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# (2R,4S,5R)-2-Chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-Sulphide, C₁₀H₁₃ClNOPS*

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**Abstract.** m.p. = 331 K, $M_r = 261 \cdot 7$, orthorhombic, $P2_12_12_1$, $a = 10 \cdot 380$ (1), $b = 11 \cdot 129$ (5), $c = 11 \cdot 151$ (1) Å, $V = 1288 \cdot 07$ Å³, $Z = 4$, $D_c = 1 \cdot 349$, $D_m = 1 \cdot 331$ Mg m⁻³ (in aqueous KI), $F(000) = 544$. Final $R = 0 \cdot 0500$ for 1010 observed reflections. The five-membered oxazaphospholidine ring exists in the crystal as a distorted envelope with C(4) deviating by $-0 \cdot 526$ (8) Å from the least-squares plane [N,P,O,C(5)].

**Introduction.** In the present paper we report the crystal structure and absolute configuration of the second member of a diastereoisomeric pair of 2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulphides, TELBAS. The first member (BASTEL) was described by Bartczak & Gałdecki (1983).

**Experimental.** Colourless single shapeless crystal fragment, approx. $0 \cdot 5 \times 0 \cdot 4 \times 0 \cdot 3$ mm, CAD-4 automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$, $\mu = 0 \cdot 498$ mm⁻¹, 1226 reflections, room temperature, range $0 \leq 2\theta \leq 54°$, 1010 with $F_o \geq 3\sigma(F_o)$, no absorption correction, maximum

$h, k, l = 13, 14, 14$; non-centrosymmetric direct methods combined with Patterson synthesis (*SHELX* 76, Sheldrick, 1976). The structure was refined by standard least-squares and difference electron density methods followed in the final stages by a blocked full-matrix technique. All H atoms, except those belonging to methyl groups C(6) and C(7), were located in a weighted difference Fourier synthesis based on reflections with sin $\theta/\lambda \leq 0 \cdot 3$Å⁻¹. C(6) appeared to be floating, the bond distance C(4)–C(6) accomplishing unrealistic values after a few cycles of refinement, due probably to some disorder of C(6). Therefore, the distance C(4)–C(6) was constrained to $1 \cdot 501$Å (value taken from BASTEL). The methyl H atoms were generated with the methyl groups assumed to be staggered (C–H constrained to $1 \cdot 08$Å). The positional parameters of all H atoms were allowed to refine in the final two cycles of refinement, with their isotropic temperature factors taken as for their parent C atoms in the last isotropic cycle of refinement. The ratio of number of reflections to number of parameters was $5 \cdot 7$. In the final $\Delta F$ map no significant density was observed. During the last cycle of refinement, the maximum shift to e.s.d. ratio for a non-H atom was $0 \cdot 385$ ($U_{22}$ for P atom). Atomic scattering factors were those from *International Tables for X-ray Crystallography* (1974).

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The refinement of the structure with isotropic temperature factors resulted in an $R$ value of 0·1053. The final refinements using anisotropic temperature factors converged with a conventional $R = 0·0500$, $R_W = 0·0537$ and $R_G = 0·0644$. The absolute configuration is described by the model $\bar{x}, \bar{y}, \bar{z}$ consistent with chemical correlations (Lesiak & Stec, 1978) and the crystal-structure determination of the diastereoisomer BASTEL (Bartczak & Gałdecki, 1983). It is confirmed additionally by the Hamilton (1965) $R$ test:

$$\mathscr{R}_{1,833,0·005} = 1·005; \frac{R_2}{R_1} = 1·010; \frac{R_{w2}}{R_{w1}} = 1·008.$$

All calculations were performed using $SHELX$ 76 (Sheldrick, 1976) and $XANADU$ (Roberts & Sheldrick, 1975).

**Discussion.** Positional and equivalent isotropic thermal parameters are listed in Table 1.* Perspective views of the molecule projected onto the least-squares plane [N, P, O, C(5)] with atomic numbering, bond distances and bond angles are given in Fig. 1. Torsion angles in the 1,3,2-oxazaphospholidine ring and asymmetry parameters are shown in Fig. 2.

The molecular geometry of (2$R$,4$S$,5$R$)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-thione (TELBAS) resembles rather closely that found for its diastereoisomer, BASTEL (see previous paper in this series) (Bartczak & Gałdecki, 1983). In the bonding pattern the difference includes P—S = 1·890 (2) Å which is significantly

shorter than P—S = 1·911 (2) Å in BASTEL. The sum of the bond angles at the ring N atom, 352°, is smaller than in BASTEL ($\sum = 357°$) and indicates a more pyramidal configuration of this atom. This affects the conformation of the 1,3,2-oxazaphospholidine ring. This ring exists in the crystal in an envelope conformation with C(4) at the flap. The deviation of this atom is −0·526 (8) Å from the least-squares plane [N, P, O,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and additional bond distances involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38089 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for the non-*H *atoms with e.s.d.'s in parentheses*

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

|       | $x$       | $y$      | $z$      | $U_{eq}(\text{Å}^2)$ |
|-------|-----------|----------|----------|----------------------|
| P     | −1776 (2) | −4588 (1)| −9803 (1)| 46 (1)               |
| S     | −1333 (2) | −3328 (2)| −863 (2) | 70 (1)               |
| Cl    | −3730 (2) | −4657 (2)| −9570 (2)| 76 (1)               |
| N     | −1289 (6) | −5944 (4)| −98 (4)  | 48 (2)               |
| O     | −1286 (5) | −4533 (4)| −8464 (4)| 54 (1)               |
| C(4)  | −1249 (9) | −6629 (6)| −8969 (7)| 55 (2)               |
| C(5)  | −774 (7)  | −5711 (6)| −8051 (5)| 51 (2)               |
| C(6)  | −426 (11) | −7735 (7)| −9063 (10)| 81 (4)              |
| C(7)  | −1551 (11)| −6527 (8)| −1241 (8)| 73 (4)               |
| C(10) | −9351 (6) | −5605 (5)| −7879 (4)| 44 (2)               |
| C(11) | −8786 (8) | −6200 (5)| −6925 (5)| 50 (2)               |
| C(12) | −7479 (8) | −6147 (6)| −6729 (5)| 58 (3)               |
| C(13) | −6739 (8) | −5479 (7)| −7489 (7)| 65 (3)               |
| C(14) | −7261 (8) | −4886 (7)| −8432 (6)| 65 (3)               |
| C(15) | 8562 (8)  | −4950 (6)| −8617 (6)| 59 (3)               |


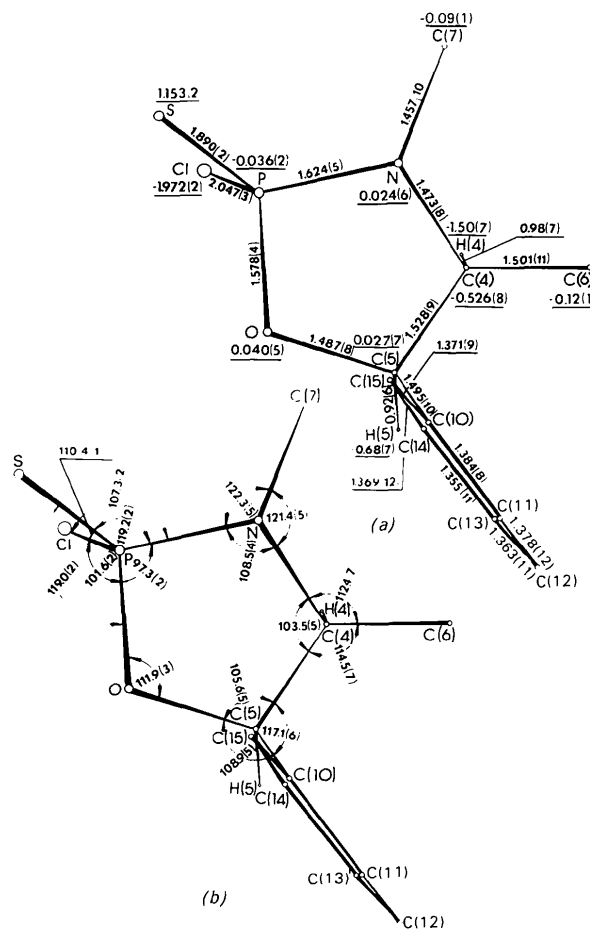
Fig. 1. (*a*) Bond distances (Å) and atomic numbering in the molecule of TELBAS projected onto the least-squares plane [N, P, O, C(5)]. Underlined are deviations of atoms from the least-squares plane (Å). E.s.d.'s in parentheses refer to the last significant digit. (*b*) Bond angles (°).
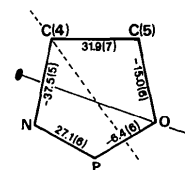


Fig. 2. The ring torsion angles and asymmetry parameters (°) (Duax & Norton, 1975). $\Delta C_s^{C(4)} = 9·4, \Delta C_2^0 = 5·0°$.

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

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**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) Å³, $D_m = 1 \cdot 64$ (by flotation in KI aqueous solution), $D_c = 1 \cdot 67$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $\mu$(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, $\theta$–$2\theta$ 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 $\sigma$'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 &

    