorinane ring adopts a flattened chair conformation. The P=Se bond points in the equatorial direction and the P—N

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38090 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond lies in the axial position. This may be explained by the anomeric effect (Hudson & Verkade, 1975; Van Nuffel, Lenstra & Geise, 1980) which causes an increase of electron density around the phosphorus. This results in a flattening of the dioxaphosphorinane ring around the P atom. The comparison of 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)] (Fig. 2a) gives a good illustration of the phenomenon. The torsion angles and asymmetry parameters (Duax & Norton, 1975) are given in Fig. 2(b). Such a flattening of the six-membered 1,3,2-dioxaphosphorinane ring has already been observed in 2-oxide, 2-sulphide and 2-selenide derivatives.
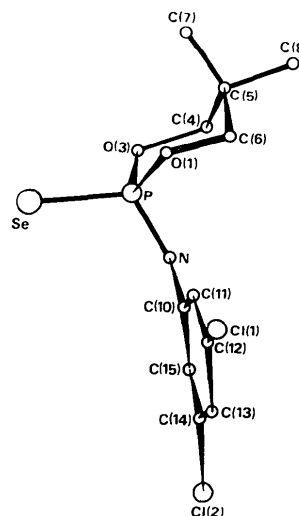

Fig. 1. View of molecule with atom numbering.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* U_{eq} ($\times 10^3$) *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} (Å^2)
Se	3457 (1)	1414 (1)	7990 (1)	64 (1)
P	3051 (1)	4173 (2)	7668 (1)	45 (1)
O(1)	1533 (3)	4778 (5)	7674 (2)	45 (1)
O(3)	3181 (4)	4467 (5)	6974 (2)	51 (1)
N	4077 (5)	5884 (7)	8045 (2)	49 (2)
C(4)	2596 (6)	6194 (9)	6634 (3)	58 (2)
C(5)	1082 (6)	6437 (9)	6650 (3)	56 (2)
C(6)	988 (6)	6531 (8)	7336 (3)	55 (2)
C(7)	206 (6)	4814 (11)	6299 (3)	75 (3)
C(8)	607 (8)	8400 (11)	6357 (4)	86 (3)
C(10)	4271 (6)	6372 (7)	8688 (3)	49 (2)
C(11)	3192 (6)	6304 (8)	8988 (3)	54 (2)
C(12)	3421 (7)	6820 (8)	9603 (3)	58 (2)
C(13)	4695 (7)	7451 (8)	9955 (3)	67 (3)
C(14)	5746 (7)	7516 (8)	9636 (3)	63 (2)
C(15)	5587 (5)	6949 (8)	9022 (3)	54 (2)
Cl(1)	2041 (2)	6722 (3)	9964 (1)	82 (1)
Cl(2)	7370 (2)	8270 (3)	56 (1)	91 (1)

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

P–Se	2·069 (2)	O(1)–P	1·573 (4)
O(3)–P	1·571 (4)	N–P	1·662 (4)
C(6)–O(1)	1·471 (6)	C(4)–O(3)	1·468 (7)
C(10)–N	1·415 (7)	C(5)–C(4)	1·526 (9)
C(6)–C(5)	1·529 (9)	C(7)–C(5)	1·526 (9)
C(8)–C(5)	1·546 (10)	C(11)–C(10)	1·389 (9)
C(15)–C(10)	1·398 (7)	C(12)–C(11)	1·361 (8)
C(13)–C(12)	1·389 (9)	Cl(1)–C(12)	1·744 (7)
C(14)–C(13)	1·393 (11)	C(15)–C(14)	1·374 (9)
Cl(2)–C(14)	1·738 (6)		
O(1)–P–Se	111·1 (2)	O(3)–P–Se	113·4 (2)
O(3)–P–O(1)	106·0 (2)	N–P–Se	117·5 (2)
N–P–O(1)	106·1 (2)	N–P–O(3)	101·6 (2)
C(6)–O(1)–P	117·5 (3)	C(4)–O(3)–P	118·9 (4)
C(10)–N–P	126·0 (4)	C(5)–C(4)–O(3)	110·8 (5)
C(6)–C(5)–C(4)	108·8 (4)	C(7)–C(5)–C(4)	110·6 (5)
C(7)–C(5)–C(6)	111·4 (5)	C(8)–C(5)–C(4)	107·2 (5)
C(8)–C(5)–C(6)	106·5 (5)	C(8)–C(5)–C(7)	112·1 (5)
C(5)–C(6)–O(1)	110·8 (5)	C(11)–C(10)–N	121·8 (5)
C(15)–C(10)–N	118·5 (5)	C(15)–C(10)–C(11)	119·8 (5)
C(12)–C(11)–C(10)	119·7 (5)	C(13)–C(12)–C(11)	123·2 (6)
Cl(1)–C(12)–C(11)	118·4 (5)	Cl(1)–C(12)–C(13)	118·4 (5)
C(14)–C(13)–C(12)	115·4 (6)	C(15)–C(14)–C(13)	123·9 (6)
Cl(2)–C(14)–C(13)	117·4 (5)	Cl(2)–C(14)–C(15)	118·6 (5)
C(14)–C(15)–C(10)	118·0 (6)		

Miller, 1978; Rømming & Songstad, 1979). The lengths of the single endocyclic P–O bonds 1·573 (4) [O(1)], 1·571 (4) [O(3)] Å are consistent with values observed in other 1,3,2-dioxaphosphorinane 2-selenides: 1·565–1·580 Å. The P–N bond distance 1·662 (4) Å is shorter than the accepted value for a P–N single bond, 1·77 Å (Rømming & Songstad, 1978). This shortening may be explained by electron transfer from the phosphorus atom to the nitrogen atom caused by the difference in electronegativity without involving the *d* orbitals on the central phosphorus atom (Rømming & Songstad, 1979). The sum of angles around N(1) is 359·1 (15)°, *i.e.* the coordination is planar. The position of the 3,5-dichlorophenyl ring results from repulsion forces between this ring and axial hydrogens connected to C(4) and C(6) on one side and Se from the opposite side. The appropriate angle between normals to the least-squares plane defined by atoms [O(1), O(3), C(4), C(6)] and to the phenyl plane (deviations of all the phenyl atoms from it are less than 0·02 Å) is 76 (1)°.
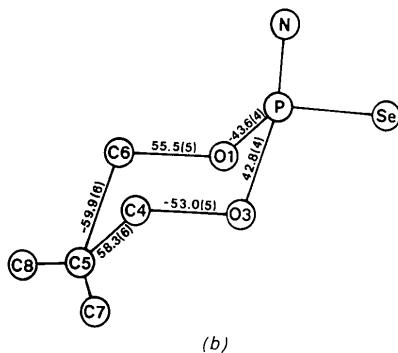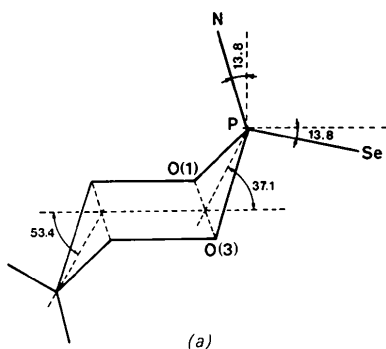
(a)

(b)

Fig. 2.(*a*) Flattening of the 1,3,2-dioxaphosphorinane ring illustrated by the dihedral angles (°) (e.s.d.'s *ca* 1·0°). (*b*) The torsion angles (°) with e.s.d.'s in parentheses. $\Delta C_5^P = 1·7°$; $\Delta C_2^{P,O(3)} = 7·0°$; $\Delta C_2^{O(1),C(6)} = 15·9°$.

The P coordination sphere is in good agreement with that found in similar compounds. The P=Se bond length 2·069 (2) Å is in the range cited in the literature (Bartczak, Christensen, Kinas & Stec, 1975*a,b*, 1976; Gałdecki, Główka, Michalski, Okruszek & Stec, 1977; Kinas, Stec & Krüger, 1978; Cameron, Howlett &

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(3R,6R)-3-Benzyl-8-thia-1,4-diazabicyclo[4.3.0]nonane-2,5-dione, $C_{13}H_{14}N_2O_2S$

BY M. VAN POUCKE, H. J. GEISE AND A. T. H. LENSTRA

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

Abstract. $M_r = 262\cdot3$, orthorhombic, $P2_12_12_1$, $Z = 8$, $a = 9\cdot256\,(2)$, $b = 10\cdot154\,(2)$, $c = 27\cdot420\,(8)$ Å, $D_c = 1\cdot352$ Mg m^{-3}. $R_w = 0\cdot039$ for 1546 reflections with $I > 2\cdot5\sigma(I)$, out of 3190 independent measurements. The benzyl group is a (pseudo-)axial substituent on the diketopiperazine ring and is folded above this ring in such a way that the overall distance is equal to the sum of the van der Waals values. The piperazine ring has a boat-like form. The molecules in the crystal occur as dimers formed through two hydrogen bridges. The geometry of the compound, also called *cyclo*|-D-Phe-L-(γS)Pro-|, is compared to *cyclo*(-D-Phe-L-Pro-).

Introduction. The title compound, shown in Fig. 1, contains the 2,5-diketopiperazine moiety (abbreviated DKP) and is a cyclic dipeptide composed of D-phenylalanine and L-γ-thiaproline, known as *trans-cyclo*|-D-Phe-L-(γS)Pro-|. It belongs to a group of compounds which show interesting biological and medical properties. Due to the restrictions brought about by the DKP ring in combination with the rigidity of the cyclic proline residue it is an attractive model compound in
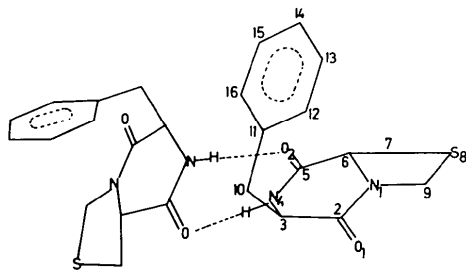
which to study side chain/side chain and side chain /backbone interactions (Ramani, Sasisekharan & Venkatesan, 1977; Anteunis, 1978). NMR spectra in CD$_3$OD had indicated a strong preference for a rotameric state in which the benzene ring is folded above the DKP ring (Schrooten, 1981). The amount of folded conformers seemed to be coupled to the concentration and to the amount of association through hydrogen bonding resulting in either long polymeric chains or dimers. The X-ray determination is one of a series, the results of which should be useful in the interpretation of NMR spectra and chemical activity.

Experimental. 3190 independent reflections $(0 \le \theta \le 27°)$, room temperature, Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo radiation; absorption correction omitted because of the small size of the crystal $(0\cdot1 \times 0\cdot2 \times 0\cdot2$ mm) and the low absorption coefficient $(\mu = 0\cdot25$ mm$^{-1})$; structure solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by a block-diagonal least-squares procedure; each reflection given a weight based on counting statistics; H atoms kept at their expected sites; their Debye–Waller temperature parameter was fixed at 5 Å^2, the value of the overall B in the Wilson plot; weighted R value converged to $0\cdot039$. The largest shift in the last cycle was 10% of the corresponding e.s.d.; the highest maximum in the final difference Fourier map was $0\cdot2$ e Å^{-3}. Relevant parameters* are listed in Table 1, the numbering of the atoms is given in Fig. 1.

Fig. 1. Structural formula, conformation and numbering of atoms.