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Crystal structure of (*E*)-2-[4-(4-hydroxyphenyl)butan-2-ylidene]hydrazine-1-carbothioamide

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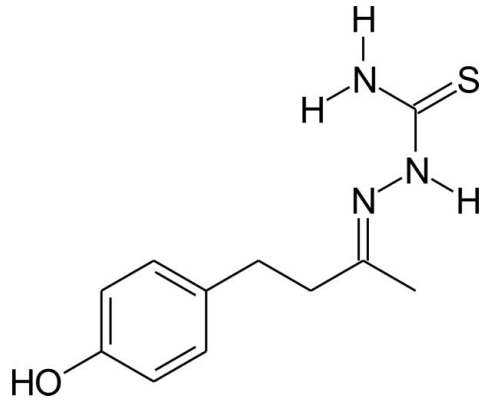
The title compound, $C_{11}H_{15}N_3OS$, is a thiosemicarbazone derivative of the raspberry ketone rheosmin [systematic name: 4-(4-hydroxyphenyl)butane-2-one]. The molecule deviates from planarity, with the bridging C—C—C═N torsion angle equal to −101.3 (2)°. The maximum deviation from the mean plane of the non-H atoms of the thiosemicarbazone fragment [C═N—N—C(═S)—N] is 0.085 (5) Å for the Schiff base N atom, and the dihedral angle between this mean plane and the aromatic ring is 50.31 (8)°. In the crystal, molecules are linked by N—H···O, N—H···S and O—H···S hydrogen bonds, forming a three-dimensional structure, with the molecules stacked along [011].

Keywords: crystal structure; thiosemicarbazone; raspberry ketone; hydrogen bonding; three-dimensional.

CCDC reference: 1036979

1. Related literature

For one of the first reports of thiosemicarbazone derivatives synthesis, see: Freund & Schander (1902). For a report concerning the synthesis of the raspberry ketone, see: Hoffmann & Degner (1981). For the biological properties of thiosemicarbazone compounds as well as for their importance in coordination chemistry, see: Lobana *et al.* (2009).



2. Experimental

2.1. Crystal data

$C_{11}H_{15}N_3OS$
M_r = 237.32
Monoclinic, $P2_1/c$
a = 13.5604 (7) Å
b = 9.7578 (6) Å
c = 9.3079 (4) Å
β = 95.194 (3)°
V = 1226.56 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 293 K
0.17 × 0.13 × 0.09 mm

2.2. Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.929, T_{max} = 0.994
12737 measured reflections
2806 independent reflections
1587 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.116
S = 0.98
2806 reflections
205 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···S1^{i}	0.89 (4)	2.32 (4)	3.206 (2)	175 (3)
N3—H10A···O1^{ii}	0.85 (2)	2.22 (2)	2.936 (2)	143 (2)
N3—H10B···S1^{iii}	0.91 (3)	2.73 (3)	3.585 (2)	156.6 (19)

Symmetry codes: (i) $x-1, -y-\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

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: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *WinGX* (Farrugia, 2012).

Acknowledgements

BRSF thanks the CNPq/UFS for the award of a PIBIC scholarship and FVR acknowledges FAPESP for a Post-Doctoral scholarship (Proc. No. 2013/20156–5).

Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5031).

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supporting information

Acta Cryst. (2015). E**71**, o33–o34 [https://doi.org/10.1107/S2056989014026401]

Crystal structure of (*E*)-2-[4-(4-hydroxyphenyl)butan-2-ylidene]hydrazine-1-carbothioamide

Adriano Bof de Oliveira, Johannes Beck, Christian Landvogt, Bárbara Regina Santos Feitosa and Fillipe Vieira Rocha

S1. Structural commentary

Our work is actually dedicated to the synthesis and structural determination of thiosemicarbazone derivatives of natural products. The thiosemicarbazone unit is well known for its biological properties as well as for its importance in coordination chemistry (Lobana *et al.*, 2009). Herein, we contribute to the thiosemicarbazone chemistry by the synthesis and crystal structure of raspberry ketone thiosemicarbazone. The raspberry ketone is a natural product with great demand on the market and its synthesis has already been reported and optimized (Hoffmann & Degner, 1981).

In the title molecule, Fig. 1, the thiosemicarbazone unit is nearly planar showing a torsion angle for the N1—N2—C10—N3 entity of -3.1 (3)°. The maximum deviation from the mean plane of the non-H atoms of the C9/C10/N1/N2/N3/S1 fragment amounts to 0.085 (5)°. The angle between this mean plane and the aromatic ring is 50.31 (8)°. This strong tilting is possiblly due to free rotation around the sp^3-hybridized C7 and C8 atoms (Fig. 1).

In the crystal, molecules are connected by N—H···O, N—H···S and O—H···S hydrogen bonds, with bridging sulfur atoms, into a three-dimensional H-bonded network (Figs. 2 and 3, and Table 1). The molecules are arranged along the [011] direction, but the hydrogen bonding interactions are present along all three directions (Fig. 3).

S2. Synthesis and crystallization

The synthesis of the title compound was adapted from a procedure reported previously (Freund & Schander, 1902). In a hydrochloric acid catalyzed reaction, a mixture of 4-(4-hydroxyphenyl)-2-butanone (raspberry ketone) (10 mmol) and thiosemicarbazide (10 mmol) in ethanol (80 mL) was refluxed for 5 h. After cooling and filtering, the title compound was obtained. Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of asolution in methanol.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All the hydrogen atoms were located in a difference Fourier map and freely refined.

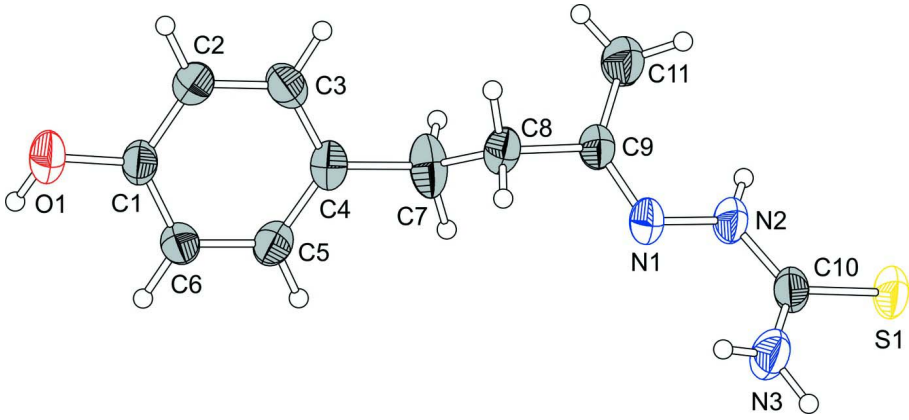

Figure 1

The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 40% probability level.

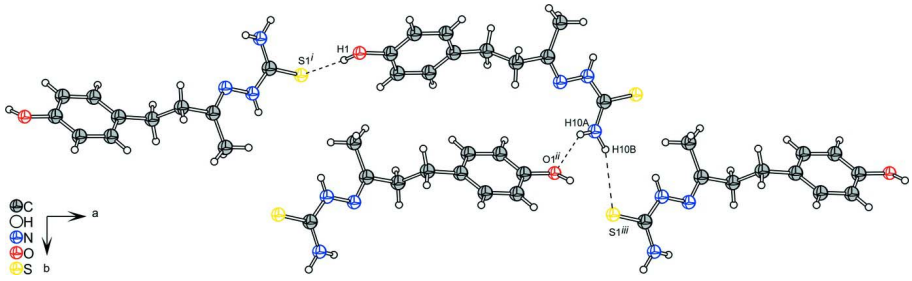

Figure 2

A view of the intermolecular hydrogen bonding (dashed lines) in the crystal of the title compound (see Table 1 for details of the hydrogen bonding and the symmetry codes).

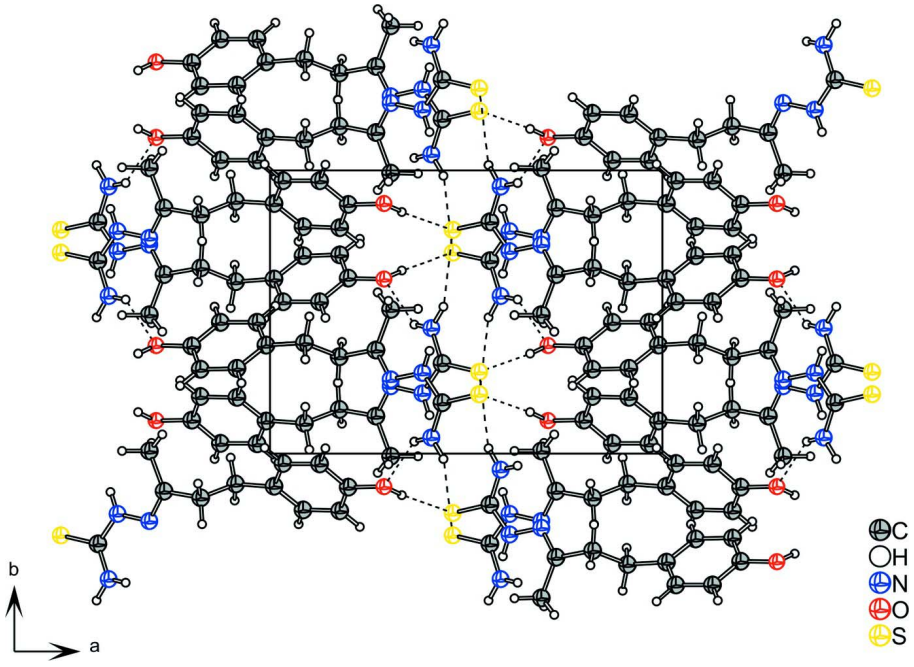

Figure 3

Crystal packing of the title compound viewed along the *c* axis, with the molecules stacking along the [011] direction. Hydrogen bonds are shown as dashed lines (see Table 1 for details).

(*E*)-2-[4-(4-Hydroxyphenyl)butan-2-ylidene]hydrazine-1-carbothioamide

Crystal data

$C_{11}H_{15}N_3OS$
$M_r = 237.32$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 13.5604\ (7)$ Å
$b = 9.7578\ (6)$ Å
$c = 9.3079\ (4)$ Å
$\beta = 95.194\ (3)°$
$V = 1226.56\ (11)$ Å^3
$Z = 4$
$F(000) = 504$
$D_x = 1.285$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4899 reflections
$\theta = 2.9–27.5°$
$\mu = 0.25$ mm^{-1}
$T = 293$ K
Rod, yellow
0.17 × 0.13 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube, Nonius KappaCCD
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
CCD rotation images, thick slices scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.929$, $T_{max} = 0.994$
12737 measured reflections
2806 independent reflections
1587 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -15\rightarrow17$
$k = -11\rightarrow12$
$l = -12\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.116$
$S = 0.98$
2806 reflections
205 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.53385 (4)	−0.71017 (6)	0.78232 (6)	0.0603 (2)
O1	−0.29137 (12)	−0.88281 (19)	0.09365 (18)	0.0714 (5)
N1	0.30776 (11)	−0.76195 (18)	0.49369 (17)	0.0513 (4)
N2	0.38871 (12)	−0.7859 (2)	0.59241 (18)	0.0522 (5)
N3	0.41152 (14)	−0.5570 (2)	0.6114 (2)	0.0635 (5)
C1	−0.19991 (14)	−0.8803 (2)	0.1707 (2)	0.0480 (5)
C2	−0.12722 (15)	−0.9634 (2)	0.1242 (2)	0.0538 (5)
C3	−0.03396 (16)	−0.9638 (2)	0.1973 (2)	0.0550 (5)
C4	−0.01049 (14)	−0.8834 (2)	0.3178 (2)	0.0493 (5)
C5	−0.08500 (15)	−0.8014 (2)	0.3617 (2)	0.0515 (5)
C6	−0.17858 (16)	−0.7981 (2)	0.2904 (2)	0.0496 (5)
C7	0.08871 (17)	−0.8918 (4)	0.4046 (3)	0.0701 (7)
C8	0.17714 (15)	−0.8434 (3)	0.3288 (2)	0.0501 (5)
C9	0.27054 (13)	−0.8668 (2)	0.42605 (19)	0.0467 (5)
C10	0.43922 (14)	−0.6808 (2)	0.6538 (2)	0.0493 (5)
C11	0.3082 (2)	−1.0096 (3)	0.4435 (3)	0.0671 (7)
H1	−0.337 (3)	−0.853 (4)	0.148 (4)	0.145 (15)*
H2	−0.1415 (17)	−1.020 (2)	0.035 (2)	0.077 (7)*
H3	0.0147 (16)	−1.022 (2)	0.1646 (19)	0.054 (6)*
H5	−0.0730 (17)	−0.750 (2)	0.449 (2)	0.069 (6)*
H6	−0.2290 (15)	−0.741 (2)	0.3238 (19)	0.051 (6)*
H7A	0.101 (2)	−0.985 (3)	0.439 (3)	0.114 (11)*
H7B	0.091 (2)	−0.833 (3)	0.499 (3)	0.103 (9)*
H8A	0.1836 (15)	−0.894 (2)	0.235 (2)	0.060 (6)*
H8B	0.1737 (14)	−0.751 (2)	0.3086 (19)	0.048 (6)*

H9	0.4068 (16)	−0.864 (2)	0.614 (2)	0.054 (7)*
H10A	0.3683 (18)	−0.544 (2)	0.541 (3)	0.077 (8)*
H10B	0.4429 (17)	−0.481 (3)	0.650 (2)	0.078 (7)*
H11A	0.377 (2)	−1.011 (3)	0.431 (3)	0.101 (9)*
H11B	0.275 (2)	−1.069 (3)	0.380 (3)	0.121 (11)*
H11C	0.302 (2)	−1.039 (3)	0.539 (3)	0.119 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0393 (3)	0.0773 (4)	0.0609 (3)	−0.0021 (3)	−0.0135 (2)	−0.0007 (3)
O1	0.0395 (9)	0.0927 (13)	0.0788 (10)	−0.0011 (8)	−0.0123 (8)	−0.0169 (9)
N1	0.0360 (9)	0.0618 (11)	0.0537 (9)	0.0004 (8)	−0.0091 (7)	−0.0022 (8)
N2	0.0378 (9)	0.0564 (13)	0.0593 (10)	0.0007 (9)	−0.0129 (7)	−0.0022 (9)
N3	0.0545 (12)	0.0599 (14)	0.0713 (13)	−0.0051 (10)	−0.0212 (9)	−0.0006 (10)
C1	0.0352 (10)	0.0496 (13)	0.0583 (11)	−0.0043 (10)	−0.0016 (8)	0.0011 (9)
C2	0.0484 (13)	0.0553 (14)	0.0575 (12)	−0.0053 (11)	0.0028 (10)	−0.0094 (10)
C3	0.0425 (12)	0.0553 (14)	0.0681 (14)	0.0078 (11)	0.0096 (10)	0.0020 (11)
C4	0.0388 (11)	0.0577 (14)	0.0504 (11)	−0.0057 (10)	−0.0006 (8)	0.0100 (9)
C5	0.0470 (12)	0.0546 (13)	0.0522 (12)	−0.0092 (11)	0.0007 (9)	−0.0043 (10)
C6	0.0403 (11)	0.0470 (13)	0.0618 (12)	0.0007 (10)	0.0052 (9)	−0.0023 (10)
C7	0.0400 (13)	0.107 (2)	0.0618 (14)	−0.0023 (13)	−0.0043 (10)	0.0199 (15)
C8	0.0413 (12)	0.0546 (14)	0.0525 (12)	−0.0065 (10)	−0.0067 (9)	0.0027 (10)
C9	0.0360 (11)	0.0555 (14)	0.0476 (11)	−0.0003 (10)	−0.0015 (8)	0.0010 (9)
C10	0.0328 (10)	0.0634 (15)	0.0513 (11)	−0.0021 (10)	0.0016 (8)	−0.0045 (10)
C11	0.0553 (16)	0.0638 (16)	0.0787 (18)	0.0031 (13)	−0.0125 (13)	−0.0031 (13)

Geometric parameters (Å, º)

S1—C10	1.6973 (19)	C4—C5	1.379 (3)
O1—C1	1.376 (2)	C4—C7	1.507 (3)
O1—H1	0.89 (4)	C5—C6	1.378 (3)
N1—C9	1.281 (2)	C5—H5	0.95 (2)
N1—N2	1.386 (2)	C6—H6	0.95 (2)
N2—C10	1.333 (3)	C7—C8	1.520 (3)
N2—H9	0.82 (2)	C7—H7A	0.98 (3)
N3—C10	1.315 (3)	C7—H7B	1.05 (3)
N3—H10A	0.85 (2)	C8—C9	1.506 (2)
N3—H10B	0.91 (3)	C8—H8A	1.01 (2)
C1—C2	1.376 (3)	C8—H8B	0.92 (2)
C1—C6	1.382 (3)	C9—C11	1.488 (3)
C2—C3	1.381 (3)	C11—H11A	0.95 (3)
C2—H2	1.00 (2)	C11—H11B	0.91 (3)
C3—C4	1.383 (3)	C11—H11C	0.95 (3)
C3—H3	0.94 (2)		
C1—O1—H1	110 (2)	C1—C6—H6	119.7 (11)
C9—N1—N2	116.39 (18)	C4—C7—C8	115.97 (18)

C10—N2—N1	120.0 (2)	C4—C7—H7A	110.2 (17)
C10—N2—H9	118.6 (14)	C8—C7—H7A	109.0 (18)
N1—N2—H9	121.4 (14)	C4—C7—H7B	112.1 (15)
C10—N3—H10A	121.7 (16)	C8—C7—H7B	104.6 (15)
C10—N3—H10B	121.1 (15)	H7A—C7—H7B	104 (2)
H10A—N3—H10B	117 (2)	C9—C8—C7	109.24 (17)
O1—C1—C2	117.58 (18)	C9—C8—H8A	108.1 (12)
O1—C1—C6	122.95 (19)	C7—C8—H8A	112.5 (12)
C2—C1—C6	119.47 (18)	C9—C8—H8B	107.2 (12)
C1—C2—C3	119.8 (2)	C7—C8—H8B	111.8 (12)
C1—C2—H2	119.8 (13)	H8A—C8—H8B	107.9 (17)
C3—C2—H2	120.4 (13)	N1—C9—C11	125.35 (18)
C2—C3—C4	122.1 (2)	N1—C9—C8	116.50 (19)
C2—C3—H3	118.7 (11)	C11—C9—C8	118.01 (19)
C4—C3—H3	119.2 (11)	N3—C10—N2	117.12 (19)
C5—C4—C3	116.66 (18)	N3—C10—S1	122.95 (16)
C5—C4—C7	121.0 (2)	N2—C10—S1	119.93 (17)
C3—C4—C7	122.2 (2)	C9—C11—H11A	109.3 (18)
C6—C5—C4	122.55 (19)	C9—C11—H11B	112.3 (19)
C6—C5—H5	118.4 (14)	H11A—C11—H11B	110 (3)
C4—C5—H5	118.8 (14)	C9—C11—H11C	108.9 (19)
C5—C6—C1	119.4 (2)	H11A—C11—H11C	106 (2)
C5—C6—H6	120.8 (11)	H11B—C11—H11C	110 (3)
C9—N1—N2—C10	171.64 (19)	C2—C1—C6—C5	−0.4 (3)
O1—C1—C2—C3	179.56 (19)	C5—C4—C7—C8	−118.0 (3)
C6—C1—C2—C3	0.0 (3)	C3—C4—C7—C8	66.8 (3)
C1—C2—C3—C4	0.4 (3)	C4—C7—C8—C9	−176.4 (2)
C2—C3—C4—C5	−0.3 (3)	N2—N1—C9—C11	−1.1 (3)
C2—C3—C4—C7	175.1 (2)	N2—N1—C9—C8	174.63 (17)
C3—C4—C5—C6	−0.1 (3)	C7—C8—C9—N1	−101.3 (2)
C7—C4—C5—C6	−175.6 (2)	C7—C8—C9—C11	74.7 (3)
C4—C5—C6—C1	0.5 (3)	N1—N2—C10—N3	−3.1 (3)
O1—C1—C6—C5	−179.97 (19)	N1—N2—C10—S1	176.21 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···S1^{i}	0.89 (4)	2.32 (4)	3.206 (2)	175 (3)
N3—H10*A*···O1^{ii}	0.85 (2)	2.22 (2)	2.936 (2)	143 (2)
N3—H10*B*···S1^{iii}	0.91 (3)	2.73 (3)	3.585 (2)	156.6 (19)

Symmetry codes: (i) *x*−1, −*y*−3/2, *z*−1/2; (ii) −*x*, *y*+1/2, −*z*+1/2; (iii) −*x*+1, *y*+1/2, −*z*+3/2.