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(2*S*,4*S*,5*R*)-2-Chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-Sulphide, C₁₀H₁₃CINOPS*

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Abstract. m.p. = 396–397 K, $M_r = 261.7$, orthorhombic, $P2_12_12_1$, $a = 9.630$ (1), $b = 10.318$ (5), $c = 12.717$ (1) Å, $V = 1263.58$ Å³, $Z = 4$, $D_c = 1.376$, $D_m = 1.362$ Mg m⁻³ (in aqueous KI), $F(000) = 544$. Final $R = 0.0451$ for 1326 observed reflections. The five-membered oxazaphospholidine ring exists in the crystal in an envelope conformation with C(4) deviating by 0.500 (4) Å upwards from the least-squares plane [N,P,O,C(5)].

Introduction. The configurations of the *cis* and *trans* isomers of 2-substituted 1,3,2-oxazaphospholidine 2-oxides, 2-sulphides and 2-selenides derived from (–)-ephedrine have been established by spectroscopic and chemical methods (Cooper, Hall, Harrison & Inch, 1977). The conversion of dialkyl(aryl) phosphoroanilidates into corresponding phosphates and phosphorothioates has been proved to be fully stereospecific and proceeding with retention of configuration at P in the case of chiral acyclic molecules as well as in 4-methyl-1,3,2-dioxaphosphorinane derivatives (Stec, Okruszek, Lesiak, Uznański & Michalski, 1976). 1,3,2-Oxazaphospholidines derived from (–)-ephedrine have been used as a model system to investigate the stereoselectivity of the above conversion when the P atom is incorporated into a five-membered ring.

The (2*S*,4*S*,5*R*)- and (2*R*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulphides (hereafter referred to as BASTEL and TELBAS) have been prepared by reaction of phosphorothioyl chloride and (–)-ephedrine in the presence of triethylamine (Lesiak & Stec, 1978). The ¹H NMR spectra of both isomers and of derivatives obtained from them were not very helpful for stereochemical analysis possibly because of different conformations of oxaza-

phospholidine rings due to spatial requirements of exocyclic substituents at the P atom (Lesiak & Stec, 1978). Therefore, four compounds have been subjected to X-ray analysis to determine the conformation of the 1,3,2-oxazaphospholidine ring in the presence of different exocyclic substituents at the P atom and to describe the geometry of the ring. Moreover, the confirmation of absolute configuration by X-ray crystallography seemed essential as the assignments for BASTEL and TELBAS given by Lesiak & Stec (1978) were contrary to those given by Cooper *et al.* (1977, p. 1978). Here and in the following paper we report the crystal and molecular structures of this diastereoisomeric pair of compounds. We believe that this is the first example of a diastereoisomeric pair examined by X-ray techniques so far for a compound incorporating the 1,3,2-oxazaphospholidine ring.

Experimental. Spherical crystals, ~0.3 mm in diameter, CAD-4 automated four-circle diffractometer, graphite-monochromatized Cu K α radiation, $\mu = 5.037$ mm⁻¹, 1371 reflections, room temperature, range $1^\circ \leq 2\theta \leq 70^\circ$, 1336 with $F_o \geq 3\sigma(F_o)$, no absorption correction, maximum $h, k, l = 11, 12, 15$; non-centrosymmetric direct methods (*SHELX* 76, Sheldrick, 1976).

The structure was refined by standard least-squares methods and difference electron density syntheses. Three cycles of full-matrix least-squares refinement using isotropic temperature factors resulted in $R = 0.077$.

Introduction of anisotropic temperature factors required the application of a blocked full-matrix technique. All H atoms, except those belonging to methyl groups, were located in a weighted difference Fourier synthesis based on reflections with $\sin \theta / \lambda \leq 0.3$ Å⁻¹. The methyl H atoms were generated with the methyl groups assumed to be staggered (C–H

* Conformation of the 1,3,2-Oxazaphospholidine Ring. I.

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constrained to 1.08 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. Apart from the reflections rejected according to the criterion $F_o \geq 3\sigma(F_o)$, ten more reflections with low h,k,l values having $(F_o - F_c)$ greater than 2σ were excluded from the last cycle of refinement. Therefore the total number of reflections used in the refinement was 1326 and the ratio of number of reflections to number of parameters was 7.5. In the final ΔF map no significant density was observed. During the last cycle of refinement, the largest positional parameter shift (z coordinate of S atom) was lower than 0.001 Å. Atomic scattering factors were those from *International Tables for X-ray Crystallography* (1974). The final refinements converged with a conventional $R = 0.0451$ and $R_w = 0.0523$ for the observed reflections. The weights were $w = k / [\sigma^2(F_o) + gF_o^2]$ where k and g refined to 1.000 and 0.0050 respectively. The final $R_G = (\sum w \Delta^2 / \sum w |F_o|^2)^{1/2} = 0.0670$ for the parameters listed in Table 1 and 0.0800 if the parameters were refined with all signs of atomic coordinates reversed and with regard to anomalous-dispersion corrections (Cromer & Liberman, 1970). According to the Hamilton (1965) R test the data in Table 1 represent the correct molecular configuration within a 99.5% confidence level:

$$\mathcal{R}_{1,1169,0.005} = 1.003; \frac{R_2}{R_1} = 1.120$$

$$\left(\frac{R_{w2}}{R_{w1}} = 1.150; \frac{R_{G2}}{R_{G1}} = 1.194 \right).$$

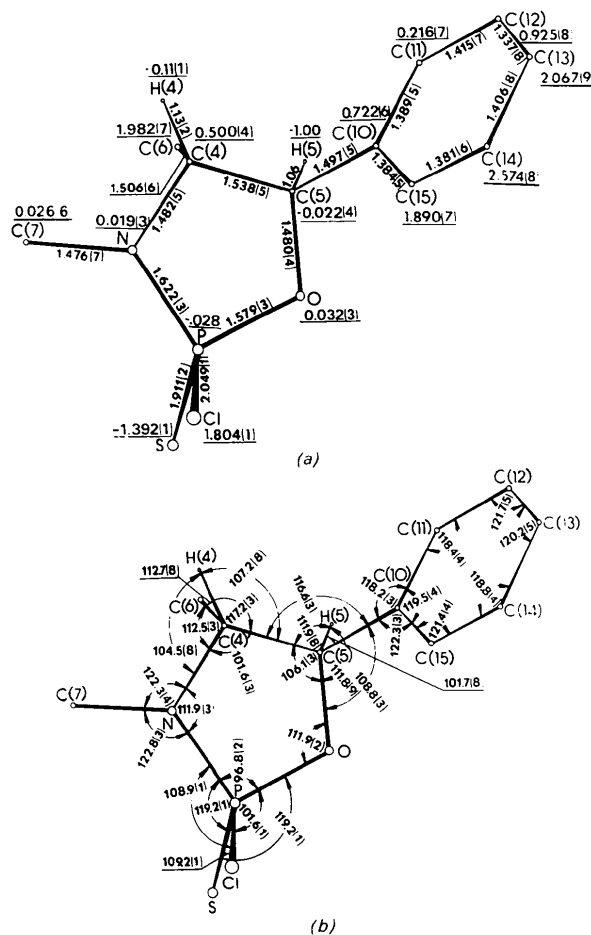
This result fully confirms the assignments given by Lesiak & Stec (1978) on the basis of NMR measurements. All calculations were performed using *SHELX 76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975).*

Discussion. Positional and equivalent isotropic thermal parameters of non-H atoms 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 shown in Fig. 1. There are four structures composed of 1,3,2-oxazaphospholidine rings described in the literature but all of them contain a five-coordinated P atom in the spiro arrangement: 1,6-dioxo-4,9-diaza-5 λ^5 -phos-

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	$U_{eq}(\text{\AA}^2)$
P	2856 (1)	235 (1)	9853 (1)	43 (1)
Cl	1850 (1)	955 (1)	1147 (1)	64 (1)
S	3993 (2)	8808 (1)	268 (1)	74 (1)
O	3564 (3)	1497 (3)	9393 (2)	49 (1)
C(4)	1562 (4)	1225 (4)	8274 (3)	52 (1)
C(5)	3018 (4)	1835 (4)	8342 (3)	46 (1)
N	1735 (4)	39 (3)	8914 (3)	53 (1)
C(6)	353 (4)	2047 (5)	8648 (4)	69 (1)
C(7)	719 (7)	8976 (5)	8911 (5)	93 (1)
C(10)	3104 (4)	3268 (4)	8197 (3)	48 (1)
C(11)	3464 (4)	3742 (5)	7211 (3)	61 (1)
C(12)	3542 (5)	5095 (5)	7066 (4)	80 (1)
C(13)	3239 (5)	5924 (5)	7854 (5)	90 (1)
C(14)	2908 (6)	5453 (4)	8842 (4)	76 (1)
C(15)	2842 (5)	4130 (4)	9005 (3)	63 (1)



* 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 38088 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. (a) Bond distances (Å) and atomic numbering in the molecule of BASTEL 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 (°).

phaspiro[4.4]nonane (I) and 2,3,7,8-dibenzo-1,6-dioxo-4,9-diaza-5 λ^5 -phosphaspiro[4.4]nona-2,7-diene (II) (Meunier, Day, Devillers & Holmes, 1978), a dioxazaspirophosphorane derived from (-)-ephedrine and tris(dimethylamino)phosphine (III) (Newton, Collier & Wolf, 1974) and 3,4-dimethyl-2,8-diphenyl-1,6-dioxo-4,9-diaza-5-phosphaspiro[4.4]nonan-7-one (IV) (Devillers, Garrigues & Wolf, 1979).

The P atom in BASTEL is a distorted tetrahedron. There are two angles smaller than tetrahedral in the environment of the P atom: the five-membered ring angles N–P–O of 96.8 (2) and Cl–P–O of 101.6 (1) $^\circ$; two angles practically equal to the tetrahedral angle: Cl–P–N = 108.9 (1) and Cl–P–S = 109.2 (1) $^\circ$ and two angles larger: N–P–S = 119.2 (1) and O–P–S = 119.2 (1) $^\circ$.

The angles formed by S–P and Cl–P bonds with the normal to the [N,P,O,C(5)] least-squares plane are 44.5 (5) and 153.4 (5) $^\circ$ respectively. It means that the Cl–P bond is in a more axial position than the S–P bond which is equatorial with respect to the ring determined by the plane defined above.

The C(6)–C(4) bond makes an angle of 169.8 (4) $^\circ$ to the normal to the least-squares plane [N,P,O,C(5)], *i.e.* this bond is in an axial position to the plane.

The sum of the bond angles at the ring N atom is 357 $^\circ$ which indicates nearly planar coordination. This planarity of the N atom testifies to sp^2 hybridization at N and the possibility of $d\pi - p\pi$ overlapping between P and N (Cameron, 1972). The ring N is also planar in (I), (III) and (IV), the sum of the bond angles being 360, 360 and 357 $^\circ$ respectively.

This interaction probably causes a shortening of the P–N single bond, 1.622 (3) Å, which is significantly shorter than in the four structures cited above: 1.640 (3) Å in (I), mean 1.653 (5) Å in (IV), mean 1.654 (3) Å in (II) and mean 1.693 (10) Å in (III). It is also shorter than the P–N bond in 2-phenyl-1,3-di-*p*-tolyl-1,3,2-diazaphospholidine (V) (Clardy, Kolpa & Verkade, 1974), 1.700 (5) Å, and shorter than the shortest P–N distances 1.65–1.66 Å found by Rømning & Songstad (1979) in tris(morpholino), tris(piperidino) and tris(dimethylamino)phosphine selenides. Only P–N bonds in some cyclophosphazenes are shorter, *e.g.* 1.58 Å in $N_3P_3Cl_6$ (Wilson & Carroll, 1960) and in $N_4P_4(NMe_2)_8$ (Bullen, 1962).

The N–C(7)(methyl) bond length of 1.476 (7) Å compares very well with a distance of 1.474 Å in methylamine (Lide, 1957), 1.474 (16) Å in (III) and 1.456 (8) Å in (IV). This bond makes an angle of 90.3 $^\circ$ with the normal to the least-squares plane described by N,P,O and C(5).

The P–O bond of 1.579 (3) Å is consistent with previously measured systems, *e.g.* in six-membered 1,3,2-dioxaphosphorinanes it ranges from 1.53 to 1.59 Å. However, this bond is significantly shorter than

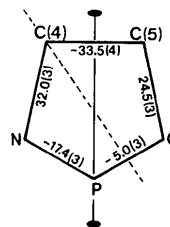


Fig. 2. The ring torsion angles and asymmetry parameters ($^\circ$) (Duax & Norton, 1975). $\Delta C_3^{C(4)} = 5.1$, $\Delta C_2^O = 10.2$.

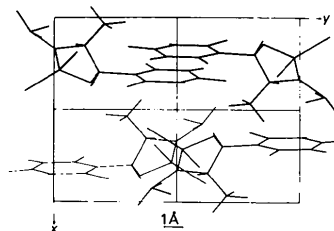


Fig. 3. The contents of the unit cell projected along z .

the P–O distance found in 1,3,2-oxazaphospholidines cited earlier, 1.663 (3) and 1.797 (3) Å in (IV), 1.700 (8) Å in (III), 1.710 (2) Å in (I) and mean 1.731 (3) Å in (II).

The 1,3,2-oxazaphospholidine ring exists in an envelope conformation with C(4) at the flap. The deviation of C(4) by 0.500 (4) Å from the least-squares plane [N,P,O,C(5)] generates an angle of 37.7 $^\circ$ between this plane and the [N,C(4),C(5)] plane. The conformation of the ring can also be characterized by the torsion angles and asymmetry parameters (Duax & Norton, 1975) given in Fig. 2.

The normal to the phenyl ring forms an angle of 121.8 (4) $^\circ$ with the normal to the least-squares plane [N,P,O,C(5)].

Fig. 3 shows the unit-cell contents.

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(2R,4S,5R)-2-Chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-Sulphide, C₁₀H₁₃CINOPS*

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Abstract. m.p. = 331 K, $M_r = 261.7$, orthorhombic, $P2_12_12_1$, $a = 10.380(1)$, $b = 11.129(5)$, $c = 11.151(1)$ Å, $V = 1288.07$ Å³, $Z = 4$, $D_c = 1.349$, $D_m = 1.331$ Mg m⁻³ (in aqueous KI), $F(000) = 544$. Final $R = 0.0500$ for 1010 observed reflections. The five-membered oxazaphospholidine ring exists in the crystal as a distorted envelope with C(4) deviating by $-0.526(8)$ 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 & Galdecki (1983).

Experimental. Colourless single shapeless crystal fragment, approx. $0.5 \times 0.4 \times 0.3$ mm, CAD-4 automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$, $\mu = 0.498$ mm⁻¹, 1226 reflections, room temperature, range $0 \leq 2\theta \leq 54^\circ$, 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 $\sin \theta/\lambda \leq 0.3$ 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 1.501 Å (value taken from BASTEL). The methyl H atoms were generated with the methyl groups assumed to be staggered (C–H constrained to 1.08 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 5.7. In the final ΔF 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 0.385 (U_{22} for P atom). Atomic scattering factors were those from *International Tables for X-ray Crystallography* (1974).

* Conformation of the 1,3,2-Oxazaphospholidine Ring. II.

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