

# Crystal structure of $(\pm)$ -(3*aR*,5*R*,8*bR*)-5-hydroperoxy-2-phenyl-6-tosyl-4,5,6,8*b*-tetrahydropyrrolo[3,4-*e*]indole-1,3(2*H*,3*aH*)-dione

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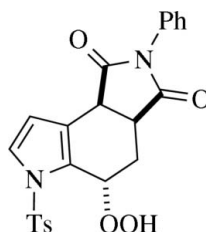
**Keywords:** crystal structure; hydroperoxide; autoxidation; cycloaddition; pyrrole; indole

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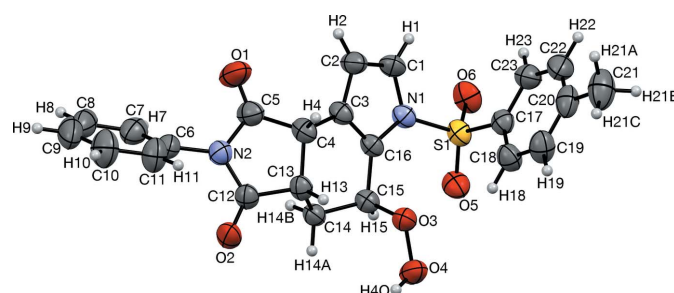
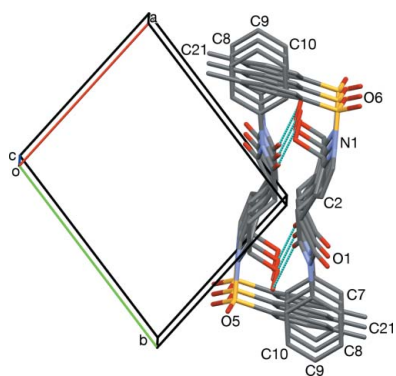
The title compound,  $C_{23}H_{20}N_2O_6S$ , crystallizes as a racemate in the space group  $P\bar{1}$ , with an overall L- or J-shape to each molecule. Centrosymmetric pairs of molecules are tandem hydrogen bonded between the hydroperoxy H atom and carbonyl O atom. A different centrosymmetric pairing has stacked *S*-tolyl rings, and a third pairing is L,J-interlocked by the short leg. Except for stacked tolyl pairs, neighboring  $\pi$ -systems are much closer to orthogonal than coaxial. The title compound is the first example of a hydroperoxide obtained from the autoxidation of a Diels–Alder adduct of a 2-vinylpyrrole.

## 1. Chemical context

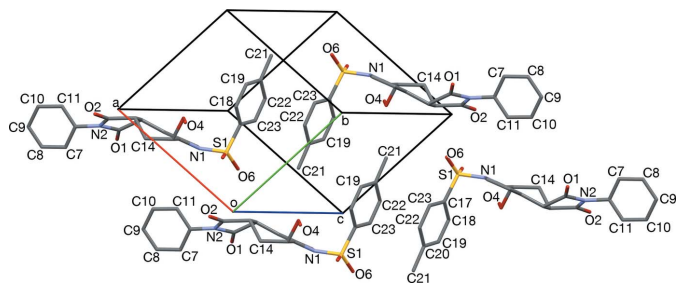
Diels–Alder reactions of vinylpyrroles with maleimides have been studied as a method to form substituted indole compounds (Nolan *et al.*, 2009; Xiao & Ketcha, 1995). Related reactions have been done with other heterocycles (Abarca *et al.*, 1985; Jones *et al.*, 1984; Nolan *et al.*, 1983). Diels–Alder reactions between vinylheterocycles and dienophiles are useful for forming fused ring systems that may have biological activity or versatility in natural product synthesis (Booth *et al.*, 2005; Kanai *et al.* 2005; Nagai *et al.* 1993; Nolan & Pardi, 2005).



The hydroperoxide title compound (I) (Fig. 1) was isolated after performing a Diels–Alder reaction between *N*-tosyl-2-vinylpyrrole (Settambolo *et al.*, 1997) and *N*-phenylmaleimide



**Figure 1**  
The molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level.

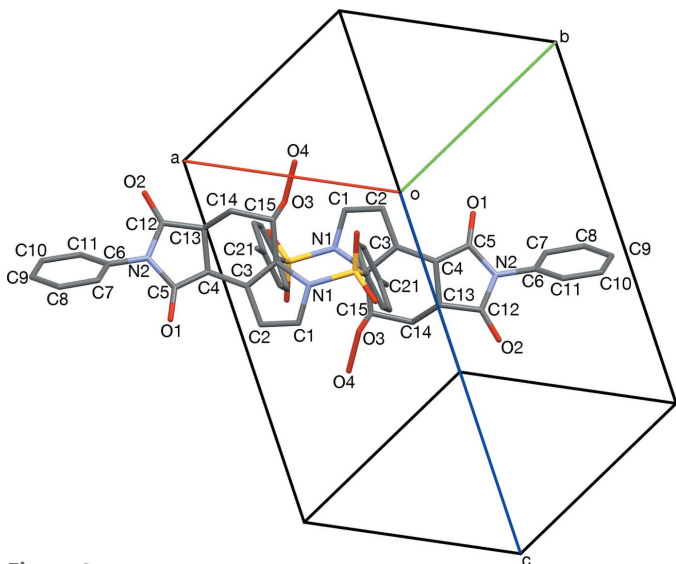

**Figure 2**

Two pairs of stacked tolyl groups, viewed along  $[1\bar{1}2]$ . The central two molecules form an interlocked pair. Twisting of the *N*-Phenyl group, and out-of-plane position of C14, are also depicted.

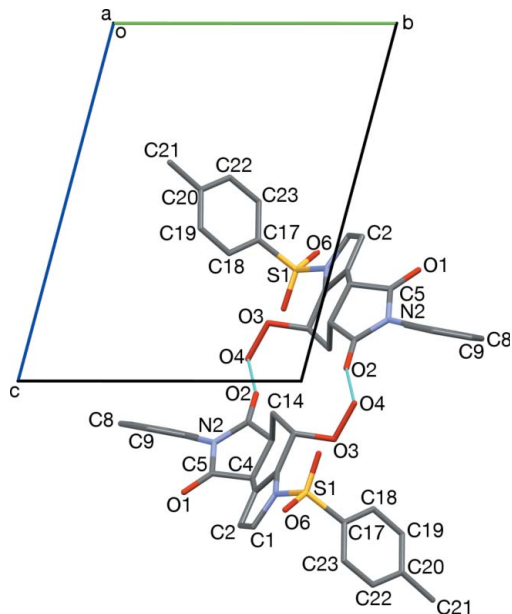
(commercially available). An analogous compound was proposed, though not isolated, as an intermediate for an alcohol product obtained from a similar reaction (Eitel & Pindur, 1988). No analogous hydroperoxides have been claimed from reactions of 2-vinyl -pyrroles, -indoles, -thiophenes, or -benzothiophenes. There are a few examples of hydroperoxides isolated from Diels–Alder reactions between 2-vinylfuran or 2-vinylbenzofuran and dienophiles, but the products were not crystallographically categorized (Brewer & Elix, 1975; Kotsuki *et al.*, 1981; Skoric *et al.*, 2001).

## 2. Structural commentary

The *N*-phenyl, *S*-phenyl, and pyrrolo rings are individually planar within 0.009, 0.011, and 0.010 Å, respectively. The *N*-phenyl ring (C7–C11) is twisted 58.3 (2)° out of plane from the imido moiety (C5, N2, C12, Figs. 2 and 4). The cyclohexene ring has a half-chair conformation with C14 out of plane in the direction *anti*- to the *S*-tolyl group (Figs. 2 and 4), which is bent 85.4 (2)° out of plane with the pyrrolo ring, giving the molecule an overall L- or J- shape.


**Figure 3**

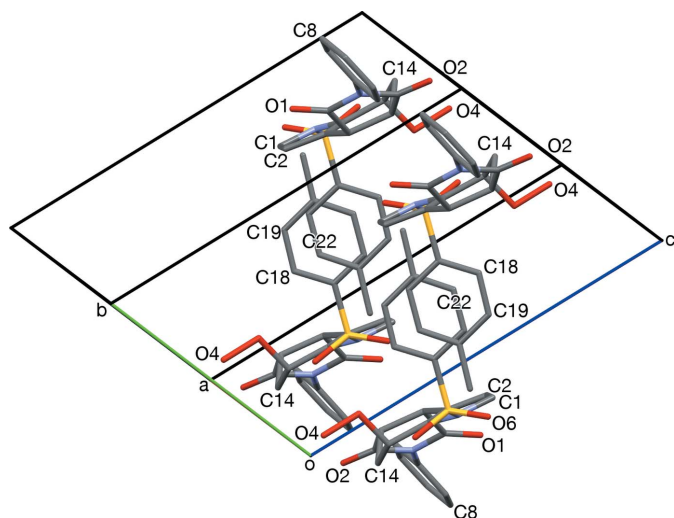
The central interlocked pair from Fig. 2, viewed along  $[221]$ . The C20,C21-axis is aligned with the face of the cyclohexene ring of its interlocked partner.


**Figure 4**

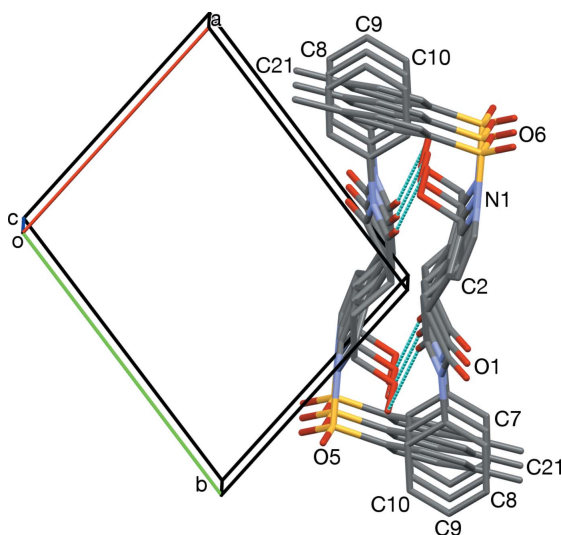
Hydrogen-bonded dimers, viewed along  $[100]$ . Hydrogen bonds (O2, O4) are shown in turquoise. Also apparent are the twisting of *N*-phenyl rings (C5, N2, C8, C9), and the half-chair conformation of the cyclohexene ring (C4, C14, lower molecule).

## 3. Supramolecular features

Interlocking pairs are aligned such that the axis of the *S*-tolyl group (C21) points toward the face of the cyclohexene ring (C3, C14, C15, Fig. 3). Hydrogen-bonded dimers form between H4O and O2 (Table 1, Figs. 4 and 6). Hydrogen bonding acts approximately along  $[4\bar{1}1]$  and twists the hydroperoxy group to have a torsion angle of 95.0°. In different pairings than those that interlock, *S*-tolyl groups stack rotated 180° about an oblique axis,  $[0.803, -0.544, 0.244]$  (Figs. 2 and 5). Each pair of *S*-tolyl pairs is sheared by approximately 3.7 Å from its neighbor. Similarly oriented


**Figure 5**

The two tolyl-stacked pairs from Fig. 2, viewed along  $[2\bar{1}0]$ . Neighboring pairs are sheared roughly 1.5 phenyl ring diameters.

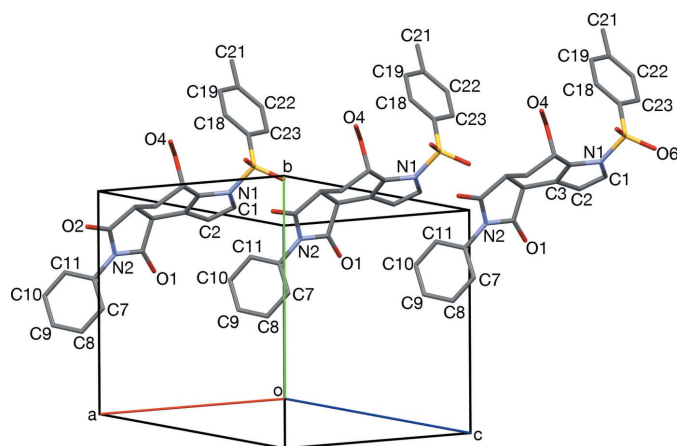


**Figure 6**  
Edge-to-face stacks of *S*-tolyl and *N*-phenyl rings, and hydrogen-bonded (turquoise) dimerization, viewed slightly off [001].

*N*-phenyl rings are separated from each other by *S*-tolyl groups (C21, Fig. 6), with an angle of  $69.26^\circ$  between the *S*-tolyl and *N*-phenyl planes. Pyrrolo groups (N1, C1, C2) each have their *endo* face toward an edge of an *N*-phenyl group (C10, C11, Fig. 7), with an angle of  $69.4(2)^\circ$  between the pyrrolo and *N*-phenyl planes.

#### 4. Database survey

The structures shown in Fig. 8 represent the cores of most compounds that could be obtained by Diels–Alder reactions of the type that gave title compound (I), using nitrogen heterocyclic dienes and dienophiles. Searching these substructures found six entries in the current database (Cambridge Structural Database, Version 5.35, November 2013; Allen 2002). Only two of these were synthesized by cycloadditions of this type [a combretastatin derivative (Ty *et al.*, 2010); carbazomycin B (Beccali *et al.*, 1996)]. Upon



**Figure 7**  
The *endo* face of pyrrole rings (N1, C1, C2) neighboring the edge of an *N*-phenyl ring (C10, C11) of an adjacent molecule of the same enantiomer, viewed along [414].

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O4–H4O...O2 <sup>i</sup>	0.82	2.00	2.7929 (19)	163

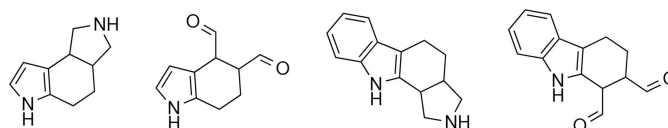
Symmetry code: (i)  $-x + 2, -y, -z$ .

expanding the search to include any combination of heteroatoms at nitrogen and oxygen sites, seven additional entries were found, all within or closely related to the caesalmin family of furanoditerpenoid antivirals (*i.e.*, Rodrigues *et al.*, 2004; Jiang *et al.*, 2002). Of 13 total entries, none was found containing sulfur atoms. Ten exhibit intermolecular hydrogen bonding, but only two of them are tandem-bonded dimers [pyrimidinone carbonyl to carboxylic acid (Obushak *et al.*, 2011); succinimide dimerization between N–H and a carbonyl oxygen (Beccali *et al.*, 1996)]. None of these structures resembles that of compound (I).

#### 5. Synthesis and crystallization

*N*-Tosyl-2-vinylpyrrole (458 mg) and *N*-phenylmaleimide (272 mg) were dissolved in chloroform (1.5 ml) and stirred for 72 h at room temperature in a vessel open to air. Column chromatography on silica gel (1:1 hexane:ethyl acetate,  $R_f = 0.30$ ), followed by recrystallization from dichloromethane–petroleum ether (b.p. 311–333 K) gave compound (I) as colourless plates (17 mg, 2.4%, m.p. 425–426 K).  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  11.96 (*s*, 1H, H4O), 7.974 (*d*,  $J = 3.4$  Hz, 2H, H18, H23), 7.483 (*t*,  $J = 8.0$  Hz, 2H, H8, H10), 7.427 (*m*, 3H, H9, H19, H22), 7.283 (*dd*,  $J = 8.8, 1.0$  Hz, 2H, H7, H11), 6.516 (*d*,  $J = 3.4$  Hz, 1H, H2), 5.485 (*dd*,  $J = 2.9, 2.7$  Hz, 1H, H15), 4.241 (*d*,  $J = 8.3$  Hz, 1H, H4), 3.375 (*ddd*,  $J = 13.7, 8.3, 5.8$  Hz, 1H, H13), 2.824 (*ddd*,  $J = 14.1, 5.8, 2.9$  Hz, 1H, H14A), 2.384 (*s*, 3H, H21), 1.886 (*ddd*,  $J = 14.1, 13.7, 2.7$  Hz, 1H, H14B);  $^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  178.09 (C12), 174.85 (C5), 145.49 (C20), 135.06 (C17), 132.36 (C6), 129.94 (C19, C22), 128.87 (C8, C10), 128.43 (C9), 127.57 (C18, C23), 127.26 (C7, C11), 125.32 (C16), 124.14 (C1), 121.63 (C3), 112.27 (C2), 70.77 (C15), 38.79 (C4), 35.32 (C13), 27.85 (C14), 21.10 (C21); IR (NaCl,  $\text{cm}^{-1}$ ) 3361 (O–H), 2917 (C–H), 1713 (C=O), 1595 (C=C), 1370 (S=O), 1177 (C–O), 808, 751, 672; MS (ESI, PEG,  $m/z$ )  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_6\text{S}$  475.0934, found 475.0921.

**Safety Note:** Hydroperoxides, particularly those bearing an  $\alpha$ -proton (*e.g.*, H15, Fig. 1), can be shock- or heat-sensitive and detonate violently (Francisco, 1993). Although sensitivity tests on our batch of title compound (I) were negative, appropriate precautions should be taken when reproducing or extending



**Figure 8**  
Substructures used for the database survey.

our work with (I) or similar compounds. Metal tools, glass or metal storage vessels, high oxygen- or nitrogen-to-carbon ratios, and large scales should all be avoided. The bulk of product should be kept in solution, with small aliquots being allowed to dry only as necessary.

## 6. Refinement

A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms except for H4O were placed in ideal positions and refined as constrained atoms with  $U_{\text{iso}}(\text{H}_n) = 1.2U_{\text{eq}}(\text{C}_n)$ , except for the methyl group, where  $U_{\text{iso}}(\text{H}21_i) = 1.5U_{\text{eq}}(\text{C}21)$ . The bond lengths (Å) specified for C–H hydrogens were 0.93 (aryl), 0.96 (methyl), 0.97 (methylene), and 0.98 (methine). H4O was found from the difference Fourier map and refined with  $U_{\text{iso}}(\text{H}4\text{O}) = 1.2U_{\text{eq}}(\text{O}4)$  and an O–H bond length of 0.82 Å. The final full-matrix least-squares refinement converged to  $R1 = 0.0364$  and  $wR2 = 0.1161$  ( $F^2$ , all data). Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

The authors thank Victor G. Young Jr (X-Ray Crystallographic Laboratory, University of Minnesota) and Dr Matthew J. Bruzek for assistance with the crystal structure analysis, and the Wayland E. Noland Research Fellowship Fund at the University of Minnesota Foundation for generous financial support of this project.

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**Table 2**

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_6\text{S}$
$M_r$	452.48
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
$a, b, c$ (Å)	8.6563 (13), 9.8819 (15), 13.533 (2)
$\alpha, \beta, \gamma$ (°)	102.068 (3), 107.786 (2), 96.364 (2)
$V$ (Å <sup>3</sup> )	1058.8 (3)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.20
Crystal size (mm)	0.60 × 0.50 × 0.20
Data collection	
Diffractometer	Bruker SMART Platform CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Blessing, 1995)
$T_{\text{min}}, T_{\text{max}}$	0.891, 0.962
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	10544, 3751, 3194
$R_{\text{int}}$	0.021
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.116, 1.06
No. of reflections	3751
No. of parameters	290
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.27, -0.28

Computer programs: *SMART* (Bruker, 2001), *SAINT* (Bruker, 2003), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae et al., 2008), *enCIFer* (Allen et al., 2004), and *publCIF* (Westrip, 2010).

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## supporting information

*Acta Cryst.* (2014). E70, 192-195 [doi:10.1107/S1600536814019874]

## Crystal structure of $(\pm)$ -(3a*R*,5*R*,8b*R*)-5-hydroperoxy-2-phenyl-6-tosyl-4,5,6,8b-tetrahydropyrrolo[3,4-*e*]indole-1,3(2*H*,3a*H*)-dione

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### Computing details

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004), and *pubCIF* (Westrip, 2010).

### $(\pm)$ -(3a*R*,5*R*,8b*R*)-5-Hydroperoxy-2-phenyl-6-tosyl-4,5,6,8b-tetrahydropyrrolo[3,4-*e*]indole-1,3(2*H*,3a*H*)-dione

#### Crystal data

C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S

*M<sub>r</sub>* = 452.48

Triclinic, *P* $\bar{1}$

*a* = 8.6563 (13) Å

*b* = 9.8819 (15) Å

*c* = 13.533 (2) Å

$\alpha$  = 102.068 (3)°

$\beta$  = 107.786 (2)°

$\gamma$  = 96.364 (2)°

*V* = 1058.8 (3) Å<sup>3</sup>

*Z* = 2

*F*(000) = 472

*D<sub>x</sub>* = 1.419 Mg m<sup>-3</sup>

Melting point: 425 K

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 2698 reflections

$\theta$  = 2.5–25.1°

$\mu$  = 0.20 mm<sup>-1</sup>

*T* = 293 K

Block, colourless

0.60 × 0.50 × 0.20 mm

#### Data collection

Bruker SMART Platform CCD  
diffractometer

Radiation source: normal-focus sealed tube

Graphite monochromator

area detector,  $\omega$  scans per phi

Absorption correction: multi-scan

(*SADABS*; Blessing, 1995)

*T<sub>min</sub>* = 0.891, *T<sub>max</sub>* = 0.962

10544 measured reflections

3751 independent reflections

3194 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.021

$\theta_{\max}$  = 25.1°,  $\theta_{\min}$  = 1.6°

*h* = -10→10

*k* = -11→11

*l* = -16→16

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.036

*wR*(*F*<sup>2</sup>) = 0.116

*S* = 1.06

3751 reflections

290 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

$$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 0.2551P]$$

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

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

$$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$$

### Special details

**Experimental.** The space group P-1 was determined based on systematic absences and intensity statistics.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.46933 (5)	0.12220 (5)	0.31067 (4)	0.04468 (16)
O1	1.0118 (2)	-0.3093 (2)	0.31048 (15)	0.0865 (6)
O2	1.09502 (19)	-0.14706 (14)	0.03647 (12)	0.0582 (4)
O3	0.74791 (17)	0.17137 (13)	0.16243 (10)	0.0499 (3)
O4	0.6719 (2)	0.20863 (16)	0.06212 (12)	0.0649 (4)
H4O	0.7339	0.2033	0.0268	0.078*
O5	0.40641 (16)	0.13010 (15)	0.20262 (10)	0.0566 (4)
O6	0.36195 (16)	0.06483 (15)	0.35954 (12)	0.0601 (4)
N1	0.60788 (18)	0.01608 (15)	0.31539 (12)	0.0418 (3)
N2	1.08339 (19)	-0.24962 (16)	0.17207 (12)	0.0474 (4)
C1	0.6732 (2)	-0.0313 (2)	0.40679 (15)	0.0480 (4)
H1	0.6284	-0.0301	0.4612	0.058*
C2	0.8110 (2)	-0.0788 (2)	0.40345 (15)	0.0502 (5)
H2	0.8770	-0.1182	0.4539	0.060*
C3	0.8381 (2)	-0.05797 (19)	0.30826 (13)	0.0420 (4)
C4	0.9808 (2)	-0.0811 (2)	0.27117 (14)	0.0457 (4)
H4	1.0786	-0.0165	0.3247	0.055*
C5	1.0216 (2)	-0.2278 (2)	0.25780 (16)	0.0539 (5)
C6	1.1781 (2)	-0.35732 (19)	0.15237 (15)	0.0486 (4)
C7	1.1125 (3)	-0.4973 (2)	0.13290 (17)	0.0610 (5)
H7	1.0042	-0.5252	0.1291	0.073*
C8	1.2118 (4)	-0.5966 (2)	0.11898 (18)	0.0739 (7)
H8	1.1700	-0.6916	0.1076	0.089*
C9	1.3694 (4)	-0.5565 (3)	0.1218 (2)	0.0801 (8)
H9	1.4336	-0.6239	0.1112	0.096*
C10	1.4322 (4)	-0.4178 (3)	0.1400 (2)	0.0857 (8)
H10	1.5393	-0.3904	0.1413	0.103*
C11	1.3370 (3)	-0.3167 (2)	0.1568 (2)	0.0669 (6)
H11	1.3811	-0.2217	0.1710	0.080*

C12	1.0551 (2)	-0.14946 (18)	0.11427 (15)	0.0443 (4)
C13	0.9635 (2)	-0.04746 (18)	0.16302 (14)	0.0429 (4)
H13	1.0188	0.0496	0.1752	0.051*
C14	0.7826 (2)	-0.06872 (18)	0.09075 (14)	0.0427 (4)
H14A	0.7783	-0.0455	0.0239	0.051*
H14B	0.7310	-0.1668	0.0739	0.051*
C15	0.6877 (2)	0.02411 (18)	0.14624 (13)	0.0415 (4)
H15	0.5697	0.0001	0.1039	0.050*
C16	0.7143 (2)	0.00040 (17)	0.25498 (13)	0.0378 (4)
C17	0.5829 (2)	0.28523 (19)	0.39512 (14)	0.0435 (4)
C18	0.6708 (3)	0.3751 (2)	0.35718 (17)	0.0550 (5)
H18	0.6656	0.3521	0.2858	0.066*
C19	0.7667 (3)	0.5001 (2)	0.42738 (19)	0.0618 (6)
H19	0.8253	0.5616	0.4024	0.074*
C20	0.7770 (3)	0.5351 (2)	0.53416 (18)	0.0592 (5)
C21	0.8857 (3)	0.6697 (3)	0.6109 (2)	0.0849 (8)
H21A	0.9501	0.6498	0.6760	0.127*
H21B	0.8180	0.7359	0.6270	0.127*
H21C	0.9582	0.7091	0.5785	0.127*
C22	0.6853 (3)	0.4442 (2)	0.56897 (17)	0.0623 (6)
H22	0.6886	0.4682	0.6399	0.075*
C23	0.5893 (3)	0.3192 (2)	0.50137 (16)	0.0561 (5)
H23	0.5297	0.2585	0.5264	0.067*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0331 (2)	0.0524 (3)	0.0469 (3)	0.00619 (19)	0.01535 (19)	0.0075 (2)
O1	0.1099 (14)	0.1116 (14)	0.0929 (12)	0.0657 (12)	0.0665 (11)	0.0702 (12)
O2	0.0736 (9)	0.0576 (8)	0.0673 (9)	0.0237 (7)	0.0473 (8)	0.0254 (7)
O3	0.0635 (8)	0.0467 (7)	0.0459 (7)	0.0136 (6)	0.0247 (6)	0.0140 (6)
O4	0.0787 (10)	0.0795 (10)	0.0667 (9)	0.0402 (8)	0.0424 (8)	0.0423 (8)
O5	0.0447 (7)	0.0696 (9)	0.0483 (8)	0.0146 (6)	0.0084 (6)	0.0091 (6)
O6	0.0425 (7)	0.0688 (9)	0.0723 (9)	0.0034 (6)	0.0314 (7)	0.0108 (7)
N1	0.0391 (8)	0.0465 (8)	0.0433 (8)	0.0059 (6)	0.0196 (6)	0.0115 (6)
N2	0.0507 (9)	0.0484 (9)	0.0504 (9)	0.0150 (7)	0.0236 (7)	0.0157 (7)
C1	0.0546 (11)	0.0550 (11)	0.0443 (10)	0.0098 (9)	0.0266 (9)	0.0189 (8)
C2	0.0535 (11)	0.0612 (12)	0.0418 (10)	0.0152 (9)	0.0183 (9)	0.0200 (9)
C3	0.0367 (9)	0.0502 (10)	0.0377 (9)	0.0062 (7)	0.0133 (7)	0.0079 (7)
C4	0.0361 (9)	0.0583 (11)	0.0408 (9)	0.0088 (8)	0.0130 (7)	0.0088 (8)
C5	0.0495 (11)	0.0702 (13)	0.0537 (11)	0.0214 (10)	0.0238 (9)	0.0255 (10)
C6	0.0549 (11)	0.0473 (10)	0.0450 (10)	0.0172 (8)	0.0162 (8)	0.0120 (8)
C7	0.0657 (13)	0.0542 (12)	0.0545 (12)	0.0097 (10)	0.0096 (10)	0.0126 (9)
C8	0.106 (2)	0.0464 (12)	0.0550 (13)	0.0230 (13)	0.0084 (13)	0.0055 (10)
C9	0.093 (2)	0.0737 (17)	0.0715 (16)	0.0450 (15)	0.0204 (14)	0.0114 (13)
C10	0.0717 (16)	0.0843 (19)	0.108 (2)	0.0351 (14)	0.0369 (15)	0.0195 (16)
C11	0.0604 (13)	0.0548 (12)	0.0870 (16)	0.0165 (10)	0.0291 (12)	0.0117 (11)
C12	0.0451 (10)	0.0424 (9)	0.0510 (10)	0.0071 (8)	0.0240 (8)	0.0127 (8)

C13	0.0429 (9)	0.0414 (9)	0.0484 (10)	0.0062 (7)	0.0227 (8)	0.0101 (8)
C14	0.0502 (10)	0.0423 (9)	0.0373 (9)	0.0078 (8)	0.0185 (8)	0.0086 (7)
C15	0.0393 (9)	0.0458 (9)	0.0382 (9)	0.0061 (7)	0.0136 (7)	0.0087 (7)
C16	0.0339 (8)	0.0419 (9)	0.0367 (8)	0.0019 (7)	0.0148 (7)	0.0065 (7)
C17	0.0371 (9)	0.0475 (10)	0.0458 (10)	0.0115 (8)	0.0136 (8)	0.0105 (8)
C18	0.0590 (12)	0.0555 (11)	0.0552 (11)	0.0105 (9)	0.0291 (10)	0.0096 (9)
C19	0.0603 (13)	0.0477 (11)	0.0815 (15)	0.0054 (9)	0.0356 (11)	0.0105 (10)
C20	0.0478 (11)	0.0485 (11)	0.0684 (14)	0.0165 (9)	0.0076 (10)	0.0023 (10)
C21	0.0708 (16)	0.0581 (14)	0.100 (2)	0.0107 (12)	0.0115 (14)	-0.0084 (13)
C22	0.0750 (15)	0.0585 (12)	0.0453 (11)	0.0179 (11)	0.0106 (10)	0.0079 (9)
C23	0.0663 (13)	0.0558 (12)	0.0466 (11)	0.0108 (10)	0.0192 (10)	0.0142 (9)

*Geometric parameters (Å, °)*

S1—O5	1.4182 (14)	C8—H8	0.9300
S1—O6	1.4278 (14)	C9—C10	1.359 (4)
S1—N1	1.6740 (15)	C9—H9	0.9300
S1—C17	1.7494 (19)	C10—C11	1.389 (3)
O1—C5	1.194 (2)	C10—H10	0.9300
O2—C12	1.208 (2)	C11—H11	0.9300
O3—C15	1.437 (2)	C12—C13	1.516 (2)
O3—O4	1.4590 (18)	C13—C14	1.536 (3)
O4—H4O	0.8200	C13—H13	0.9800
N1—C1	1.393 (2)	C14—C15	1.528 (2)
N1—C16	1.407 (2)	C14—H14A	0.9700
N2—C12	1.383 (2)	C14—H14B	0.9700
N2—C5	1.407 (2)	C15—C16	1.491 (2)
N2—C6	1.443 (2)	C15—H15	0.9800
C1—C2	1.340 (3)	C17—C18	1.382 (3)
C1—H1	0.9300	C17—C23	1.389 (3)
C2—C3	1.429 (2)	C18—C19	1.384 (3)
C2—H2	0.9300	C18—H18	0.9300
C3—C16	1.356 (2)	C19—C20	1.386 (3)
C3—C4	1.492 (2)	C19—H19	0.9300
C4—C5	1.517 (3)	C20—C22	1.381 (3)
C4—C13	1.535 (2)	C20—C21	1.510 (3)
C4—H4	0.9800	C21—H21A	0.9600
C6—C11	1.369 (3)	C21—H21B	0.9600
C6—C7	1.373 (3)	C21—H21C	0.9600
C7—C8	1.396 (3)	C22—C23	1.374 (3)
C7—H7	0.9300	C22—H22	0.9300
C8—C9	1.364 (4)	C23—H23	0.9300
O5—S1—O6	120.26 (9)	C10—C11—H11	120.1
O5—S1—N1	106.58 (8)	O2—C12—N2	124.70 (16)
O6—S1—N1	104.10 (8)	O2—C12—C13	126.41 (16)
O5—S1—C17	110.99 (9)	N2—C12—C13	108.87 (15)
O6—S1—C17	108.79 (9)	C12—C13—C4	103.09 (14)



N1—S1—C17	104.77 (8)	C12—C13—C14	111.55 (14)
C15—O3—O4	107.67 (12)	C4—C13—C14	112.69 (14)
O3—O4—H4O	109.5	C12—C13—H13	109.8
C1—N1—C16	108.04 (14)	C4—C13—H13	109.8
C1—N1—S1	120.64 (12)	C14—C13—H13	109.8
C16—N1—S1	127.91 (12)	C15—C14—C13	110.81 (14)
C12—N2—C5	112.50 (15)	C15—C14—H14A	109.5
C12—N2—C6	123.69 (15)	C13—C14—H14A	109.5
C5—N2—C6	123.61 (15)	C15—C14—H14B	109.5
C2—C1—N1	108.87 (15)	C13—C14—H14B	109.5
C2—C1—H1	125.6	H14A—C14—H14B	108.1
N1—C1—H1	125.6	O3—C15—C16	106.51 (13)
C1—C2—C3	107.45 (17)	O3—C15—C14	111.80 (14)
C1—C2—H2	126.3	C16—C15—C14	108.60 (14)
C3—C2—H2	126.3	O3—C15—H15	110.0
C16—C3—C2	108.74 (16)	C16—C15—H15	110.0
C16—C3—C4	121.81 (16)	C14—C15—H15	110.0
C2—C3—C4	129.26 (17)	C3—C16—N1	106.87 (15)
C3—C4—C5	117.02 (16)	C3—C16—C15	125.22 (15)
C3—C4—C13	113.64 (15)	N1—C16—C15	127.44 (15)
C5—C4—C13	104.65 (14)	C18—C17—C23	120.96 (18)
C3—C4—H4	107.0	C18—C17—S1	119.98 (14)
C5—C4—H4	107.0	C23—C17—S1	118.99 (15)
C13—C4—H4	107.0	C17—C18—C19	118.74 (19)
O1—C5—N2	124.96 (19)	C17—C18—H18	120.6
O1—C5—C4	128.61 (19)	C19—C18—H18	120.6
N2—C5—C4	106.36 (16)	C18—C19—C20	121.3 (2)
C11—C6—C7	120.53 (19)	C18—C19—H19	119.3
C11—C6—N2	118.49 (18)	C20—C19—H19	119.3
C7—C6—N2	120.95 (18)	C22—C20—C19	118.47 (19)
C6—C7—C8	118.6 (2)	C22—C20—C21	120.6 (2)
C6—C7—H7	120.7	C19—C20—C21	121.0 (2)
C8—C7—H7	120.7	C20—C21—H21A	109.5
C9—C8—C7	120.9 (2)	C20—C21—H21B	109.5
C9—C8—H8	119.5	H21A—C21—H21B	109.5
C7—C8—H8	119.5	C20—C21—H21C	109.5
C10—C9—C8	119.9 (2)	H21A—C21—H21C	109.5
C10—C9—H9	120.1	H21B—C21—H21C	109.5
C8—C9—H9	120.1	C23—C22—C20	121.6 (2)
C9—C10—C11	120.2 (3)	C23—C22—H22	119.2
C9—C10—H10	119.9	C20—C22—H22	119.2
C11—C10—H10	119.9	C22—C23—C17	118.9 (2)
C6—C11—C10	119.8 (2)	C22—C23—H23	120.5
C6—C11—H11	120.1	C17—C23—H23	120.5
O5—S1—N1—C1	-169.75 (14)	O2—C12—C13—C14	70.7 (2)
O6—S1—N1—C1	-41.65 (15)	N2—C12—C13—C14	-107.92 (17)
C17—S1—N1—C1	72.53 (15)	C3—C4—C13—C12	-148.89 (15)

O5—S1—N1—C16	33.70 (17)	C5—C4—C13—C12	-20.06 (18)
O6—S1—N1—C16	161.79 (14)	C3—C4—C13—C14	-28.5 (2)
C17—S1—N1—C16	-84.02 (16)	C5—C4—C13—C14	100.34 (17)
C16—N1—C1—C2	-1.8 (2)	C12—C13—C14—C15	174.11 (14)
S1—N1—C1—C2	-162.56 (14)	C4—C13—C14—C15	58.70 (19)
N1—C1—C2—C3	1.6 (2)	O4—O3—C15—C16	-159.65 (12)
C1—C2—C3—C16	-0.8 (2)	O4—O3—C15—C14	81.87 (16)
C1—C2—C3—C4	174.24 (19)	H4O—O4—O3—C15	-95.0
C16—C3—C4—C5	-128.24 (19)	C13—C14—C15—O3	65.49 (18)
C2—C3—C4—C5	57.3 (3)	C13—C14—C15—C16	-51.74 (18)
C16—C3—C4—C13	-6.0 (2)	C2—C3—C16—N1	-0.4 (2)
C2—C3—C4—C13	179.55 (18)	C4—C3—C16—N1	-175.81 (15)
C12—N2—C5—O1	169.9 (2)	C2—C3—C16—C15	-173.01 (16)
C6—N2—C5—O1	-15.1 (3)	C4—C3—C16—C15	11.5 (3)
C12—N2—C5—C4	-12.9 (2)	C1—N1—C16—C3	1.32 (19)
C6—N2—C5—C4	162.11 (16)	S1—N1—C16—C3	160.22 (13)
C3—C4—C5—O1	-35.7 (3)	C1—N1—C16—C15	173.76 (16)
C13—C4—C5—O1	-162.4 (2)	S1—N1—C16—C15	-27.3 (2)
C3—C4—C5—N2	147.29 (16)	O3—C15—C16—C3	-102.19 (19)
C13—C4—C5—N2	20.51 (19)	C14—C15—C16—C3	18.4 (2)
C12—N2—C6—C11	56.6 (3)	O3—C15—C16—N1	86.68 (19)
C5—N2—C6—C11	-117.8 (2)	C14—C15—C16—N1	-152.76 (16)
C12—N2—C6—C7	-125.4 (2)	O5—S1—C17—C18	-32.44 (18)
C5—N2—C6—C7	60.2 (3)	O6—S1—C17—C18	-166.93 (15)
C11—C6—C7—C8	0.7 (3)	N1—S1—C17—C18	82.23 (16)
N2—C6—C7—C8	-177.25 (18)	O5—S1—C17—C23	150.62 (15)
C6—C7—C8—C9	-1.7 (3)	O6—S1—C17—C23	16.13 (18)
C7—C8—C9—C10	1.1 (4)	N1—S1—C17—C23	-94.71 (16)
C8—C9—C10—C11	0.5 (4)	C23—C17—C18—C19	0.3 (3)
C7—C6—C11—C10	0.9 (4)	S1—C17—C18—C19	-176.53 (16)
N2—C6—C11—C10	178.9 (2)	C17—C18—C19—C20	0.7 (3)
C9—C10—C11—C6	-1.5 (4)	C18—C19—C20—C22	-1.8 (3)
C5—N2—C12—O2	-179.12 (19)	C18—C19—C20—C21	178.3 (2)
C6—N2—C12—O2	5.9 (3)	C19—C20—C22—C23	2.0 (3)
C5—N2—C12—C13	-0.4 (2)	C21—C20—C22—C23	-178.1 (2)
C6—N2—C12—C13	-175.46 (16)	C20—C22—C23—C17	-1.0 (3)
O2—C12—C13—C4	-168.10 (19)	C18—C17—C23—C22	-0.2 (3)
N2—C12—C13—C4	13.25 (18)	S1—C17—C23—C22	176.73 (15)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O4—H4O···O2 <sup>i</sup>	0.82	2.00	2.7929 (19)	163

Symmetry code: (i)  $-x+2, -y, -z$ .