Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of *N*-(2-amino-5-cyano-4-methylsulfanyl-6-oxo-1,6-dihydropyrimidin-1-yl)-4-bromobenzenesulfonamide dimethylformamide monosolvate

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Received 18 September 2015
Accepted 7 October 2015

Edited by A. J. Lough, University of Toronto, Canada

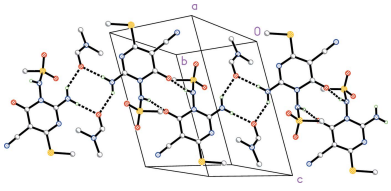
Keywords: crystal structure; pyrimidine; bromobenzenesulfonamide; hydrogen bonding

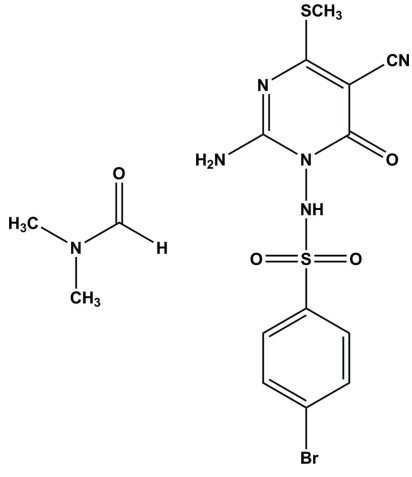
CCDC reference: 1430044
Supporting information: this article has supporting information at journals.iucr.org/e

The title compound, $C_{12}H_{10}BrN_5O_3S_2\cdot C_3H_7NO$, displays an almost planar amine group. The interplanar angle between the rings is 31.72 (6)°. The residues are associated into ribbons parallel to [110] by three classical hydrogen bonds; one from each amine H_{amine} to O_{DMF} and one from NH_{amide} to O_{oxo}. Adjacent ribbons are connected by translation parallel to the *c* axis by a 'weak' hydrogen bond $H_{methyl}\cdots O_{sulfonyl}$ to form a layer structure parallel to $(1\bar{1}0)$, while a further contact $H_{bromophenyl}\cdots O_{sulfonyl}$ connects the residues in the third dimension.

1. Chemical context

We are conducting studies directed towards exploring the synthetic potential of dimethyl *N*-cyanoimido-*S*,*S*-dimethyldithiocarbonate and other ketene dithioacetals for synthesizing new classes of antimetabolites (Elgemeie & Mohamed, 2014; Elgemeie *et al.*, 2007, 2009). We have recently reported various successful approaches to the synthesis of mercaptopyrimidines by the reaction of this compound with active methylene functions (Elgemeie & Sood, 2001; Elgemeie *et al.*, 2003). In an extension of this work, we describe a one-pot synthesis of *N*-(2-amino-5-cyano-4-(methylthio)-6-oxopyrimidin-1(6*H*)-yl)-4-bromobenzenesulfonamide (I) by the reaction of dimethyl *N*-cyanodithioiminocarbonate with *N*′-(4-bromophenyl)sulfonyl-2-cyanoethanehydrazide. The chemical nature was proposed on the basis of elemental analysis and spectroscopic data and its X-ray structure determination was undertaken to confirm the nature of the product. We have recently presented the structure of a related pyrimidine (Elgemeie *et al.*, 2015).





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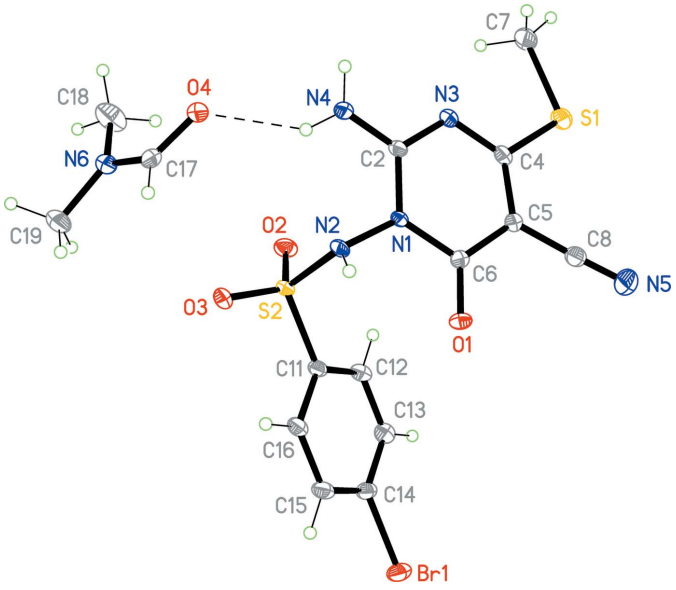

Figure 1
The formula unit of compound (I)·DMF in the crystal. Displacement ellipsoids correspond to 50% probability levels. The hydrogen bond H03···O4 is drawn as a thin dashed line.

2. Structural commentary

The structure of the title compound, which proved to be the dimethylformamide solvate (I)·DMF, is shown in Fig. 1. The ring systems are as expected almost planar, with r.m.s. deviations of 0.002 Å for the phenyl and 0.04 Å for the pyrimidine ring. The substituent atoms N4 and S1 deviate significantly from the pyrimidine plane [by 0.199 (2) and 0.257 (2) Å respectively, to opposite sides of the plane]. The interplanar angle is 31.72 (6)°, and is also associated with the torsion angles C12—C11—S2—N2 88.10 (12), C11—S2—N2—N1 78.98 (11) and S2—N2—N1—C2 100.31 (12)°. The amino group at N4 is almost planar, with the nitrogen atom lying just 0.035 (11) Å out of the plane of its substituents.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H01···O1^{i}	0.80 (2)	2.00 (2)	2.7784 (15)	165.5 (19)
N4—H02···O4^{ii}	0.86 (2)	1.98 (2)	2.8382 (16)	177.9 (19)
N4—H03···O4	0.85 (2)	2.07 (2)	2.8005 (16)	143.1 (18)
C12—H12···O2^{iii}	0.95	2.46	3.4096 (18)	173
C7—H7B···O3^{iv}	0.98	2.45	3.2848 (19)	143
C17—H17···Br1^{v}	0.95	3.05	3.6686 (15)	124

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y, z+1$; (v) $x, y-1, z$.

3. Supramolecular features

The components are associated into ribbons parallel to [110] (Fig. 2) by three classical hydrogen bonds (Table 1). Two of these, H02···O4($1-x, -y, 1-z$) and H03···O4, involve the dimethylformamide oxygen atom and lead to the formation of inversion-symmetric rings of graph set $R_4^2(8)$. The third hydrogen bond, H01···O1($2-x, 1-y, 1-z$), also forms inversion-symmetric rings, but of graph set $R_2^2(10)$.

There are two short and acceptably linear C—H···O contacts that may be assumed to represent 'weak' hydrogen bonds; H7B···O3 connects neighbouring ribbons by translation parallel to the c axis, thus completing a layer structure parallel to ($1\bar{1}0$), while H12···O2 connects the residues in the third dimension via the inversion operator ($1-x, 1-y, 1-z$).

The bromine atom is involved in two secondary contacts: a halogen bond of 3.4582 (10) Å with O1($2-x, 2-y, 1-z$) and a weak hydrogen bond of 3.05 Å from H17($x, 1+y, z$), with an angle of 124° at hydrogen. These interactions also connect the residues in the third dimension.

4. Synthesis and crystallization

Dimethyl *N*-cyanoimido-*S*,*S*-dimethyl-dithiocarbonate (0.01 mol) was added to a stirred solution of *N*′-(4-bromo-

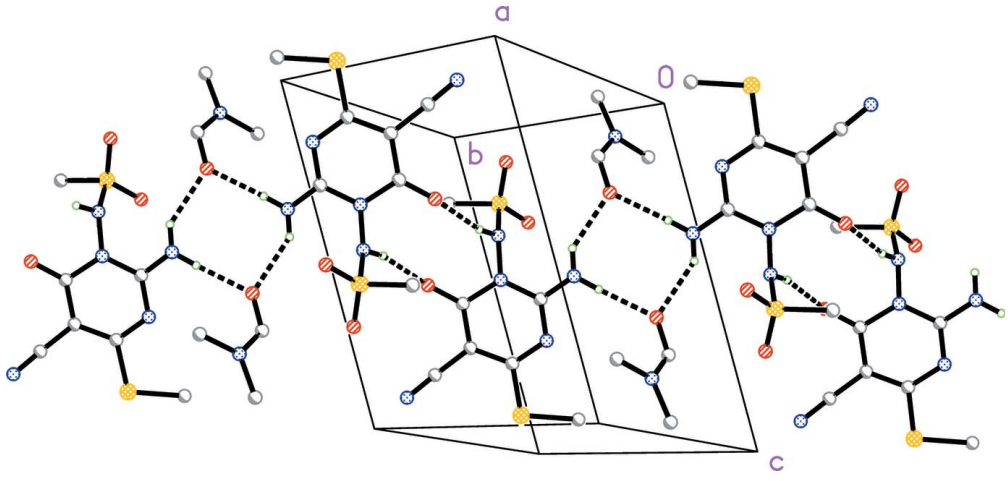

Figure 2
Packing diagram of compound (I)· DMF viewed perpendicular to ($1\bar{1}0$). For clarity, only the *ipso* carbons of the bromophenyl groups are shown. Classical hydrogen bonds are indicated by dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{10}BrN_5O_3S_2\cdot C_3H_7NO$
M_r	489.38
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	9.1107 (4), 9.9911 (4), 11.6498 (6)
α, β, γ (°)	96.482 (4), 107.802 (4), 99.322 (4)
V (Å^3)	981.33 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.34
Crystal size (mm)	0.45 × 0.40 × 0.40
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.824, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	52130, 5844, 5306
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.722
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.061, 1.06
No. of reflections	5844
No. of parameters	268
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.39

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS97*, *SHELXL97* and *XP* in *SHELXTL* (Sheldrick, 2008).

phenyl)sulfonyl-2-cyanoethanehydrazide (0.01 mol) in dry dioxane (50 mL) containing potassium hydroxide (0.01 mol) at room temperature. The reaction mixture was stirred for 30 min at room temperature; the precipitated solid was collected by filtration and crystallized from dimethyl formamide to give pale yellow crystals, m.p. 483–485 K, yield 85%.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH hydrogens were refined freely. The methyl groups were refined as idealized rigid groups allowed to rotate but not tip. Other H were included using a riding model starting from calculated positions [C—H = 0.95–0.98 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms].

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supporting information

Acta Cryst. (2015). E**71**, 1322-1324 [https://doi.org/10.1107/S2056989015018903]

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

N-(2-Amino-5-cyano-4-methylsulfanyl-6-oxo-1,6-dihydropyrimidin-1-yl)-4-bromobenzenesulfonamide dimethylformamide monosolvate

Crystal data

$C_{12}H_{10}BrN_5O_3S_2 \cdot C_3H_7NO$
$M_r = 489.38$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 9.1107$ (4) Å
$b = 9.9911$ (4) Å
$c = 11.6498$ (6) Å
$\alpha = 96.482$ (4)°
$\beta = 107.802$ (4)°
$\gamma = 99.322$ (4)°
$V = 981.33$ (8) Å^3
$Z = 2$
$F(000) = 496$
$D_x = 1.656$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 16424 reflections
$\theta = 2.6$–30.4°
$\mu = 2.34$ mm^{-1}
$T = 100$ K
Block, colourless
0.45 × 0.40 × 0.40 mm

Data collection

Oxford Diffraction Xcalibur, Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1419 pixels mm^{-1}
ω–scan
Absorption correction: multi-scan (CrysAlisPro; Agilent, 2013)
$T_{min} = 0.824$, $T_{max} = 1.000$
52130 measured reflections
5844 independent reflections
5306 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 30.9°$, $\theta_{min} = 2.4°$
$h = -12 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.061$
$S = 1.06$
5844 reflections
268 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 atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2 + 0.6489P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ 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.
Non-bonded contact:
3.4582 (0.0010) Br1 - O1_$6
Operator for generating equivalent atoms: $6 - *x* + 2, -*y* + 2, -*z* + 1
==========
Least-squares planes (*x*,*y*,*z* in crystal coordinates) and deviations from them (* indicates atom used to define plane)
8.0547 (0.0765) *x* - 4.9253 (0.0915) *y* + 0.8579 (0.2093) *z* = 4.7396 (0.0731)
* 0.0000 (0.0001) C2 * 0.0000 (0.0001) H02 * 0.0000 (0.0000) H03 0.0352 (0.0108) N4
Rms deviation of fitted atoms = 0.0000
7.4457 (0.0028) *x* - 5.9260 (0.0044) *y* + 1.6748 (0.0062) *z* = 4.4689 (0.0045)
Angle to previous plane (with approximate e.s.d.) = 7.74 (1.41)
* -0.0578 (0.0009) N1 * 0.0522 (0.0009) C2 * 0.0025 (0.0009) N3 * -0.0485 (0.0010) C4 * 0.0394 (0.0010) C5 * 0.0122 (0.0009) C6 0.1986 (0.0021) N4 - 0.2565 (0.0018) S1 - 0.3373 (0.0028) C7 0.1276 (0.0023) C8 0.2186 (0.0028) N5 0.0409 (0.0018) O1 - 0.0581 (0.0020) N2
Rms deviation of fitted atoms = 0.0411
6.0229 (0.0041) *x* - 2.3534 (0.0057) *y* + 5.9679 (0.0059) *z* = 4.9873 (0.0043)
Angle to previous plane (with approximate e.s.d.) = 31.72 (0.06)
* -0.0028 (0.0010) C11 * 0.0004 (0.0010) C12 * 0.0025 (0.0010) C13 * -0.0031 (0.0010) C14 * 0.0007 (0.0010) C15 * 0.0023 (0.0010) C16 - 0.0142 (0.0020) Br1 0.0055 (0.0019) S2
Rms deviation of fitted atoms = 0.0022

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	0.74640 (5)	0.49517 (4)	0.94893 (3)	0.02271 (8)
S2	0.64492 (4)	0.41433 (3)	0.34915 (3)	0.01389 (7)
Br1	0.903097 (18)	1.043895 (15)	0.333551 (15)	0.02167 (5)
N1	0.78069 (13)	0.40042 (11)	0.57992 (10)	0.0118 (2)
C2	0.70629 (16)	0.30239 (14)	0.62952 (12)	0.0132 (2)
N2	0.77711 (15)	0.36204 (12)	0.45978 (10)	0.0130 (2)
H01	0.863 (2)	0.3749 (19)	0.4545 (17)	0.020 (5)*
N3	0.69682 (14)	0.33056 (12)	0.74159 (11)	0.0151 (2)
C4	0.77293 (17)	0.45373 (14)	0.80858 (12)	0.0147 (3)
C5	0.87008 (16)	0.55054 (14)	0.77173 (12)	0.0142 (2)
C6	0.87526 (15)	0.52734 (13)	0.65034 (12)	0.0122 (2)
C7	0.6131 (2)	0.34218 (18)	0.95215 (15)	0.0254 (3)
H7A	0.5211	0.3215	0.8774	0.038*
H7B	0.5787	0.3573	1.0236	0.038*

H7C	0.6669	0.2646	0.9572	0.038*
C8	0.96232 (18)	0.67418 (15)	0.85179 (13)	0.0186 (3)
N4	0.64153 (15)	0.17814 (13)	0.56513 (12)	0.0169 (2)
H02	0.597 (2)	0.119 (2)	0.5990 (18)	0.024 (5)*
H03	0.633 (2)	0.159 (2)	0.4900 (19)	0.025 (5)*
N5	1.03702 (19)	0.77174 (15)	0.91924 (14)	0.0298 (3)
O1	0.95091 (12)	0.60446 (10)	0.60406 (9)	0.01553 (19)
O2	0.50567 (12)	0.40373 (11)	0.38292 (10)	0.0196 (2)
O3	0.64611 (14)	0.33408 (11)	0.23994 (9)	0.0215 (2)
C11	0.71531 (16)	0.58768 (14)	0.34507 (12)	0.0140 (2)
C12	0.68353 (17)	0.69127 (15)	0.41854 (13)	0.0162 (3)
H12	0.6237	0.6690	0.4703	0.019*
C13	0.74062 (17)	0.82758 (15)	0.41502 (13)	0.0175 (3)
H13	0.7206	0.8999	0.4646	0.021*
C14	0.82751 (17)	0.85737 (15)	0.33814 (13)	0.0167 (3)
C15	0.86007 (17)	0.75425 (15)	0.26524 (13)	0.0179 (3)
H15	0.9202	0.7767	0.2137	0.021*
C16	0.80332 (17)	0.61764 (15)	0.26891 (13)	0.0162 (3)
H16	0.8244	0.5454	0.2199	0.019*
N6	0.33893 (15)	0.04126 (13)	0.14664 (11)	0.0182 (2)
O4	0.50814 (13)	0.02165 (11)	0.32929 (10)	0.0198 (2)
C17	0.48080 (18)	0.04576 (14)	0.22375 (13)	0.0174 (3)
H17	0.5681	0.0692	0.1963	0.021*
C18	0.2020 (2)	0.0087 (2)	0.18574 (17)	0.0322 (4)
H18A	0.1941	−0.0837	0.2071	0.048*
H18B	0.1066	0.0117	0.1191	0.048*
H18C	0.2132	0.0762	0.2574	0.048*
C19	0.3164 (2)	0.08261 (18)	0.02765 (15)	0.0274 (3)
H19A	0.4184	0.1036	0.0146	0.041*
H19B	0.2700	0.1646	0.0248	0.041*
H19C	0.2456	0.0075	−0.0366	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0325 (2)	0.02259 (18)	0.01318 (16)	0.00060 (15)	0.01114 (15)	0.00105 (13)
S2	0.01596 (16)	0.01541 (15)	0.01050 (14)	0.00078 (12)	0.00523 (12)	0.00418 (11)
Br1	0.02029 (8)	0.01729 (7)	0.02730 (9)	0.00028 (5)	0.00798 (6)	0.00829 (6)
N1	0.0146 (5)	0.0130 (5)	0.0090 (5)	0.0013 (4)	0.0062 (4)	0.0024 (4)
C2	0.0140 (6)	0.0143 (6)	0.0120 (6)	0.0018 (5)	0.0050 (5)	0.0048 (5)
N2	0.0151 (6)	0.0159 (5)	0.0107 (5)	0.0033 (4)	0.0077 (4)	0.0034 (4)
N3	0.0178 (6)	0.0167 (5)	0.0110 (5)	0.0015 (4)	0.0058 (4)	0.0033 (4)
C4	0.0160 (6)	0.0179 (6)	0.0106 (6)	0.0041 (5)	0.0046 (5)	0.0037 (5)
C5	0.0155 (6)	0.0141 (6)	0.0124 (6)	0.0023 (5)	0.0040 (5)	0.0018 (5)
C6	0.0105 (6)	0.0124 (6)	0.0141 (6)	0.0032 (5)	0.0038 (5)	0.0034 (5)
C7	0.0280 (8)	0.0315 (8)	0.0170 (7)	−0.0022 (6)	0.0117 (6)	0.0051 (6)
C8	0.0223 (7)	0.0173 (6)	0.0167 (7)	0.0042 (5)	0.0067 (6)	0.0044 (5)
N4	0.0226 (6)	0.0150 (5)	0.0125 (6)	−0.0014 (5)	0.0075 (5)	0.0026 (4)

N5	0.0357 (8)	0.0210 (7)	0.0259 (7)	0.0004 (6)	0.0043 (6)	0.0005 (5)
O1	0.0151 (5)	0.0149 (4)	0.0189 (5)	0.0013 (4)	0.0091 (4)	0.0051 (4)
O2	0.0147 (5)	0.0246 (5)	0.0205 (5)	0.0017 (4)	0.0069 (4)	0.0091 (4)
O3	0.0318 (6)	0.0194 (5)	0.0113 (5)	−0.0003 (4)	0.0077 (4)	0.0014 (4)
C11	0.0146 (6)	0.0153 (6)	0.0132 (6)	0.0028 (5)	0.0047 (5)	0.0062 (5)
C12	0.0161 (6)	0.0194 (6)	0.0163 (6)	0.0053 (5)	0.0076 (5)	0.0075 (5)
C13	0.0175 (7)	0.0187 (7)	0.0176 (7)	0.0058 (5)	0.0061 (5)	0.0045 (5)
C14	0.0140 (6)	0.0166 (6)	0.0182 (7)	0.0012 (5)	0.0032 (5)	0.0071 (5)
C15	0.0171 (7)	0.0212 (7)	0.0179 (7)	0.0027 (5)	0.0083 (5)	0.0084 (5)
C16	0.0173 (7)	0.0199 (7)	0.0129 (6)	0.0040 (5)	0.0063 (5)	0.0051 (5)
N6	0.0199 (6)	0.0184 (6)	0.0158 (6)	0.0022 (5)	0.0054 (5)	0.0049 (5)
O4	0.0222 (5)	0.0175 (5)	0.0161 (5)	−0.0018 (4)	0.0036 (4)	0.0044 (4)
C17	0.0203 (7)	0.0134 (6)	0.0174 (7)	−0.0009 (5)	0.0071 (5)	0.0016 (5)
C18	0.0204 (8)	0.0526 (11)	0.0288 (9)	0.0110 (8)	0.0106 (7)	0.0167 (8)
C19	0.0315 (9)	0.0315 (8)	0.0177 (7)	0.0026 (7)	0.0059 (6)	0.0101 (6)

Geometric parameters (Å, º)

S1—C4	1.7392 (14)	C15—C16	1.389 (2)
S1—C7	1.8036 (16)	N6—C17	1.320 (2)
S2—O3	1.4292 (11)	N6—C19	1.4551 (19)
S2—O2	1.4305 (11)	N6—C18	1.455 (2)
S2—N2	1.6707 (13)	O4—C17	1.2373 (18)
S2—C11	1.7580 (14)	N2—H01	0.80 (2)
Br1—C14	1.8920 (14)	C7—H7A	0.9800
N1—C2	1.3801 (16)	C7—H7B	0.9800
N1—N2	1.3979 (15)	C7—H7C	0.9800
N1—C6	1.4150 (17)	N4—H02	0.86 (2)
C2—N4	1.3167 (18)	N4—H03	0.85 (2)
C2—N3	1.3361 (17)	C12—H12	0.9500
N3—C4	1.3342 (18)	C13—H13	0.9500
C4—C5	1.3971 (19)	C15—H15	0.9500
C5—C6	1.4235 (18)	C16—H16	0.9500
C5—C8	1.4235 (19)	C17—H17	0.9500
C6—O1	1.2281 (16)	C18—H18A	0.9800
C8—N5	1.147 (2)	C18—H18B	0.9800
C11—C12	1.392 (2)	C18—H18C	0.9800
C11—C16	1.3918 (19)	C19—H19A	0.9800
C12—C13	1.387 (2)	C19—H19B	0.9800
C13—C14	1.391 (2)	C19—H19C	0.9800
C14—C15	1.388 (2)		
C4—S1—C7	101.66 (7)	C17—N6—C18	119.55 (13)
O3—S2—O2	121.50 (7)	C19—N6—C18	118.46 (13)
O3—S2—N2	103.18 (6)	O4—C17—N6	124.64 (14)
O2—S2—N2	106.00 (6)	N1—N2—H01	111.8 (14)
O3—S2—C11	107.29 (6)	S2—N2—H01	113.5 (14)
O2—S2—C11	109.08 (7)	S1—C7—H7A	109.5

N2—S2—C11	109.23 (6)	S1—C7—H7B	109.5
C2—N1—N2	116.88 (11)	H7A—C7—H7B	109.5
C2—N1—C6	122.54 (11)	S1—C7—H7C	109.5
N2—N1—C6	120.02 (11)	H7A—C7—H7C	109.5
N4—C2—N3	118.74 (12)	H7B—C7—H7C	109.5
N4—C2—N1	119.66 (12)	C2—N4—H02	117.5 (13)
N3—C2—N1	121.60 (12)	C2—N4—H03	121.9 (14)
N1—N2—S2	117.24 (9)	H02—N4—H03	120.2 (19)
C4—N3—C2	117.70 (12)	C13—C12—H12	120.5
N3—C4—C5	123.85 (13)	C11—C12—H12	120.5
N3—C4—S1	117.37 (10)	C12—C13—H13	120.3
C5—C4—S1	118.77 (11)	C14—C13—H13	120.3
C4—C5—C6	119.61 (12)	C14—C15—H15	120.6
C4—C5—C8	121.71 (13)	C16—C15—H15	120.6
C6—C5—C8	118.67 (12)	C15—C16—H16	120.3
O1—C6—N1	119.46 (12)	C11—C16—H16	120.3
O1—C6—C5	126.95 (13)	O4—C17—H17	117.7
N1—C6—C5	113.59 (11)	N6—C17—H17	117.7
N5—C8—C5	177.93 (16)	N6—C18—H18A	109.5
C12—C11—C16	121.64 (13)	N6—C18—H18B	109.5
C12—C11—S2	119.54 (10)	H18A—C18—H18B	109.5
C16—C11—S2	118.82 (11)	N6—C18—H18C	109.5
C13—C12—C11	118.95 (13)	H18A—C18—H18C	109.5
C12—C13—C14	119.35 (13)	H18B—C18—H18C	109.5
C15—C14—C13	121.82 (13)	N6—C19—H19A	109.5
C15—C14—Br1	119.39 (11)	N6—C19—H19B	109.5
C13—C14—Br1	118.79 (11)	H19A—C19—H19B	109.5
C14—C15—C16	118.90 (13)	N6—C19—H19C	109.5
C15—C16—C11	119.35 (13)	H19A—C19—H19C	109.5
C17—N6—C19	121.65 (13)	H19B—C19—H19C	109.5

N2—N1—C2—N4	2.44 (19)	C4—C5—C6—O1	177.72 (13)
C6—N1—C2—N4	−168.95 (13)	C8—C5—C6—O1	−1.0 (2)
N2—N1—C2—N3	−176.97 (12)	C4—C5—C6—N1	−2.16 (18)
C6—N1—C2—N3	11.6 (2)	C8—C5—C6—N1	179.16 (12)
C2—N1—N2—S2	100.31 (12)	O3—S2—C11—C12	160.71 (11)
C6—N1—N2—S2	−88.07 (13)	O2—S2—C11—C12	27.34 (13)
O3—S2—N2—N1	−167.13 (9)	N2—S2—C11—C12	−88.10 (12)
O2—S2—N2—N1	−38.42 (11)	O3—S2—C11—C16	−19.99 (13)
C11—S2—N2—N1	78.98 (11)	O2—S2—C11—C16	−153.36 (11)
N4—C2—N3—C4	175.25 (13)	N2—S2—C11—C16	91.20 (12)
N1—C2—N3—C4	−5.3 (2)	C16—C11—C12—C13	0.3 (2)
C2—N3—C4—C5	−4.6 (2)	S2—C11—C12—C13	179.59 (11)
C2—N3—C4—S1	174.66 (10)	C11—C12—C13—C14	0.2 (2)
C7—S1—C4—N3	−0.12 (13)	C12—C13—C14—C15	−0.6 (2)
C7—S1—C4—C5	179.14 (12)	C12—C13—C14—Br1	179.51 (11)
N3—C4—C5—C6	8.4 (2)	C13—C14—C15—C16	0.4 (2)
S1—C4—C5—C6	−170.82 (10)	Br1—C14—C15—C16	−179.69 (11)

N3—C4—C5—C8	−172.98 (14)	C14—C15—C16—C11	0.1 (2)
S1—C4—C5—C8	7.81 (19)	C12—C11—C16—C15	−0.5 (2)
C2—N1—C6—O1	172.81 (12)	S2—C11—C16—C15	−179.77 (11)
N2—N1—C6—O1	1.68 (19)	C19—N6—C17—O4	174.49 (15)
C2—N1—C6—C5	−7.29 (18)	C18—N6—C17—O4	1.3 (2)
N2—N1—C6—C5	−178.42 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H01···O1^{i}	0.80 (2)	2.00 (2)	2.7784 (15)	165.5 (19)
N4—H02···O4^{ii}	0.86 (2)	1.98 (2)	2.8382 (16)	177.9 (19)
N4—H03···O4	0.85 (2)	2.07 (2)	2.8005 (16)	143.1 (18)
C12—H12···O2^{iii}	0.95	2.46	3.4096 (18)	173
C7—H7*B*···O3^{iv}	0.98	2.45	3.2848 (19)	143
C17—H17···Br1^{v}	0.95	3.05	3.6686 (15)	124

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