

Fig. 2. (100) projection of the structure. Symmetry code: (I) x, y, z ; (II) $x, y, z-1$; (III) $\bar{x}, 1-y, 2-z$; (IV) $\bar{x}, 1-y, 1-z$; (V) $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; (VI) $\bar{x}, \frac{1}{2}+y, \frac{3}{2}-z$; (VII) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (VIII) $x, \frac{1}{2}-y, z-\frac{1}{2}$.

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(2R,4S,5R)-2-Anilino-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-Sulphide,
C₁₆H₁₉N₂OPS*

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Abstract. $M_r = 318.4$, orthorhombic, $P2_12_12_1$, $a = 10.935(1)$, $b = 16.757(5)$, $c = 9.192(1)$ Å, $V = 1684.3$ Å³, $Z = 4$, $D_c = 2.084$ Mg m⁻³, graphite-monochromated Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.242$ mm⁻¹, $F(000) = 672$, room temperature, $R = 0.0682$ for 1324 observed reflections. The five-membered oxazaphospholidine ring exists in the crystal in an envelope conformation with P deviating by $-0.339(2)$ Å downwards from the least-squares plane N(1), C(4), C(5), O.

Introduction. The compound was synthesized by reaction of (2*S*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulphide (Lesiak & Stec, 1978; Bartczak & Galdecki, 1983) with lithium anilide.

Experimental. Irregular plate, approximately $0.4 \times 0.5 \times 0.6$ mm, CAD-4 automated four-circle diffrac-

tometer, 1778 unique reflections, $1 \leq 2\theta \leq 54^\circ$, 1324 with $F_o \geq 3\sigma(F_o)$, no absorption correction, maximum $hkl = 13,21,11$, noncentrosymmetric direct methods (SHELX 76, Sheldrick, 1976), standard least-squares methods and difference electron density syntheses, then blocked full-matrix technique. All H atoms, except those belonging to methyl groups C(6) and C(7), were located in subsequent difference Fourier syntheses based on reflections with $\sin \theta/\lambda \leq 0.3$ Å⁻¹. C(4) and C(6) and some C atoms of the phenyl rings were resolved with some difficulty in the initial stages of the structure solution, so the phenyl rings were converted into regular hexagons and refined as rigid groups. The constraints were released when passing to anisotropic refinements. Some final thermal parameters of C(4), C(6), C(22), C(23), C(24), C(25) and C(12) have rather high values which may indicate some degree of conformational disorder. However, a difference Fourier synthesis calculated without C(4) and C(6) did not reveal significantly extended regions of electron density. Methyl H atoms were generated in the final stages of refinement with the methyl groups C(6) and C(7)

References

- BOHLMANN, F., NIEBALLA, U. & SCHULZ, J. (1969). *Chem. Ber.* **102**, 864–871.
 BOIS, C. (1970). *Acta Cryst.* **B26**, 2086–2092.
 DHEKNE, V. V. & RAO, A. S. (1980a). *Indian J. Chem.* **19B**, 852–855.
 DHEKNE, V. V. & RAO, A. S. (1980b). *Synthesis*, pp. 58–60.
 GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *LALS. Full-Matrix Least-Squares Refinement of Positional and Thermal Parameters and Scale Factors*.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 PIPPY, M. E. & AHMED, F. R. (1978). *NRC-12. Scan of Interatomic Distances and Angles. NRC-22. Mean Plane and Torsion Angles*. NRC Crystallographic Programs for the IBM/360 System.
 PORTE, A. L. & ROBERTSON, J. M. (1959). *J. Chem. Soc.* pp. 817–824.

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

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assumed to be staggered (C—H constrained to 1.08 Å) and refined as rigid groups. The positional parameters of H(2), H(4) and H(5) atoms were refined with isotropic temperature factors taken as for their parent C atoms. The final refinements converged with $R = 0.0682$, $R_w = 0.0685$, $w = k/[\sigma^2(F_o) + gF_o^2]$, $k = 1.2994$, $g = 0.0022$, and $R_G = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2} = 0.769$. Reversing the hand of the molecule did not make a significant difference to the final R factor: $R = 0.0684$ (model $\bar{x}, \bar{y}, \bar{z}$). The absolute configuration is indicated by chemical correlations (Lesiak & Stec, 1978) and by our previous crystal structure determinations (Bartczak & Gałdecki, 1983; Bartczak, Gałdecki & Rutkowska, 1983). In the final difference Fourier map no significant density was observed. Shift-to-error ratio for all parameters was less than 0.4 in the last cycle of refinement. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). All calculations were performed using *SHELX 76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975).

Discussion. Positional and equivalent thermal parameters of non-H atoms are listed in Table 1.* A perspective view of the molecule projected onto the least-squares plane [N(1),P,O,C(5)] with numbering and bond distances is shown in Fig. 1.

The environment of the P atom in the title compound is, as had been expected, a distorted tetrahedron but more regular than that found in previously reported structures of (2*S*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulphide (Bartczak & Gałdecki, 1983) and its diastereoisomeric pair (Bartczak, Gałdecki & Rutkowska, 1983). There is only one angle in the present structure smaller than tetrahedral: the five-membered-ring angle (Table 2) N(1)—P—O = 95.5 (3)°. This is the smallest ring angle at the P atom in the three structures cited. Three angles are close to tetrahedral: N(1)—P—N(2) = 108.3 (3), N(2)—P—O = 107.6 (3) and N(2)—P—S = 109.8 (2)° and two angles are larger: N(1)—P—S = 119.1 (2) and O—P—S = 115.3 (2)°. The bonds at the ring N atom are not quite coplanar as in (2*R*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulphide (the sum of angles $\Sigma = 354^\circ$) and the internal ring angle C(4)—N—P = 113.8 (5)° is the largest one in the three structures. The angle at the O atom, C(5)—O—P = 113.4 (4)°, is also the largest in the series as are the angles at C(4) and C(5): 106.1 (7) and 107.1 (6)°, respectively.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and deviations of C atoms from the least-squares planes of the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38333 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional* ($\times 10^4$) and *equivalent isotropic thermal parameters* ($\times 10^3$) of non-H atoms

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

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} (Å ²) |
|-------|------------|----------|-----------|----------------------------|
| N(2) | 11725 (5) | 6164 (3) | 1849 (7) | 66 (1) |
| C(20) | 10965 (7) | 6811 (4) | 1369 (8) | 65 (1) |
| C(21) | 10183 (7) | 6697 (5) | 208 (9) | 78 (2) |
| C(22) | 9419 (8) | 7328 (6) | -188 (10) | 93 (2) |
| C(23) | 9433 (10) | 8036 (6) | 560 (11) | 108 (2) |
| C(24) | 10193 (10) | 8125 (5) | 1680 (11) | 111 (2) |
| C(25) | 10983 (9) | 7517 (4) | 2106 (9) | 88 (2) |
| P | 11463 (2) | 5626 (1) | 3313 (2) | 48 (1) |
| S | 12713 (2) | 4825 (1) | 3520 (3) | 62 (1) |
| O | 10106 (4) | 5296 (3) | 3205 (5) | 59 (1) |
| N(1) | 11192 (6) | 6234 (3) | 4672 (7) | 62 (1) |
| C(7) | 12185 (9) | 6641 (5) | 5418 (10) | 88 (2) |
| C(4) | 10091 (7) | 6050 (6) | 5465 (9) | 84 (2) |
| C(6) | 9397 (10) | 6802 (8) | 5808 (13) | 189 (2) |
| C(5) | 9387 (7) | 5428 (5) | 4532 (9) | 65 (1) |
| C(10) | 8107 (5) | 5656 (4) | 4092 (8) | 55 (1) |
| C(11) | 7111 (8) | 5379 (6) | 4860 (13) | 103 (2) |
| C(12) | 5920 (7) | 5605 (6) | 4444 (14) | 110 (2) |
| C(13) | 5745 (7) | 6065 (6) | 3271 (13) | 98 (2) |
| C(14) | 6686 (7) | 6351 (5) | 2522 (9) | 78 (2) |
| C(15) | 7892 (6) | 6161 (4) | 2923 (8) | 58 (1) |

Table 2. *Bond angles* (°)

| | | | |
|-------------------|-----------|-------------------|-----------|
| P—N(2)—H(2) | 111 (3) | C(14)—C(15)—C(10) | 120.0 (6) |
| P—N(2)—C(20) | 124.3 (5) | C(21)—C(20)—N(2) | 119.4 (6) |
| C(20)—N(2)—H(2) | 123 (3) | C(25)—C(20)—C(21) | 120.9 (7) |
| C(25)—C(20)—N(2) | 119.6 (7) | C(23)—C(22)—C(21) | 121.2 (8) |
| C(22)—C(21)—C(20) | 117.9 (8) | C(25)—C(24)—C(23) | 121.5 (8) |
| C(24)—C(23)—C(22) | 119.5 (9) | S—P—N(2) | 109.8 (2) |
| C(24)—C(25)—C(20) | 119.1 (8) | O—P—S | 115.3 (2) |
| O—P—N(2) | 107.6 (3) | N(1)—P—S | 119.1 (2) |
| N(1)—P—N(2) | 108.3 (3) | C(5)—O—P | 113.4 (4) |
| N(1)—P—O | 95.5 (3) | C(4)—N(1)—P | 113.8 (5) |
| C(7)—N(1)—P | 121.0 (5) | C(6)—C(4)—N(1) | 110.4 (8) |
| C(4)—N(1)—C(7) | 119.1 (7) | C(5)—C(4)—C(6) | 115.4 (7) |
| C(5)—C(4)—N(1) | 106.1 (6) | C(10)—C(5)—O | 108.2 (6) |
| C(4)—C(5)—O | 107.1 (6) | C(11)—C(10)—C(5) | 120.7 (7) |
| C(10)—C(5)—C(4) | 115.9 (6) | C(15)—C(10)—C(11) | 117.9 (7) |
| C(15)—C(10)—C(5) | 121.3 (6) | C(13)—C(12)—C(11) | 120.3 (9) |
| C(12)—C(11)—C(10) | 120.1 (9) | C(15)—C(14)—C(13) | 120.6 (8) |
| C(14)—C(13)—C(12) | 121.0 (8) | | |

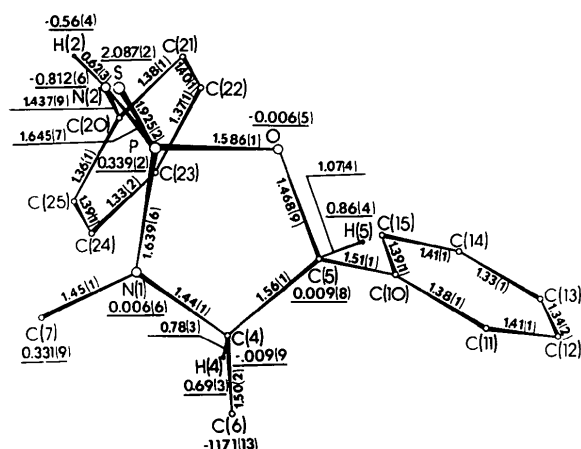


Fig. 1. Bond lengths (Å) and atomic numbering in the molecule of (2*R*,4*S*,5*R*)-2-anilino-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-sulphide projected onto the plane formed by N(1), O, C(5) and C(4). Underlined are deviations of atoms above the least-squares plane (Å). E.s.d.'s in parentheses refer to the last significant digit.

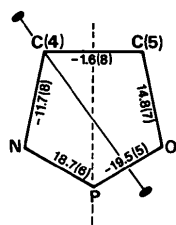


Fig. 2. The ring torsion angles and asymmetry parameters ($^{\circ}$) (Duax & Norton, 1975). $\Delta C_2^3 = 2.3(8)^{\circ}$, $\Delta C_2^4 = 7.7(8)^{\circ}$.

The C(7)–N and C(6)–C(4) bonds form angles of $102.9(9)$ and $39.4(9)^{\circ}$ with the normal to the least-squares plane [N(1),O,C(4),C(5)].

The oxazaphospholidine ring is almost an ideal envelope with the P atom deviating by $-0.339(2)$ Å from the least-squares plane [N(1),O,C(4),C(5)], Fig. 1. The angle between this plane and the [O,P,N(1)] plane is $18.2(9)^{\circ}$. The substituents at the aniline N atom are nearly coplanar ($\Sigma = 358^{\circ}$). The plane [P,N(2),C(20)] is almost exactly perpendicular to the [N(1),O,C(5),C(4)] plane; the angle between normals to these planes is $88.1(9)^{\circ}$. The S–P bond is practically coplanar with the plane [P,N(2),C(20)] and forms the angle of $89.8(6)^{\circ}$ with the normal to this plane. The plane is also very nearly coplanar with a pseudo plane of symmetry passing through C(23),C(20) and the middle of the C(4)–C(5) bond. It is illustrated by the distances

of the following atoms from the plane: $-1.147(7)$ and $1.098(10)$ Å for C(22) and C(24), $-1.217(5)$ and $1.166(6)$ Å for O and N(1), $-0.844(8)$ and $0.707(9)$ Å for C(5) and C(4). The phenyl rings show normal geometry. The normals to them form the angles $108(1)$ and $102(1)^{\circ}$ respectively with the normal to the [N(1),O,C(5),C(4)] plane.

Fig. 2 shows torsion angles and asymmetry parameters for the oxazaphospholidine ring.

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References

- BARTCZAK, T. J. & GALDECKI, Z. (1983). *Acta Cryst.* **C39**, 219–222, and references cited therein.
 BARTCZAK, T. J., GALDECKI, Z. & RUTKOWSKA, M. (1983). *Acta Cryst.* **C39**, 222–224.
 DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, pp. 16–22. New York: Plenum Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 LESIAK, K. & STEC, W. J. (1978). *Z. Naturforsch. Teil B*, **33**, 782–785.
 ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of *p*-(*p*-Nitroanilino)phenyl Isothiocyanate, C₁₃H₉N₃O₂S*

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Abstract. $M_r = 271.30$, monoclinic, $P2_1/n$, $a = 9.1998(3)$, $b = 10.6690(4)$, $c = 12.6690(4)$ Å, $\beta = 98.725(2)^{\circ}$, $V = 1229.1$ Å³, $Z = 4$, $D_m = 1.44(2)$, $D_x = 1.466$ g cm⁻³, $\lambda(\text{Cu } K\alpha_1) = 1.54056$ Å, $\mu = 23.0$ cm⁻¹, $F(000) = 560$, $T = 296(1)$ K. Final $R(F) = 0.039$ for 1964 counter reflections. The two planar benzene rings, connected by an imino N atom, make an

angle of $47.28(6)^{\circ}$ with each other. The SCNC group is nearly linear, with S–C–N and C–N–C angles of $178.1(2)$ and $168.9(3)^{\circ}$ respectively. The C–NH–C group is nearly planar; the C–N–C angle has the large value $127.6(1)^{\circ}$, due mainly to steric repulsion between the two aromatic rings.

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Introduction. Hycanthonone is a drug still widely used in Africa, the Middle East, and Brazil for the treatment of schistosomiasis despite its potential risks to human health implied by the carcinogenic, mutagenic, and teratogenic activities observed in experimental animals