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Crystal structure of rac-3-[2,3-bis(phenylsulfanyl)-3H-indol-3-yl]propanoic acid

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The title compound, $C_{23}H_{19}NO_2S_2$, was obtained as an unexpected regioisomer from an attempted synthesis of an intermediate for a substituent-effect study on ergot alkaloids. This is the first report of a 1H-indole monothioating at the 2- and 3-positions to give a 3H-indole. In the crystal, the acid H atom is twisted roughly 180° from the typical carboxy conformation and forms centrosymmetric O—H···N hydrogen-bonded dimers with the indole N atom of an inversion-related molecule. Together with a weak C—H···O hydrogen bond involving the carbonyl O atom, chains are formed along [100].

1. Chemical context

The ergot alkaloids, a family of natural and synthetic compounds based on a tetracyclic skeleton [(2), Fig. 1], have been long known to exhibit various pharmacological activities (Hofmann, 1978). Examples include pergolide (Gilbert et al., 2000), bromocriptine (Weber et al., 1981), and cabergoline (Dosa et al., 2013), which have been used as treatments for Tourette's syndrome, psoriasis, and Parkinson's disease, respectively. Uhle's ketone (3) is a commonly used intermediate in the synthesis of some ergot alkaloids (Moldvai et al., 2004; Uhle, 1951).
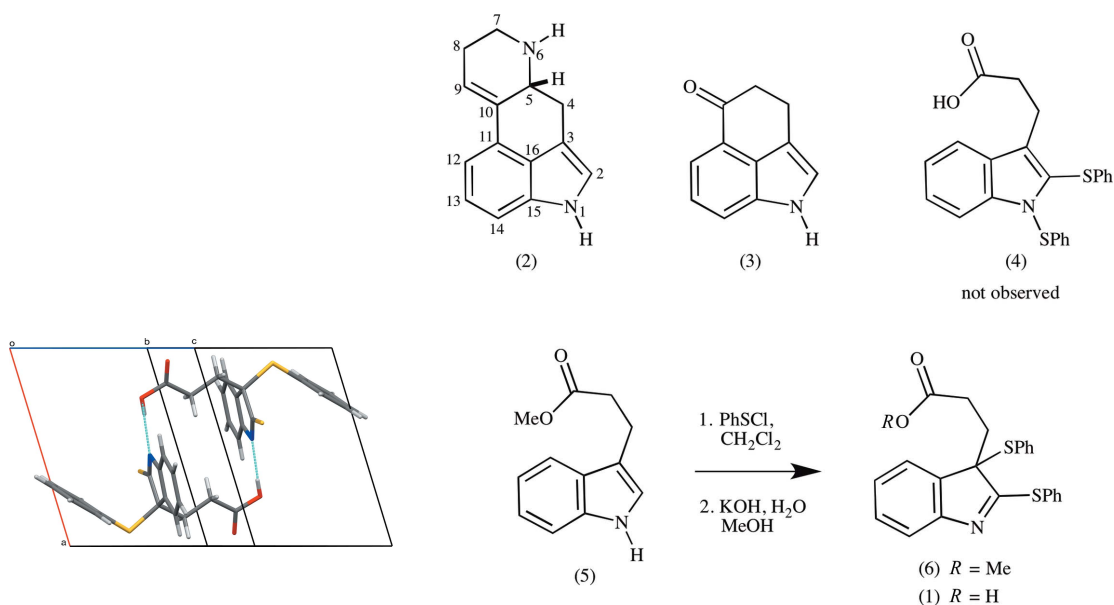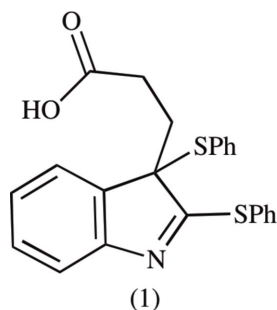

Figure 1
The ergot alkaloid skeleton, (2), Uhle's ketone, (3), the intended product, (4), and the synthesis of the title compound (bottom row).

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(1)

Our group envisioned the synthesis of novel Uhle's ketone derivatives bearing a reductively removable thio functionality at the 1- or 2-position to facilitate study of substituent effects at the 12–14 positions of several ergot alkaloids. 1,2-Bis(phenylthio)indole-3-propanoic acid (4) was a planned intermediate. However, phenylthioation and hydrolysis of methyl indole-3-propanoate (5) gave the title compound (1) as the only observed bisthioation product. 2,3-bis(thio)-3*H*-indoles such as (1) have not previously been reported as a product of 3-alkylindoles reacting with sulfenyl chlorides.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 2. The O1—H1*O* bond is *syn*-periplanar with C1—C2 (Fig. 3), in contrast to the *anti*-periplanar hydroxyl conformation usually observed in carboxyl groups. This is a consequence of an O1—H1*O*···N1 hydrogen bond (Table 1; §3). The remaining structural features are typical. The atoms of the indole unit (N1/C4–C11) have an r.m.s. deviation of 0.010 (2) Å from the mean plane, with quaternary carbon C4 only 0.012 (2) Å out of plane. The O1/C1–C4/S2/C18 (O1–C18) chain adopts a staggered conformation whose plane of best fit is inclined by 87.97 (8)° to that of the indole unit. Phenyl ring C18–C23 is inclined by 79.39 (10)° to the mean
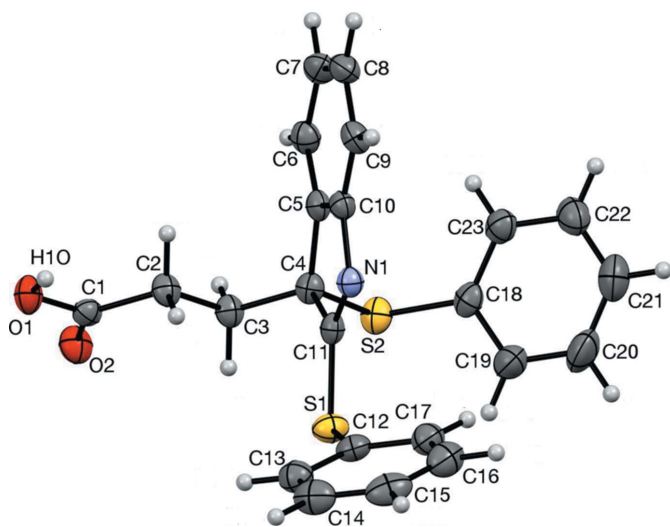
plane of the O1–C18 chain. Phenyl ring C12–C17 ring is inclined by 71.91 (7)° to the mean plane of the indole unit (Fig. 2). The C12—S1 bond is *syn*-periplanar with bond N1=C11, supporting conjugation between atom S1 and the indole system.

3. Supramolecular features

In the crystal, an O1—H1*O*···N1 hydrogen bond (Table 1) forms inversion dimers with an $R_2^2(16)$ ring motif (Fig. 3). Molecules are also linked by a non-classical C3—H3*A*···O2 hydrogen bond, forming inversion dimers with an $R_2^2(10)$ motif (Fig. 4). Collectively, these interactions form chains along [100].

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1[i]	0.84	1.96	2.7622 (18)	159
C3—H3A···O2[ii]	0.99	2.57	3.356 (2)	136

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$.

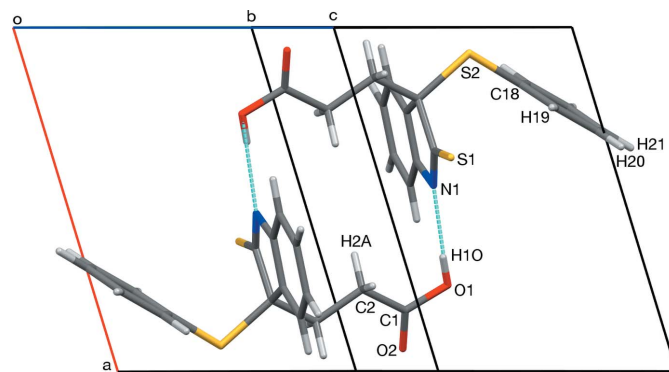**Figure 3**
A view along [04$\bar{3}$] of the O1—H1*O*···N1 hydrogen-bonded inversion dimer. The C12–C17 ring has been omitted for clarity.

Figure 2
The molecular structure of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level.
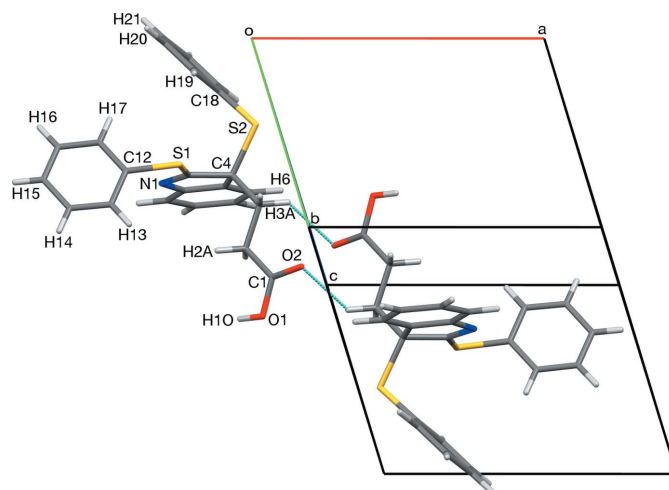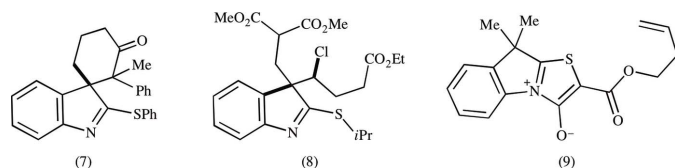

Figure 4
A view along [0$\bar{3}$4] of the C3—H3*A*···O2 hydrogen-bonded inversion dimer.

Figure 5
The three 2-thio-3*H*-indoles found in the Cambridge Structural Database (CSD; Groom & Allen, 2014).

4. Database survey

A search was performed for variously substituted 3*H*-indoles in the Cambridge Structural Database (CSD, Version 5.36, update 3; Groom & Allen, 2014). No entries were found containing a 3-thio or 3-propanoic functionality. Three examples of 2-thio-3*H*-indoles were found. Spiro-fused cyclohexanone (7) contains a 2-phenylthio group with similar geometry as is found in the title compound (Fig. 5; Feldman & Nuriye, 2009). The long chain in chlorotriester (8) is primarily staggered and normal to the indole unit, akin to the title compound (Novikov *et al.*, 2003). The third example, (9), is a thiazolium-4-oxide (Moody *et al.*, 2003).

5. Synthesis and crystallization

Methyl indole-3-propanoate (5) was prepared according to Pedras & Jha (2006), using *p*-toluenesulfonic acid in place of sulfuric acid. Benzenesulfenyl chloride (PhSCl) solution was prepared according to Li *et al.* (2013). In an argon atmosphere, methyl indole-3-propanoate (2.69 g) was dissolved in dichloromethane (30 ml) and then cooled in an ice bath. PhSCl solution (28 mmol, 32 ml) was added dropwise over 30 minutes. The resulting mixture was allowed to warm to room temperature and then was stirred for 2 h. Saturated $NaHCO_3$ solution (aq., 30 ml) was added, followed by extraction with dichloromethane (3 × 25 ml). The organic portion was dried with $MgSO_4$, concentrated, and then purified by column chromatography (SiO_2, 9:1 hexane–ethyl acetate), giving methyl 2,3-bis(phenylthio)-3*H*-indole-3-propanoate [(6), R_f = 0.41 in 2:1] as a yellow powder (3.29 g, 59%, m.p. 360-363 K); ¹H NMR (500 MHz, CD_2Cl_2) δ 7.572–7.553 (*m*, 2H), 7.455–7.416 (*m*, 4H), 7.222 (*m*, 1H), 7.194–7.171 (*m*, 4H), 7.104–7.073 (*m*, 2H), 7.045 (*m*, 1H), 3.563 (*s*, 3H), 2.647 (*ddd*, *J* = 13.8, 11.4, 5.1 Hz, 1H), 2.475 (*ddd*, *J* = 13.8, 11.2, 5.1 Hz, 1H), 2.174 (*ddd*, *J* = 16.3, 11.4, 5.1 Hz, 1H), 1.798 (*ddd*, *J* = 16.3, 11.2, 5.1 Hz, 1H); ¹³C NMR (126 MHz, CD_2Cl_2) δ 182.70 (1C), 175.84 (1C), 154.68 (1C), 139.60 (1C), 136.18 (2C), 135.44 (2C), 130.06 (1C), 129.95 (1C), 129.79 (2C), 129.74 (1C), 129.42 (1C), 128.85 (2C), 128.57 (1C), 125.31 (1C), 123.62 (1C), 119.50 (1C), 68.10 (1C), 52.14 (1C), 31.92 (1C), 29.55 (1C); IR (KBr, cm⁻¹) 3057 (*w*), 2956, 2926, 2851 (*w*), 1734 (*s*, C=O), 1508, 1440 (*s*), 1372, 1298 (O—CH_3), 1173, 744 (*s*), 689; MS (ESI, *m/z*) [*M*+H]⁺ calculated for $C_{24}H_{21}NO_2S_2$ 420.1086, found 420.1081.

Bisthioated ester [(6), 0.52 g] was dissolved in methanol (20 ml). KOH (0.12 g) and water (5 ml) were added. The resulting mixture was refluxed for 1 h and then cooled to room

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{23}H_{19}NO_2S_2$
M_r	405.51
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, *b*, *c* (Å)	9.6498 (12), 9.8610 (12), 10.8812 (13)
α, β, γ (°)	87.626 (1), 79.331 (1), 76.022 (1)
V (Å³)	987.4 (2)
Z	2
Radiation type	Mo *Kα*
μ (mm⁻¹)	0.29
Crystal size (mm)	0.23 × 0.12 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.698, 0.746
No. of measured, independent and observed [*I* > 2σ(*I*)] reflections	11689, 4499, 3396
R_{int}	0.032
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.092, 1.06
No. of reflections	4499
No. of parameters	254
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.27, −0.26

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

temperature. Hydrochloric acid was added drop wise until the reaction mixture pH reached 1. The resulting mixture was extracted with dichloromethane (3 × 25 ml). The organic portion was dried with $MgSO_4$ and then concentrated giving the title compound (1) as a pale-yellow powder (0.43 g, 90%, m.p. 443–445 K); R_f = 0.49 (SiO_2, 1:1 hexane–ethyl acetate); ¹H NMR (500 MHz, CD_2Cl_2; acid proton H1*O* not observed) δ 7.520–7.389 (*m*, 6H), 7.245–7.168 (*m*, 5H), 7.108–7.078 (*m*, 2H), 7.045 (*m*, 1H), 2.619 (*ddd*, *J* = 13.9, 11.8, 4.7 Hz, H3*A*), 2.447 (*ddd*, *J* = 13.9, 11.0, 5.0 Hz, H3*B*), 2.130 (*ddd*, *J* = 16.4, 11.8, 5.0 Hz, H2*A*), 1.734 (*ddd*, *J* = 16.4, 11.0, 4.7 Hz, H2*B*); ¹³C NMR (126 MHz, CD_2Cl_2) δ 183.24 (C11), 175.84 (C1), 154.38 (C10), 139.52 (C5), 136.20 (2C), 135.50 (2C), 130.16 (1C), 130.14 (1C), 129.91 (2C), 129.61 (1C), 128.90 (2C), 128.15 (1C), 127.48 (1C), 125.52 (1C), 123.65 (1C), 119.36 (1C), 67.93 (C4), 31.67 (C3), 29.18 (C2); IR (KBr, cm⁻¹) 3407 (O—H), 3056 (*w*), 2925, 2854 (*w*), 1745 (*s*, C=O), 1514, 1383, 746 (*s*), 689; MS (ESI, *m/z*) [*M* − H]⁻ calculated for $C_{23}H_{19}NO_2S_2$ 404.0784, found 404.0797.

Crystals of the title compound were grown by slow evaporation of a solution in dichloromethane at 270 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in calculated positions and refined as riding atoms: O—H = 0.84 Å and C—

H = 0.95–0.99 Å with $U_{iso}(H) = 1.5U_{eq}(O1)$ for atom H1 and $1.2U_{eq}(C)$ for other H atoms.

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Bruker (2007). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dosa, P. I., Ward, T., Walters, M. A. & Kim, S. W. (2013). *ACS Med. Chem. Lett.* **4**, 254–258.

Feldman, K. S. & Nuriye, A. Y. (2009). *Tetrahedron Lett.* **50**, 1914–1916.

Gilbert, D. L., Sethuraman, G., Sine, L., Peters, S. & Sallee, F. R. (2000). *Neurology*, **54**, 1310–1315.

Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.

Hofmann, A. (1978). *Pharmacology*, **16**, 1–11.

Li, Z.-S., Wang, W.-M., Lu, W., Niu, C.-W., Li, Y.-H., Li, Z.-M. & Wang, J.-G. (2013). *Bioorg. Med. Chem. Lett.* **23**, 3723–3727.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Moldvai, I., Temesvári-Major, E., Incze, M., Szentirmay, É., Gács-Baitz, E. & Szántay, C. (2004). *J. Org. Chem.* **69**, 5993–6000.

Moody, C. J., Slawin, A. M. Z. & Willows, D. (2003). *Org. Biomol. Chem.* **1**, 2716–2722.

Novikov, A. V., Kennedy, A. R. & Rainier, J. D. (2003). *J. Org. Chem.* **68**, 993–996.

Pedras, M. S. C. & Jha, M. (2006). *Bioorg. Med. Chem.* **14**, 4958–4979.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Uhle, F. C. (1951). *J. Am. Chem. Soc.* **73**, 2402–2403.

Weber, G., Neidhardt, M., Frey, H., Galle, K. & Geiger, A. (1981). *Arch. Dermatol. Res.* **271**, 437–439.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Crystal structure of *rac*-3-[2,3-bis(phenylsulfanyl)-3*H*-indol-3-yl]propanoic acid

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

rac-**3-[2,3-Bis(phenylsulfanyl)-3*H*-indol-3-yl]propanoic acid**

Crystal data

$C_{23}H_{19}NO_2S_2$	$F(000) = 424$
$M_r = 405.51$	$D_x = 1.364$ Mg m^{-3}
Triclinic, $P\overline{1}$	Melting point: 444 K
$a = 9.6498$ (12) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.8610$ (12) Å	Cell parameters from 2977 reflections
$c = 10.8812$ (13) Å	$\theta = 2.7–27.3°$
$\alpha = 87.626$ (1)°	$\mu = 0.29$ mm^{-1}
$\beta = 79.331$ (1)°	$T = 173$ K
$\gamma = 76.022$ (1)°	Block, colourless
$V = 987.4$ (2) Å^3	$0.23 \times 0.12 \times 0.10$ mm
$Z = 2$	

Data collection

Bruker APEXII CCD diffractometer	4499 independent reflections
Radiation source: sealed tube	3396 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.032$
Absorption correction: multi-scan (SADABS; Bruker, 2007)	$\theta_{max} = 27.6°$, $\theta_{min} = 1.9°$
$T_{min} = 0.698$, $T_{max} = 0.746$	$h = -12 \rightarrow 12$
11689 measured reflections	$k = -12 \rightarrow 12$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.1618P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
4499 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
254 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
0 restraints	

Special details

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.62197 (5)	0.45034 (5)	0.16673 (4)	0.03266 (13)
S2	0.92472 (5)	0.19331 (5)	0.20164 (4)	0.03283 (13)
O1	0.74866 (13)	0.71335 (13)	0.58120 (12)	0.0338 (3)
H1	0.6688	0.6928	0.6075	0.051*
O2	0.93299 (13)	0.65100 (13)	0.42699 (12)	0.0370 (3)
N1	0.54112 (14)	0.29215 (14)	0.36472 (13)	0.0251 (3)
C1	0.82262 (18)	0.62905 (17)	0.48697 (16)	0.0262 (4)
C2	0.76080 (18)	0.50855 (18)	0.46281 (16)	0.0289 (4)
H2A	0.6624	0.5453	0.4433	0.035*
H2B	0.7514	0.4515	0.5395	0.035*
C3	0.85486 (18)	0.41595 (17)	0.35510 (16)	0.0279 (4)
H3A	0.9532	0.3789	0.3747	0.033*
H3B	0.8644	0.4731	0.2784	0.033*
C4	0.79162 (17)	0.29341 (17)	0.33029 (15)	0.0258 (4)
C5	0.75579 (18)	0.20556 (17)	0.44228 (15)	0.0254 (4)
C6	0.84042 (19)	0.13254 (18)	0.52368 (17)	0.0310 (4)
H6	0.9401	0.1332	0.5147	0.037*
C7	0.7755 (2)	0.05780 (18)	0.61945 (17)	0.0350 (4)
H7	0.8320	0.0052	0.6757	0.042*
C8	0.6292 (2)	0.05935 (18)	0.63364 (17)	0.0350 (4)
H8	0.5872	0.0073	0.6994	0.042*
C9	0.54286 (19)	0.13564 (17)	0.55330 (16)	0.0295 (4)
H9	0.4424	0.1380	0.5637	0.035*
C10	0.60945 (18)	0.20787 (16)	0.45758 (15)	0.0251 (4)
C11	0.64132 (17)	0.34029 (17)	0.29370 (15)	0.0250 (4)
C12	0.43242 (19)	0.48511 (19)	0.16692 (15)	0.0295 (4)
C13	0.3474 (2)	0.6178 (2)	0.20041 (17)	0.0363 (4)
H13	0.3887	0.6865	0.2283	0.044*
C14	0.2017 (2)	0.6485 (2)	0.19258 (18)	0.0432 (5)
H14	0.1427	0.7391	0.2152	0.052*
C15	0.1417 (2)	0.5497 (2)	0.15248 (18)	0.0442 (5)
H15	0.0420	0.5726	0.1459	0.053*
C16	0.2255 (2)	0.4172 (2)	0.12167 (18)	0.0422 (5)
H16	0.1828	0.3482	0.0962	0.051*
C17	0.3717 (2)	0.3847 (2)	0.12777 (17)	0.0358 (4)
H17	0.4301	0.2939	0.1052	0.043*
C18	0.83442 (18)	0.06781 (19)	0.16376 (16)	0.0307 (4)
C19	0.7666 (2)	0.0890 (2)	0.06019 (18)	0.0444 (5)
H19	0.7669	0.1712	0.0115	0.053*

C20	0.6988 (3)	−0.0091 (3)	0.0277 (2)	0.0563 (6)
H20	0.6528	0.0057	−0.0433	0.068*
C21	0.6979 (2)	−0.1282 (2)	0.0980 (2)	0.0506 (6)
H21	0.6496	−0.1947	0.0764	0.061*
C22	0.7667 (2)	−0.1509 (2)	0.19934 (19)	0.0444 (5)
H22	0.7674	−0.2341	0.2467	0.053*
C23	0.8348 (2)	−0.05393 (19)	0.23299 (17)	0.0355 (4)
H23	0.8820	−0.0703	0.3034	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0282 (2)	0.0393 (3)	0.0309 (2)	−0.0096 (2)	−0.00598 (19)	0.0068 (2)
S2	0.0249 (2)	0.0364 (3)	0.0345 (3)	−0.00567 (19)	0.00119 (19)	−0.0076 (2)
O1	0.0281 (7)	0.0349 (7)	0.0405 (7)	−0.0121 (6)	−0.0035 (6)	−0.0088 (6)
O2	0.0303 (7)	0.0405 (8)	0.0426 (8)	−0.0175 (6)	0.0000 (6)	−0.0020 (6)
N1	0.0236 (7)	0.0249 (7)	0.0271 (7)	−0.0060 (6)	−0.0048 (6)	−0.0018 (6)
C1	0.0255 (9)	0.0273 (9)	0.0282 (9)	−0.0072 (7)	−0.0101 (7)	0.0035 (7)
C2	0.0246 (9)	0.0300 (9)	0.0326 (9)	−0.0104 (7)	−0.0011 (7)	−0.0025 (7)
C3	0.0223 (8)	0.0299 (9)	0.0325 (9)	−0.0089 (7)	−0.0038 (7)	−0.0017 (7)
C4	0.0208 (8)	0.0271 (9)	0.0279 (9)	−0.0035 (7)	−0.0027 (7)	−0.0034 (7)
C5	0.0262 (9)	0.0216 (8)	0.0274 (9)	−0.0041 (7)	−0.0033 (7)	−0.0047 (7)
C6	0.0290 (9)	0.0268 (9)	0.0361 (10)	−0.0031 (7)	−0.0075 (8)	−0.0026 (8)
C7	0.0397 (11)	0.0265 (9)	0.0368 (11)	0.0001 (8)	−0.0127 (8)	0.0012 (8)
C8	0.0449 (11)	0.0254 (9)	0.0337 (10)	−0.0089 (8)	−0.0050 (9)	0.0037 (8)
C9	0.0287 (9)	0.0239 (9)	0.0362 (10)	−0.0082 (7)	−0.0042 (8)	−0.0006 (7)
C10	0.0273 (9)	0.0212 (8)	0.0265 (9)	−0.0048 (7)	−0.0046 (7)	−0.0024 (7)
C11	0.0241 (8)	0.0231 (8)	0.0270 (9)	−0.0040 (7)	−0.0036 (7)	−0.0065 (7)
C12	0.0291 (9)	0.0360 (10)	0.0223 (9)	−0.0058 (8)	−0.0054 (7)	0.0048 (7)
C13	0.0371 (10)	0.0378 (11)	0.0320 (10)	−0.0065 (8)	−0.0043 (8)	0.0006 (8)
C14	0.0363 (11)	0.0459 (12)	0.0380 (11)	0.0020 (9)	0.0014 (9)	0.0029 (9)
C15	0.0280 (10)	0.0677 (15)	0.0333 (11)	−0.0099 (10)	−0.0007 (8)	0.0100 (10)
C16	0.0385 (11)	0.0565 (13)	0.0360 (11)	−0.0199 (10)	−0.0072 (9)	0.0033 (10)
C17	0.0376 (11)	0.0377 (11)	0.0327 (10)	−0.0090 (9)	−0.0075 (8)	0.0004 (8)
C18	0.0264 (9)	0.0330 (10)	0.0291 (9)	−0.0006 (7)	−0.0022 (7)	−0.0085 (8)
C19	0.0580 (14)	0.0411 (12)	0.0346 (11)	−0.0078 (10)	−0.0146 (10)	−0.0018 (9)
C20	0.0702 (16)	0.0599 (15)	0.0451 (13)	−0.0130 (12)	−0.0271 (12)	−0.0136 (11)
C21	0.0531 (14)	0.0479 (13)	0.0542 (14)	−0.0160 (11)	−0.0092 (11)	−0.0176 (11)
C22	0.0538 (13)	0.0347 (11)	0.0425 (12)	−0.0113 (10)	−0.0007 (10)	−0.0057 (9)
C23	0.0374 (10)	0.0328 (10)	0.0335 (10)	−0.0013 (8)	−0.0072 (8)	−0.0050 (8)

Geometric parameters (Å, º)

S1—C11	1.7305 (17)	C8—H8	0.9500
S1—C12	1.7773 (18)	C9—C10	1.385 (2)
S2—C18	1.7767 (18)	C9—H9	0.9500
S2—C4	1.8493 (16)	C12—C17	1.383 (2)
O1—C1	1.328 (2)	C12—C13	1.389 (3)

O1—H1	0.8400	C13—C14	1.382 (3)
O2—C1	1.2040 (19)	C13—H13	0.9500
N1—C11	1.293 (2)	C14—C15	1.370 (3)
N1—C10	1.435 (2)	C14—H14	0.9500
C1—C2	1.504 (2)	C15—C16	1.378 (3)
C2—C3	1.525 (2)	C15—H15	0.9500
C2—H2A	0.9900	C16—C17	1.382 (3)
C2—H2B	0.9900	C16—H16	0.9500
C3—C4	1.533 (2)	C17—H17	0.9500
C3—H3A	0.9900	C18—C19	1.389 (3)
C3—H3B	0.9900	C18—C23	1.390 (2)
C4—C5	1.502 (2)	C19—C20	1.382 (3)
C4—C11	1.533 (2)	C19—H19	0.9500
C5—C6	1.379 (2)	C20—C21	1.375 (3)
C5—C10	1.386 (2)	C20—H20	0.9500
C6—C7	1.392 (2)	C21—C22	1.374 (3)
C6—H6	0.9500	C21—H21	0.9500
C7—C8	1.388 (3)	C22—C23	1.379 (3)
C7—H7	0.9500	C22—H22	0.9500
C8—C9	1.392 (2)	C23—H23	0.9500
C11—S1—C12	102.47 (8)	C9—C10—N1	126.35 (15)
C18—S2—C4	102.65 (8)	C5—C10—N1	111.96 (14)
C1—O1—H1	109.5	N1—C11—C4	114.43 (14)
C11—N1—C10	106.38 (14)	N1—C11—S1	127.16 (13)
O2—C1—O1	119.92 (15)	C4—C11—S1	118.40 (12)
O2—C1—C2	123.81 (16)	C17—C12—C13	120.40 (17)
O1—C1—C2	116.27 (14)	C17—C12—S1	120.78 (14)
C1—C2—C3	112.44 (13)	C13—C12—S1	118.72 (14)
C1—C2—H2A	109.1	C14—C13—C12	119.08 (19)
C3—C2—H2A	109.1	C14—C13—H13	120.5
C1—C2—H2B	109.1	C12—C13—H13	120.5
C3—C2—H2B	109.1	C15—C14—C13	120.61 (19)
H2A—C2—H2B	107.8	C15—C14—H14	119.7
C2—C3—C4	112.42 (13)	C13—C14—H14	119.7
C2—C3—H3A	109.1	C14—C15—C16	120.29 (19)
C4—C3—H3A	109.1	C14—C15—H15	119.9
C2—C3—H3B	109.1	C16—C15—H15	119.9
C4—C3—H3B	109.1	C15—C16—C17	119.99 (19)
H3A—C3—H3B	107.9	C15—C16—H16	120.0
C5—C4—C3	115.35 (14)	C17—C16—H16	120.0
C5—C4—C11	99.58 (13)	C16—C17—C12	119.61 (18)
C3—C4—C11	113.08 (13)	C16—C17—H17	120.2
C5—C4—S2	113.36 (11)	C12—C17—H17	120.2
C3—C4—S2	104.98 (11)	C19—C18—C23	119.20 (18)
C11—C4—S2	110.69 (11)	C19—C18—S2	119.45 (15)
C6—C5—C10	120.95 (16)	C23—C18—S2	121.31 (14)
C6—C5—C4	131.39 (15)	C20—C19—C18	120.20 (19)

C10—C5—C4	107.65 (14)	C20—C19—H19	119.9
C5—C6—C7	118.04 (17)	C18—C19—H19	119.9
C5—C6—H6	121.0	C21—C20—C19	120.1 (2)
C7—C6—H6	121.0	C21—C20—H20	119.9
C8—C7—C6	120.76 (17)	C19—C20—H20	119.9
C8—C7—H7	119.6	C22—C21—C20	119.9 (2)
C6—C7—H7	119.6	C22—C21—H21	120.0
C7—C8—C9	121.26 (17)	C20—C21—H21	120.0
C7—C8—H8	119.4	C21—C22—C23	120.6 (2)
C9—C8—H8	119.4	C21—C22—H22	119.7
C10—C9—C8	117.26 (16)	C23—C22—H22	119.7
C10—C9—H9	121.4	C22—C23—C18	119.89 (18)
C8—C9—H9	121.4	C22—C23—H23	120.1
C9—C10—C5	121.70 (16)	C18—C23—H23	120.1
O2—C1—C2—C3	0.9 (2)	C10—N1—C11—S1	−179.11 (12)
O1—C1—C2—C3	−178.65 (14)	C5—C4—C11—N1	−0.43 (18)
C1—C2—C3—C4	−179.85 (13)	C3—C4—C11—N1	−123.38 (16)
C2—C3—C4—C5	−52.58 (19)	S2—C4—C11—N1	119.15 (13)
C2—C3—C4—C11	61.13 (19)	C5—C4—C11—S1	178.90 (11)
C2—C3—C4—S2	−178.10 (12)	C3—C4—C11—S1	55.95 (17)
C18—S2—C4—C5	60.67 (13)	S2—C4—C11—S1	−61.52 (14)
C18—S2—C4—C3	−172.58 (11)	C12—S1—C11—N1	3.10 (17)
C18—S2—C4—C11	−50.24 (13)	C12—S1—C11—C4	−176.13 (12)
C3—C4—C5—C6	−57.2 (2)	C11—S1—C12—C17	−74.16 (15)
C11—C4—C5—C6	−178.58 (17)	C11—S1—C12—C13	109.44 (14)
S2—C4—C5—C6	63.8 (2)	C17—C12—C13—C14	−0.8 (3)
C3—C4—C5—C10	121.86 (15)	S1—C12—C13—C14	175.62 (14)
C11—C4—C5—C10	0.53 (16)	C12—C13—C14—C15	0.1 (3)
S2—C4—C5—C10	−117.07 (13)	C13—C14—C15—C16	1.3 (3)
C10—C5—C6—C7	1.9 (2)	C14—C15—C16—C17	−1.8 (3)
C4—C5—C6—C7	−179.11 (16)	C15—C16—C17—C12	1.1 (3)
C5—C6—C7—C8	−1.2 (3)	C13—C12—C17—C16	0.2 (3)
C6—C7—C8—C9	−0.2 (3)	S1—C12—C17—C16	−176.11 (14)
C7—C8—C9—C10	1.0 (3)	C4—S2—C18—C19	100.86 (16)
C8—C9—C10—C5	−0.4 (2)	C4—S2—C18—C23	−81.59 (15)
C8—C9—C10—N1	179.83 (15)	C23—C18—C19—C20	0.9 (3)
C6—C5—C10—C9	−1.1 (3)	S2—C18—C19—C20	178.48 (16)
C4—C5—C10—C9	179.70 (15)	C18—C19—C20—C21	0.2 (3)
C6—C5—C10—N1	178.71 (14)	C19—C20—C21—C22	−1.2 (3)
C4—C5—C10—N1	−0.51 (18)	C20—C21—C22—C23	1.2 (3)
C11—N1—C10—C9	−179.99 (16)	C21—C22—C23—C18	−0.2 (3)
C11—N1—C10—C5	0.23 (18)	C19—C18—C23—C22	−0.9 (3)
C10—N1—C11—C4	0.15 (18)	S2—C18—C23—C22	−178.43 (14)

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯N1[i]	0.84	1.96	2.7622 (18)	159
C3—H3*A*⋯O2[ii]	0.99	2.57	3.356 (2)	136

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*+1, −*z*+1.