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Crystal structure of *N*,*N*′-[(ethane-1,2-diyl)bis(azanediylcarbonothioyl)]bis(benzamide)

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The reaction of benzoyl chloride and ethylendiamine in the presence of potassium thiocyanate yielded a white solid, $C_{18}H_{18}N_4O_2S_2$, which consists of two benzoylthioureido moieties connected by an ethylene chain. The asymmetric unit consists of one half of the molecule, the complete molecule being generated by crystallographic inversion symmetry. Both thiourea moieties are in a *trans* conformation. An intramolecular N—H⋯O hydrogen bond occurs. In the crystal, C—H⋯S and C—H⋯O hydrogen bonds link the molecules, forming layers parallel to the *ac* plane.

1. Chemical context

Thiourea derivatives have been successfully used in the extraction of some transition metals (*i.e.* Cu[II], Ni[II] and Co[II]) from acidic media. Thiourea derivatives have also been shown to possess antibacterial, antifungal, antitubercular, antithyroid and insecticidal properties (Arslan *et al.*, 2004; Cunha *et al.*, 2007). The structures of several types of thiourea derivatives and its metal complexes have been determined in recent decades. These compounds possess two arms which can act as a tetradentate ligand coordinating through the S atom and the benzoyl O atom of each arm. Urea and thiourea derivatives can behave as catalysts through double interaction by hydrogen bonding with the substrate (Sigman & Jacobsen, 1998; Cortes-Clerget *et al.*, 2016). Thiourea derivatives with alkyl bridges can adopt diverse conformations (Thiam *et al.*, 2008; Pansuriya *et al.*, 2011). We have recently begun to examine the coordination behaviour of a series of substituted benzoylthiourea derivatives that possess a number of interesting properties and reported a thioureido ligand in which the two thioureido moieties are bridged by a 1,2-phenylene ring (Thiam *et al.*, 2008). In this paper, we report the synthesis and the characterization of a molecule where the two thioureidos are bridged by an ethane-1,2-diyl group.
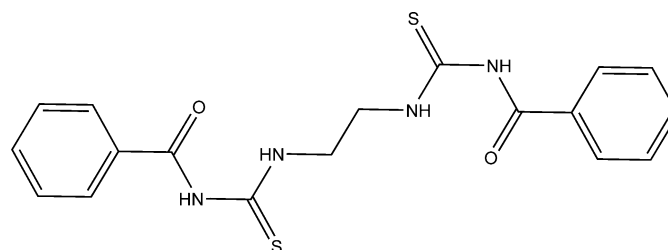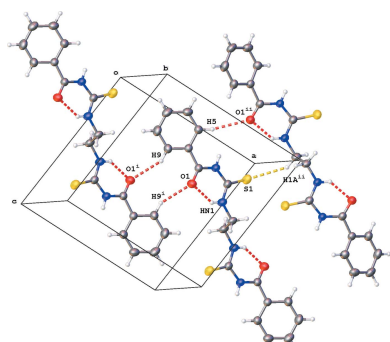
Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—HN1$\cdots$O1	0.86 (2)	1.95 (2)	2.6528 (16)	138 (2)
C5—H5$\cdots$O1^{i}	0.93	2.58	3.478 (16)	162
C9—H9$\cdots$O1^{ii}	0.93	2.52	3.311 (16)	143
C1—H1$A\cdots$S1^{iii}	0.97	2.97	3.8375 (16)	150

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

2. Structural commentary

The asymmetric unit of the title compound is a half-molecule with the other half being generated by an inversion centre located at the mid-point of the C1—C1a bond [Fig. 1; symmetry code: (a) $-x + 2, -y + 1, -z + 1$]. The benzoyl groups of each thiourea subunit are *trans* with respect to the thiono S atoms across the respective C2—N2 bonds. The 1-benzoyl-3-ethylthiourea fragments adopt a *cis* conformation with respect to the thiono S atom across the respective C2—N1 bonds. The S1—C2 [1.6626 (15) Å] and O1—C3 [1.2209 (16) Å] distances indicate that these correspond to double bonds and are comparable to those observed for 1,2-bis(N-benzoylthioureido)benzene [1.6574 (18) Å for S—C and 1.222 (2) Å for O7—C16] (Thiam *et al.*, 2008). The C—N bond lengths [1.3744 (17)–1.3971 (17) Å] are in the normal range observed for a single C—N bond. The thiourea fragments S1/N1/N2/C1/C2 are planar, with a maximum deviation from the least-squares plane of 0.015 (1) Å for the N1 atom. The dihedral angle between this plane and that of the benzene ring (r.m.s. deviation = 0.006 Å) is 26.97 (5)° *versus ca* 34° when the benzene ring is chlorinated (Abusaadiya *et al.*, 2016). As regularly noticed with carbonylurea derivatives, the molecule also forms intramolecular N1—H1 hydrogen bonds between the carbonyl O and thioamide H atoms producing $S(6)$ rings (N1—H1$\cdots$O1, Table 1).

3. Supramolecular features

In the crystal, the molecules, which feature an overall Z-form, have both halves roughly parallel to the *ac* plane, whereas the mid-point of the C1—C1a bond lies orthogonally parallel to the (100) plane. Molecular layers running almost parallel to the *ac* plane are formed by intermolecular C—H$\cdots$O and C—H$\cdots$S interactions (Table 1 and Fig. 2). These layers stack along the *b* direction. Despite the presence of phenyl rings, no π–π interactions are observed in the crystal packing. However,

the carbonyl function C3=O1 stacks on phenyl group C4–C9 of a neighbouring layer [O1$\cdots Cg$1^{iv} = 3.5543 (14) Å; Cg1 is the centroid of ring C4–C9; symmetry code: (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$].

4. Database survey

Reflecting the interest in compounds similar to the title compound, no less than 35 associated structures are included in the Cambridge Structural Database (Version 5.38; Groom *et al.*, 2016). The match APALEK (Abusaadiya *et al.*, 2016) is the most similar structure to the title compound, the only difference being the substitution of the phenyl ring on the C3 position by a Cl atom. In both cases, the benzoyl functions of each thiourea subunit are *trans* with respect to the thiono S atom across the C—N bond. The 1-benzoyl-3-ethylthiourea fragment adopts a *cis* conformation with respect to the thiono S atom across the respective C—N bond. Six structures in which the spacer is different from the spacer in the symmetrical bis(thioureido) molecule studied here appear in the literature. The angles between the phenyl rings are: 63.1° for DAVHOZ (Aydın *et al.*, 2012), 10.2° for EGUYAH (Sow *et al.*, 2009), 35.4° for NEWJIL (Light, 2018), 0.0° for QIXQUK (Ding *et al.*, 2008), 3.2° for TIFQAD (Oyeka *et al.*, 2018) and 0.0° for XIQPAP (Dong *et al.*, 2007). In addition, 23 structures which contain only one arm with a thioureido moiety similar to the studied molecules are reported, while the other arm consists of diverse moieties: CIGDAZ (Karipcin *et al.*, 2013), DELMUD (Ngah *et al.*, 2006), EYACIQ (Shutalev *et al.*, 2004), GIHMIV (Haynes *et al.*, 2014), GIHMOB (Haynes *et al.*, 2014), IFUZOZ (Hassan *et al.*, 2008a,b), NIQROV (Yamin & Malik, 2007), NIQROV01 (Nguyen & Abram, 2008), POFKIG (Ngah *et al.*, 2014), QEWHUY (Rakhshani *et al.*, 2018), RUGKOU (Hassan *et al.*, 2009), SAFPAT (Wei, 2016),
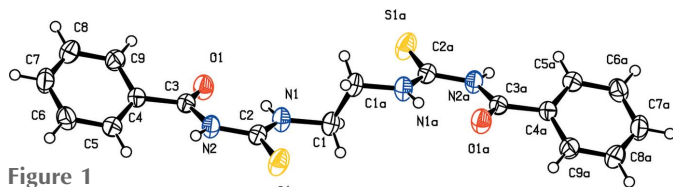

Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme and intramolecular contacts. Displacement ellipsoids are plotted at the 50% probability level. [Symmetry code: (a) $-x + 2, -y + 1, -z + 1$]
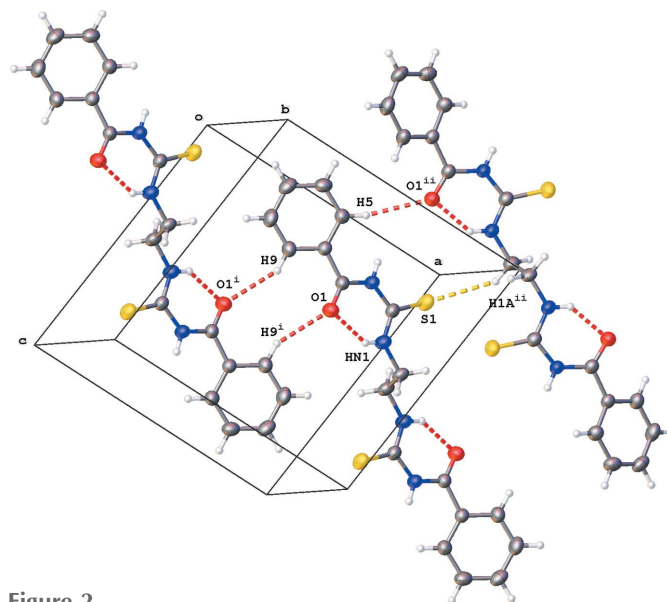

Figure 2
Partial crystal packing of the title compound, showing C—H$\cdots$O (red dashed lines) and C—H$\cdots$S (yellow dashed lines) interactions (see Table 1 for details).

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Crystal data	
Chemical formula	$C_{18}H_{18}N_4O_2S_2$
M_r	386.48
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	11.2250 (6), 7.2547 (5), 11.1397 (6)
β (°)	100.978 (5)
V (Å^3)	890.55 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.32
Crystal size (mm)	$0.36 \times 0.14 \times 0.11$
Data collection	
Diffractometer	XtaLAB AFC12 (RINC): Kappa single
Absorption correction	Multi-scan *CrysAlis PRO* (Rigaku OD, 2018)
T_{min}, T_{max}	0.513, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7264, 2328, 1942
R_{int}	0.040
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.704
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.121, 1.05
No. of reflections	2325
No. of parameters	124
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.31

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2014* (Sheldrick, 2015a) and *SHELXL2018* (Sheldrick, 2015b).

SITKUC (Yamin *et al.*, 2008), TADSIB (Zhang *et al.*, 2003), TADTEY (Yusof & Yamin, 2003), TIBLEW (Khawar Rauf *et al.*, 2007). TIHJAW (Yusof *et al.*, 2007), UNUBAH (Hassan *et al.*, 2011), WOGTUI (Hassan *et al.*, 2008a,b), XEBQOM (Adan *et al.*, 2012), YICDEU (Othman *et al.*, 2007), YUPYEO (Zheng *et al.*, 2010) and YUPYEO01 (Khan *et al.*, 2018).

5. Synthesis and crystallization

All purchased chemicals and solvents were of reagent grade and were used without further purification. Melting points were determined with a Büchi 570 melting-point apparatus and were uncorrected. To a mixture of 7.02 g (72 mmol) of potassium thiocyanate and 100 ml of acetone was added dropwise a solution of 10.116 g (72 mmol) of benzoyl chloride in 50 ml of acetone. The resulting mixture was stirred under reflux for 1 h and cooled to room temperature. A solution of 2.2 g (36.6 mmol) of 1,2-ethylenediamine in 20 ml of acetone was added. The yellow solution obtained was stirred at room temperature during 2 h. Hydrochloric acid (0.1 *N*, 300 ml) was added and a white solid appeared after a few minutes. The compound was filtered off, washed with 3 × 50 ml of water and dried under vacuum. The solid product was washed with water and purified by recrystallization from an ethanol/dichloro-methane mixture (1:1 *v/v*). 12.3 g of the title compound were obtained (yield 88.5%). A small quantity of powder was recrystallized from 5 ml of DMF. Colourless single crystals suitable to XRD grew within six days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Aromatic H atoms were first located by HFIX and other H atoms were located in the difference Fourier map, positioned geometrically and allowed to ride on their respective parent atoms, with C—H = 0.93 (C$_{ar}$H) or 0.97 Å (CH$_2$). The NH H atoms were located in a difference Fourier map and freely refined.

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Crystal structure of *N*,*N*′-[(ethane-1,2-diyl)bis(azanediylcarbonothioyl)]bis-(benzamide)

Issa Samb, Nango Gaye, Rokhaya Sylla-Gueye, Elhadj Ibrahima Thiam, Mohamed Gaye and Pascal Retailleau

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b).

***N*,*N*′-[(Ethane-1,2-diyl)bis(azanediylcarbonothioyl)]bis(benzamide)**

Crystal data

$C_{18}H_{18}N_4O_2S_2$	$F(000) = 404$
$M_r = 386.48$	$D_x = 1.441$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.2250$ (6) Å	Cell parameters from 3377 reflections
$b = 7.2547$ (5) Å	$\theta = 4.7–30.2°$
$c = 11.1397$ (6) Å	$\mu = 0.32$ mm^{-1}
$\beta = 100.978$ (5)°	$T = 293$ K
$V = 890.55$ (9) Å^3	Prism, colourless
$Z = 2$	$0.36 \times 0.14 \times 0.11$ mm

Data collection

XtaLAB AFC12 (RINC): Kappa single diffractometer	7264 measured reflections
	2328 independent reflections
Radiation source: micro-focus sealed X-ray tube, Rigaku (Mo)mm03 X-ray Source	1942 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.040$
Rigaku MaxFlux mirror monochromator	$\theta_{max} = 30.0°$, $\theta_{min} = 3.7°$
ω scans	$h = -15 \rightarrow 14$
Absorption correction: multi-scan	$k = -10 \rightarrow 9$
CrysAlis PRO (Rigaku OD, 2018)	$l = -15 \rightarrow 15$
$T_{min} = 0.513$, $T_{max} = 1.000$	

Refinement

Refinement on F^2	2 restraints
Least-squares matrix: full	Primary atom site location: dual
$R[F^2 > 2\sigma(F^2)] = 0.042$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.121$	
$S = 1.05$	Hydrogen site location: mixed
2325 reflections	H atoms treated by a mixture of independent and constrained refinement
124 parameters	

$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.1222P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.85736 (10)	0.61198 (19)	0.41958 (11)	0.0399 (3)
HN1	0.8022 (15)	0.636 (3)	0.4606 (15)	0.048*
O1	0.62565 (9)	0.65743 (17)	0.43252 (9)	0.0452 (3)
C1	0.98347 (12)	0.5989 (2)	0.48195 (13)	0.0398 (3)
H1A	0.996007	0.675814	0.554503	0.048*
H1AB	1.035920	0.643780	0.428470	0.048*
S1	0.90847 (3)	0.53047 (7)	0.20190 (4)	0.05100 (17)
N2	0.69512 (10)	0.59494 (18)	0.25797 (10)	0.0372 (3)
HN2	0.6711 (17)	0.573 (2)	0.1826 (14)	0.045*
C2	0.82013 (12)	0.58234 (19)	0.30120 (12)	0.0351 (3)
C3	0.60474 (11)	0.62787 (19)	0.32261 (12)	0.0332 (3)
C4	0.47845 (11)	0.61990 (18)	0.25055 (12)	0.0323 (3)
C5	0.44876 (13)	0.6519 (2)	0.12543 (12)	0.0380 (3)
H5	0.508903	0.681492	0.081672	0.046*
C6	0.32849 (14)	0.6391 (2)	0.06642 (14)	0.0446 (3)
H6	0.308060	0.662390	−0.017073	0.054*
C7	0.23884 (13)	0.5923 (2)	0.13013 (16)	0.0466 (4)
H7	0.158787	0.581443	0.089304	0.056*
C8	0.26809 (14)	0.5617 (2)	0.25436 (16)	0.0469 (4)
H8	0.207621	0.530909	0.297439	0.056*
C9	0.38722 (13)	0.5766 (2)	0.31507 (13)	0.0396 (3)
H9	0.406519	0.557780	0.399116	0.048*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0294 (6)	0.0525 (7)	0.0365 (6)	0.0051 (5)	0.0025 (4)	−0.0034 (5)
O1	0.0362 (5)	0.0667 (7)	0.0327 (5)	0.0038 (5)	0.0061 (4)	−0.0008 (5)
C1	0.0288 (6)	0.0468 (8)	0.0405 (7)	−0.0030 (5)	−0.0013 (5)	−0.0052 (6)
S1	0.0316 (2)	0.0798 (3)	0.0436 (2)	−0.00179 (16)	0.01212 (16)	−0.00785 (18)
N2	0.0274 (5)	0.0518 (7)	0.0316 (5)	0.0025 (5)	0.0039 (4)	−0.0014 (5)
C2	0.0282 (6)	0.0395 (7)	0.0371 (6)	−0.0016 (5)	0.0049 (5)	0.0012 (5)
C3	0.0291 (6)	0.0373 (7)	0.0333 (6)	0.0012 (5)	0.0063 (5)	0.0036 (5)
C4	0.0283 (6)	0.0338 (6)	0.0347 (6)	0.0024 (5)	0.0058 (5)	0.0027 (5)
C5	0.0348 (6)	0.0427 (7)	0.0362 (6)	−0.0003 (5)	0.0063 (5)	0.0053 (5)
C6	0.0410 (7)	0.0497 (8)	0.0390 (7)	0.0026 (6)	−0.0030 (6)	0.0041 (6)

C7	0.0285 (6)	0.0490 (9)	0.0586 (9)	0.0040 (6)	−0.0009 (6)	0.0005 (7)
C8	0.0313 (7)	0.0552 (9)	0.0571 (9)	0.0028 (6)	0.0155 (6)	0.0040 (7)
C9	0.0331 (7)	0.0486 (8)	0.0387 (7)	0.0034 (6)	0.0108 (5)	0.0048 (6)

Geometric parameters (Å, º)

N1—C2	1.3228 (17)	C4—C5	1.3894 (17)
N1—C1	1.4564 (17)	C4—C9	1.3944 (18)
N1—HN1	0.854 (14)	C5—C6	1.388 (2)
O1—C3	1.2209 (16)	C5—H5	0.9300
C1—C1^i	1.518 (3)	C6—C7	1.380 (2)
C1—H1A	0.9700	C6—H6	0.9300
C1—H1AB	0.9700	C7—C8	1.378 (2)
S1—C2	1.6633 (14)	C7—H7	0.9300
N2—C3	1.3723 (17)	C8—C9	1.383 (2)
N2—C2	1.3971 (16)	C8—H8	0.9300
N2—HN2	0.846 (14)	C9—H9	0.9300
C3—C4	1.4913 (17)		
C2—N1—C1	123.98 (12)	C5—C4—C9	119.69 (12)
C2—N1—HN1	116.3 (12)	C5—C4—C3	123.74 (12)
C1—N1—HN1	119.7 (12)	C9—C4—C3	116.58 (12)
N1—C1—C1^i	110.75 (14)	C6—C5—C4	119.34 (13)
N1—C1—H1A	109.5	C6—C5—H5	120.3
C1^i—C1—H1A	109.5	C4—C5—H5	120.3
N1—C1—H1AB	109.5	C7—C6—C5	120.78 (14)
C1^i—C1—H1AB	109.5	C7—C6—H6	119.6
H1A—C1—H1AB	108.1	C5—C6—H6	119.6
C3—N2—C2	128.67 (11)	C8—C7—C6	119.91 (13)
C3—N2—HN2	115.1 (13)	C8—C7—H7	120.0
C2—N2—HN2	116.1 (13)	C6—C7—H7	120.0
N1—C2—N2	116.03 (12)	C7—C8—C9	120.11 (14)
N1—C2—S1	125.77 (10)	C7—C8—H8	119.9
N2—C2—S1	118.19 (10)	C9—C8—H8	119.9
O1—C3—N2	122.46 (12)	C8—C9—C4	120.15 (14)
O1—C3—C4	121.88 (12)	C8—C9—H9	119.9
N2—C3—C4	115.64 (11)	C4—C9—H9	119.9
C2—N1—C1—C1^i	−84.6 (2)	N2—C3—C4—C9	154.33 (13)
C1—N1—C2—N2	177.90 (13)	C9—C4—C5—C6	−0.4 (2)
C1—N1—C2—S1	−1.5 (2)	C3—C4—C5—C6	179.28 (13)
C3—N2—C2—N1	−2.5 (2)	C4—C5—C6—C7	−1.1 (2)
C3—N2—C2—S1	177.01 (12)	C5—C6—C7—C8	1.5 (3)
C2—N2—C3—O1	2.4 (2)	C6—C7—C8—C9	−0.4 (3)
C2—N2—C3—C4	−175.85 (13)	C7—C8—C9—C4	−1.0 (2)
O1—C3—C4—C5	156.36 (14)	C5—C4—C9—C8	1.4 (2)

| N2—C3—C4—C5 | −25.33 (19) | C3—C4—C9—C8 | −178.28 (14) |
| O1—C3—C4—C9 | −23.98 (19) | | |

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H*N*1···O1	0.86 (2)	1.95 (2)	2.6528 (16)	138 (2)
C5—H5···O1ii	0.93	2.58	3.478 (16)	162
C9—H9···O1iii	0.93	2.52	3.311 (16)	143
C1—H1*A*···S1iv	0.97	2.97	3.8375 (16)	150

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