

# Crystal structure and Hirshfeld surface analysis of dimethyl(phenyl)phosphine sulfide

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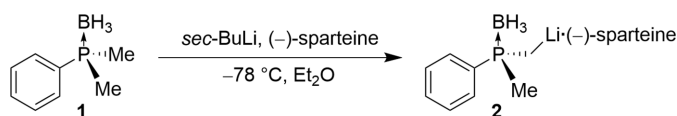
**Keywords:** crystal structure; Hirshfeld surface analysis; phosphine sulfide.**CCDC reference:** 2362349**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound,  $C_8H_{11}PS$ , which melts below room temperature, was crystallized at low temperature. The P–S bond length is 1.9623 (5) Å and the major contributors to the Hirshfeld surface are H···H (58.1%), S···H/H···S (13.4%) and C···H/H···C contacts (11.7%).

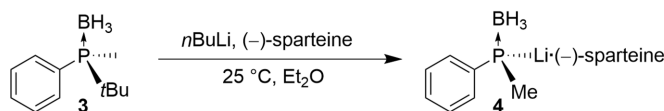
## 1. Chemical context

The structure of the title compound,  $C_8H_{11}PS$ , **11**, is interesting for two reasons: firstly, the crystals are very temperature sensitive and secondly the chemical background of the substance itself. Although **11** has been known since 1962 (Monsanto Chemicals, 1962) and even commercially available, no crystal structure has been obtained until now. This might be due to its low melting point, which made measurements very difficult and only feasible with X-Temp 2 (Stalke, 1998), which makes crystal picking and mounting possible at very low temperatures. Phosphorus-based molecules are used in a large variety of different chemical applications as chiral ligands for enantioselective catalysis (Grabulosa, 2011). Compound **11** is a prochiral building block for *P*-stereogenic biphosphine ligands, which are used for transition-metal-catalyzed asymmetric reactions (Tang & Zhang, 2003). This application makes an enantioselective synthesis indispensable, which is why different approaches have been reported. For the chemically similar phosphine–boranes, the desired enantiomer can be synthesized either under kinetic control with *sec*-BuLi and (–)-sparteine *via* an asymmetric deprotonation (Muci *et al.*, 1995) or a thermodynamically controlled reaction with *n*-BuLi and (–)-sparteine *via* dynamic resolution (Wolfe & Livinghouse, 1998) (Fig. 1). For phosphine sulfides like compound **11**, the synthetic approach is quite similar. Using *n*-BuLi and (–)-sparteine in  $Et_2O$  results in an enantiometric

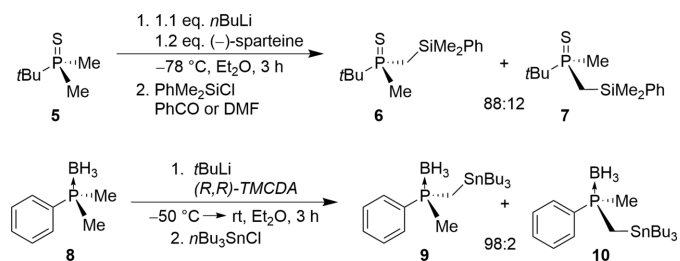
### Asymmetric Deprotonation (Kinetic control)



### Dynamic Resolution (Thermodynamic control)

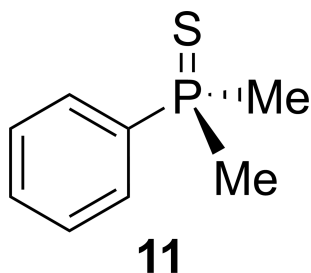
**Figure 1**

Kinetic and thermodynamic approaches to synthesize chiral phosphine boranes.



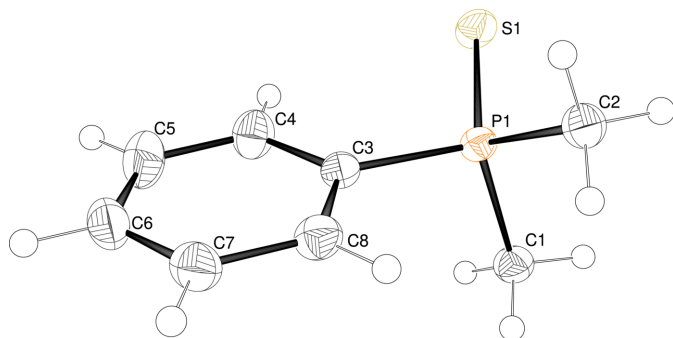
**Figure 2**  
More recent synthetic approaches for chiral phosphine sulfides and boranes.

ratio (*e.r.*) of 88:12 via a kinetically controlled reaction (Gammon *et al.*, 2010) (Fig. 2). By trapping the lithiated intermediate, not only has a higher enantioselectivity of *e.r.* = 93:7 been achieved, but it has also been discovered that the enantiomers can interconvert at temperatures above 253 K. One of the most recent synthetic approaches for phosphine-boranes relies on the much cheaper (*R,R*)-TMCDA instead of (–)-sparteine and crystallization-induced dynamic resolution (CIDR). This synthesis achieves up to 80% yield and enantioselectivity of 98:2 (Kuzu *et al.*, 2024).



## 2. Structural commentary

Compound **11**, which was crystallized from toluene at 193 K, forms colorless needles in the monoclinic space group  $P2_1/n$ . The P-tetrahedral molecule consists of two methyl groups and one phenyl group bound to the phosphine sulfide unit. The P1–S1 bond length of 1.9623 (5) Å matches the typical bond length for this species (Verschoor-Kirss *et al.*, 2016; Blake *et al.*, 1981). The phosphorus bond angles vary from 105.58 (6)° for C1–P1–C3 to 113.55 (5)° for C2–P1–S1. These angles

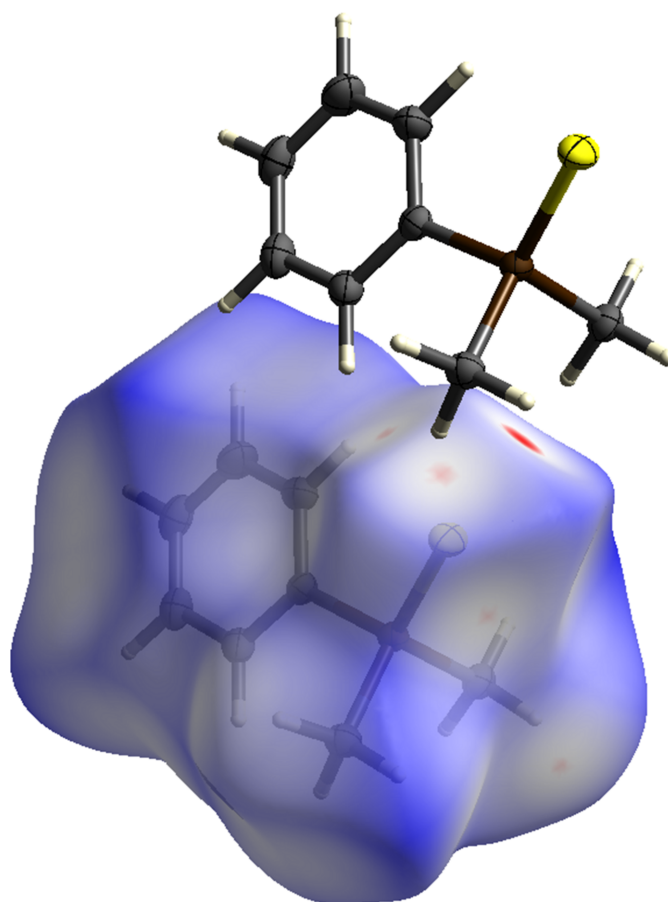


**Figure 3**  
The molecular structure of **11** showing 50% displacement ellipsoids.

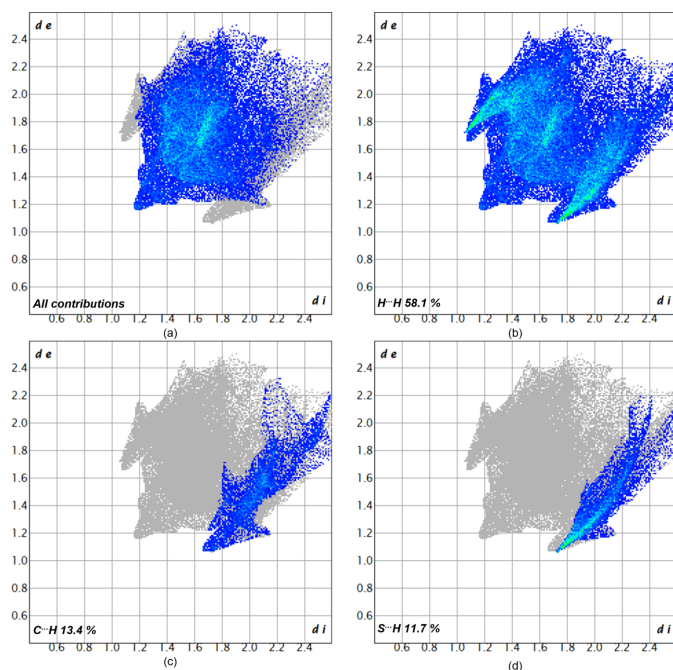
are slightly distorted from the nominal angle of 109.5°, which is probably caused by the different steric effects of the substituents. The bond lengths and angles of the C3–C8 phenyl ring match with the typical lengths and angles for this familiar group (Lide, 2005). Atom S1 is displaced from the plane of the C3–C8 ring by –0.549 (1) Å with corresponding deviations for atoms C1 and C2 of the methyl groups of 1.839 (2) and –0.781 (1) Å, respectively; the C4–C3–P1–S1 torsion angle is 23.85 (12)°.

## 3. Supramolecular features

To better understand the intermolecular interactions of **11**, a Hirshfeld surface analysis was performed. In Fig. 3 the Hirshfeld surface analysis is mapped over  $d_{\text{norm}}$  in the range of –0.07 to 1.20 a.u. (Spackman & Jayatilaka, 2009) and generated by *CrystalExplorer21* (Spackman *et al.*, 2021) using red dots to represent close contacts. Atom S1 has close contacts to atoms H1A (H··S = 2.87 Å) and H2C (2.95 Å) of the methyl groups of a neighboring molecule displaced by translation in the *a*-axis direction. For further visualization of the percentage of the respective interactions, two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were generated and these are shown in Fig. 4. The most significant contacts in the solid state are the H··H interactions, contributing 58.1% of the total



**Figure 4**  
Hirshfeld surface analysis of **11** showing close contacts in the crystal.



**Figure 5**  
Two-dimensional fingerprint plots for compound **11**, showing (a) all contributions and (b)–(d) contributions between specific interacting atom pairs.

surface (Fig. 5). The  $S \cdots H/H \cdots S$  (13.4%) and  $C \cdots H/H \cdots C$  interactions (11.7%) are less impactful in comparison.

#### 4. Database survey

Similar molecules to **11** can vary either in the attached heteroatom such as the previously discussed phosphine boranes (Muci *et al.*, 1995; Kuzu *et al.*, 2024) or they can vary in their organic substituents (Gammon *et al.*, 2010). A search in the Cambridge Structural Database (WebCSD, March 2024; Groom *et al.*, 2016) for phosphine sulfides lead to many similar structures with different organic substituents. Some of those structures contain aromatic substituents such as three phenyl rings (CSD refcode BAQTOC; Arca *et al.*, 1999) or even larger substituents like an anthracene group (BARWEA; Schillmüller *et al.*, 2021). Structures with smaller substituents are also known, for example, butyronitrile (KADJEE; Blake *et al.*, 1981).

#### 5. Synthesis and crystallization

In a round-bottom flask equipped with a condenser dimethyl(phenyl)phosphane (1.00 g, 7.24 mmol, 1 eq.) and sulfur (2.23 g, 8.69 mmol, 1.2 eq.) were dissolved in 20 ml of toluene. While stirring, the mixture was heated under reflux to 373 K and then stirred overnight without heating. The resulting mixture was filtered through 3 cm of celite and washed with diethyl ether. The organic phase was dried with magnesium sulfate and the solvent was removed *in vacuo*, yielding a slightly yellow oil of dimethyl(phenyl)phosphine sulfide

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	$C_8H_{11}PS$
$M_r$	170.20
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
$a, b, c$ (Å)	6.2805 (2), 7.6549 (2), 19.3578 (8)
$\beta$ (°)	99.372 (2)
$V$ (Å <sup>3</sup> )	918.23 (5)
$Z$	4
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	4.17
Crystal size (mm)	0.14 × 0.13 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}, T_{\max}$	0.465, 0.587
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	12606, 1886, 1745
$R_{\text{int}}$	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.064, 1.06
No. of reflections	1886
No. of parameters	93
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.34, -0.23

Computer programs: APEX2 and SAINT (Bruker, 2018), SHELXT (Sheldrick, 2015a), SHELXL2014/7 (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

(1.04 g, 85%). The oil was dissolved in hot toluene and recrystallized at 193 K, forming colorless needles.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were geometrically placed ( $C-H = 0.95-0.98$  Å) and refined as riding atoms with  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$  or  $1.5U_{\text{eq}}(\text{methyl } C)$ .

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#### References

- Arca, M., Demartin, F., Devillanova, F. A., Garau, A., Isaia, F., Lippolis, V. & Verani, G. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3069–3073.
- Blake, A. J., Howie, R. A. & McQuillan, G. P. (1981). *Acta Cryst.* **B37**, 1959–1962.
- Bruker (2018). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

- Gammon, J. J., Gessner, V. H., Barker, G. R., Granander, J., Whitwood, A. C., Strohmann, C., O'Brien, P. & Kelly, B. (2010). *J. Am. Chem. Soc.* **132**, 13922–13927.
- Grabulosa, A. (2011). *P-Stereogenic Ligands in Enantioselective Catalysis*. Cambridge: RSC Publishing, .
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Kuzu, M. Y., Schmidt, A. & Strohmann, C. (2024). *Angew. Chem. Int. Ed.* e202319665.
- Lide (2005). Editor. *CRC Handbook of Chemistry and Physics, Internet Version*. Boca Raton, FL: CRC Press.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Monsanto Chemicals (1962). American Patent No. US3053900A
- Muci, A. R., Campos, K. R. & Evans, D. A. (1995). *J. Am. Chem. Soc.* **117**, 9075–9076.
- Schillmöller, T., Herbst-Irmer, R. & Stalke, D. (2021). *Adv. Opt. Mater.* **9**, 2001814.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
- Stalke, D. (1998). *Chem. Soc. Rev.* **27**, 171.
- Tang, W. & Zhang, X. (2003). *Chem. Rev.* **103**, 3029–3070.
- Verschoor-Kirss, M. J., Hendricks, O., Verschoor, C. M., Conry, R. & Kirss, R. U. (2016). *Inorg. Chim. Acta*, **450**, 30–38.
- Wolfe, B. & Livinghouse, T. (1998). *J. Am. Chem. Soc.* **120**, 5116–5117.

## supporting information

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## Crystal structure and Hirshfeld surface analysis of dimethyl(phenyl)phosphine sulfide

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### Computing details

#### Dimethyl(phenyl)phosphanethione

##### Crystal data

$C_8H_{11}PS$

$M_r = 170.20$

Monoclinic,  $P2_1/n$

$a = 6.2805$  (2) Å

$b = 7.6549$  (2) Å

$c = 19.3578$  (8) Å

$\beta = 99.372$  (2)°

$V = 918.23$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 360$

$D_x = 1.231$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å

Cell parameters from 3458 reflections

$\theta = 4.6$ – $79.2$ °

$\mu = 4.17$  mm<sup>-1</sup>

$T = 100$  K

Needle, colourless

$0.14 \times 0.13 \times 0.10$  mm

##### Data collection

Bruker APEXII CCD  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.465$ ,  $T_{\max} = 0.587$

12606 measured reflections

1886 independent reflections

1745 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 74.7$ °,  $\theta_{\min} = 4.6$ °

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 7$

$l = -24 \rightarrow 23$

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.064$

$S = 1.06$

1886 reflections

93 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.342P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.34$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.23$  e Å<sup>-3</sup>

##### Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.42807 (5)	0.75930 (4)	0.57224 (2)	0.02071 (10)
S1	0.73232 (5)	0.79603 (5)	0.56424 (2)	0.02966 (11)
C3	0.3919 (2)	0.57849 (16)	0.62992 (6)	0.0225 (3)
C8	0.1928 (2)	0.49493 (18)	0.62617 (7)	0.0280 (3)
H8	0.0754	0.5285	0.5913	0.034*
C2	0.2586 (2)	0.71634 (18)	0.48984 (7)	0.0267 (3)
H2A	0.3014	0.6055	0.4708	0.040*
H2B	0.2743	0.8110	0.4570	0.040*
H2C	0.1078	0.7091	0.4968	0.040*
C1	0.3115 (2)	0.94645 (17)	0.60830 (7)	0.0268 (3)
H1A	0.1620	0.9205	0.6133	0.040*
H1B	0.3142	1.0466	0.5769	0.040*
H1C	0.3950	0.9741	0.6543	0.040*
C4	0.5618 (2)	0.52745 (19)	0.68113 (7)	0.0320 (3)
H4	0.6990	0.5816	0.6836	0.038*
C7	0.1657 (2)	0.36298 (19)	0.67315 (8)	0.0331 (3)
H7	0.0303	0.3056	0.6700	0.040*
C6	0.3345 (3)	0.31482 (19)	0.72440 (8)	0.0357 (3)
H6	0.3152	0.2250	0.7567	0.043*
C5	0.5320 (3)	0.3975 (2)	0.72876 (8)	0.0398 (4)
H5	0.6477	0.3654	0.7645	0.048*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
P1	0.01838 (17)	0.02128 (17)	0.02246 (17)	0.00095 (11)	0.00330 (12)	0.00012 (12)
S1	0.01915 (17)	0.03201 (19)	0.0385 (2)	0.00062 (12)	0.00678 (13)	0.00507 (14)
C3	0.0253 (6)	0.0205 (6)	0.0223 (6)	0.0025 (5)	0.0058 (5)	-0.0015 (5)
C8	0.0261 (7)	0.0248 (6)	0.0337 (7)	-0.0002 (5)	0.0066 (5)	-0.0004 (5)
C2	0.0266 (7)	0.0291 (7)	0.0238 (6)	0.0010 (5)	0.0021 (5)	-0.0011 (5)
C1	0.0285 (7)	0.0236 (6)	0.0293 (6)	0.0023 (5)	0.0075 (5)	-0.0008 (5)
C4	0.0304 (7)	0.0315 (7)	0.0321 (7)	-0.0014 (6)	-0.0011 (6)	0.0027 (6)
C7	0.0377 (8)	0.0251 (7)	0.0396 (8)	-0.0021 (6)	0.0152 (6)	-0.0005 (6)
C6	0.0553 (10)	0.0250 (7)	0.0300 (7)	0.0032 (6)	0.0165 (7)	0.0035 (6)
C5	0.0478 (9)	0.0368 (8)	0.0319 (7)	0.0039 (7)	-0.0027 (7)	0.0077 (6)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

P1—S1	1.9623 (5)	C1—H1A	0.9800
P1—C3	1.8158 (13)	C1—H1B	0.9800
P1—C2	1.7977 (13)	C1—H1C	0.9800
P1—C1	1.8004 (13)	C4—H4	0.9500
C3—C8	1.3957 (19)	C4—C5	1.390 (2)
C3—C4	1.3893 (18)	C7—H7	0.9500
C8—H8	0.9500	C7—C6	1.379 (2)

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C8—C7	1.388 (2)	C6—H6	0.9500
C2—H2A	0.9800	C6—C5	1.383 (2)
C2—H2B	0.9800	C5—H5	0.9500
C2—H2C	0.9800		
C3—P1—S1	112.26 (4)	P1—C1—H1A	109.5
C2—P1—S1	113.55 (5)	P1—C1—H1B	109.5
C2—P1—C3	106.91 (6)	P1—C1—H1C	109.5
C2—P1—C1	105.68 (6)	H1A—C1—H1B	109.5
C1—P1—S1	112.28 (5)	H1A—C1—H1C	109.5
C1—P1—C3	105.58 (6)	H1B—C1—H1C	109.5
C8—C3—P1	121.21 (10)	C3—C4—H4	119.9
C4—C3—P1	119.64 (10)	C3—C4—C5	120.24 (14)
C4—C3—C8	119.08 (12)	C5—C4—H4	119.9
C3—C8—H8	119.9	C8—C7—H7	119.9
C7—C8—C3	120.25 (13)	C6—C7—C8	120.26 (14)
C7—C8—H8	119.9	C6—C7—H7	119.9
P1—C2—H2A	109.5	C7—C6—H6	120.1
P1—C2—H2B	109.5	C7—C6—C5	119.89 (13)
P1—C2—H2C	109.5	C5—C6—H6	120.1
H2A—C2—H2B	109.5	C4—C5—H5	119.9
H2A—C2—H2C	109.5	C6—C5—C4	120.26 (14)
H2B—C2—H2C	109.5	C6—C5—H5	119.9
P1—C3—C8—C7	-176.66 (10)	C8—C7—C6—C5	-0.4 (2)
P1—C3—C4—C5	175.48 (12)	C2—P1—C3—C8	-34.24 (12)
S1—P1—C3—C8	-159.38 (10)	C2—P1—C3—C4	148.99 (11)
S1—P1—C3—C4	23.85 (12)	C1—P1—C3—C8	77.98 (12)
C3—C8—C7—C6	0.8 (2)	C1—P1—C3—C4	-98.79 (12)
C3—C4—C5—C6	1.7 (2)	C4—C3—C8—C7	0.1 (2)
C8—C3—C4—C5	-1.4 (2)	C7—C6—C5—C4	-0.8 (2)

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