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(*E*)-Methyl 3-(2-nitrobenzylidene)dithiocarbazate

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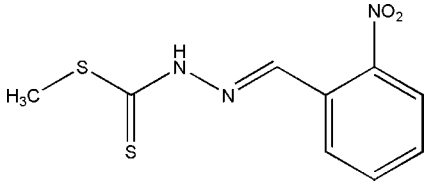
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.116; data-to-parameter ratio = 17.6.

The asymmetric unit of the title compound, $C_9H_9N_3O_2S_2$, contains two independent molecules, *A* and *B*, with similar bond dimensions. In both molecules, the nitro group is tilted with respect to the aromatic ring [dihedral angles 32.0 (1)° in molecule *A* and 34.0 (1)° in molecule *B*]. The dithiocarbazate unit is nearly coplanar with the aromatic ring in both molecules. For molecule *B*, pairs of molecules are linked by N—H···O and C—H···O hydrogen bonds about a centre of symmetry to form a dimer, whereas molecules *A* are not involved in hydrogen bonding in the crystal structure.

Related literature

For general background, see: Okabe *et al.* (1993); Hu *et al.* (2001). For related structures, see: Chen *et al.* (2007); Shan & Zhang, 2006; Zhang *et al.* 2005). For synthesis, see: Hu *et al.* (2001).



Experimental

Crystal data

$C_9H_9N_3O_2S_2$
M_r = 255.31
Triclinic, $P\overline{1}$
a = 7.5261 (12) Å
b = 10.7128 (16) Å
c = 14.5343 (17) Å
α = 78.588 (6)°
β = 87.095 (5)°
γ = 84.612 (6)°
V = 1143.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 291 (2) K
0.36 × 0.30 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.795, T_{max} = 0.930
11206 measured reflections
5127 independent reflections
3773 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.116
S = 1.10
5127 reflections
291 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N13—H13N···O11^{i}	0.86	2.16	3.014 (3)	174
C17—H17···O12^{i}	0.93	2.55	3.373 (3)	148

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2380).

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supporting information

Acta Cryst. (2008). E**64**, o53 [https://doi.org/10.1107/S160053680706059X]

(*E*)-Methyl 3-(2-nitrobenzylidene)dithiocarbazate

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S1. Comment

Hydrazone and its derivatives have attracted our much attention because of their application in biological field (Okabe *et al.*, 1993). As part of our ongoing investigation on anti-cancer compounds (Hu *et al.*, 2001), the title compound has been prepared and its structure is presented here.

The asymmetric unit of the title compound contains two crystallographic independent molecules, A (C1-containing molecule) and B (C11-containing molecule), with the similar structure (Fig. 1). In the two molecules, the nitro groups are tilted with respect to the connected benzene rings by dihedral angles of 31.96 (11) and 33.96 (11)°, respectively; while dithiocarbazate moieties are nearly co-planar with the benzene rings, dihedral angles being 3.00 (6) and 4.03 (6)°, respectively. The centro-symmetry related B molecules are linked by N—H···O hydrogen bonding to form the supramolecular dimer (Table 2). Whereas the A molecules are not involved in hydrogen bonding in the crystal structure. The N2?C7 and N12?C17 bond distances (Table 1) indicate the typical N?C double bonds. Around the N?C double bonds, both molecules A and B exhibit the E configuration, similar to those found in related compounds (Chen *et al.*, 2007; Shan & Zhang, 2006; Zhang *et al.*, 2005).

S2. Experimental

Methyl dithiocarbazate was synthesized in the manner reported previously (Hu *et al.*, 2001). Methyl dithiocarbazate (1.24 g, 10 mmol) and 2-nitrobenzaldehyde (1.51 g, 10 mmol) were dissolved in ethanol (10 ml) and refluxed for 4 h. Fine yellow crystals appeared on cooling. They were separated and washed with cold water three times. Single crystals of the title compound were obtained by recrystallization from an absolute ethanol solution.

S3. Refinement

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and torsion angle was refined to fit electron density, U_{iso}(H) = 1.5U_{eq}(C). Other H atoms were placed in calculated positions with C—H = 0.97 and N—H = 0.86 Å, and refined in the riding mode, with U_{iso}(H) = 1.2U_{eq}(C,*N*).

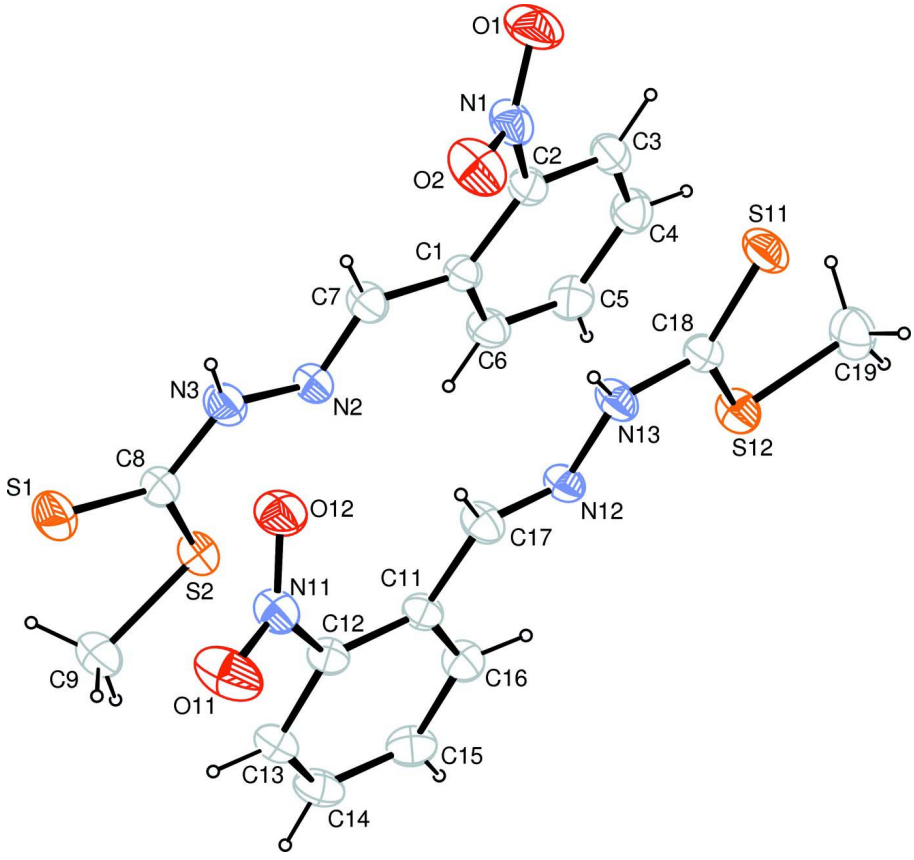

Figure 1

The molecular structure of the title compound with 40% probability displacement ellipsoids (arbitrary spheres for H atoms).

(*E*)-Methyl 3-(2-nitrobenzylidene)dithiocarbazate

Crystal data

$C_9H_9N_3O_2S_2$
$M_r = 255.31$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.5261\ (12)$ Å
$b = 10.7128\ (16)$ Å
$c = 14.5343\ (17)$ Å
$\alpha = 78.588\ (6)°$
$\beta = 87.095\ (5)°$
$\gamma = 84.612\ (6)°$
$V = 1143.0\ (3)$ Å^3
$Z = 4$
$F(000) = 528$
$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8768 reflections
$\theta = 3.5–25.2°$
$\mu = 0.45$ mm^{-1}
$T = 291$ K
Prism, yellow
0.36 × 0.30 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.00 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.795$, $T_{max} = 0.930$
11206 measured reflections
5127 independent reflections
3773 reflections with $I > 2\sigma(I)$

R_{int} = 0.024
θ_{max} = 27.4°, θ_{min} = 3.0°
h = −9→9
k = −13→13
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.116
S = 1.10
5127 reflections
291 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
$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.2566P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 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	−0.10244 (10)	0.28477 (6)	0.50066 (5)	0.0686 (2)
S2	−0.04064 (8)	0.25046 (5)	0.29873 (4)	0.05480 (17)
S11	0.67348 (9)	0.86939 (5)	0.15976 (5)	0.06155 (19)
S12	0.62739 (8)	0.64462 (5)	0.06773 (4)	0.05198 (16)
N1	0.1634 (3)	0.88846 (18)	0.18824 (14)	0.0555 (5)
N2	0.0369 (2)	0.50343 (16)	0.26593 (12)	0.0470 (4)
N3	−0.0124 (3)	0.46023 (17)	0.35805 (13)	0.0545 (5)
H3N	−0.0185	0.5114	0.3970	0.065*
N11	0.3762 (3)	0.30552 (17)	0.50958 (12)	0.0499 (4)
N12	0.5421 (2)	0.52269 (15)	0.24812 (12)	0.0420 (4)
N13	0.5836 (3)	0.64538 (16)	0.24503 (12)	0.0477 (4)
H13N	0.5823	0.6745	0.2961	0.057*
O1	0.1188 (3)	1.00252 (16)	0.16247 (14)	0.0801 (6)
O2	0.2133 (3)	0.84171 (18)	0.26726 (13)	0.0751 (5)
O11	0.4082 (3)	0.23524 (18)	0.58419 (12)	0.0875 (7)
O12	0.3194 (3)	0.41716 (15)	0.50380 (12)	0.0646 (5)
C1	0.1201 (3)	0.67717 (18)	0.14835 (14)	0.0404 (4)
C2	0.1581 (3)	0.80514 (18)	0.12003 (14)	0.0427 (4)
C3	0.1920 (3)	0.8603 (2)	0.02687 (15)	0.0496 (5)
H3	0.2125	0.9463	0.0103	0.060*
C4	0.1951 (3)	0.7869 (2)	−0.04046 (16)	0.0535 (5)
H4	0.2187	0.8226	−0.1031	0.064*

C5	0.1629 (3)	0.6593 (2)	−0.01493 (16)	0.0532 (5)
H5	0.1668	0.6091	−0.0605	0.064*
C6	0.1251 (3)	0.6061 (2)	0.07770 (16)	0.0494 (5)
H6	0.1025	0.5205	0.0933	0.059*
C7	0.0663 (3)	0.6209 (2)	0.24519 (15)	0.0480 (5)
H7	0.0539	0.6708	0.2911	0.058*
C8	−0.0516 (3)	0.3381 (2)	0.38814 (16)	0.0504 (5)
C9	−0.0977 (4)	0.0963 (2)	0.3612 (2)	0.0689 (7)
H9A	−0.0182	0.0664	0.4121	0.103*
H9B	−0.0869	0.0369	0.3193	0.103*
H9C	−0.2183	0.1032	0.3857	0.103*
C11	0.4580 (3)	0.32678 (17)	0.33941 (13)	0.0382 (4)
C12	0.4033 (3)	0.25252 (18)	0.42419 (13)	0.0390 (4)
C13	0.3699 (3)	0.12543 (18)	0.43353 (15)	0.0453 (5)
H13	0.3341	0.0789	0.4914	0.054*
C14	0.3904 (3)	0.06946 (19)	0.35602 (16)	0.0514 (5)
H14	0.3677	−0.0155	0.3608	0.062*
C15	0.4450 (3)	0.1400 (2)	0.27100 (16)	0.0511 (5)
H15	0.4585	0.1020	0.2185	0.061*
C16	0.4798 (3)	0.2658 (2)	0.26259 (15)	0.0451 (5)
H16	0.5186	0.3109	0.2048	0.054*
C17	0.5029 (3)	0.45918 (19)	0.32906 (14)	0.0454 (5)
H17	0.5028	0.4967	0.3816	0.054*
C18	0.6263 (3)	0.72055 (18)	0.16279 (14)	0.0427 (5)
C19	0.6919 (4)	0.7682 (3)	−0.02735 (17)	0.0663 (7)
H19A	0.5985	0.8366	−0.0368	0.099*
H19B	0.7119	0.7340	−0.0836	0.099*
H19C	0.7996	0.8002	−0.0124	0.099*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0862 (5)	0.0596 (4)	0.0520 (3)	−0.0072 (3)	0.0147 (3)	0.0049 (3)
S2	0.0588 (3)	0.0460 (3)	0.0564 (3)	−0.0097 (3)	0.0041 (3)	−0.0011 (2)
S11	0.0834 (4)	0.0354 (3)	0.0657 (4)	−0.0174 (3)	0.0141 (3)	−0.0080 (3)
S12	0.0637 (4)	0.0490 (3)	0.0444 (3)	−0.0098 (3)	−0.0008 (3)	−0.0096 (2)
N1	0.0720 (13)	0.0434 (10)	0.0562 (12)	−0.0216 (9)	0.0085 (10)	−0.0167 (9)
N2	0.0487 (10)	0.0401 (9)	0.0482 (10)	−0.0041 (8)	0.0011 (8)	0.0004 (7)
N3	0.0682 (12)	0.0446 (10)	0.0471 (10)	−0.0055 (9)	0.0062 (9)	−0.0023 (8)
N11	0.0681 (12)	0.0432 (10)	0.0405 (9)	−0.0102 (9)	0.0001 (9)	−0.0114 (8)
N12	0.0511 (10)	0.0315 (8)	0.0441 (9)	−0.0073 (7)	−0.0019 (8)	−0.0068 (7)
N13	0.0674 (12)	0.0347 (8)	0.0425 (9)	−0.0142 (8)	0.0037 (8)	−0.0078 (7)
O1	0.1226 (17)	0.0372 (9)	0.0830 (13)	−0.0105 (10)	0.0093 (12)	−0.0194 (9)
O2	0.1115 (16)	0.0655 (11)	0.0557 (11)	−0.0289 (11)	−0.0109 (10)	−0.0178 (9)
O11	0.164 (2)	0.0608 (11)	0.0367 (9)	−0.0046 (12)	−0.0097 (11)	−0.0065 (8)
O12	0.0928 (13)	0.0452 (9)	0.0593 (10)	−0.0055 (9)	0.0089 (9)	−0.0219 (7)
C1	0.0378 (10)	0.0347 (9)	0.0481 (11)	−0.0036 (8)	−0.0020 (8)	−0.0063 (8)
C2	0.0452 (11)	0.0369 (10)	0.0475 (11)	−0.0076 (8)	0.0004 (9)	−0.0105 (8)

C3	0.0563 (13)	0.0400 (11)	0.0509 (12)	−0.0102 (9)	0.0048 (10)	−0.0038 (9)
C4	0.0555 (13)	0.0572 (13)	0.0467 (12)	−0.0055 (11)	0.0023 (10)	−0.0085 (10)
C5	0.0584 (13)	0.0542 (13)	0.0519 (13)	−0.0078 (11)	−0.0006 (11)	−0.0206 (10)
C6	0.0528 (12)	0.0370 (10)	0.0610 (13)	−0.0088 (9)	−0.0024 (10)	−0.0139 (10)
C7	0.0537 (12)	0.0409 (11)	0.0491 (12)	−0.0083 (9)	−0.0005 (10)	−0.0067 (9)
C8	0.0464 (11)	0.0455 (11)	0.0530 (12)	−0.0008 (9)	0.0043 (10)	0.0027 (10)
C9	0.0703 (16)	0.0472 (13)	0.0838 (19)	−0.0125 (12)	0.0040 (14)	0.0016 (12)
C11	0.0435 (10)	0.0327 (9)	0.0396 (10)	−0.0055 (8)	−0.0058 (8)	−0.0079 (8)
C12	0.0455 (11)	0.0346 (9)	0.0385 (10)	−0.0037 (8)	−0.0069 (8)	−0.0096 (8)
C13	0.0546 (12)	0.0329 (10)	0.0476 (11)	−0.0077 (9)	−0.0073 (10)	−0.0026 (8)
C14	0.0628 (14)	0.0309 (10)	0.0635 (14)	−0.0070 (9)	−0.0164 (11)	−0.0113 (9)
C15	0.0617 (14)	0.0444 (11)	0.0527 (12)	0.0000 (10)	−0.0101 (10)	−0.0230 (10)
C16	0.0522 (12)	0.0437 (11)	0.0417 (10)	−0.0062 (9)	−0.0022 (9)	−0.0129 (9)
C17	0.0615 (13)	0.0379 (10)	0.0398 (10)	−0.0119 (9)	−0.0023 (9)	−0.0110 (8)
C18	0.0462 (11)	0.0357 (10)	0.0457 (11)	−0.0050 (8)	0.0023 (9)	−0.0072 (8)
C19	0.0759 (17)	0.0732 (17)	0.0450 (12)	−0.0097 (14)	0.0031 (12)	0.0006 (11)

Geometric parameters (Å, º)

S1—C8	1.660 (2)	C3—H3	0.9300
S2—C8	1.742 (3)	C4—C5	1.385 (3)
S2—C9	1.800 (2)	C4—H4	0.9300
S11—C18	1.657 (2)	C5—C6	1.381 (3)
S12—C18	1.736 (2)	C5—H5	0.9300
S12—C19	1.797 (2)	C6—H6	0.9300
N1—O2	1.221 (3)	C7—H7	0.9300
N1—O1	1.225 (2)	C9—H9A	0.9600
N1—C2	1.464 (3)	C9—H9B	0.9600
N2—C7	1.272 (3)	C9—H9C	0.9600
N2—N3	1.372 (2)	C11—C12	1.394 (3)
N3—C8	1.350 (3)	C11—C16	1.396 (3)
N3—H3N	0.8600	C11—C17	1.466 (3)
N11—O11	1.212 (2)	C12—C13	1.387 (3)
N11—O12	1.220 (2)	C13—C14	1.373 (3)
N11—C12	1.461 (3)	C13—H13	0.9300
N12—C17	1.273 (3)	C14—C15	1.380 (3)
N12—N13	1.371 (2)	C14—H14	0.9300
N13—C18	1.345 (2)	C15—C16	1.378 (3)
N13—H13N	0.8600	C15—H15	0.9300
C1—C6	1.391 (3)	C16—H16	0.9300
C1—C2	1.403 (3)	C17—H17	0.9300
C1—C7	1.470 (3)	C19—H19A	0.9600
C2—C3	1.387 (3)	C19—H19B	0.9600
C3—C4	1.369 (3)	C19—H19C	0.9600
C8—S2—C9	101.93 (12)	N3—C8—S2	113.24 (16)
C18—S12—C19	101.57 (11)	S1—C8—S2	126.39 (13)
O2—N1—O1	123.3 (2)	S2—C9—H9A	109.5

O2—N1—C2	118.83 (19)	S2—C9—H9B	109.5
O1—N1—C2	117.9 (2)	H9A—C9—H9B	109.5
C7—N2—N3	115.10 (19)	S2—C9—H9C	109.5
C8—N3—N2	120.7 (2)	H9A—C9—H9C	109.5
C8—N3—H3N	119.7	H9B—C9—H9C	109.5
N2—N3—H3N	119.7	C12—C11—C16	116.26 (17)
O11—N11—O12	122.41 (19)	C12—C11—C17	123.88 (18)
O11—N11—C12	118.20 (18)	C16—C11—C17	119.74 (18)
O12—N11—C12	119.38 (17)	C13—C12—C11	123.03 (19)
C17—N12—N13	115.97 (17)	C13—C12—N11	115.63 (18)
C18—N13—N12	120.58 (17)	C11—C12—N11	121.34 (17)
C18—N13—H13N	119.7	C14—C13—C12	118.95 (19)
N12—N13—H13N	119.7	C14—C13—H13	120.5
C6—C1—C2	116.07 (19)	C12—C13—H13	120.5
C6—C1—C7	120.58 (18)	C13—C14—C15	119.60 (19)
C2—C1—C7	123.24 (19)	C13—C14—H14	120.2
C3—C2—C1	122.61 (19)	C15—C14—H14	120.2
C3—C2—N1	116.12 (17)	C16—C15—C14	121.1 (2)
C1—C2—N1	121.27 (18)	C16—C15—H15	119.5
C4—C3—C2	119.33 (19)	C14—C15—H15	119.5
C4—C3—H3	120.3	C15—C16—C11	121.1 (2)
C2—C3—H3	120.3	C15—C16—H16	119.5
C3—C4—C5	119.7 (2)	C11—C16—H16	119.5
C3—C4—H4	120.1	N12—C17—C11	119.89 (18)
C5—C4—H4	120.1	N12—C17—H17	120.1
C6—C5—C4	120.4 (2)	C11—C17—H17	120.1
C6—C5—H5	119.8	N13—C18—S11	120.14 (16)
C4—C5—H5	119.8	N13—C18—S12	113.32 (14)
C5—C6—C1	121.75 (19)	S11—C18—S12	126.54 (12)
C5—C6—H6	119.1	S12—C19—H19A	109.5
C1—C6—H6	119.1	S12—C19—H19B	109.5
N2—C7—C1	119.6 (2)	H19A—C19—H19B	109.5
N2—C7—H7	120.2	S12—C19—H19C	109.5
C1—C7—H7	120.2	H19A—C19—H19C	109.5
N3—C8—S1	120.37 (19)	H19B—C19—H19C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N13—H13*N*···O11^{i}	0.86	2.16	3.014 (3)	174
C17—H17···O12^{i}	0.93	2.55	3.373 (3)	148

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