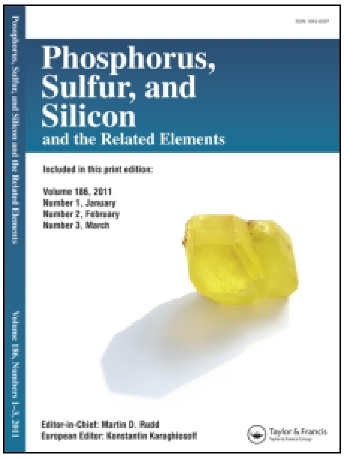

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CRYSTAL AND MOLECULAR STRUCTURE OF (2 *R*, 4*S*, 5*R*)-2-THIOMETHYL-3,4-DIMETHYL-5-PHENYL-1,3,2-OXAZAPHOSPHOLIDINE 2-OXIDE

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CRYSTAL AND MOLECULAR STRUCTURE OF (2*R*,4*S*,5*R*)-2-THIOMETHYL-3,4-DIMETHYL-5-PHENYL-1,3,2-OXAZAPHOSPHOLIDINE 2-OXIDE[†]

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The five-membered 1,3,2-oxazaphospholidine ring exists in the crystal in an envelope C(5) conformation combined with N half-chair. C(5) atom deviates by −0.49(1) Å from the C(4), N, P, O plane.

INTRODUCTION

Cis- and *trans*- isomers of 2-substituted 1,3,2-oxazaphospholidine 2-oxides, 2-sulfides and 2-selenides derived from (−)-ephedrine were synthesized and their configurations established by spectroscopic and chemical methods.[1] The conversion of dialkyl (aryl) phosphoroanilidates into corresponding phosphates and phosphorothioates proceeds fully stereospecifically with retention of configuration at P atom in the case of chiral acyclic molecules as well as in 4-methyl-1,3,2-dioxaphosphorinane derivatives.[2] Oxazaphospholidines derived from (−)-ephedrine were used as model compounds to investigate the stereoselectivity of above mentioned conversion when the P atom is incorporated into a five-membered ring.[3] The ^1H NMR of both starting 2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulfide isomers and of derivatives obtained from them were not very helpful for stereochemical analysis, possibly because of different conformations of the oxazaphospholidine ring due to spatial requirements of exocyclic substituents at the P atom.[3] Therefore, it seemed essential to establish the stereochemistry of these compounds by x-ray crystallography. The crystal and molecular structures of the diastereoisomeric pair: (2*S*,4*S*,5*R*)- (**1**) and (2*R*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulfides[1,3] (**2**) as well as of (2*R*,4*S*,5*R*)-2-anilido-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulfide[3] (**3**) were described elsewhere.[4–6] Here

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[†] *Conformation of 1,3,2-Oxazaphospholidine Ring IV. Parts I–III.*[4–6]

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we report the crystal structure of the title compound established by x-ray crystallography.

DISCUSSION

The P atom in the title compound is a distorted tetrahedron, similarly as in the three parent compounds cited.[4-6] The angles around the P atom in the oxide resemble rather those found in (**1**)[4] than in its isomer (**3**).[5] Thus, there are two angles smaller: the five-membered ring angle N—P—O(1) at 96.8(5) and S—P—O(2) = 104.8(4)°, two angles approximating: N—P—S = 111.5(4) and O(1)—P—S = 107.0(3)° and two angles larger than the tetrahedral one: N—P—O(2) = 117.5(5)° and O(1)—P—O(2) = 119.0(6)°. The P—S = 2.059(5) Å is typical for a single bond and the phosphoryl bond P—O(2) of 1.491(10) Å is in the range commonly encountered for a double bond P=O. These bonds are at an angle 104.7(4)° which is smaller than the angles formed by P—Cl and P—S bonds found in (**2**)[4] and (**3**)[5] 109.2(1) and 110.4(1) ° respectively. The positions of the substituents at the P atom and the angle between them is resultant of several interactions: the attraction of these substituents of various negativity and H(4) and H(5), the interaction with π system of the phenyl ring and the influence of methyl groups C(6) and C(7).

The endocyclic 1,3,2-oxazaphospholidine bond lengths and angles are similar to observed in above mentioned parent compounds, with two exceptions. The P—N bond being 1.669(10) Å is the longest one in the series described here. Of the other 1,3,2-oxazaphospholidines described in the literature[13-15] only for a dioxazaspirophosphorane derived from (−)-ephedrine and tris(dimethylamino)phosphine,[14] a longer value of 1.693(10) Å was reported. Also the P—O endocyclic bond 1.598(9) is slightly longer than in reported 2-sulfides.[4-6] The exocyclic N—C(7) distance of 1.37(2) is shortest found in the reported compounds.[4-6,14,15] This bond makes an angle of 87.1(5)° with the normal to the least-squares plane defined by the atoms C(4), N, P, O. This means that the bond, like in the other structures cited[4-6] is almost exactly equatorial. Consequently, the ring N atom is practically planar: $\Sigma = 359°$. The bonds C(6)—C(4) and C(10)—C(5) form the angles 150.4(5) and 71.1(5)° respectively with the above mentioned plane.

The 1,3,2-oxazaphospholidine ring in the title oxide is a combination of envelope with C(5) deviating by −0.49(1) Å and half-chair N what is illustrated by the asymmetry parameters,[10] Figure 2. The asymmetry parameters given in the Figure 2 were calculated using the formulae:

$$\Delta C_S = \sqrt{\frac{\sum_{i=1}^{m} (\phi_i + \phi_i')^2}{m}};$$

for the mirror plane shown in Figure 2.

$$\Delta C_2 = \sqrt{\frac{\sum_{i=1}^{m} (\phi_i - \phi_i')^2}{m}};$$

for the two-fold axis shown in the Figure 2, where m is the number of the symmetrical pairs of the torsion angles. ϕ_i and ϕ_i' are values of the torsion angles taking signs into account.

EXPERIMENTAL

$C_{11}H_{16}NO_2PS$, mol. weight 257.29. The compound was synthesized by the reaction of 2-anilido-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulfide[3,6] (**3**) with sodium hydride, followed by saturation of the reaction mixture with anhydrous CO_2 and alkylation of the resulting sodium phosphorothioate with methyl iodide.[3] Colorless, tiny crystals were kindly provided by Professor W. J. Stec of the Polish Academy of Sciences, Łódź, Poland. Preliminary Weissenberg photographs showed the crystal system to be orthorhombic with $a = 21.744(6)$, $b = 8.409(1)$, $c = 6.9704(5)$ Å, $Z = 4$, $D_m = 1.33_8$, $D_c = 1.341$ g/cm^3. Systematic extinctions were consistent with the space group $P2_12_12_1$. Attempts to grow larger crystals failed and a small specimen, approx. 0.15 × 0.10 × 0.10 mm, was used for intensity measurements on a Syntex $P2_1$ automated four-circle diffractometer with graphite-monochromatized CuK_α radiation ($\lambda = 1.54178$ Å). The small dimensions of the crystal available, made impossible application of the Mo radiation what would diminish the absorption effect. 1365 reflections were measured at room temperature within the max. $\sin\theta/\lambda$ value 0.544; of these 960 had $F_0 \geqslant 2\sigma(F_0)$ and were used for all calculations. The data were corrected for Lorentz and polarization effects but not for absorption: $\mu(\text{Cu}K_\alpha) = 3.19$ mm^{-1}. The max. hkl = 23, 9, 7.

The structure was solved by interpretation of a Patterson synthesis and refined by standard least-squares methods and difference electron density syntheses.[7] All H atoms, except those belonging to methyl groups, were located in a weighted difference electron density synthesis based on reflections with $\sin\theta/\lambda \leqslant 0.3$ Å^{-1}. The H atoms belonging to C(7) and C(6) methyl groups were generated geometrically and refined as rigid groups. Final anisotropic refinements converged with a conventional R_1 factor 0.120, a weighted R_{w1} factor 0.125 and R_{G1} factor 0.152. The small dimensions of the crystal used for data collection and its rather poor quality precluded achievement of lower R values. These rather high R values may be also explained by some degree of disorder visible particularly in C(1), C(7) and in carbon atoms of the phenyl ring (Table II, Figure 1). The absolute configuration of the molecule was confirmed by the chemical correlations (Ref. 3, Scheme 2) and by the established configuration of parent compounds by x-ray diffraction.[4-6] It was additionally confirmed by refinement of the crystal structure parameters with regard to anomalous-dispersion corrections for P and S atoms.[8] The final R_2, R_{w2} and R_{G2} values for molecule with all positional parameters given negative signs were 0.113, 0.116 and 0.142 respectively. The significance test on the R factor[9] showed that the proper configuration is described by the model

TABLE I

Final atomic positional parameters

Atom	*X*	*Y*	*Z*
P	−0.41201(11)	−0.49919(33)	−0.42726(56)
S	−0.34240(16)	−0.38364(41)	−0.57118(76)
C(1)	−0.29802(89)	−0.5389(21)	−0.6673(39)
O(1)	−0.38024(33)	−0.6074(10)	−0.2669(14)
O(2)	−0.45492(41)	−0.3704(11)	−0.3665(17)
N	−0.44111(39)	−0.6477(11)	−0.5577(16)
C(7)	−0.47685(89)	−0.6281(25)	−0.7169(26)
C(4)	−0.43195(44)	−0.8029(13)	−0.4669(18)
C(5)	−0.41253(54)	−0.7644(15)	−0.2570(21)
C(6)	−0.38698(53)	−0.9047(13)	−0.5805(20)
C(10)	−0.37161(50)	−0.8780(16)	−0.1608(18)
C(11)	−0.31537(50)	−0.8393(16)	−0.0833(24)
C(12)	−0.28202(51)	−0.9526(19)	−0.9856(22)
C(13)	−0.30394(55)	−0.1070(18)	−0.9566(33)
C(14)	0.35759(72)	−0.1433(18)	−0.0476(27)
C(15)	−0.3960(57)	−0.0372(18)	−0.1302(20)

The estimated standard deviations of the least significant digits are given in parentheses.

(x, y, z). The final difference Fourier synthesis was featureless, showing two peaks ca. 0.3 e/Å^3 close to the sulfur atom. The analysis of variance of the final calculated structure factor versus various classes of reflections was "flat".[7] The weights were $w = k/[\sigma^2(F_0) + gF_0^2]$ where k and g refined to 0.5093 and 0.0313 respectively.

Final atomic positional parameters and anisotropic temperature factors appear in Tables I and II. Bond lengths and angles are given in Tables III and IV, respectively. Figure 1 shows the computer-generated drawing of the title compound with atom labelling[11] and Figure 2 shows the torsion angles in the 1,3,2-oxazaphospholidine ring with their estimated standard deviations.[12]

TABLE Ia

Final atomic parameters of the hydrogen atoms

Atom	Parent atom	X	Y	Z	Uiso
H(1)	C(1)	−0.2812	−0.4779	−0.7640	0.0835
H(2)		−0.2676	−0.6063	−0.5525	0.0835
H(3)		−0.3116	−0.6143	−0.7730	0.0835
H(4)	C(4)	−0.4727	−0.8701	−0.4511	0.0596
H(5)	C(5)	−0.4469	−0.7393	−0.2169	0.0525
H(61)	C(6)	−0.3969	0.0142	−0.5360	0.0520
H(62)		−0.4067	−0.8897	−0.7234	0.0520
H(63)		−0.3409	−0.8537	−0.5787	0.0520
H(71)	C(7)	−0.4769	−0.5182	−0.8142	0.0658
H(72)		−0.4688	−0.7015	−0.8076	0.0658
H(73)		−0.5250	−0.6552	−0.6366	0.0658
H(11)	C(11)	−0.7350	−0.2611	−0.4144	0.0580
H(12)	C(12)	−0.7604	−0.4303	−0.5258	0.0613
H(13)	C(13)	−0.7322	−0.6811	−0.5959	0.0587
H(14)	C(14)	−0.6272	−0.7712	−0.4856	0.0572
H(15)	C(15)	−0.5527	−0.5497	−0.3760	0.0542

TABLE II

Anisotropic thermal parameters (in square Angstroms) times 10.000

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
P	482(15)	353(17)	595(21)	−25(18)	9(14)	43(13)
S	831(21)	390(19)	925(31)	132(21)	200(23)	−91(15)
C(1)	1008(114)	572(96)	1751(226)	−300(126)	721(147)	−65(91)
O(1)	488(36)	420(50)	689(64)	−29(49)	−60(40)	−137(36)
O(2)	600(43)	500(51)	1011(85)	−170(61)	18(52)	163(42)
N	507(42)	370(50)	493(60)	70(55)	3(49)	58(39)
C(7)	1270(131)	691(111)	625(114)	9(107)	−113(97)	161(105)
C(4)	398(49)	319(55)	409(72)	90(56)	30(49)	−60(46)
C(5)	503(54)	396(70)	572(84)	71(64)	18(68)	−112(55)
C(6)	674(62)	406(66)	393(70)	−169(62)	−153(62)	102(55)
C(10)	552(57)	409(69)	371(72)	37(62)	−73(54)	25(53)
C(11)	499(58)	535(82)	618(92)	−176(79)	209(66)	−58(54)
C(12)	418(49)	748(101)	634(95)	93(83)	−45(56)	85(60)
C(13)	484(59)	599(90)	1295(156)	215(120)	213(90)	167(63)
C(14)	931(88)	465(79)	612(111)	130(93)	115(86)	−98(71)
C(15)	614(62)	648(85)	433(77)	−17(72)	−133(57)	−7(64)

The estimated standard deviations of the least significant digits are given in parentheses.

TABLE III

Bond lengths (Å)

S—P	2.059(5)	O(1)—P	1.598(9)
O(2)—P	1.491(10)	N—P	1.669(10)
C(1)—S	1.756(20)	C(5)—O(1)	1.497(15)
C(7)—N	1.365(21)	C(4)—N	1.464(15)
C(4)—C(5)	1.557(19)	C(4)—C(6)	1.522(16)
O(1)—C(5)	1.497(15)	C(5)—C(10)	1.468(18)
C(10)—C(11)	1.376(17)	C(10)—C(15)	1.453(20)
C(11)—C(12)	1.378(20)	C(12)—C(13)	1.398(22)
C(13)—C(14)	1.363(22)	C(14)—C(15)	1.351(21)

The estimated standard deviations of the least significant digits are given in parentheses.

TABLE IV

Bond angles (°)

O(1)—P—S	107.0(0.3)	O(2)—P—S	104.8(0.4)
O(2)—P—O(1)	119.0(0.6)	N—P—S	111.5(0.4)
N—P—O(1)	96.8(0.5)	N—P—O(2)	117.5(0.5)
C(1)—S—P	103.8(0.7)	C(5)—O(1)—P	109.4(0.7)
C(7)—N—P	124.6(1.1)	C(4)—N—P	112.3(0.8)
C(4)—N—C(7)	122.5(1.2)	C(5)—C(4)—N	104.9(0.9)
C(6)—C(4)—N	111.3(1.0)	C(6)—C(4)—C(5)	115.6(0.9)
C(10)—C(5)—O(1)	108.1(0.9)	C(10)—C(5)—C(4)	117.3(1.1)
C(11)—C(10)—C(5)	124.4(1.2)	C(15)—C(10)—C(5)	116.4(1.0)
C(15)—C(10)—C(11)	118.9(1.2)	C(12)—C(11)—C(10)	119.9(1.2)
C(13)—C(12)—C(11)	122.3(1.2)	C(14)—C(13)—C(12)	115.7(1.5)
C(15)—C(14)—C(13)	125.4(1.5)	C(14)—C(15)—C(10)	116.4(1.2)

The estimated standard deviations of the least significant digits are given in parentheses.

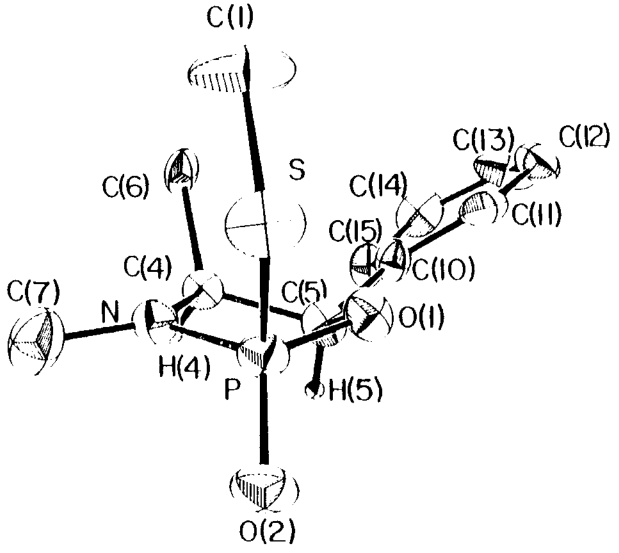

FIGURE 1 Computer-generated drawing of the title compound. The thermal ellipsoids are shown with 30% probability.[11]

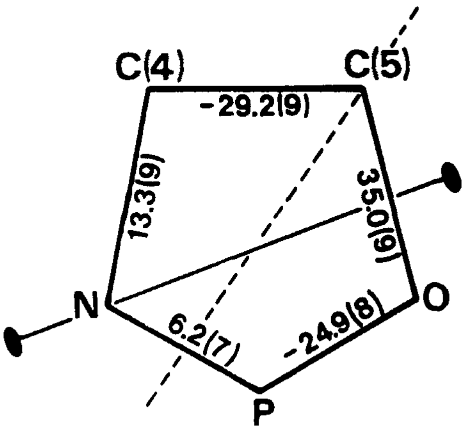

FIGURE 2 The torsion angles (°) with their estimated standard deviations and asymmetry parameters:[10]

$$\Delta C_S^{C(5)} = 9.2°, \qquad \Delta C_2^{P} = 5.9°.$$

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REFERENCES

1. D. B. Cooper, C. R. Hall, J. M. Harrison and T. D. Inch, *J. Chem. Soc. Perkin Trans.*, **1** (1977), 1969.
2. W. J. Stec, A. Okruszek, K. Lesiak, B. Uznański and J. Michalski, *J. Org. Chem.*, **41** (1976), 227.
3. K. Lesiak and W. J. Stec, *Z. Naturforsch. Teil B*, **33** (1978), 782.
4. T. J. Bartczak and Z. Gałdecki, *Acta Cryst.*, **C39** (1983), 219–222.
5. T. J. Bartczak, Z. Gałdecki and M. Rutkowska, *Acta Cryst.* **C39** (1983), 222–224.
6. T. J. Bartczak, Z. Gałdecki and M. Rutkowska, *Acta Cryst.* **C39** (1983), 614–616.
7. G. M. Sheldrick, *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.
8. D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891–1898.
9. W. C. Hamilton, *Acta Cryst.* **18** (1965), 502–510.
10. W. L. Duax and D. A. Norton, *Atlas of Steroid Structure*, pp. 16–22, New York: Plenum Press (1975).
11. C. A. Johnson, ORTEP II, *A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, U.S. Atomic Energy Report ORNYL-3794, Second Revision with Supplemental Instructions, Oak Ridge National Laboratory, Oak Ridge, Tenn., (1971).
12. The table of atomic co-ordinates together with the tables of bond lengths & angles have been deposited with the Cambridge Crystallographic Data Centre, United Kingdom, and is available on request from the Director, CCDC, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation.
13. P. F. Meunier, R. O. Day, J. R. Devilliers and R. R. Holmes, *Inorg. Chem.*, **17** (1978), 3270–3276.
14. J. Devilliers, B. Garrigues and R. Wolf, *Acta Cryst.* **B35** (1979), 2153–2161.
15. M. G. Newton, J. E. Collier and R. Wolf, *J. Am. Chem. Soc.*, **96** (1974), 6888–6892.