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Triethylammonium *N*′-(benzylsulfanylthiocarbonyl)-2-hydroxybenzohydrazidate

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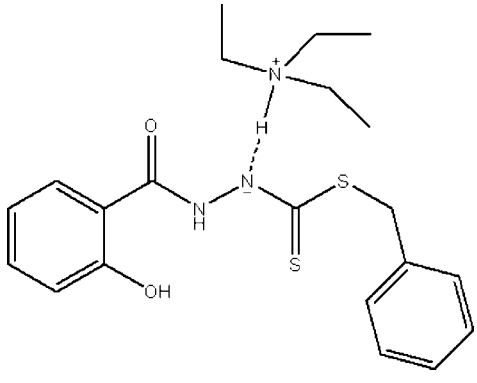
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.005 Å; R factor = 0.056; wR factor = 0.118; data-to-parameter ratio = 15.3.

In the title compound, $C_6H_{16}N^+\cdot C_{15}H_{13}N_2O_2S_2^-$, the thione S atom is in a *cis* configuration with respect to the phenyl and benzene rings, while it adopts a *trans* configuration with respect to the carbonyl group. The dihedral angle between the benzene and phenyl rings is 78.81 (2)°. The molecular conformation is stabilized by intramolecular O—H···O and N—H···S hydrogen bonds, while intermolecular N—H···O, N—H···N and weak C—H···O interactions help to stabilize the crystal structure.

Related literature

For related literature, see: Scovill *et al.* (1982, 1984); West *et al.* (1989); Gou *et al.* (1990); Abu-Raqabah *et al.* (1992); Marchi *et al.* (1990); Ali & Livingston, (1974); Wu *et al.* (2000); Boga *et al.* (1990).



Experimental

Crystal data

$C_6H_{16}N^+\cdot C_{15}H_{13}N_2O_2S_2^-$
M_r = 419.59
Orthorhombic, *Pbca*
a = 10.7109 (4) Å
b = 18.6807 (6) Å
c = 22.1814 (7) Å
V = 4438.2 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 173 (2) K
0.08 × 0.08 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
26195 measured reflections
3928 independent reflections
2542 reflections with $I > 2\sigma(I)$
R_{int} = 0.138

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.118
S = 1.05
3928 reflections
257 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.84	1.79	2.538 (3)	147
N1—H1A···S2	0.88	2.39	2.855 (3)	114
N3—H3A···O2	0.93	2.18	2.929 (3)	137
N3—H3A···N2	0.93	2.27	3.094 (4)	148
C9—H9A···S2	0.99	2.59	3.200 (3)	120
C21—H21A···O1^{i}	0.98	2.56	3.377 (5)	141

Symmetry code: (i) $x-\frac{1}{2}, y, -z+\frac{1}{2}$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2550).

References

Abu-Raqabah, A., Davies, G., El-Sayed, M. A., El-Toukhy, A., Shaikh, S. N. & Zubieta, J. (1992). *Inorg. Chim. Acta*, **193**, 43–56.
Ali, M. A. & Livingston, S. E. (1974). *Coord. Chem. Rev.* **13**, 101–132.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Boga, C., Forlani, L., Silverstoni, C., Corradi, A. B. & Sgarabotto, P. (1999). *J. Chem. Soc. Perkin Trans. 1*, pp. 1363–1368.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gou, S. H., You, X. Z., Xu, Z., Yu, K. B. & Zhou, Z. Y. (1990). *Polyhedron*, **9**, 2981–2985.
Marchi, A., Rossi, R., Magon, L., Duttai, A., Pasqualini, R., Ferretti, V. & Bertolasi, V. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1411–1416.
Nonius (1998). *COLLECT* Nonius BV Delft The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Scovill, J. P., Klayman, D. L. & Franchino, C. F. (1982). *J. Med. Chem.* **25**, 1261–1264.
Scovill, J. P., Klayman, D. L., Lambros, C., Childs, G. E. & Nortsh, J. D. (1984). *J. Med. Chem.* **27**, 87–91.
Sheldrick, G. M. (1997). *SHELXL97*, University of Göttingen, Germany.
West, D. X. & Pannell, L. K. (1989). *Transition Met. Chem.* **14**, 457–462.

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Triethylammonium *N*′-(benzylsulfanylthiocarbonyl)-2-hydroxybenzohydrazidate

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S1. Comment

Dithiocarbazates and their derivatives have attracted much attention as they have potential applications as antitumor, antibacterial and antifungal agents (Scovill *et al.*, 1982,1984, West & Pannell, 1989, Gou *et al.*, 1990). Interest in these systems is also stimulated by their unusual physico-chemical (Abu-Raquabah *et al.*1992, Marchi *et al.*, 1990) and chemotherapeutic properties (Ali & Livingston, 1974). Although *N*′-acyl hydrazine carbodithioates are structurally similar to the derivatives of dithiocarbazates, little data is available on their synthesis and characterization. As part of our ongoing investigation, we report here the synthesis and structure determination of the title compound (I) which was obtained from the reaction of salicylic acid hydrazide, CS_2 and benzyl chloride in the presence of triethylamine.

The molecular structure of (I), together with atom labeling scheme is shown in Fig 1. The Hydrazinic H atom on N1 is *trans* with respect to the carbonyl group and *cis* with respect to the thione S atom. The C7—N1 distance of 1.329 (4) Å is intermediate between 1.47 Å for a C—N single bond and 1.29 Å for a double bond (Boga *et al.*, 1999). The N1—N2 distance of 1.396 (3) Å [single bond (N—N) = 1.45 Å and double bond (N=N) = 1.25 Å] and the O2—C7 distance of 1.257 (4) Å suggest extensive delocalization in this part of the molecule. In the crystal structure, there is a weak C—H···π interaction (Fig 2) [C5—H5···*Cg* = 140.65°, H5···*Cg* = 2.976 Å and C5···*Cg* = 3.759 Å, where *Cg* is the centroid of the phenyl ring]. The molecular conformation is stabilized by intramolecular O—H···O and N—H···S hydrogen bonds while intermolecular N—H···O, N—H···N and weak C—H···O interactions help stabilize the crystal structure.

S2. Experimental

The title compound was synthesized by the reaction of CS_2 (1.99 g, 26.29 mmol) with a solution of salicylic acid hydrazide (4 g, 24.09 mmol) in $CHCl_3$ (15 ml) in the presence of triethylamine (2 ml, 24.09 mmol). Benzyl chloride (3.5 ml, 26.30 mmol) was added dropwise to the above clear solution, which was stirred continuously for 2 h at room temperature. The product was obtained on evaporation of the solvent at room temperature. Colorless single crystals of (I) (m.p., 418 K) suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution over a period of 10 days. (Yield 58%). Elemental analysis: Anal. Calcd (%): C, 60.11; H, 6.97; N, 10.01; S, 15.28; Found (%) for $C_{21}H_{29}N_3O_2S_2$ (419.59): C,60.01; H, 6.87; N, 10.30; S, 15.06. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, TMS, δ, p.p.m.) 11.66, 12.38 (s, 2H, NH), 7.92–6.9 (m, 4H, benzene ring), 7.18 - 6.89 (m, 5H, phenyl), 4.48 (s, 1H, OH), 4.25 (s, 2H, CH_2), 2.49 (s, 6H, CH_2 of Et_3NH^+), 1.15 (s, 9H, CH_3 of Et_3NH^+).^{13}C NMR ($CDCl_3$, TMS, δ, p.p.m.): 117.25 (C1), 158.94 (C2), 116.30 (C3),134.06 (C4), 118.99 (C5), 128.42 (C6), 165.85 (C7), 174.23 (C8), 35.66 (C9), 139.52 (C10),127.60 (C11,C15), 129.09 (C12,C14),126.38 (C13),45.77 (C16,C18, C20), 8.59 (C17, C19, C21).

S3. Refinement

All H atoms were initially located in a diffrence Fourier map. They were then placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95–0.99 Å; N—H = 0.88Å and O—H = 0.84Å and U_{iso}(H) =

1.2 U_{eq}(C,*N*) or 1.5U_{eq}(C_{methyl},*O*).

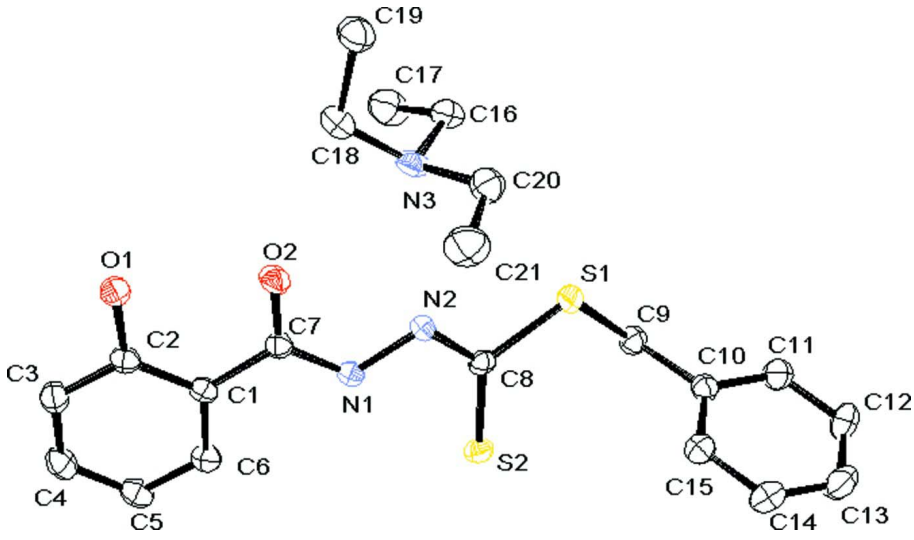

Figure 1

The molecular structure showing the atom-numbering scheme and displacement ellipsoids the 30% probability level. Hydrogen atoms are not shown.

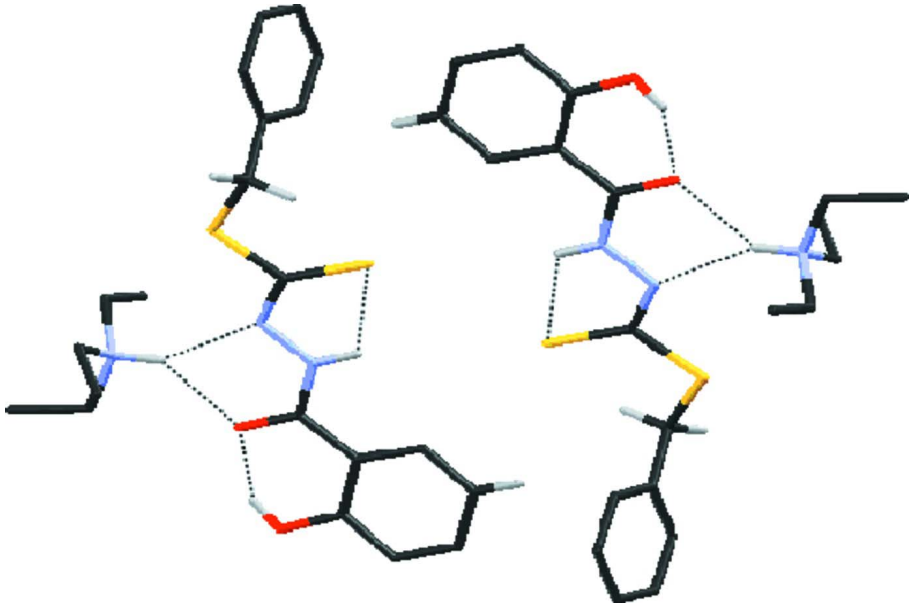

Figure 2

Part of the crystal structure showing hydrogen bonds as dashed lines. Some H atoms have not been shown but the H atom of the benzene ring which is involved in a C—H···π interaction with the phenyl ring is shown.

Triethylammonium *N*′-(benzylsulfanylthiocarbonyl)-2-hydroxybenzohydrazidate

Crystal data

$C_6H_{16}N^+·C_{15}H_{13}N_2O_2S_2^-$
M_r = 419.59
Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab
a = 10.7109 (4) Å
b = 18.6807 (6) Å

c = 22.1814 (7) Å
V = 4438.2 (3) Å^3
Z = 8
F(000) = 1792
D_x = 1.256 Mg m^{-3}
Melting point: 418 K
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 16320 reflections
θ = 1.0–26.0°
μ = 0.26 mm^{-1}
T = 173 K
Chip, yellow
0.08 × 0.08 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Horizonally mounted graphite crystal monochromator
φ scans and ω scans with κ offsets
26195 measured reflections

3928 independent reflections
2542 reflections with $I > 2\sigma(I)$
R_{int} = 0.138
θ_{max} = 25.0°, θ_{min} = 2.4°
h = −12→12
k = −22→20
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.118
S = 1.05
3928 reflections
257 parameters

0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 3.4211P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.15592 (9)	0.33158 (5)	−0.05488 (4)	0.0436 (2)
S2	0.34667 (8)	0.44725 (4)	−0.01971 (4)	0.0380 (2)
O1	0.5287 (2)	0.23266 (12)	0.22154 (10)	0.0454 (6)
H1	0.4638	0.2259	0.2010	0.068*
O2	0.3691 (2)	0.25376 (12)	0.13887 (10)	0.0427 (6)
N1	0.3824 (2)	0.35026 (14)	0.07825 (12)	0.0351 (7)
H1A	0.4152	0.3928	0.0719	0.042*
N2	0.2880 (2)	0.32553 (13)	0.04023 (11)	0.0335 (6)
C1	0.5386 (3)	0.33468 (16)	0.15530 (13)	0.0302 (7)
C2	0.5870 (3)	0.29257 (17)	0.20199 (14)	0.0348 (8)
C3	0.6992 (3)	0.31114 (19)	0.22951 (15)	0.0434 (9)
H3	0.7313	0.2825	0.2613	0.052*
C4	0.7638 (3)	0.3707 (2)	0.21095 (16)	0.0462 (9)
H4	0.8408	0.3826	0.2297	0.055*

C5	0.7178 (3)	0.41331 (19)	0.16532 (15)	0.0431 (9)
H5	0.7627	0.4546	0.1528	0.052*
C6	0.6067 (3)	0.39574 (17)	0.13812 (15)	0.0376 (8)
H6	0.5751	0.4256	0.1070	0.045*
C7	0.4235 (3)	0.31073 (17)	0.12389 (14)	0.0332 (8)
C8	0.2719 (3)	0.36876 (16)	−0.00578 (14)	0.0320 (7)
C9	0.1697 (3)	0.38403 (17)	−0.12303 (14)	0.0395 (8)
H9A	0.2505	0.4097	−0.1220	0.047*
H9B	0.1719	0.3509	−0.1579	0.047*
C10	0.0678 (3)	0.43768 (17)	−0.13339 (14)	0.0355 (8)
C11	0.0125 (4)	0.4435 (2)	−0.18983 (16)	0.0501 (10)
H11	0.0358	0.4115	−0.2212	0.060*
C12	−0.0765 (4)	0.4959 (2)	−0.20057 (19)	0.0637 (12)
H12	−0.1135	0.4995	−0.2394	0.076*
C13	−0.1118 (4)	0.5423 (2)	−0.1562 (2)	0.0597 (11)
H13	−0.1723	0.5782	−0.1641	0.072*
C14	−0.0587 (4)	0.53656 (19)	−0.09972 (17)	0.0498 (10)
H14	−0.0833	0.5684	−0.0685	0.060*
C15	0.0300 (3)	0.48471 (17)	−0.08859 (15)	0.0394 (8)
H15	0.0659	0.4812	−0.0495	0.047*
N3	0.1590 (3)	0.18429 (14)	0.07791 (13)	0.0420 (7)
H3A	0.2145	0.2224	0.0807	0.050*
C16	0.1821 (3)	0.14954 (19)	0.01787 (16)	0.0476 (9)
H16A	0.1311	0.1055	0.0149	0.057*
H16B	0.1549	0.1825	−0.0146	0.057*
C17	0.3143 (4)	0.1311 (2)	0.0086 (2)	0.0683 (12)
H17A	0.3663	0.1730	0.0173	0.102*
H17B	0.3271	0.1163	−0.0333	0.102*
H17C	0.3374	0.0919	0.0357	0.102*
C18	0.1836 (3)	0.13709 (19)	0.13117 (17)	0.0498 (10)
H18A	0.1716	0.1655	0.1684	0.060*
H18B	0.2721	0.1218	0.1300	0.060*
C19	0.1015 (4)	0.0707 (2)	0.13475 (18)	0.0589 (11)
H19A	0.0137	0.0851	0.1377	0.088*
H19B	0.1243	0.0426	0.1704	0.088*
H19C	0.1135	0.0416	0.0985	0.088*
C20	0.0303 (4)	0.2161 (2)	0.07594 (17)	0.0527 (10)
H20A	0.0230	0.2461	0.0393	0.063*
H20B	−0.0313	0.1768	0.0725	0.063*
C21	−0.0019 (4)	0.2601 (2)	0.1287 (2)	0.0746 (13)
H21A	−0.0068	0.2295	0.1645	0.112*
H21B	−0.0827	0.2833	0.1220	0.112*
H21C	0.0625	0.2967	0.1347	0.112*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0456 (5)	0.0354 (5)	0.0496 (5)	−0.0055 (4)	−0.0148 (5)	0.0072 (4)

S2	0.0395 (5)	0.0281 (4)	0.0464 (5)	−0.0009 (4)	−0.0008 (4)	0.0027 (4)
O1	0.0535 (16)	0.0388 (14)	0.0439 (14)	−0.0102 (12)	−0.0090 (12)	0.0085 (11)
O2	0.0475 (15)	0.0396 (13)	0.0410 (13)	−0.0169 (12)	−0.0066 (11)	0.0058 (11)
N1	0.0346 (16)	0.0280 (14)	0.0427 (16)	−0.0063 (12)	−0.0066 (13)	0.0005 (12)
N2	0.0323 (16)	0.0312 (15)	0.0371 (15)	−0.0019 (12)	−0.0062 (12)	−0.0018 (12)
C1	0.0301 (18)	0.0315 (17)	0.0289 (17)	−0.0010 (15)	0.0045 (14)	−0.0056 (14)
C2	0.038 (2)	0.0342 (18)	0.0325 (18)	−0.0005 (15)	0.0032 (15)	−0.0045 (15)
C3	0.041 (2)	0.048 (2)	0.041 (2)	0.0036 (17)	−0.0057 (17)	−0.0026 (17)
C4	0.032 (2)	0.057 (2)	0.050 (2)	−0.0019 (18)	−0.0008 (18)	−0.0114 (19)
C5	0.037 (2)	0.045 (2)	0.047 (2)	−0.0115 (17)	0.0063 (17)	−0.0070 (17)
C6	0.042 (2)	0.038 (2)	0.0331 (19)	−0.0028 (16)	0.0044 (16)	−0.0010 (15)
C7	0.035 (2)	0.0324 (18)	0.0322 (18)	0.0019 (15)	−0.0003 (15)	−0.0051 (15)
C8	0.0289 (18)	0.0287 (17)	0.0384 (18)	0.0060 (14)	0.0033 (15)	−0.0024 (15)
C9	0.045 (2)	0.0400 (19)	0.0338 (18)	0.0037 (17)	−0.0032 (16)	−0.0013 (15)
C10	0.0373 (19)	0.0338 (18)	0.0354 (19)	−0.0067 (15)	−0.0019 (16)	0.0044 (15)
C11	0.062 (3)	0.046 (2)	0.043 (2)	0.001 (2)	−0.0073 (19)	0.0019 (17)
C12	0.077 (3)	0.056 (3)	0.058 (3)	0.011 (2)	−0.025 (2)	0.017 (2)
C13	0.059 (3)	0.043 (2)	0.078 (3)	0.010 (2)	−0.002 (2)	0.014 (2)
C14	0.054 (3)	0.041 (2)	0.054 (2)	0.0064 (19)	0.009 (2)	0.0055 (18)
C15	0.041 (2)	0.040 (2)	0.0371 (19)	−0.0008 (17)	0.0039 (16)	0.0043 (16)
N3	0.0357 (16)	0.0339 (15)	0.0564 (18)	−0.0110 (13)	0.0012 (15)	−0.0074 (14)
C16	0.051 (2)	0.040 (2)	0.052 (2)	−0.0060 (18)	−0.0023 (19)	−0.0038 (18)
C17	0.053 (3)	0.066 (3)	0.086 (3)	−0.002 (2)	0.005 (2)	−0.018 (2)
C18	0.046 (2)	0.051 (2)	0.053 (2)	−0.0111 (18)	−0.0063 (19)	−0.0081 (18)
C19	0.062 (3)	0.057 (3)	0.058 (3)	−0.016 (2)	−0.007 (2)	0.006 (2)
C20	0.046 (2)	0.053 (2)	0.059 (2)	−0.0035 (19)	−0.001 (2)	−0.0003 (19)
C21	0.076 (3)	0.068 (3)	0.080 (3)	0.013 (2)	0.008 (3)	−0.021 (2)

Geometric parameters (Å, º)

S1—C8	1.793 (3)	C12—H12	0.9500
S1—C9	1.807 (3)	C13—C14	1.379 (5)
S2—C8	1.699 (3)	C13—H13	0.9500
O1—C2	1.353 (4)	C14—C15	1.379 (5)
O1—H1	0.8400	C14—H14	0.9500
O2—C7	1.258 (4)	C15—H15	0.9500
N1—C7	1.328 (4)	N3—C18	1.498 (4)
N1—N2	1.395 (3)	N3—C20	1.502 (4)
N1—H1A	0.8800	N3—C16	1.502 (4)
N2—C8	1.313 (4)	N3—H3A	0.9300
C1—C2	1.400 (4)	C16—C17	1.471 (5)
C1—C6	1.407 (4)	C16—H16A	0.9900
C1—C7	1.485 (4)	C16—H16B	0.9900
C2—C3	1.392 (5)	C17—H17A	0.9800
C3—C4	1.374 (5)	C17—H17B	0.9800
C3—H3	0.9500	C17—H17C	0.9800
C4—C5	1.379 (5)	C18—C19	1.523 (5)
C4—H4	0.9500	C18—H18A	0.9900

C5—C6	1.374 (4)	C18—H18B	0.9900
C5—H5	0.9500	C19—H19A	0.9800
C6—H6	0.9500	C19—H19B	0.9800
C9—C10	1.499 (4)	C19—H19C	0.9800
C9—H9A	0.9900	C20—C21	1.470 (5)
C9—H9B	0.9900	C20—H20A	0.9900
C10—C15	1.387 (4)	C20—H20B	0.9900
C10—C11	1.389 (5)	C21—H21A	0.9800
C11—C12	1.387 (5)	C21—H21B	0.9800
C11—H11	0.9500	C21—H21C	0.9800
C12—C13	1.365 (6)		

C8—S1—C9	103.99 (15)	C13—C14—C15	120.1 (4)
C2—O1—H1	109.5	C13—C14—H14	120.0
C7—N1—N2	121.1 (3)	C15—C14—H14	120.0
C7—N1—H1A	119.4	C14—C15—C10	121.2 (3)
N2—N1—H1A	119.4	C14—C15—H15	119.4
C8—N2—N1	111.2 (3)	C10—C15—H15	119.4
C2—C1—C6	117.7 (3)	C18—N3—C20	114.7 (3)
C2—C1—C7	119.0 (3)	C18—N3—C16	114.6 (3)
C6—C1—C7	123.2 (3)	C20—N3—C16	107.3 (3)
O1—C2—C3	117.7 (3)	C18—N3—H3A	106.6
O1—C2—C1	122.1 (3)	C20—N3—H3A	106.6
C3—C2—C1	120.3 (3)	C16—N3—H3A	106.6
C4—C3—C2	120.4 (3)	C17—C16—N3	112.5 (3)
C4—C3—H3	119.8	C17—C16—H16A	109.1
C2—C3—H3	119.8	N3—C16—H16A	109.1
C3—C4—C5	120.5 (3)	C17—C16—H16B	109.1
C3—C4—H4	119.8	N3—C16—H16B	109.1
C5—C4—H4	119.8	H16A—C16—H16B	107.8
C6—C5—C4	119.6 (3)	C16—C17—H17A	109.5
C6—C5—H5	120.2	C16—C17—H17B	109.5
C4—C5—H5	120.2	H17A—C17—H17B	109.5
C5—C6—C1	121.6 (3)	C16—C17—H17C	109.5
C5—C6—H6	119.2	H17A—C17—H17C	109.5
C1—C6—H6	119.2	H17B—C17—H17C	109.5
O2—C7—N1	121.2 (3)	N3—C18—C19	114.8 (3)
O2—C7—C1	121.0 (3)	N3—C18—H18A	108.6
N1—C7—C1	117.8 (3)	C19—C18—H18A	108.6
N2—C8—S2	127.6 (2)	N3—C18—H18B	108.6
N2—C8—S1	109.0 (2)	C19—C18—H18B	108.6
S2—C8—S1	123.40 (18)	H18A—C18—H18B	107.6
C10—C9—S1	115.5 (2)	C18—C19—H19A	109.5
C10—C9—H9A	108.4	C18—C19—H19B	109.5
S1—C9—H9A	108.4	H19A—C19—H19B	109.5
C10—C9—H9B	108.4	C18—C19—H19C	109.5
S1—C9—H9B	108.4	H19A—C19—H19C	109.5
H9A—C9—H9B	107.5	H19B—C19—H19C	109.5

C15—C10—C11	118.2 (3)	C21—C20—N3	114.4 (3)
C15—C10—C9	121.7 (3)	C21—C20—H20A	108.7
C11—C10—C9	120.0 (3)	N3—C20—H20A	108.7
C12—C11—C10	120.2 (4)	C21—C20—H20B	108.7
C12—C11—H11	119.9	N3—C20—H20B	108.7
C10—C11—H11	119.9	H20A—C20—H20B	107.6
C13—C12—C11	121.0 (4)	C20—C21—H21A	109.5
C13—C12—H12	119.5	C20—C21—H21B	109.5
C11—C12—H12	119.5	H21A—C21—H21B	109.5
C12—C13—C14	119.4 (4)	C20—C21—H21C	109.5
C12—C13—H13	120.3	H21A—C21—H21C	109.5
C14—C13—H13	120.3	H21B—C21—H21C	109.5

C7—N1—N2—C8	−172.4 (3)	C9—S1—C8—N2	−167.1 (2)
C6—C1—C2—O1	−179.7 (3)	C9—S1—C8—S2	12.3 (2)
C7—C1—C2—O1	−3.5 (4)	C8—S1—C9—C10	−105.5 (3)
C6—C1—C2—C3	−0.5 (4)	S1—C9—C10—C15	48.7 (4)
C7—C1—C2—C3	175.7 (3)	S1—C9—C10—C11	−134.3 (3)
O1—C2—C3—C4	178.9 (3)	C15—C10—C11—C12	0.9 (5)
C1—C2—C3—C4	−0.3 (5)	C9—C10—C11—C12	−176.2 (3)
C2—C3—C4—C5	0.7 (5)	C10—C11—C12—C13	−0.2 (6)
C3—C4—C5—C6	−0.3 (5)	C11—C12—C13—C14	−0.6 (6)
C4—C5—C6—C1	−0.6 (5)	C12—C13—C14—C15	0.6 (6)
C2—C1—C6—C5	0.9 (5)	C13—C14—C15—C10	0.1 (5)
C7—C1—C6—C5	−175.1 (3)	C11—C10—C15—C14	−0.9 (5)
N2—N1—C7—O2	−8.7 (5)	C9—C10—C15—C14	176.2 (3)
N2—N1—C7—C1	169.2 (3)	C18—N3—C16—C17	−64.9 (4)
C2—C1—C7—O2	0.4 (4)	C20—N3—C16—C17	166.6 (3)
C6—C1—C7—O2	176.4 (3)	C20—N3—C18—C19	62.5 (4)
C2—C1—C7—N1	−177.5 (3)	C16—N3—C18—C19	−62.2 (4)
C6—C1—C7—N1	−1.5 (4)	C18—N3—C20—C21	58.6 (4)
N1—N2—C8—S2	−2.5 (4)	C16—N3—C20—C21	−172.9 (3)
N1—N2—C8—S1	176.84 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.84	1.79	2.538 (3)	147
N1—H1*A*···S2	0.88	2.39	2.855 (3)	114
N3—H3*A*···O2	0.93	2.18	2.929 (3)	137
N3—H3*A*···N2	0.93	2.27	3.094 (4)	148
C9—H9*A*···S2	0.99	2.59	3.200 (3)	120
C21—H21*A*···O1^{i}	0.98	2.56	3.377 (5)	141

Symmetry code: (i) *x*−1/2, *y*, −*z*+1/2.