The amino nitrogen N(12) presents a quaternary character: this quaternization is produced by proton transfer from the carboxyl group to N(12); thus, a 'zwitterion' structure is present, with the carboxyl group deprotonated and the amino N protonated. The distances of 2·75 (1), 2·74 (1) and 2·86 (1) Å between N(12) and O(11*A*) of the molecule at (1·5−*x*, −*y*, 0·5+*z*), O(11*A*) at (1+*x*, *y*, *z*) and O(3) at (1·5−*x*, −*y*, −0·5+*z*) indicate the presence of three independent intermolecular hydrogen bonds. Fig. 3 shows the molecular packing.

The authors thank Dr Y. Oka for helpful discussion and Ms K. Higashikawa for technical assistance.

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Acta Cryst. (1987). C**43**, 1788–1790

The Stereochemistry of the Phosphorus–Selenium Bond. VI.* Structure of 5,5-Dimethyl-2-methylseleno-1,3,2-dioxaphosphorinane 2-Selenide

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(*Received* 25 *November* 1986; *accepted* 21 *April* 1987)

Abstract. $C_6H_{13}O_2PSe_2$, $M_r = 306{\cdot}06$, monoclinic, $P2_1/n$, $a = 6{\cdot}9528\ (5)$, $b = 12{\cdot}234\ (1)$, $c = 12{\cdot}235\ (2)$ Å, $\beta = 93{\cdot}77\ (1)°$, $U = 1038{\cdot}4\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}94$ (by flotation in aqueous KI solution), $D_x = 1{\cdot}958$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 7{\cdot}16$ mm^{-1}, $F(000) = 592$, $T = 133$ K, $R = 0{\cdot}021$ for 1649 observed reflections [$I > 3\sigma(I)$]. The dioxaphosphorinane ring exists in the solid state in a flattened chair conformation with P=Se [2·071 (1) Å] positioned equatorially and P–Se [2·227 (1) Å] in the axial position. The geometrical features compare well with those of other 1,3,2-dioxaphosphorinane 2-selenides.

Introduction. Reactions of Na derivatives of *O,O*-diallylphosphoroanilidates and their thio and seleno analogues with CS_2 give the corresponding phosphoroselenoates and phosphorodiselenoates (Lesiak, Leśnikowski, Stec & Zielińska, 1979). In the case of chiral phosphoroanilidates the PN → PSe conversion proceeds with high stereospecificity and the configuration at the P atom is retained. It seemed desirable to investigate the title compound, synthesized in the course of the above research, by means of X-ray crystallography to reveal the conformation of the 1,3,2-dioxaphosphorinane ring in the presence of two Se atoms bonded to the P atom. Here we report the results of this study, which forms a continuation of investigations of 1,3,2-dioxaphosphorinane 2-selenides performed at the Institute of General Chemistry, Technical University of Łódź, since 1975 (Bartczak, Christensen, Kinas & Stec, 1975*a,b*, 1976; Bartczak & Wolf, 1983; Bartczak, Gałdecki, Trezeźwińska & Wolf, 1983; Bartczak, Gałdecki, Wolf, Lesiak & Stec, 1986).

Experimental. Colourless crystal shaped to sphere *ca* 0·03 mm in diameter, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; 2θ–ω scan mode; low-temperature system based on a design by Huffman (1974); lattice constants refined by least-squares fit of 25 reflections in the θ range 16·5–24·1°; empirical absorption correction (North, Phillips & Mathews, 1968) based on ψ scan, transmission factors 0·999 max. and 0·919 min.; h −8→8,

* Part V: Bartczak, Gałdecki, Wolf, Lesiak & Stec (1986).

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$k0\rightarrow15$, $l0\rightarrow15$; max. $\sin\theta/\lambda=0{\cdot}6168$ Å^{-1}; six standard reflections with no significant intensity variations; 2247 reflections measured, 1649 observed [$I > 3\sigma(I)$]; solution by direct methods and refined by full-matrix least squares using F's; H atoms found from difference Fourier map and calculated geometrically; $wR = 0{\cdot}031$; $w = 1/\sigma(F^2)$; max. $\Delta/\sigma = 0{\cdot}01$ in the final cycle; largest $\Delta\rho$ peak in the final difference electron density map 0·42 e Å^{-3}; all calculations carried out with the Enraf–Nonius *SDP* crystallographic computing package (Frenz, 1979); scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Positional parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B(Å^2)
Se(1)	0·28702 (4)	0·19654 (3)	0·42499 (3)	1·862 (6)
Se(2)	0·79556 (5)	0·23575 (3)	0·50965 (3)	1·831 (6)
P	0·5704 (1)	0·17034 (6)	0·38925 (6)	1·35 (1)
O(1)	0·6226 (3)	0·2261 (2)	0·2778 (2)	1·67 (4)
O(2)	0·6127 (3)	0·0444 (2)	0·3754 (2)	1·62 (4)
C(1)	0·7957 (5)	0·1873 (3)	0·2252 (2)	1·57 (6)
C(2)	0·7900 (4)	0·0122 (3)	0·3245 (3)	1·66 (6)
C(3)	0·6278 (5)	0·0270 (3)	0·1360 (3)	2·56 (7)
C(4)	0·9871 (5)	0·0328 (3)	0·1643 (3)	2·19 (6)
C(5)	0·7957 (4)	0·0640 (3)	0·2121 (2)	1·53 (6)
C(6)	0·7236 (5)	0·1437 (3)	0·6306 (3)	2·31 (7)

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

P–Se(1)	2·071 (1)	P–Se(2)	2·227 (1)
Se(2)–C(6)	1·951 (4)	P–O(1)	1·588 (2)
P–O(2)	1·580 (2)	O(1)–C(1)	1·480 (4)
O(2)–C(2)	1·471 (4)	C(1)–C(5)	1·517 (5)
C(2)–C(5)	1·517 (4)	C(3)–C(5)	1·514 (5)
C(4)–C(5)	1·535 (5)		

P–Se(2)–C(6)	98·2 (1)	Se(1)–P–Se(2)	116·23 (4)
Se(1)–P–O(1)	112·90 (9)	Se(1)–P–O(2)	111·10 (9)
Se(2)–P–O(1)	102·9 (1)	Se(2)–P–O(2)	107·08 (9)
O(1)–P–O(2)	105·8 (1)	P–O(1)–C(1)	118·28 (9)
P–O(2)–C(2)	118·2 (2)	O(1)–C(1)–C(5)	111·8 (3)
O(2)–C(2)–C(5)	111·0 (3)	C(1)–C(5)–C(2)	108·6 (3)
C(1)–C(5)–C(3)	110·9 (3)	C(1)–C(5)–C(4)	107·1 (3)
C(2)–C(5)–C(3)	111·6 (3)	C(2)–C(5)–C(4)	108·4 (3)
C(3)–C(5)–C(4)	110·1 (3)		

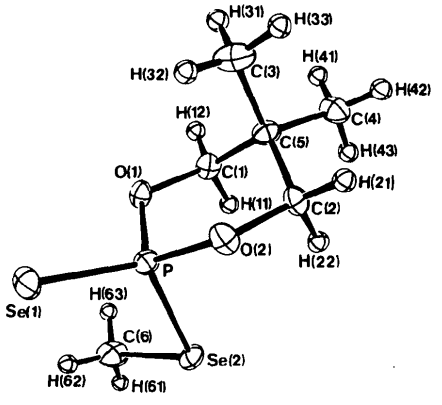

Fig. 1. Conformation of the molecule and numbering of the atoms.

Discussion. Relevant parameters are listed in Table 1,* bond lengths and angles in Table 2, and the numbering of the atoms is given in Fig. 1. The P=Se(1) [2·071 (1) Å] and P–Se(2) [2·227 (1) Å] bonds are within their normal values (Kinas, Stec & Krüger, 1978; Bartczak & Wolf, 1983). The single-bond length [P–Se(2) = 2·227 (1) Å] is to our best knowledge the most accurate value found in any crystallographic work published before May 1985 (Husebye & Helland-Madsen, 1969; Husebye, 1966, 1969; Penney & Sheldrick, 1971; Keulen & Vos, 1959). The P=Se bond lies in the equatorial position while the P–Se single bond is axial to the ring. This can be explained by the generalized anomeric effect (Kirby, 1983; Hudson & Verkade, 1975; Van Nuffel, Van Alsenoy, Lenstra, Geise & Van den Berg, 1984), transmitted through phosphorus. The flattened chair conformation observed in the ring is typical for this class of compounds. The dihedral angles of the O(1)–P–O(2) and C(1)–C(5)–C(2) planes with the O(1)–O(2)–C(2)–C(1) plane are 39·8 (5) and 61·3 (5)° respectively. Also, inspection of asymmetry parameters (Duax & Norton, 1975) shows good agreement with the ideal chair form: $\Delta C_s^P = 3{\cdot}6$ (5), $\Delta C_2^{O(1),C(1)} = 19{\cdot}1$ (5)°.

The authors wish to thank Professor W. J. Stec for the gift of the crystals. TJB and WW were supported financially by project RP.11.10 of the Polish Ministry of Science and Higher Education.

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43988 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1987). C**43**, 1790–1793

A Structural Study of 3′-Deoxytubercidin and 3-Deaza-3′-deoxyadenosine

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(*Received* 31 *January* 1987; *accepted* 8 *May* 1987)

Abstract. 3′-Deoxytubercidin (3′-dTu), $C_{11}H_{14}N_4O_3$, $M_r = 250{\cdot}26$, monoclinic, $P2_1$, $a = 5{\cdot}299\ (1)$, $b = 9{\cdot}945\ (3)$, $c = 11{\cdot}107\ (1)$ Å, $\beta = 100{\cdot}75\ (1)°$, $V = 575{\cdot}13$ Å^3, $Z = 2$, $D_x = 1{\cdot}445$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 86{\cdot}2$ mm^{-1}, $F(000) = 264$, $T = 298$ K. Final $R = 0{\cdot}030$ for 1266 observed reflections with $I \geq 1{\cdot}5\sigma(I)$. 3-Deaza-3′-deoxyadenosine (3′-ddA), $C_{11}H_{14}N_4O_3$, $M_r = 250{\cdot}26$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}826\ (1)$, $b = 9{\cdot}075\ (2)$, $c = 21{\cdot}887\ (3)$ Å, $V = 1157{\cdot}27$ Å^3, $Z = 4$, $D_x = 1{\cdot}436$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 85{\cdot}6$ mm^{-1}, $F(000) = 528$, $T = 298$ K. Final $R = 0{\cdot}030$ for 1075 observed reflections with $I \geq 1{\cdot}5\sigma(I)$. 3-Deaza-3′-deoxyadenosine (3′-ddA) and 3′-deoxytubercidin (3′-dTu) are analogues of the nucleoside 3′-deoxyadenosine (3′-dA). The sugar pucker for both structures is the C3′-*endo* conformation. For 3′-dTu the C4′—C5 bond conformation is *gauche*(+)–*trans* whereas for 3′-ddA it is *gauche*(+)–*gauche*(−). Where the substitutions of N by C have been made in the purine bases, the relevant bond lengths have increased by 0·05 Å and the bond angles by 3° compared with adenosine, which causes significant deviation from the usual planar purine-ring structure.

Introduction. The title structures are analogues of cordycepin, the nucleoside antitumour antibiotic 3′-deoxyadenosine (3′-dA) (Radwan & Wilson, 1980). This has been shown to inhibit the growth of human tumour cells in culture (Rich, Meyers, Weinbaum, Cory & Suhadolnik, 1965). 3′-dA primarily inhibits RNA synthesis and, as a consequence, blocks DNA and protein synthesis in cells. Its mode of action involves incorporation into the 3′-end of an RNA molecule and this prevents further elongation, thereby acting as a chain terminator (Suhadolnik, 1979). A major problem associated with the clinical use of these nucleoside antitumour antibiotics is that the enzyme adenosine deaminase (ADAase) (Montgomery, 1970) causes deamination of purine antimetabolites and hence limits their activity. The aim of the structural studies detailed in this paper is to examine compounds potentially active in chain termination of RNA that are, at the same time, resistant to ADAase, although without being an inhibitor (Montgomery, Thomas, Zell, Einspahr & Bugg, 1985), which causes other toxic effects produced by excess adenosine (Plagemann & Wohlhueter, 1981). Syntheses are described elsewhere (Serafinowski, 1987).

3-Deaza-3′-deoxyadenosine (3′-ddA) has a C atom substituted for the N atom at the 3-position of the adenine base; 3′-deoxytubercidin (3′-dTu) has a C atom substituted for an N atom at position 7. The substitutions of a C for an N atom in these nucleoside antibiotics have electronic effects which are manifested in changes in bond geometry. These are discussed in this paper and compared with the crystal structures of the parent nucleosides adenosine (Lai & Marsh, 1972), 2′-deoxyadenosine (Watson, Sutor & Tollin, 1965),

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