Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 2-(4-Methoxyphenyl)-4*H*-1,3,2-benzoxathiaphosphinine 2-sulfide

**Vitaly A. Osyanin,[a] Elena A. Ivleva,[a] Victor B. Rybakov[b]* and Yurij N. Klimochkin[a]**

[a]Samara State Technical University, Molodogvardeyskay Str. 244, 443100 Samara, Russian Federation, and [b]Department of Chemistry, Moscow State University, 119992 Moscow, Russian Federation
Correspondence e-mail: rybakov20021@yandex.ru

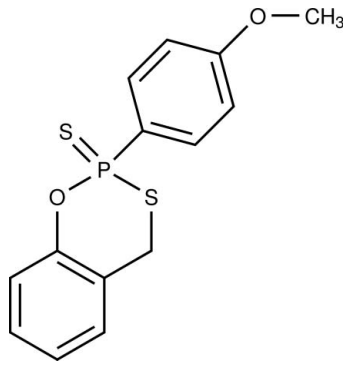
Received 3 December 2010; accepted 17 December 2010

Key indicators: single-crystal X-ray study; $T$ = 150 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.031; $wR$ factor = 0.078; data-to-parameter ratio = 14.3.

The asymmetric unit of the title compound, $C_{14}H_{13}O_2PS_2$, contains two crystallographically independent molecules, which differ in the conformation of the 1,3,2-benzoxathiaphosphinine moieties (screw boat in the first molecule and envelope in the second molecule). In the crystal, neither classical nor non-classical hydrogen bonds are found. Weak interactions (about 2.9–3.0 Å) between the lone pair of the terminal S atoms with H atoms occur. This compound was further characterized by $^1$H NMR and IR spectroscopy.

## Related literature

Lawesson's reagent is widely used for transformation of a carbonyl functional group into a thiocarbonyl, see: Ozturk *et al.* (2007). Lawesson's reagent reacts with 1,2-naphthoquinone-1-methide precursors to give 1*H*-naphtho[1,2-*e*][1,3,2]oxathiaphosphinine 2-sulfide derivatives, which are of interest as herbicides, see: El-Kateb & El-Rahman (2006); El-Kateb *et al.* (1991); Maigali *et al.* (2009). For conformational calculations, see: Cremer & Pople (1975); Zefirov *et al.* (1990); Zotov *et al.* (1997). For a description of the Cambridge Structural Database, see: Allen (2002).




## Experimental

### Crystal data

$C_{14}H_{13}O_2PS_2$
$M_r$ = 308.35
Triclinic, $P\overline{1}$
$a$ = 10.0548 (5) Å
$b$ = 10.0804 (5) Å
$c$ = 14.8913 (7) Å
$\alpha$ = 94.322 (4)°
$\beta$ = 91.121 (4)°
$\gamma$ = 111.675 (4)°
$V$ = 1396.79 (12) Å$^3$
$Z$ = 4
Cu $K\alpha$ radiation
$\mu$ = 4.50 mm$^{-1}$
$T$ = 150 K
0.20 × 0.14 × 0.05 mm

### Data collection

Oxford Diffraction Xcalibur Atlas Gemini ultra diffractometer
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2010); based on expressions derived by Clark & Reid (1995)]
$T_{min}$ = 0.499, $T_{max}$ = 0.816
27233 measured reflections
4926 independent reflections
4175 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.051

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.078
$S$ = 1.05
4926 reflections
345 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *OLEX2* (Dolomanov *et al.*, 2009); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *OLEX2*.

The authors are indebted to the Russian Foundation for Basic Research for covering the licence fee for use of the Cambridge Structural Database (Allen, 2002). The authors thank Dr Alex Griffin (Agilent Technologies) for the X-ray diffraction experiment.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VM2065).

## References


Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
El-Kateb, A. A. & El-Rahman, N. M. A. (2006). *Phosphorus Sulfur Silicon Relat. Elem.* **181**, 249–254.
El-Kateb, A. A., Hennawy, I. T., Shabana, R. & Abdel-Malek, H. A. (1991). *Phosphorus Sulfur Silicon Relat. Elem.* **63**, 13–17.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Maigali, S. S., Shabana, R., El-Hussieny, M. & Soliman, F. M. (2009). *Phosphorus Sulfur Silicon Relat. Elem.* **184**, 2408–2426.
Oxford Diffraction (2010). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Ozturk, T., Ertas, E. & Mert, O. (2007). *Chem. Rev*. **107**, 5210–5278.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zefirov, N. S., Palyulin, V. A. & Dashevskaya, E. E. (1990). *J. Phys. Org. Chem.* **3**, 147–158.
Zotov, A. Yu., Palyulin, V. A. & Zefirov, N. S. (1997). *J. Chem. Inf. Comput. Sci.* **37**, 766–773.

# supporting information

*Acta Cryst.* (2011). E**67**, o388–o389 [doi:10.1107/S1600536810053146]

## 2-(4-Methoxyphenyl)-4*H*-1,3,2-benzoxathiaphosphinine 2-sulfide

**Vitaly A. Osyanin, Elena A. Ivleva, Victor B. Rybakov and Yurij N. Klimochkin**

### S1. Comment

Lawesson's reagent is widely used for transformation of a carbonyl functional group into a thiocarbonyl (Ozturk *et al.*, 2007). At the same time, the reaction of Lawesson's reagent with compounds having two nucleophilic or one nucleophilic and one electrophilic centers may lead to heterocyclic rings incorporating part of Lawesson's reagent.

It was shown that Lawesson's reagent reacts with 1,2-naphthoquinone-1-methide precursors to give 1*H*-naphtho[1,2-e][1,3,2]oxathiaphosphinine 2-sulfide derivatives which are interesting as herbicides (El-Kateb & El-Rahman, 2006; El-Kateb *et al.*, 1991; Maigali *et al.*, 2009). However, preparation of 4*H*-1,3,2-benzoxathiaphosphinine 2-sulfides from salicylic alcohols was not described in literature. The 2-(4-methoxyphenyl)-4*H*-1,3,2-benzoxathiaphosphinine 2-sulfide was prepared from Lawesson's reagent and *o*-hydroxybenzyl alcohol in *o*-xylene at reflux in 35% yield. A mechanism accounting for the formation of structure **I** is depicted in Fig. 1. The hydroxybenzyl alcohol loses a molecule of water to give the *o*-quinone methide **II**. A nucleophilic attack on the methylene group of **II** by the sulfur anion of the monomeric form of Lawesson's reagent produces the zwitterionic intermediate which is cyclized to give the end product **I**.

The asymmetric unit of a crystal of **I** contains two crystallographically independent molecules, which are different by the conformation of the 1,3,2-benzoxathiaphosphinine moieties: in molecule **a** - screw boat, and in molecule **b** - distorted envelope. The Zotov-Palyulin puckering parameters for molecule **a** are: $S$ = 0.886, $\theta$ = 80.83°, $\psi_2$ = 347.94°, $\sigma$ = 4.21 (Zefirov *et al.*, 1990; Zotov *et al.*, 1997). Cremer-Pople parameters for comparison: $Q$ = 0.750 Å, $\theta$ = 76.92°, $\varphi_2$ = 341.43° (Cremer & Pople, 1975). For molecule **b**: $S$ = 0.751, $\theta$ = 35.92°, $\psi_2$ = 356.11°, $\sigma$ = 3.86 (Zotov-Palyulin), and $Q$ = 0.666 Å, $\theta$ = 52.87°, $\varphi_2$ = 2.08° (Cremer-Pople).

In the crystal structure neither classical nor non-classical hydrogen bonds are found, but weak interactions between lone pairs of terminal S atoms with H atoms are found: C12*a*–H12*a*···S21*a* [C12*a*–H12*a* = 0.95 Å, C12*a*···S21*a* = 3.379 (2) Å, H12*a*···S21*a* = 2.894 Å, angle C12*a*–H12*a*···S21*a* = 113°]; C17*a*–H17*b*···S21*b*Å [C17*a*–H17*b* = 0.98 Å, C17*a*···S21*b* = 3.817 (3) Å, H17*b*···S21*b* = 2.847 Å, angle C17*a*–H17*b*···S21*b* = 170°]; C17*a*–H17*c*···S21*a*$^{i}$ [C17*a*–H17*c* = 0.98 Å, C17*a*···S21*a*$^{i}$ = 3.906 (3) Å, H17*c*···S21*a*$^{i}$ = 2.978 Å, angle C17*a*–H17*c*···S21*a*$^{i}$ = 159°]; C4b–H4*b*2···S3a$^{ii}$ [C4b–H4*b*2 = 0.99 Å, C4b···S3a$^{ii}$ = 3.796 (2) Å, H4*b*2···S3a$^{ii}$ = 2.996 Å, angle C4b–H4*b*2···S3a$^{ii}$ = 139°]; C8b–H8b···S21*b*$^{iii}$ [C8b–H8b = 0.95 Å, C8b···S21*b*$^{iii}$ = 3.657 (3) Å, H8b···S21*b*$^{iii}$ = 2.944 Å, angle C8b–H8b···S21*b*$^{iii}$ = 133°]. Symmetry codes: (i) -*x* + 1, -*y* + 1, -*z*; (ii) *x*, *y* + 1, *z* + 1; (iii) *x*, *y* + 1, *z*.

### S2. Experimental

A mixture of Lawesson's reagent (3.31 g, 8.2 mmol) and *o*-hydroxybenzyl alcohol (1 g, 8.2 mmol) in *o*-xylene (30 ml) was refluxed for 2 h. The solvent was removed *in vacuo* and the residue was dissolved in 15 ml of methanol at reflux and cooled to room temperature. Insoluble impurity was filtered off and filtrate then stored at 253 K overnight. The precipitate formed was then filtered, washed ice-cold methanol. Recrystallization of the crude product from methanol gave 0.88 g of colourless crystals. Yield 35%, m.p. 357-358 K. IR-spectra, $\nu$, cm$^{-1}$: 3067 (CH-aromatic.), 2966, 2928,

2839 (CH-aliphatic), 1593 (C═C), 1562, 1497, 1481, 1474, 1447 (P–C), 1300, 1261, 1211, 1173, 1111, 1022, 926, 833, 763, 729, 698, 683. MS(ESI): m/*z* 308 $[M]^+$ (100), 275 $[M\text{-SH}]^+$ (36), 243 (14), 242 (15), 169 (13), 153 (50), 139 (57), 137 $[C_7H_5OS]^+$ (23), 122 (15). $^1$H NMR, $\delta$: 3.82 s (3*H*, $OCH_3$), 4.14-4.27 m (2*H*, $CH_2$), 7.11 dd (2*H*, $^3$J = 8.86 Hz, $^4$J PH = 3.76 Hz, $CH_3OCCH$), 7.18-7.21 m (2*H*, H-6,8), 7.36-7.40 m (2*H*, H-5,7), 7.90 dd (2*H*, $^3$J PH = 14.50 Hz, $^3$J = 8.86 Hz, PCCH). Anal. calc. for $C_{14}H_{13}O_2PS_2$, %: C 54.53; H 4.25; S 20.80. Found, %: C 54.61; H 4.21; S 20.71.

Single crystals for *X*-ray analysis were obtained by slow evaporation of a methanol solution. IR-spectrum was recorded (in KBr) on Shimadzu FTIR-8400S. Mass-spectrum was measured on Finnigan Trance DSQ spectrometer. $^1$H NMR spectrum was obtained in DMSO-$d_6$ on Jeol JNM-ECX400 (400 MHz), using TMS as internal standard. Elemental composition was determined on Euro Vector EA-3000 elemental analyzer.

### S3. Refinement

C-bound H-atoms were placed in calculated positions with C–H 0.95 Å for aromatic, 0.99 Å for methylene with $U_{iso}$(H) = 1.2$U_{eq}$(C) and 0.98 Å for methyl with $U_{iso}$(H) = 1.5$U_{eq}$(C). All H atoms refined as riding.

Technical problems during the diffraction experiment led to the loss of 87 reflections.

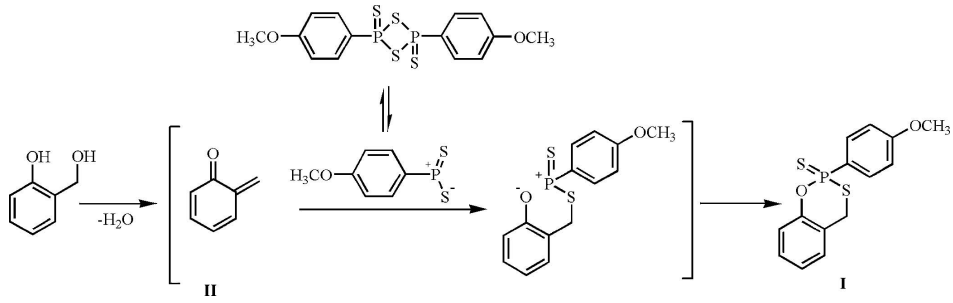



**Figure 1**

Synthesis of the title compound.

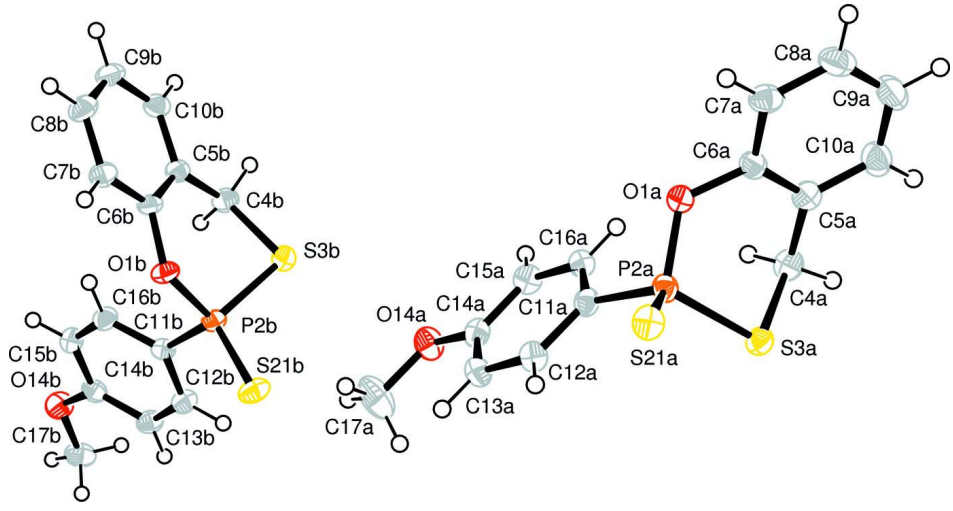



**Figure 2**

*ORTEP-3* (Farrugia, 1997) plot of molecular structure of the title compound showing the atom-numbering scheme. Thermal displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

**2-(4-Methoxyphenyl)-4*H*-1,3,2-benzoxathiaphosphinine 2-sulfide**

*Crystal data*

$C_{14}H_{13}O_2PS_2$
$M_r = 308.35$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 10.0548$ (5) Å
$b = 10.0804$ (5) Å
$c = 14.8913$ (7) Å
$\alpha = 94.322$ (4)°
$\beta = 91.121$ (4)°
$\gamma = 111.675$ (4)°
$V = 1396.79$ (12) Å$^3$
$Z = 4$
$F(000) = 640$
$D_x = 1.466$ Mg m$^{-3}$
Melting point = 357–358 K
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 11905 reflections
$\theta = 3.0$–67.2°
$\mu = 4.50$ mm$^{-1}$
$T = 150$ K
Prism, colourless
0.20 × 0.14 × 0.05 mm

*Data collection*

Oxford Diffraction Xcalibur Atlas Gemini ultra diffractometer
Radiation source: fine-focus sealed tube
Mirror monochromator
$\omega$ scans
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2010); based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.499$, $T_{max} = 0.816$
27233 measured reflections
4926 independent reflections
4175 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 67.4°$, $\theta_{min} = 3.0°$
$h = -12 \rightarrow 12$
$k = -11 \rightarrow 12$
$l = -17 \rightarrow 17$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.078$
$S = 1.05$
4926 reflections
345 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.5302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å$^{-3}$
$\Delta\rho_{min} = -0.28$ e Å$^{-3}$

*Special details*

**Experimental**. *CrysAlis Pro*(Oxford Diffraction, 2010); Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid (1995).

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1a | 0.02926 (16) | 0.29773 (15) | −0.14746 (10) | 0.0277 (3) |

| | | | | |
|---|---|---|---|---|
| P2a | 0.15135 (6) | 0.24002 (6) | −0.11687 (3) | 0.02317 (13) |
| S3a | 0.04617 (6) | 0.01896 (6) | −0.12506 (4) | 0.02639 (13) |
| C4a | −0.1381 (2) | 0.0133 (2) | −0.12138 (15) | 0.0292 (5) |
| H4a1 | −0.2060 | −0.0876 | −0.1243 | 0.035* |
| H4a2 | −0.1500 | 0.0630 | −0.0640 | 0.035* |
| C5a | −0.1703 (2) | 0.0843 (2) | −0.19912 (14) | 0.0267 (5) |
| C6a | −0.0826 (2) | 0.2236 (2) | −0.21191 (14) | 0.0250 (5) |
| C7a | −0.1048 (2) | 0.2957 (3) | −0.28197 (15) | 0.0301 (5) |
| H7a | −0.0420 | 0.3910 | −0.2891 | 0.036* |
| C8a | −0.2218 (3) | 0.2251 (3) | −0.34208 (16) | 0.0377 (6) |
| H8a | −0.2404 | 0.2728 | −0.3906 | 0.045* |
| C9a | −0.3108 (3) | 0.0866 (3) | −0.33152 (17) | 0.0415 (6) |
| H9a | −0.3900 | 0.0392 | −0.3732 | 0.050* |
| C10a | −0.2862 (3) | 0.0153 (3) | −0.26080 (17) | 0.0365 (6) |
| H10a | −0.3481 | −0.0805 | −0.2543 | 0.044* |
| S21a | 0.32266 (6) | 0.29002 (6) | −0.18310 (4) | 0.02974 (14) |
| C11a | 0.1791 (2) | 0.3094 (2) | −0.00060 (14) | 0.0236 (4) |
| C12a | 0.3126 (2) | 0.3441 (2) | 0.04299 (14) | 0.0264 (5) |
| H12a | 0.3898 | 0.3382 | 0.0093 | 0.032* |
| C13a | 0.3357 (2) | 0.3873 (2) | 0.13437 (14) | 0.0268 (5) |
| H13a | 0.4278 | 0.4110 | 0.1631 | 0.032* |
| C14a | 0.2221 (2) | 0.3953 (2) | 0.18358 (14) | 0.0256 (5) |
| C15a | 0.0881 (2) | 0.3626 (2) | 0.14060 (15) | 0.0274 (5) |
| H15a | 0.0112 | 0.3697 | 0.1741 | 0.033* |
| C16a | 0.0669 (2) | 0.3200 (2) | 0.04959 (15) | 0.0266 (5) |
| H16a | −0.0248 | 0.2977 | 0.0207 | 0.032* |
| O14a | 0.23190 (17) | 0.43446 (17) | 0.27326 (10) | 0.0320 (4) |
| C17a | 0.3668 (3) | 0.4683 (4) | 0.32061 (17) | 0.0509 (7) |
| H17a | 0.3959 | 0.3856 | 0.3137 | 0.076* |
| H17b | 0.3582 | 0.4921 | 0.3847 | 0.076* |
| H17c | 0.4390 | 0.5505 | 0.2959 | 0.076* |
| O1b | 0.33103 (15) | 0.89365 (15) | 0.58572 (10) | 0.0249 (3) |
| P2b | 0.26816 (6) | 0.73662 (6) | 0.62048 (4) | 0.02184 (13) |
| S3b | 0.05104 (6) | 0.66625 (6) | 0.59061 (4) | 0.02646 (13) |
| C4b | 0.0279 (2) | 0.8259 (2) | 0.64340 (15) | 0.0277 (5) |
| H4b1 | −0.0733 | 0.8152 | 0.6335 | 0.033* |
| H4b2 | 0.0480 | 0.8318 | 0.7092 | 0.033* |
| C5b | 0.1228 (2) | 0.9638 (2) | 0.60826 (13) | 0.0236 (4) |
| C6b | 0.2616 (2) | 0.9922 (2) | 0.58256 (14) | 0.0227 (4) |
| C7b | 0.3455 (2) | 1.1212 (2) | 0.55097 (15) | 0.0275 (5) |
| H7b | 0.4394 | 1.1363 | 0.5323 | 0.033* |
| C8b | 0.2900 (3) | 1.2277 (2) | 0.54712 (16) | 0.0325 (5) |
| H8b | 0.3464 | 1.3171 | 0.5262 | 0.039* |
| C9b | 0.1529 (3) | 1.2042 (2) | 0.57358 (15) | 0.0316 (5) |
| H9b | 0.1156 | 1.2779 | 0.5717 | 0.038* |
| C10b | 0.0702 (2) | 1.0739 (2) | 0.60266 (14) | 0.0280 (5) |
| H10b | −0.0248 | 1.0582 | 0.6193 | 0.034* |
| S21b | 0.35029 (6) | 0.60954 (6) | 0.56361 (4) | 0.03111 (14) |

| | | | | |
|---|---|---|---|---|
| C11b | 0.2993 (2) | 0.7683 (2) | 0.74075 (14) | 0.0224 (4) |
| C12b | 0.2885 (2) | 0.6534 (2) | 0.79025 (15) | 0.0278 (5) |
| H12b | 0.2694 | 0.5616 | 0.7596 | 0.033* |
| C13b | 0.3052 (2) | 0.6707 (2) | 0.88353 (15) | 0.0274 (5) |
| H13b | 0.2974 | 0.5916 | 0.9168 | 0.033* |
| C14b | 0.3335 (2) | 0.8054 (2) | 0.92778 (14) | 0.0251 (5) |
| C15b | 0.3472 (2) | 0.9212 (2) | 0.87922 (15) | 0.0286 (5) |
| H15b | 0.3687 | 1.0134 | 0.9099 | 0.034* |
| C16b | 0.3299 (2) | 0.9033 (2) | 0.78634 (15) | 0.0265 (5) |
| H16b | 0.3387 | 0.9830 | 0.7534 | 0.032* |
| O14b | 0.34857 (18) | 0.83466 (17) | 1.01926 (10) | 0.0333 (4) |
| C17b | 0.3349 (3) | 0.7191 (3) | 1.07348 (15) | 0.0344 (5) |
| H17d | 0.2394 | 0.6441 | 1.0620 | 0.052* |
| H17e | 0.3481 | 0.7547 | 1.1374 | 0.052* |
| H17f | 0.4079 | 0.6794 | 1.0581 | 0.052* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1a | 0.0310 (8) | 0.0231 (8) | 0.0286 (8) | 0.0104 (6) | −0.0055 (6) | 0.0001 (6) |
| P2a | 0.0256 (3) | 0.0229 (3) | 0.0193 (3) | 0.0072 (2) | −0.0004 (2) | 0.0017 (2) |
| S3a | 0.0313 (3) | 0.0222 (3) | 0.0255 (3) | 0.0100 (2) | −0.0008 (2) | 0.0022 (2) |
| C4a | 0.0276 (11) | 0.0264 (12) | 0.0311 (12) | 0.0065 (9) | 0.0054 (9) | 0.0046 (10) |
| C5a | 0.0270 (11) | 0.0287 (12) | 0.0253 (11) | 0.0116 (9) | 0.0051 (9) | 0.0018 (9) |
| C6a | 0.0251 (11) | 0.0292 (12) | 0.0224 (11) | 0.0127 (9) | −0.0002 (8) | −0.0014 (9) |
| C7a | 0.0344 (12) | 0.0346 (13) | 0.0268 (12) | 0.0186 (10) | 0.0044 (9) | 0.0052 (10) |
| C8a | 0.0458 (15) | 0.0510 (16) | 0.0269 (12) | 0.0304 (13) | −0.0016 (10) | 0.0036 (11) |
| C9a | 0.0369 (14) | 0.0535 (17) | 0.0358 (14) | 0.0220 (13) | −0.0118 (11) | −0.0099 (12) |
| C10a | 0.0275 (12) | 0.0388 (14) | 0.0406 (14) | 0.0112 (11) | −0.0020 (10) | −0.0054 (11) |
| S21a | 0.0317 (3) | 0.0305 (3) | 0.0249 (3) | 0.0086 (2) | 0.0063 (2) | 0.0038 (2) |
| C11a | 0.0255 (11) | 0.0197 (11) | 0.0224 (11) | 0.0048 (9) | 0.0014 (8) | 0.0024 (8) |
| C12a | 0.0247 (11) | 0.0280 (12) | 0.0248 (11) | 0.0074 (9) | 0.0044 (9) | 0.0031 (9) |
| C13a | 0.0252 (11) | 0.0291 (12) | 0.0229 (11) | 0.0067 (9) | −0.0011 (9) | 0.0024 (9) |
| C14a | 0.0317 (12) | 0.0218 (11) | 0.0212 (11) | 0.0072 (9) | 0.0031 (9) | 0.0028 (9) |
| C15a | 0.0253 (11) | 0.0294 (12) | 0.0273 (12) | 0.0095 (9) | 0.0071 (9) | 0.0027 (9) |
| C16a | 0.0252 (11) | 0.0258 (11) | 0.0283 (12) | 0.0094 (9) | −0.0013 (9) | −0.0001 (9) |
| O14a | 0.0348 (9) | 0.0405 (9) | 0.0191 (8) | 0.0126 (7) | 0.0020 (6) | −0.0009 (7) |
| C17a | 0.0446 (16) | 0.082 (2) | 0.0207 (12) | 0.0191 (15) | −0.0041 (11) | −0.0052 (13) |
| O1b | 0.0264 (8) | 0.0223 (8) | 0.0302 (8) | 0.0125 (6) | 0.0061 (6) | 0.0094 (6) |
| P2b | 0.0266 (3) | 0.0201 (3) | 0.0214 (3) | 0.0109 (2) | 0.0028 (2) | 0.0049 (2) |
| S3b | 0.0268 (3) | 0.0240 (3) | 0.0277 (3) | 0.0084 (2) | 0.0004 (2) | 0.0021 (2) |
| C4b | 0.0283 (11) | 0.0286 (12) | 0.0291 (12) | 0.0138 (10) | 0.0048 (9) | 0.0033 (9) |
| C5b | 0.0305 (11) | 0.0251 (11) | 0.0173 (10) | 0.0129 (9) | −0.0013 (8) | 0.0019 (8) |
| C6b | 0.0290 (11) | 0.0223 (11) | 0.0212 (10) | 0.0145 (9) | 0.0000 (8) | 0.0037 (9) |
| C7b | 0.0316 (12) | 0.0265 (12) | 0.0265 (11) | 0.0124 (10) | 0.0038 (9) | 0.0070 (9) |
| C8b | 0.0459 (14) | 0.0238 (12) | 0.0294 (12) | 0.0140 (11) | 0.0018 (10) | 0.0071 (10) |
| C9b | 0.0453 (14) | 0.0281 (13) | 0.0288 (12) | 0.0224 (11) | −0.0026 (10) | 0.0021 (10) |
| C10b | 0.0333 (12) | 0.0318 (13) | 0.0233 (11) | 0.0178 (10) | −0.0018 (9) | −0.0001 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| S21b | 0.0435 (3) | 0.0294 (3) | 0.0286 (3) | 0.0226 (3) | 0.0073 (2) | 0.0039 (2) |
| C11b | 0.0215 (10) | 0.0252 (11) | 0.0229 (11) | 0.0109 (9) | 0.0019 (8) | 0.0040 (9) |
| C12b | 0.0336 (12) | 0.0254 (12) | 0.0272 (11) | 0.0142 (10) | 0.0031 (9) | 0.0022 (9) |
| C13b | 0.0326 (12) | 0.0274 (12) | 0.0254 (11) | 0.0138 (10) | 0.0031 (9) | 0.0076 (9) |
| C14b | 0.0236 (11) | 0.0317 (12) | 0.0214 (11) | 0.0115 (9) | 0.0014 (8) | 0.0041 (9) |
| C15b | 0.0303 (12) | 0.0249 (12) | 0.0294 (12) | 0.0098 (9) | −0.0016 (9) | −0.0015 (9) |
| C16b | 0.0317 (12) | 0.0216 (11) | 0.0268 (11) | 0.0098 (9) | 0.0013 (9) | 0.0060 (9) |
| O14b | 0.0442 (9) | 0.0359 (9) | 0.0215 (8) | 0.0169 (8) | 0.0004 (7) | 0.0037 (7) |
| C17b | 0.0404 (14) | 0.0466 (15) | 0.0242 (12) | 0.0245 (12) | 0.0035 (10) | 0.0081 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1a—C6a | 1.404 (3) | O1b—C6b | 1.412 (2) |
| O1a—P2a | 1.6119 (15) | O1b—P2b | 1.6033 (15) |
| P2a—C11a | 1.794 (2) | P2b—C11b | 1.796 (2) |
| P2a—S21a | 1.9219 (8) | P2b—S21b | 1.9197 (7) |
| P2a—S3a | 2.0766 (8) | P2b—S3b | 2.0586 (8) |
| S3a—C4a | 1.835 (2) | S3b—C4b | 1.831 (2) |
| C4a—C5a | 1.497 (3) | C4b—C5b | 1.505 (3) |
| C4a—H4a1 | 0.9900 | C4b—H4b1 | 0.9900 |
| C4a—H4a2 | 0.9900 | C4b—H4b2 | 0.9900 |
| C5a—C6a | 1.385 (3) | C5b—C6b | 1.385 (3) |
| C5a—C10a | 1.396 (3) | C5b—C10b | 1.401 (3) |
| C6a—C7a | 1.375 (3) | C6b—C7b | 1.386 (3) |
| C7a—C8a | 1.392 (3) | C7b—C8b | 1.385 (3) |
| C7a—H7a | 0.9500 | C7b—H7b | 0.9500 |
| C8a—C9a | 1.375 (4) | C8b—C9b | 1.380 (3) |
| C8a—H8a | 0.9500 | C8b—H8b | 0.9500 |
| C9a—C10a | 1.386 (4) | C9b—C10b | 1.377 (3) |
| C9a—H9a | 0.9500 | C9b—H9b | 0.9500 |
| C10a—H10a | 0.9500 | C10b—H10b | 0.9500 |
| C11a—C12a | 1.389 (3) | C11b—C12b | 1.392 (3) |
| C11a—C16a | 1.398 (3) | C11b—C16b | 1.396 (3) |
| C12a—C13a | 1.385 (3) | C12b—C13b | 1.386 (3) |
| C12a—H12a | 0.9500 | C12b—H12b | 0.9500 |
| C13a—C14a | 1.393 (3) | C13b—C14b | 1.390 (3) |
| C13a—H13a | 0.9500 | C13b—H13b | 0.9500 |
| C14a—O14a | 1.355 (3) | C14b—O14b | 1.365 (3) |
| C14a—C15a | 1.393 (3) | C14b—C15b | 1.384 (3) |
| C15a—C16a | 1.378 (3) | C15b—C16b | 1.380 (3) |
| C15a—H15a | 0.9500 | C15b—H15b | 0.9500 |
| C16a—H16a | 0.9500 | C16b—H16b | 0.9500 |
| O14a—C17a | 1.428 (3) | O14b—C17b | 1.434 (3) |
| C17a—H17a | 0.9800 | C17b—H17d | 0.9800 |
| C17a—H17b | 0.9800 | C17b—H17e | 0.9800 |
| C17a—H17c | 0.9800 | C17b—H17f | 0.9800 |
| | | | |
| C6a—O1a—P2a | 124.10 (13) | C6b—O1b—P2b | 127.23 (13) |

| | | | |
|---|---|---|---|
| O1a—P2a—C11a | 99.46 (9) | O1b—P2b—C11b | 104.09 (9) |
| O1a—P2a—S21a | 118.15 (7) | O1b—P2b—S21b | 112.57 (6) |
| C11a—P2a—S21a | 114.65 (7) | C11b—P2b—S21b | 114.84 (7) |
| O1a—P2a—S3a | 103.99 (6) | O1b—P2b—S3b | 104.42 (6) |
| C11a—P2a—S3a | 109.24 (7) | C11b—P2b—S3b | 108.63 (7) |
| S21a—P2a—S3a | 110.34 (3) | S21b—P2b—S3b | 111.54 (3) |
| C4a—S3a—P2a | 98.13 (8) | C4b—S3b—P2b | 95.79 (8) |
| C5a—C4a—S3a | 109.77 (15) | C5b—C4b—S3b | 113.98 (15) |
| C5a—C4a—H4a1 | 109.7 | C5b—C4b—H4b1 | 108.8 |
| S3a—C4a—H4a1 | 109.7 | S3b—C4b—H4b1 | 108.8 |
| C5a—C4a—H4a2 | 109.7 | C5b—C4b—H4b2 | 108.8 |
| S3a—C4a—H4a2 | 109.7 | S3b—C4b—H4b2 | 108.8 |
| H4a1—C4a—H4a2 | 108.2 | H4b1—C4b—H4b2 | 107.7 |
| C6a—C5a—C10a | 117.8 (2) | C6b—C5b—C10b | 116.7 (2) |
| C6a—C5a—C4a | 119.70 (19) | C6b—C5b—C4b | 124.61 (18) |
| C10a—C5a—C4a | 122.5 (2) | C10b—C5b—C4b | 118.6 (2) |
| C7a—C6a—C5a | 123.1 (2) | C5b—C6b—C7b | 122.63 (19) |
| C7a—C6a—O1a | 118.32 (19) | C5b—C6b—O1b | 123.69 (19) |
| C5a—C6a—O1a | 118.51 (19) | C7b—C6b—O1b | 113.68 (18) |
| C6a—C7a—C8a | 118.1 (2) | C8b—C7b—C6b | 118.9 (2) |
| C6a—C7a—H7a | 121.0 | C8b—C7b—H7b | 120.6 |
| C8a—C7a—H7a | 121.0 | C6b—C7b—H7b | 120.6 |
| C9a—C8a—C7a | 120.3 (2) | C9b—C8b—C7b | 120.1 (2) |
| C9a—C8a—H8a | 119.8 | C9b—C8b—H8b | 119.9 |
| C7a—C8a—H8a | 119.8 | C7b—C8b—H8b | 119.9 |
| C8a—C9a—C10a | 120.8 (2) | C10b—C9b—C8b | 120.0 (2) |
| C8a—C9a—H9a | 119.6 | C10b—C9b—H9b | 120.0 |
| C10a—C9a—H9a | 119.6 | C8b—C9b—H9b | 120.0 |
| C9a—C10a—C5a | 120.0 (2) | C9b—C10b—C5b | 121.6 (2) |
| C9a—C10a—H10a | 120.0 | C9b—C10b—H10b | 119.2 |
| C5a—C10a—H10a | 120.0 | C5b—C10b—H10b | 119.2 |
| C12a—C11a—C16a | 118.58 (19) | C12b—C11b—C16b | 119.02 (19) |
| C12a—C11a—P2a | 119.61 (16) | C12b—C11b—P2b | 118.69 (16) |
| C16a—C11a—P2a | 121.64 (16) | C16b—C11b—P2b | 122.27 (16) |
| C13a—C12a—C11a | 121.5 (2) | C13b—C12b—C11b | 121.0 (2) |
| C13a—C12a—H12a | 119.2 | C13b—C12b—H12b | 119.5 |
| C11a—C12a—H12a | 119.2 | C11b—C12b—H12b | 119.5 |
| C12a—C13a—C14a | 119.1 (2) | C12b—C13b—C14b | 119.1 (2) |
| C12a—C13a—H13a | 120.5 | C12b—C13b—H13b | 120.4 |
| C14a—C13a—H13a | 120.5 | C14b—C13b—H13b | 120.4 |
| O14a—C14a—C13a | 124.18 (19) | O14b—C14b—C15b | 115.25 (19) |
| O14a—C14a—C15a | 115.77 (19) | O14b—C14b—C13b | 124.3 (2) |
| C13a—C14a—C15a | 120.05 (19) | C15b—C14b—C13b | 120.4 (2) |
| C16a—C15a—C14a | 120.14 (19) | C16b—C15b—C14b | 120.3 (2) |
| C16a—C15a—H15a | 119.9 | C16b—C15b—H15b | 119.9 |
| C14a—C15a—H15a | 119.9 | C14b—C15b—H15b | 119.9 |
| C15a—C16a—C11a | 120.6 (2) | C15b—C16b—C11b | 120.2 (2) |
| C15a—C16a—H16a | 119.7 | C15b—C16b—H16b | 119.9 |

| | | | |
|---|---|---|---|
| C11a—C16a—H16a | 119.7 | C11b—C16b—H16b | 119.9 |
| C14a—O14a—C17a | 117.98 (18) | C14b—O14b—C17b | 117.99 (17) |
| O14a—C17a—H17a | 109.5 | O14b—C17b—H17d | 109.5 |
| O14a—C17a—H17b | 109.5 | O14b—C17b—H17e | 109.5 |
| H17a—C17a—H17b | 109.5 | H17d—C17b—H17e | 109.5 |
| O14a—C17a—H17c | 109.5 | O14b—C17b—H17f | 109.5 |
| H17a—C17a—H17c | 109.5 | H17d—C17b—H17f | 109.5 |
| H17b—C17a—H17c | 109.5 | H17e—C17b—H17f | 109.5 |
| | | | |
| C6a—O1a—P2a—C11a | −146.02 (17) | C6b—O1b—P2b—C11b | −82.72 (17) |
| C6a—O1a—P2a—S21a | 89.32 (17) | C6b—O1b—P2b—S21b | 152.30 (14) |
| C6a—O1a—P2a—S3a | −33.33 (17) | C6b—O1b—P2b—S3b | 31.14 (17) |
| O1a—P2a—S3a—C4a | −19.97 (10) | O1b—P2b—S3b—C4b | −50.90 (9) |
| C11a—P2a—S3a—C4a | 85.47 (11) | C11b—P2b—S3b—C4b | 59.70 (10) |
| S21a—P2a—S3a—C4a | −147.62 (8) | S21b—P2b—S3b—C4b | −172.74 (8) |
| P2a—S3a—C4a—C5a | 59.70 (15) | P2b—S3b—C4b—C5b | 55.70 (16) |
| S3a—C4a—C5a—C6a | −55.1 (2) | S3b—C4b—C5b—C6b | −35.7 (3) |
| S3a—C4a—C5a—C10a | 124.4 (2) | S3b—C4b—C5b—C10b | 145.92 (17) |
| C10a—C5a—C6a—C7a | 0.1 (3) | C10b—C5b—C6b—C7b | −1.2 (3) |
| C4a—C5a—C6a—C7a | 179.6 (2) | C4b—C5b—C6b—C7b | −179.7 (2) |
| C10a—C5a—C6a—O1a | 176.18 (19) | C10b—C5b—C6b—O1b | 178.88 (18) |
| C4a—C5a—C6a—O1a | −4.2 (3) | C4b—C5b—C6b—O1b | 0.4 (3) |
| P2a—O1a—C6a—C7a | −128.39 (18) | P2b—O1b—C6b—C5b | −1.6 (3) |
| P2a—O1a—C6a—C5a | 55.3 (2) | P2b—O1b—C6b—C7b | 178.51 (15) |
| C5a—C6a—C7a—C8a | 0.6 (3) | C5b—C6b—C7b—C8b | 1.8 (3) |
| O1a—C6a—C7a—C8a | −175.56 (19) | O1b—C6b—C7b—C8b | −178.33 (18) |
| C6a—C7a—C8a—C9a | −0.8 (3) | C6b—C7b—C8b—C9b | −0.6 (3) |
| C7a—C8a—C9a—C10a | 0.4 (4) | C7b—C8b—C9b—C10b | −0.9 (3) |
| C8a—C9a—C10a—C5a | 0.3 (4) | C8b—C9b—C10b—C5b | 1.5 (3) |
| C6a—C5a—C10a—C9a | −0.5 (3) | C6b—C5b—C10b—C9b | −0.4 (3) |
| C4a—C5a—C10a—C9a | 180.0 (2) | C4b—C5b—C10b—C9b | 178.1 (2) |
| O1a—P2a—C11a—C12a | −150.77 (17) | O1b—P2b—C11b—C12b | −164.91 (16) |
| S21a—P2a—C11a—C12a | −23.7 (2) | S21b—P2b—C11b—C12b | −41.39 (19) |
| S3a—P2a—C11a—C12a | 100.70 (17) | S3b—P2b—C11b—C12b | 84.27 (17) |
| O1a—P2a—C11a—C16a | 33.9 (2) | O1b—P2b—C11b—C16b | 16.9 (2) |
| S21a—P2a—C11a—C16a | 160.92 (16) | S21b—P2b—C11b—C16b | 140.42 (16) |
| S3a—P2a—C11a—C16a | −74.66 (19) | S3b—P2b—C11b—C16b | −93.92 (18) |
| C16a—C11a—C12a—C13a | 0.6 (3) | C16b—C11b—C12b—C13b | 1.1 (3) |
| P2a—C11a—C12a—C13a | −174.86 (17) | P2b—C11b—C12b—C13b | −177.12 (17) |
| C11a—C12a—C13a—C14a | 0.3 (3) | C11b—C12b—C13b—C14b | −0.2 (3) |
| C12a—C13a—C14a—O14a | 179.2 (2) | C12b—C13b—C14b—O14b | 178.4 (2) |
| C12a—C13a—C14a—C15a | −1.1 (3) | C12b—C13b—C14b—C15b | −1.1 (3) |
| O14a—C14a—C15a—C16a | −179.2 (2) | O14b—C14b—C15b—C16b | −178.10 (19) |
| C13a—C14a—C15a—C16a | 1.1 (3) | C13b—C14b—C15b—C16b | 1.4 (3) |
| C14a—C15a—C16a—C11a | −0.1 (3) | C14b—C15b—C16b—C11b | −0.4 (3) |
| C12a—C11a—C16a—C15a | −0.7 (3) | C12b—C11b—C16b—C15b | −0.8 (3) |
| P2a—C11a—C16a—C15a | 174.71 (17) | P2b—C11b—C16b—C15b | 177.37 (17) |
| C13a—C14a—O14a—C17a | −0.6 (3) | C15b—C14b—O14b—C17b | 179.73 (19) |

| | | | |
|---|---|---|---|
| C15a—C14a—O14a—C17a | 179.7 (2) | C13b—C14b—O14b—C17b | 0.2 (3) |