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3-Benzoyl-1-[4-(methylsulfanyl)phenyl]-thiourea

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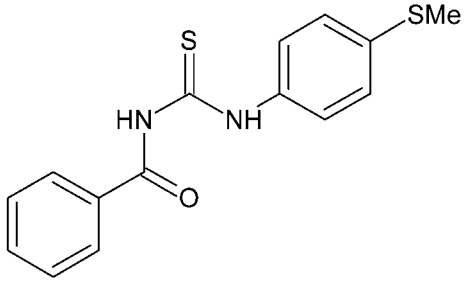
Key indicators: single-crystal X-ray study; T = 308 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.099; data-to-parameter ratio = 18.0.

The title compound, $C_{15}H_{14}N_2OS_2$, adopts a helix conformation. An intramolecular N—H···O hydrogen bond leads to a six-membered pseudo-ring [r.m.s. deviation = 0.0212 Å, maximum deviation = 0.033 (1) Å for the N atom bearing the benzoyl group] in the central unit. The benzene and (methylsulfanyl)benzene ring [r.m.s = 0.0028 Å and largest deviation of 0.067 (3) Å for the methylsulfanyl C atom] make dihedral angles of 31.76 (8) and 54.68 (6)°, respectively, with the pseudo-ring plane. The dihedral angle between the benzene rings is 85.71 (8)°. In the crystal, pairs of weak N—H···S interactions form inversion dimers and mediate a linear chain along [001].

Related literature

For related compounds found in CSD (Allen, 2002) see: Al-abbasi *et al.* (2010); Cao *et al.* (1996). For the structure of the unsubstituted compound, see: Yamin & Yusof (2003). For details of the synthesis, see: Zhang *et al.* (2001).



Experimental

Crystal data

$C_{15}H_{14}N_2OS_2$
M_r = 302.42
Triclinic, $P\overline{1}$
a = 5.9131 (2) Å
b = 9.5826 (3) Å
c = 13.3149 (4) Å
α = 96.729 (1)°
β = 91.533 (1)°
γ = 94.503 (1)°
V = 746.46 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 308 K
0.7 × 0.34 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
T_{min} = 0.917, T_{max} = 1.0
11518 measured reflections
3285 independent reflections
2908 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.099
S = 1
3285 reflections
183 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1	0.86	1.93	2.6250 (16)	137
N1—H1···S1^{i}	0.86	2.61	3.4358 (12)	161

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2097).

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supporting information

Acta Cryst. (2013). E**69**, o923 [doi:10.1107/S1600536813013159]

3-Benzoyl-1-[4-(methylsulfanyl)phenyl]thiourea

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S1. Comment

In the title compound, $C_{15}H_{14}N_2OS_2$, an intramolecular hydrogen bond of type N2—H2···O1 completes a nearly planar six-membered pseudo-ring involving the N2/C1/N1/C2/O1 atoms [r.m.s = 0.0212 Å and largest deviation = 0.033 (1) Å for N1]. The dihedral angle between the benzene ring [r.m.s = 0.0036 Å] and the (methylsulfanyl)benzene ring [r.m.s = 0.0028 Å and largest deviation of 0.067 (3) Å for C15] is 85.71 (8)°. The benzene ring and the (methylsulfanyl)benzene group make dihedral angles of 31.76 (8)° and 54.68 (6)°, respectively, with the plane of the pseudo-ring.

The crystal packing is stabilized by weak N1—H1···S1^{i} [(^{i}): -*x* + 1, -*y* + 2, -*z* + 2] interactions (Table 2), which lead to centrosymmetric dimer formation around the inversion center on (1/2,0,0) and arranged in a linear chain along [001]. The helix conformation of the title compound is justified by the supramolecular array.

The bond lengths and bond angles are in agreement with similar benzoylthiourea derivatives found in the CSD (Allen, 2002): 1-Benzoyl-3-(4-hydroxyphenyl)thiourea [CSD refcode:WADSAX (Al-abbasi *et al.*, 2010)], 1-Benzoyl-3-(4-methoxyphenyl)thiourea [CSD refcode: WIRZAY (Cao *et al.*, 1996)] and *N*-Benzoyl-*N*′-phenylthiourea [CSD refcode: HURYAU (Yamin *et al.*, 2003)].

S2. Experimental

The procedure employed for synthesis of the title compound was described by Zhang *et al.* (2001). Benzoyl chloride (11 mmol) was added to a solution of ammonium thiocyanate (11 mmol) in anhydrous acetone (25 ml). The reaction mixture was heated under reflux for 15 minutes and then cooled to room temperature. A solution of 4-methylthiophenylamine (11 mmol) in acetone (10 ml) was added and the resulting mixture was stirred under reflux for 30 minutes. The reaction mixture was then poured into crushed ice under stirred. The solid product was filtered under and washed with deionized water and purified by recrystallization from ethanol to give fine crystals of the title compound, with an overall yield of 84%.

Spectroscopic data: ^{1}H NMR (400 MHz, $CDCl_3$, p.p.m.): 2.48 (s, 3H, OCH_3), 7.27 (dt, J= 8,7 Hz &2,2 Hz, 2H), 7.52 (m, 2H), 7.63 (m, 3H), 7.87 (m, 2H), 9.08 (s, 1H, CONH), 12.54 (s, 1H, CSNH). ^{13}C and DEPT-135 NMR (400 MHz, $CDCl_3$, p.p.m.): 16.13(+) (OCH_3); 124.87(+); 127.04(+); 127.68(+); 129.44(+); 131.77; 133.99(+); 134.92; 137.42; 167.14 (*C*=O); 178.34 (*C*=S). FT—IR (KBr, cm^{-1}): 3216 *v*(amide N—H), 3019 *v*(thiourea N—H), 1670 *v*(C=O), 1265 *v*(C=S).

S3. Refinement

All H atoms were placed in calculated positions (C–H = 0.93 and 0.96 Å, N–H = 0.86) and treated as riding atoms [U_{iso}(H) = 1.2U_{eq}(C,*N*) orU_{iso}(H) = 1.5U_{eq}(methyl)]

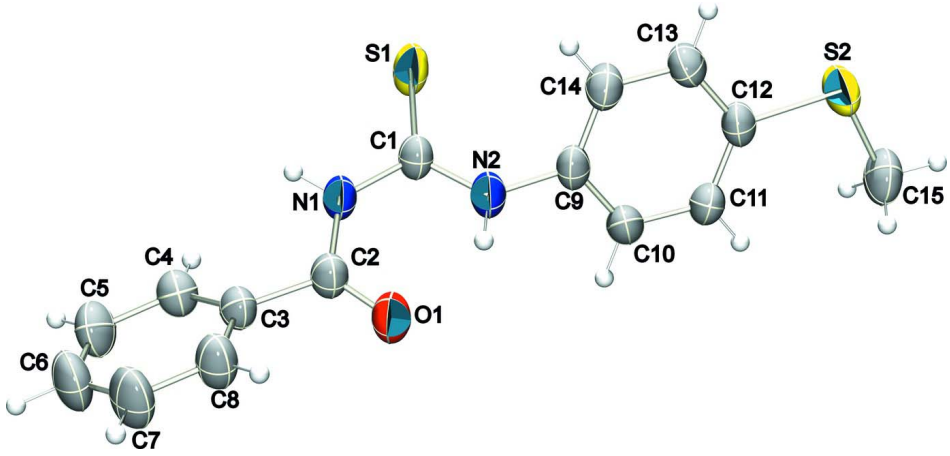

Figure 1

The structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level

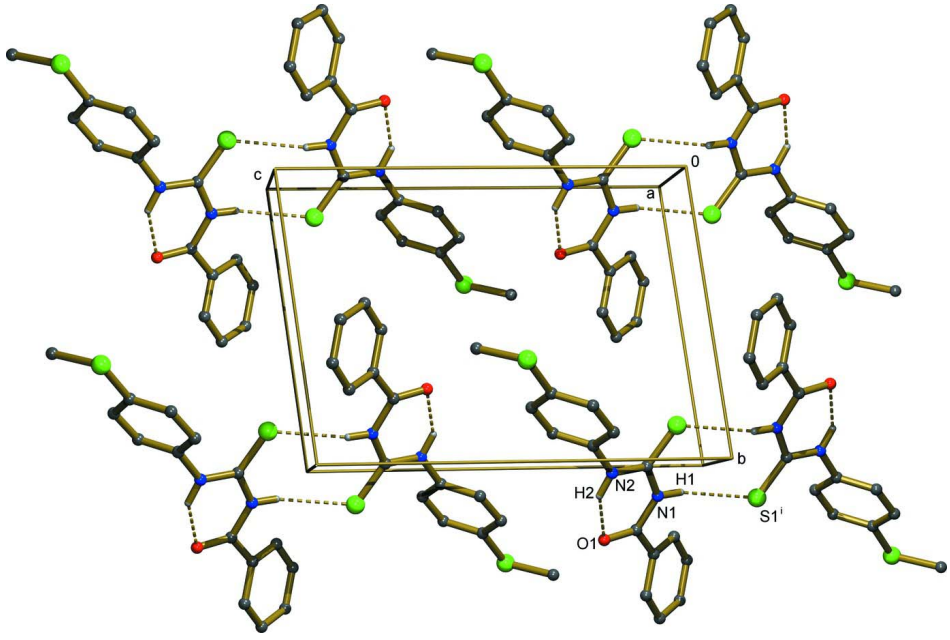

Figure 2

The packing diagram of the title compound. Intermolecular hydrogen bonds are shown as dashed line. Symmetry code: (i) -*x* + 1, -*y* + 2, -*z* + 2.

3-Benzoyl-1-[4-(methylsulfanyl)phenyl]thiourea

Crystal data

$C_{15}H_{14}N_2OS_2$
M_r = 302.42
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 5.9131 (2) Å
b = 9.5826 (3) Å
c = 13.3149 (4) Å
α = 96.729 (1)°
β = 91.533 (1)°
γ = 94.503 (1)°
V = 746.46 (4) Å^3
Z = 2
F(000) = 316
D_x = 1.345 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7480 reflections
θ = 5.0–54.1°
μ = 0.35 mm^{-1}
T = 308 K
Prism, colourless
0.7 × 0.34 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer
Multilayer optics monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
T_{min} = 0.917, T_{max} = 1.0
11518 measured reflections
3285 independent reflections
2908 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 27.1°, θ_{min} = 1.5°
h = −7→7
k = −12→11
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.099
S = 1
3285 reflections
183 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
$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.2312P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.029
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.038 (4)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N2	0.6544 (2)	0.96378 (13)	0.72447 (9)	0.0477 (3)
H2	0.6015	0.8875	0.6881	0.057*
S1	0.66478 (9)	1.12397 (4)	0.90198 (3)	0.06291 (17)
C7	−0.0806 (4)	0.4643 (2)	0.83445 (17)	0.0745 (6)
H7	−0.1007	0.368	0.8133	0.089*
C4	−0.0192 (3)	0.75005 (17)	0.89870 (12)	0.0506 (3)
H4	0.0007	0.8462	0.9205	0.061*
C11	0.9002 (3)	1.18452 (18)	0.53854 (11)	0.0519 (4)
H11	0.8552	1.2143	0.4776	0.062*
C1	0.5795 (2)	0.98624 (14)	0.81784 (10)	0.0418 (3)
C2	0.3113 (3)	0.77171 (15)	0.78408 (11)	0.0460 (3)

C5	−0.1955 (3)	0.6678 (2)	0.93446 (15)	0.0647 (5)
H5	−0.2941	0.7087	0.9803	0.078*
C12	1.1161 (2)	1.22405 (16)	0.57927 (11)	0.0453 (3)
C13	1.1798 (3)	1.17840 (18)	0.67070 (12)	0.0518 (4)
H13	1.3244	1.2054	0.699	0.062*
N1	0.4143 (2)	0.88724 (12)	0.84430 (9)	0.0433 (3)
H1	0.3711	0.8995	0.9056	0.052*
O1	0.3658 (2)	0.73896 (13)	0.69735 (9)	0.0679 (4)
C10	0.7507 (3)	1.10043 (17)	0.58862 (11)	0.0509 (4)
H10	0.6051	1.0746	0.5611	0.061*
C3	0.1268 (2)	0.68897 (15)	0.83058 (11)	0.0445 (3)
C14	1.0303 (3)	1.09336 (18)	0.71986 (12)	0.0504 (4)
H14	1.0751	1.0624	0.7804	0.061*
C9	0.8147 (2)	1.05463 (14)	0.67869 (10)	0.0428 (3)
S2	1.32148 (7)	1.32969 (6)	0.52237 (4)	0.06877 (17)
C8	0.0945 (3)	0.54539 (17)	0.79760 (14)	0.0604 (4)
H8	0.1906	0.5041	0.7508	0.072*
C6	−0.2246 (3)	0.5255 (2)	0.90207 (17)	0.0748 (6)
H6	−0.343	0.4706	0.9263	0.09*
C15	1.1792 (3)	1.3752 (2)	0.41292 (15)	0.0684 (5)
H15A	1.1327	1.2911	0.3684	0.103*
H15B	1.2801	1.4357	0.3787	0.103*
H15C	1.0482	1.4235	0.4326	0.103*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0555 (7)	0.0429 (6)	0.0431 (6)	−0.0071 (5)	0.0160 (5)	0.0024 (5)
S1	0.0905 (3)	0.0470 (2)	0.0462 (2)	−0.0230 (2)	0.0246 (2)	−0.00146 (16)
C7	0.0898 (14)	0.0473 (9)	0.0854 (14)	−0.0157 (9)	0.0241 (11)	0.0132 (9)
C4	0.0487 (8)	0.0492 (8)	0.0547 (9)	0.0025 (6)	0.0078 (6)	0.0100 (7)
C11	0.0503 (8)	0.0663 (10)	0.0393 (7)	−0.0055 (7)	0.0054 (6)	0.0138 (7)
C1	0.0477 (7)	0.0374 (7)	0.0416 (7)	0.0016 (5)	0.0110 (6)	0.0095 (5)
C2	0.0521 (8)	0.0418 (7)	0.0440 (7)	−0.0021 (6)	0.0100 (6)	0.0065 (6)
C5	0.0528 (9)	0.0740 (11)	0.0698 (11)	0.0033 (8)	0.0211 (8)	0.0161 (9)
C12	0.0423 (7)	0.0493 (8)	0.0451 (7)	0.0007 (6)	0.0133 (6)	0.0085 (6)
C13	0.0373 (7)	0.0671 (10)	0.0525 (8)	0.0004 (6)	0.0061 (6)	0.0148 (7)
N1	0.0512 (7)	0.0402 (6)	0.0384 (6)	−0.0042 (5)	0.0125 (5)	0.0070 (5)
O1	0.0822 (9)	0.0649 (7)	0.0496 (7)	−0.0246 (6)	0.0248 (6)	−0.0069 (5)
C10	0.0470 (8)	0.0623 (9)	0.0406 (7)	−0.0116 (7)	0.0048 (6)	0.0043 (6)
C3	0.0480 (8)	0.0426 (7)	0.0433 (7)	−0.0032 (6)	0.0057 (6)	0.0107 (6)
C14	0.0465 (8)	0.0622 (9)	0.0463 (8)	0.0070 (7)	0.0092 (6)	0.0187 (7)
C9	0.0471 (7)	0.0409 (7)	0.0403 (7)	0.0000 (6)	0.0151 (6)	0.0041 (5)
S2	0.0501 (3)	0.0899 (4)	0.0694 (3)	−0.0149 (2)	0.0089 (2)	0.0348 (3)
C8	0.0725 (11)	0.0450 (8)	0.0630 (10)	−0.0055 (7)	0.0204 (8)	0.0063 (7)
C6	0.0698 (12)	0.0687 (12)	0.0873 (14)	−0.0163 (9)	0.0230 (10)	0.0250 (10)
C15	0.0701 (11)	0.0769 (12)	0.0640 (11)	0.0050 (9)	0.0201 (9)	0.0291 (9)

Geometric parameters (Å, º)

N2—C1	1.3303 (18)	C5—H5	0.93
N2—C9	1.4331 (17)	C12—C13	1.393 (2)
N2—H2	0.86	C12—S2	1.7635 (14)
S1—C1	1.6643 (15)	C13—C14	1.384 (2)
C7—C6	1.370 (3)	C13—H13	0.93
C7—C8	1.380 (2)	N1—H1	0.86
C7—H7	0.93	C10—C9	1.378 (2)
C4—C3	1.381 (2)	C10—H10	0.93
C4—C5	1.386 (2)	C3—C8	1.391 (2)
C4—H4	0.93	C14—C9	1.380 (2)
C11—C12	1.380 (2)	C14—H14	0.93
C11—C10	1.386 (2)	S2—C15	1.778 (2)
C11—H11	0.93	C8—H8	0.93
C1—N1	1.3890 (17)	C6—H6	0.93
C2—O1	1.2193 (17)	C15—H15A	0.96
C2—N1	1.3783 (18)	C15—H15B	0.96
C2—C3	1.4891 (19)	C15—H15C	0.96
C5—C6	1.377 (3)		
C1—N2—C9	126.20 (12)	C2—N1—H1	116.1
C1—N2—H2	116.9	C1—N1—H1	116.1
C9—N2—H2	116.9	C9—C10—C11	120.90 (14)
C6—C7—C8	120.07 (17)	C9—C10—H10	119.5
C6—C7—H7	120	C11—C10—H10	119.5
C8—C7—H7	120	C4—C3—C8	119.70 (14)
C3—C4—C5	119.86 (15)	C4—C3—C2	122.95 (13)
C3—C4—H4	120.1	C8—C3—C2	117.22 (13)
C5—C4—H4	120.1	C9—C14—C13	119.77 (14)
C12—C11—C10	119.89 (14)	C9—C14—H14	120.1
C12—C11—H11	120.1	C13—C14—H14	120.1
C10—C11—H11	120.1	C10—C9—C14	119.61 (13)
N2—C1—N1	116.19 (12)	C10—C9—N2	117.94 (13)
N2—C1—S1	124.91 (11)	C14—C9—N2	122.42 (13)
N1—C1—S1	118.88 (10)	C12—S2—C15	104.62 (8)
O1—C2—N1	122.34 (13)	C7—C8—C3	119.92 (16)
O1—C2—C3	121.47 (13)	C7—C8—H8	120
N1—C2—C3	116.18 (12)	C3—C8—H8	120
C6—C5—C4	119.95 (16)	C7—C6—C5	120.50 (16)
C6—C5—H5	120	C7—C6—H6	119.8
C4—C5—H5	120	C5—C6—H6	119.8
C11—C12—C13	119.09 (13)	S2—C15—H15A	109.5
C11—C12—S2	124.05 (12)	S2—C15—H15B	109.5
C13—C12—S2	116.87 (11)	H15A—C15—H15B	109.5
C14—C13—C12	120.74 (14)	S2—C15—H15C	109.5
C14—C13—H13	119.6	H15A—C15—H15C	109.5
C12—C13—H13	119.6	H15B—C15—H15C	109.5

C2—N1—C1	127.82 (12)		
C9—N2—C1—N1	176.58 (13)	O1—C2—C3—C8	30.6 (2)
C9—N2—C1—S1	−2.0 (2)	N1—C2—C3—C8	−150.00 (15)
C3—C4—C5—C6	0.0 (3)	C12—C13—C14—C9	−0.8 (2)
C10—C11—C12—C13	−0.1 (2)	C11—C10—C9—C14	0.2 (2)
C10—C11—C12—S2	179.62 (12)	C11—C10—C9—N2	−177.77 (14)
C11—C12—C13—C14	0.7 (2)	C13—C14—C9—C10	0.4 (2)
S2—C12—C13—C14	−179.05 (12)	C13—C14—C9—N2	178.27 (13)
O1—C2—N1—C1	3.7 (3)	C1—N2—C9—C10	−124.24 (17)
C3—C2—N1—C1	−175.71 (13)	C1—N2—C9—C14	57.8 (2)
N2—C1—N1—C2	−3.1 (2)	C11—C12—S2—C15	3.27 (17)
S1—C1—N1—C2	175.56 (12)	C13—C12—S2—C15	−177.03 (13)
C12—C11—C10—C9	−0.4 (2)	C6—C7—C8—C3	1.1 (3)
C5—C4—C3—C8	0.6 (2)	C4—C3—C8—C7	−1.2 (3)
C5—C4—C3—C2	176.20 (15)	C2—C3—C8—C7	−177.03 (17)
O1—C2—C3—C4	−145.13 (17)	C8—C7—C6—C5	−0.5 (4)
N1—C2—C3—C4	34.3 (2)	C4—C5—C6—C7	−0.1 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.86	1.93	2.6250 (16)	137
N1—H1···S1^{i}	0.86	2.61	3.4358 (12)	161

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