

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Triethylammonium *N'*-(benzylsulfanylthiocarbonyl)-2-hydroxybenzohydrazidateMamata Singh,^{a*} Ajay K. Srivastava,^a N. K. Singh,^a Anuraag Shrivastav^b and R. K. Sharma^b^aDepartment of Chemistry, Banaras Hindu University, Varanasi 221 005, India, and^bDepartment of Pathology and Laboratory Medicine, College of Medicine, University of Saskatchewan, 20 Campus Drive, Saskatoon, SK, Canada S7N 4H4

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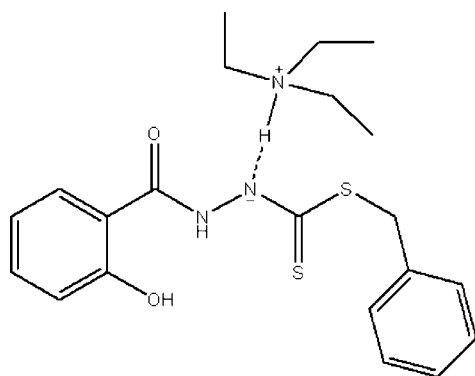
Received 2 November 2007; accepted 14 December 2007

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.056; wR factor = 0.118; data-to-parameter ratio = 15.3.

In the title compound, $\text{C}_6\text{H}_{16}\text{N}^+\cdot\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2\text{S}_2^-$, 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 $78.81(2)^\circ$. The molecular conformation is stabilized by intramolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, while intermolecular $\text{N}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{N}$ and weak $\text{C}-\text{H}\cdots\text{O}$ 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-Raquabah *et al.* (1992); Marchi *et al.* (1990); Ali & Livingston, (1974); Wu *et al.* (2000); Boga *et al.* (1990).



Experimental

Crystal data

$\text{C}_6\text{H}_{16}\text{N}^+\cdot\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2\text{S}_2^-$
 $M_r = 419.59$
 Orthorhombic, *Pbca*

$a = 10.7109(4)$ Å
 $b = 18.6807(6)$ Å
 $c = 22.1814(7)$ Å

$V = 4438.2(3)$ Å³
 $Z = 8$
 Mo $K\alpha$ radiation

$\mu = 0.26$ mm⁻¹
 $T = 173(2)$ K
 $0.08 \times 0.08 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: none
 26195 measured reflections

3928 independent reflections
 2542 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.138$

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
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}$	0.84	1.79	2.538 (3)	147
$\text{N1}-\text{H1A}\cdots\text{S2}$	0.88	2.39	2.855 (3)	114
$\text{N3}-\text{H3A}\cdots\text{O2}$	0.93	2.18	2.929 (3)	137
$\text{N3}-\text{H3A}\cdots\text{N2}$	0.93	2.27	3.094 (4)	148
$\text{C9}-\text{H9A}\cdots\text{S2}$	0.99	2.59	3.200 (3)	120
$\text{C21}-\text{H21A}\cdots\text{O1}^{\ddagger}$	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*.

The authors thank Professor W. Quail, Saskatchewan Structural Sciences Centre, Canada, for the X-ray diffraction facility.

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

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supplementary materials

Acta Cryst. (2008). E64, o339 [doi:10.1107/S1600536807067037]

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

M. Singh, A. K. Srivastava, N. K. Singh, A. Shrivastav and R. K. Sharma

Comment

Dithiocarbazates and their derivatives have attracted much attention as they have potential applications as antitumor, anti-bacterial 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, CS₂ 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 \cdots π interaction (Fig 2) [C5—H5 \cdots Cg = 140.65°, H5 \cdots Cg = 2.976 Å and C5 \cdots Cg = 3.759 Å, where Cg is the centroid of the phenyl ring]. The molecular conformation is stabilized by intramolecular O—H \cdots O and N—H \cdots S hydrogen bonds while intermolecular N—H \cdots O, N—H \cdots N and weak C—H \cdots O interactions help stabilize the crystal structure.

Experimental

The title compound was synthesized by the reaction of CS₂ (1.99 g, 26.29 mmol) with a solution of salicylic acid hydrazide (4 g, 24.09 mmol) in CHCl₃ (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 C₂₁H₂₉N₃O₂S₂ (419.59): C,60.01; H, 6.87; N, 10.30; S, 15.06. Spectroscopic analysis: ¹H NMR (CDCl₃, 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, CH₂), 2.49 (s, 6H, CH₂ of Et₃NH⁺), 1.15 (s, 9H, CH₃ of Et₃NH⁺). ¹³C NMR (CDCl₃, 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).

Refinement

All H atoms were initially located in a difference 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 = 0.88 Å and O—H = 0.84 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$ or $1.5 U_{\text{eq}}(\text{C}_{\text{methyl}}, \text{O})$.

Figures

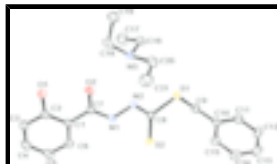


Fig. 1. The molecular structure showing the atom-numbering scheme and displacement ellipsoids the 30% probability level. Hydrogen atoms are not shown.

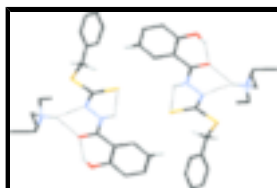


Fig. 2. Part of the crystal structure showing hydrogen bonds as dashed lines. Some H atoms have not been shown but the H atom of the benzene ring which is involved in a C—H... π interaction with the phenyl ring is shown.

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

Crystal data

$\text{C}_6\text{H}_{16}\text{N}^+ \cdot \text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2\text{S}_2^-$

$M_r = 419.59$

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) Å³

$Z = 8$

$F_{000} = 1792$

$D_x = 1.256$ Mg m⁻³

Melting point: 418 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 16320 reflections

$\theta = 1.0$ – 26.0°

$\mu = 0.26$ mm⁻¹

$T = 173$ (2) K

Chip, yellow

$0.08 \times 0.08 \times 0.05$ mm

Data collection

Nonius KappaCCD
diffractometer

2542 reflections with $I > 2\sigma(I)$

Radiation source: fine-focus sealed tube

$R_{\text{int}} = 0.138$

Monochromator: horizontally mounted graphite crystal

$\theta_{\text{max}} = 25.0^\circ$

$T = 173$ (2) K

$\theta_{\text{min}} = 2.4^\circ$

φ scans and ω scans with κ offsets

$h = -12 \rightarrow 12$

Absorption correction: none

$k = -22 \rightarrow 20$

26195 measured reflections
3928 independent reflections

$l = -26 \rightarrow 26$

Refinement

Refinement on F^2

H-atom parameters constrained

Least-squares matrix: full

$$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 3.4211P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$R[F^2 > 2\sigma(F^2)] = 0.056$$

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

$$wR(F^2) = 0.118$$

$$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$$

$$S = 1.05$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

3928 reflections

Extinction correction: none

257 parameters

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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)

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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 (\AA^2)

	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, °)

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

supplementary materials

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 (\AA , $^\circ$)

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

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

Fig. 1

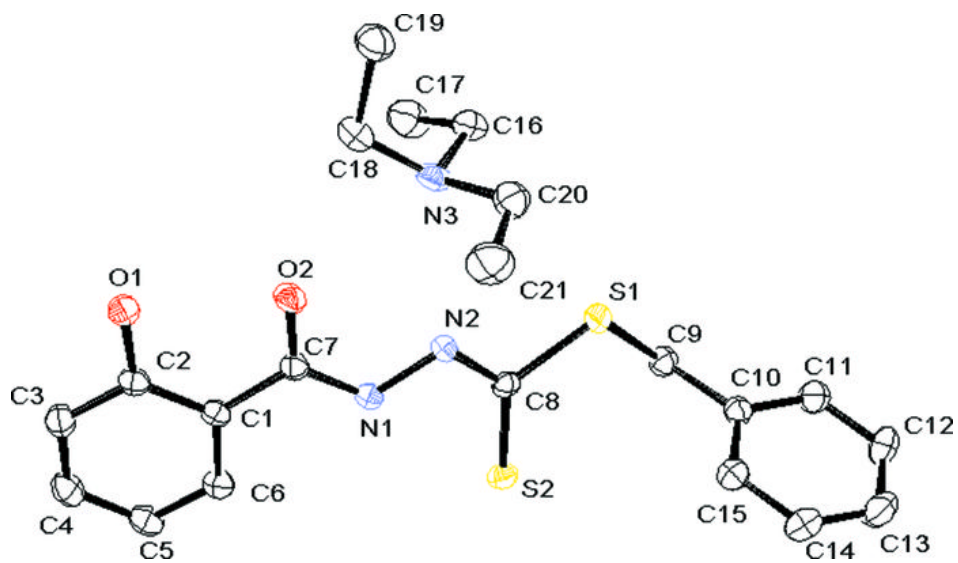


Fig. 2

