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2-[(4,6-Diaminopyrimidin-2-yl)sulfanyl]-*N*-(4-methoxyphenyl)acetamide

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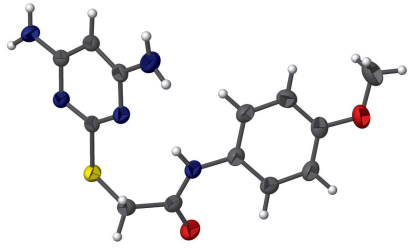
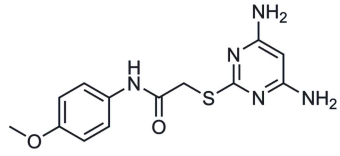
In the title compound, $C_{13}H_{15}N_5O_2S$, the acetamide N—C(=O)—C plane makes dihedral angles of 30.51 (11) and 51.93 (11)°, respectively, with the benzene ring and the pyrimidine ring. The dihedral angle between the benzene and pyrimidine rings is 43.40 (6)°. There is an intramolecular N—H···N hydrogen bond with an *S*(7) ring motif. In the crystal, molecules are linked by pairs of intermolecular N—H···N hydrogen bonds, forming inversion dimers with an $R_2^2(8)$ ring motif. The molecules are further linked by intermolecular N—H···O hydrogen bonds, forming a *C*(9) chain along [100]. Intermolecular C—H···π and N—H···π interactions are also observed.

3D view



Chemical scheme



Structure description

2,4-Diaminopyrimidine derivatives are reported to be potent antimalarial and anti-filarial agents because of their inhibition of dihydrofolate reductase (DHFR) (Neekhara *et al.*, 2006; Sharma *et al.*, 2013). Furthermore, they have also exhibited anti-retroviral activity (Hocková *et al.*, 2004), antibacterial (Kandeel *et al.*, 1994) and potential anti-microbial properties (Holla *et al.*, 2006). As part of our own studies in this area, we report herein the synthesis and crystal structure of the title compound.

The title molecule has an intramolecular N—H···N hydrogen bond with an *S*(7) ring motif (Table 1 and Fig. 1). The methyl group (C1) is oriented *syn*-periplanar to atom C7 [C7—C2—O2—C1 = 5.7 (3)°] and *anti*-periplanar to atom C3 [C3—C2—O2—C1 = −174.8 (2)°]. The pyrimidine ring makes a dihedral angle of 43.40 (6)° with the benzene ring. The acetamide N5/C8/O1/C9 plane makes dihedral angles of 30.51 (11) and 51.93 (11)°, respectively, with the benzene and pyrimidine rings. The bond lengths C10—

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

*Cg*1 and *Cg*2 are the centroids of the N3/C10/N4/C11–C13 and C2–C7 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*D*···N4^{i}	0.91 (2)	2.17 (2)	3.048 (2)	164.2 (2)
N2—H2*B*···O1^{ii}	0.87 (2)	2.08 (2)	2.922 (2)	163.1 (2)
N5—H5···N3	0.84 (2)	2.06 (2)	2.863 (2)	160.3 (2)
N2—H2*A*···*Cg*1^{iii}	0.91 (2)	2.62 (1)	3.533 (2)	156.7 (2)
C4—H4···*Cg*2^{iv}	0.93	2.76	3.623 (2)	134

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

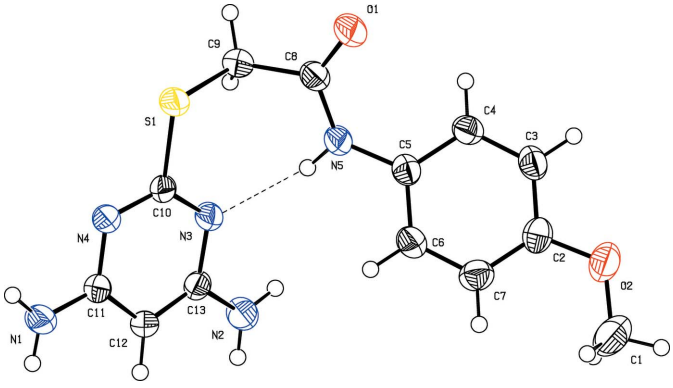


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. The N—H···N hydrogen bond is shown as thin dashed line.

S1 [1.7664 (17) Å] and C9—S1 [1.808 (2) Å] are comparable with the values reported in the literature (1.751 and 1.813 Å, respectively; Allen *et al.*, 1987).

In the crystal, the molecules are linked into inversion dimers with an $R_2^2(8)$ ring motif by pairs of N—H···N hydrogen bonds (Table 1, Fig. 2). Adjacent molecules are further linked *via* N—H···O hydrogen bonds, forming a *C*(9)

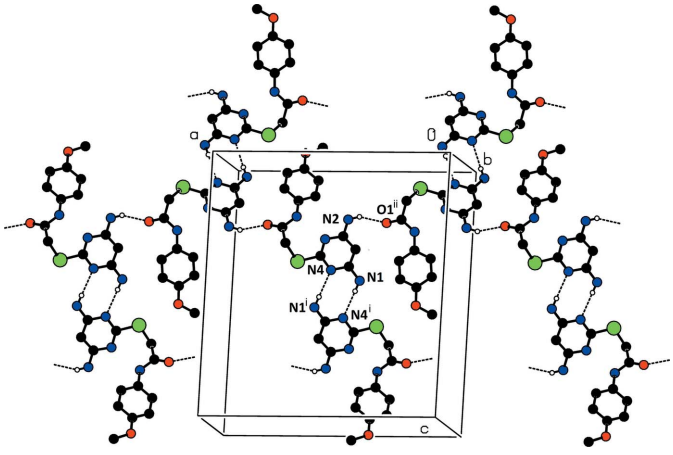


Figure 2
A packing diagram of the title compound, showing the N—H···N and N—H···O hydrogen bonds (dashed lines). Hydrogen atoms not involved in the hydrogen bonds have been omitted for clarity. [Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$.]

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{15}N_5O_2S$
M_r	305.36
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	293
a, *b*, *c* (Å)	18.2763 (6), 7.5909 (2), 20.0571 (6)
V (Å^3)	2782.59 (14)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.25
Crystal size (mm)	0.30 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker SMART APEXII area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.753, 0.823
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14130, 3471, 2119
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.042, 0.110, 1.02
No. of reflections	3471
No. of parameters	211
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.27

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2015).

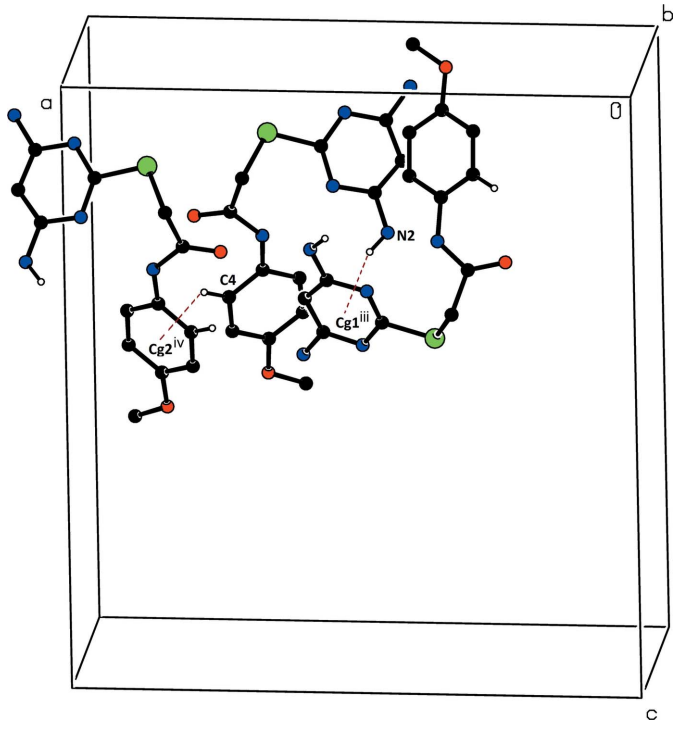


Figure 3
A packing diagram of the title compound, showing the C—H···π and N—H···π interactions (dashed lines). Hydrogen atoms not involved in these interactions have been omitted for clarity. [Symmetry codes: (iii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, y-\frac{1}{2}, z$.]

chain along [100]. The crystal packing also features C—H$\cdots\pi$ and N—H$\cdots\pi$ interactions (Table 1 and Fig. 3).

Synthesis and crystallization

To a solution of 4,6-diamino-pyrimidine-2-thiol (0.5 g, 3.52 mmol) in 25 ml of ethanol was added (0.2g, 3.52 mmol) potassium hydroxide and the mixture was refluxed for about 30 min. An equimolar quantity of 2-chloro-*N*-(4-methoxyphenyl)acetamide (3.52 mmol) was then added and reflux was continued for 4 h. Evaporation of the organic layer in a vacuum provided the title compound. After purification, single crystals were obtained from an ethanol solution by slow evaporation of the solvent.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2018). **3**, x180600 [https://doi.org/10.1107/S2414314618006004]

2-[(4,6-Diaminopyrimidin-2-yl)sulfanyl]-*N*-(4-methoxyphenyl)acetamide

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2-[(4,6-Diaminopyrimidin-2-yl)sulfanyl]-*N*-(4-methoxyphenyl)acetamide

Crystal data

$C_{13}H_{15}N_5O_2S$
M_r = 305.36
Orthorhombic, *Pbca*
a = 18.2763 (6) Å
b = 7.5909 (2) Å
c = 20.0571 (6) Å
V = 2782.59 (14) Å^3
Z = 8
F(000) = 1280
D_x = 1.458 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 3471 reflections
θ = 2.0–28.3°
μ = 0.25 mm^{-1}
T = 293 K
Block, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.753, T_{max} = 0.823
14130 measured reflections
3471 independent reflections
2119 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 28.3°, θ_{min} = 2.0°
h = −24→15
k = −10→8
l = −13→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.110
S = 1.02
3471 reflections
211 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.2859P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 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.

Refinement. The C-bound H atoms were placed in calculated positions with C—H = 0.93–0.97 Å and refined as riding with U_{iso}(H) = 1.5U_{eq}(C) for methyl group or U_{iso}(H) = 1.2U_{eq}(C) for other groups. The N-bound H atoms were located in a difference Fourier map and refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
H1D	−0.0645 (12)	0.581 (3)	0.0150 (12)	0.064 (7)*
H1E	−0.1267 (12)	0.591 (3)	0.0632 (11)	0.052 (7)*
H2A	−0.0275 (12)	0.190 (3)	0.2877 (11)	0.048 (7)*
H2B	−0.1027 (12)	0.269 (3)	0.2704 (10)	0.045 (6)*
H5	0.1243 (11)	0.295 (3)	0.2612 (9)	0.042 (6)*
C1	0.11212 (15)	0.6519 (4)	0.56365 (12)	0.0726 (8)
H1A	0.1009	0.7542	0.5375	0.109*
H1B	0.1226	0.6868	0.6086	0.109*
H1C	0.0710	0.5731	0.5634	0.109*
C2	0.16810 (11)	0.5039 (3)	0.47250 (9)	0.0387 (5)
C3	0.22722 (11)	0.4076 (3)	0.44951 (9)	0.0399 (5)
H3	0.2665	0.3864	0.4778	0.048*
C4	0.22885 (10)	0.3426 (3)	0.38539 (9)	0.0375 (5)
H4	0.2690	0.2781	0.3707	0.045*
C5	0.17026 (10)	0.3739 (3)	0.34272 (9)	0.0337 (5)
C6	0.11077 (10)	0.4671 (3)	0.36636 (10)	0.0404 (5)
H6	0.0710	0.4867	0.3383	0.049*
C7	0.10898 (11)	0.5321 (3)	0.43086 (10)	0.0425 (5)
H7	0.0684	0.5942	0.4460	0.051*
C8	0.22034 (10)	0.2696 (3)	0.23446 (9)	0.0363 (5)
C9	0.19429 (11)	0.1899 (3)	0.16929 (9)	0.0406 (5)
H9A	0.1574	0.1017	0.1791	0.049*
H9B	0.2352	0.1303	0.1482	0.049*
C10	0.06326 (9)	0.3615 (3)	0.13367 (9)	0.0299 (4)
C11	−0.04605 (9)	0.4777 (3)	0.10243 (9)	0.0325 (4)
C12	−0.07491 (10)	0.4288 (3)	0.16389 (9)	0.0349 (5)
H12	−0.1223	0.4598	0.1760	0.042*
C13	−0.03109 (10)	0.3332 (3)	0.20616 (9)	0.0325 (5)
N1	−0.08541 (11)	0.5584 (3)	0.05502 (9)	0.0468 (5)
N2	−0.05566 (11)	0.2679 (3)	0.26481 (8)	0.0457 (5)
N3	0.04068 (8)	0.3016 (2)	0.19228 (7)	0.0335 (4)
N4	0.02461 (8)	0.4414 (2)	0.08647 (7)	0.0339 (4)
N5	0.16624 (9)	0.3033 (2)	0.27763 (8)	0.0366 (4)
O1	0.28525 (7)	0.2957 (2)	0.24536 (7)	0.0565 (5)
O2	0.17327 (8)	0.5664 (2)	0.53655 (7)	0.0524 (4)
S1	0.15638 (2)	0.34642 (8)	0.11078 (2)	0.03976 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.091 (2)	0.083 (2)	0.0438 (14)	0.0218 (17)	0.0071 (13)	−0.0136 (14)
C2	0.0467 (11)	0.0393 (13)	0.0301 (10)	−0.0042 (10)	0.0000 (9)	0.0051 (9)
C3	0.0375 (11)	0.0489 (14)	0.0331 (10)	−0.0014 (10)	−0.0062 (8)	0.0058 (10)
C4	0.0302 (9)	0.0455 (13)	0.0368 (10)	0.0031 (9)	0.0001 (8)	0.0029 (10)
C5	0.0320 (10)	0.0369 (12)	0.0322 (10)	−0.0021 (9)	−0.0023 (8)	0.0037 (9)

C6	0.0361 (10)	0.0487 (14)	0.0365 (10)	0.0056 (10)	−0.0048 (8)	0.0044 (10)
C7	0.0446 (11)	0.0403 (13)	0.0425 (11)	0.0078 (10)	0.0043 (9)	0.0003 (10)
C8	0.0305 (10)	0.0429 (13)	0.0356 (10)	0.0038 (10)	−0.0027 (8)	0.0036 (9)
C9	0.0361 (10)	0.0468 (14)	0.0390 (11)	0.0108 (10)	−0.0029 (9)	−0.0053 (10)
C10	0.0272 (9)	0.0354 (12)	0.0270 (9)	−0.0013 (8)	−0.0012 (7)	−0.0045 (8)
C11	0.0310 (9)	0.0356 (12)	0.0309 (9)	0.0021 (8)	−0.0030 (8)	−0.0060 (9)
C12	0.0268 (9)	0.0479 (14)	0.0300 (10)	0.0044 (9)	0.0009 (7)	−0.0046 (9)
C13	0.0305 (9)	0.0394 (13)	0.0278 (9)	−0.0027 (9)	0.0014 (7)	−0.0060 (9)
N1	0.0378 (10)	0.0685 (15)	0.0341 (10)	0.0194 (10)	0.0001 (8)	0.0072 (10)
N2	0.0324 (10)	0.0698 (15)	0.0349 (10)	−0.0007 (10)	0.0029 (8)	0.0128 (10)
N3	0.0267 (8)	0.0445 (11)	0.0292 (8)	−0.0003 (8)	−0.0001 (6)	0.0015 (7)
N4	0.0293 (8)	0.0437 (11)	0.0286 (8)	0.0028 (8)	0.0006 (6)	0.0013 (8)
N5	0.0261 (8)	0.0518 (12)	0.0319 (8)	−0.0013 (8)	−0.0032 (7)	−0.0015 (8)
O1	0.0273 (7)	0.0955 (13)	0.0466 (8)	−0.0007 (8)	−0.0033 (6)	−0.0068 (9)
O2	0.0659 (10)	0.0570 (11)	0.0343 (7)	0.0039 (9)	−0.0024 (7)	−0.0048 (7)
S1	0.0274 (2)	0.0607 (4)	0.0311 (3)	0.0034 (2)	0.00268 (19)	0.0036 (2)

Geometric parameters (Å, º)

C1—O2	1.402 (3)	C9—S1	1.808 (2)
C1—H1A	0.9600	C9—H9A	0.9700
C1—H1B	0.9600	C9—H9B	0.9700
C1—H1C	0.9600	C10—N3	1.326 (2)
C2—O2	1.373 (2)	C10—N4	1.328 (2)
C2—C7	1.382 (3)	C10—S1	1.7664 (17)
C2—C3	1.384 (3)	C11—N1	1.341 (2)
C3—C4	1.378 (3)	C11—N4	1.359 (2)
C3—H3	0.9300	C11—C12	1.391 (2)
C4—C5	1.391 (2)	C12—C13	1.373 (3)
C4—H4	0.9300	C12—H12	0.9300
C5—C6	1.381 (3)	C13—N2	1.353 (2)
C5—N5	1.413 (2)	C13—N3	1.362 (2)
C6—C7	1.385 (3)	N1—H1D	0.91 (2)
C6—H6	0.9300	N1—H1E	0.81 (2)
C7—H7	0.9300	N2—H2A	0.91 (2)
C8—O1	1.222 (2)	N2—H2B	0.87 (2)
C8—N5	1.339 (2)	N5—H5	0.84 (2)
C8—C9	1.517 (3)		
O2—C1—H1A	109.5	S1—C9—H9A	108.6
O2—C1—H1B	109.5	C8—C9—H9B	108.6
H1A—C1—H1B	109.5	S1—C9—H9B	108.6
O2—C1—H1C	109.5	H9A—C9—H9B	107.6
H1A—C1—H1C	109.5	N3—C10—N4	128.54 (16)
H1B—C1—H1C	109.5	N3—C10—S1	120.52 (13)
O2—C2—C7	124.45 (19)	N4—C10—S1	110.91 (13)
O2—C2—C3	116.15 (17)	N1—C11—N4	115.81 (17)
C7—C2—C3	119.40 (18)	N1—C11—C12	123.17 (17)

C4—C3—C2	121.13 (18)	N4—C11—C12	121.00 (16)
C4—C3—H3	119.4	C13—C12—C11	117.83 (17)
C2—C3—H3	119.4	C13—C12—H12	121.1
C3—C4—C5	119.78 (18)	C11—C12—H12	121.1
C3—C4—H4	120.1	N2—C13—N3	115.64 (17)
C5—C4—H4	120.1	N2—C13—C12	122.45 (17)
C6—C5—C4	118.82 (18)	N3—C13—C12	121.89 (16)
C6—C5—N5	118.06 (16)	C11—N1—H1D	119.2 (15)
C4—C5—N5	122.95 (18)	C11—N1—H1E	119.7 (16)
C5—C6—C7	121.46 (18)	H1D—N1—H1E	121 (2)
C5—C6—H6	119.3	C13—N2—H2A	119.3 (14)
C7—C6—H6	119.3	C13—N2—H2B	116.0 (14)
C2—C7—C6	119.38 (19)	H2A—N2—H2B	120 (2)
C2—C7—H7	120.3	C10—N3—C13	114.85 (15)
C6—C7—H7	120.3	C10—N4—C11	115.47 (15)
O1—C8—N5	124.76 (19)	C8—N5—C5	129.15 (17)
O1—C8—C9	121.55 (17)	C8—N5—H5	114.1 (13)
N5—C8—C9	113.67 (16)	C5—N5—H5	116.1 (14)
C8—C9—S1	114.65 (15)	C2—O2—C1	117.90 (17)
C8—C9—H9A	108.6	C10—S1—C9	104.07 (9)

O2—C2—C3—C4	−178.18 (19)	S1—C10—N3—C13	175.11 (14)
C7—C2—C3—C4	1.4 (3)	N2—C13—N3—C10	177.94 (18)
C2—C3—C4—C5	0.0 (3)	C12—C13—N3—C10	−3.5 (3)
C3—C4—C5—C6	−1.3 (3)	N3—C10—N4—C11	5.3 (3)
C3—C4—C5—N5	−176.38 (19)	S1—C10—N4—C11	−172.79 (14)
C4—C5—C6—C7	1.1 (3)	N1—C11—N4—C10	179.97 (18)
N5—C5—C6—C7	176.5 (2)	C12—C11—N4—C10	−1.5 (3)
O2—C2—C7—C6	178.01 (19)	O1—C8—N5—C5	0.2 (4)
C3—C2—C7—C6	−1.5 (3)	C9—C8—N5—C5	178.83 (19)
C5—C6—C7—C2	0.3 (3)	C6—C5—N5—C8	152.0 (2)
O1—C8—C9—S1	−102.2 (2)	C4—C5—N5—C8	−32.9 (3)
N5—C8—C9—S1	79.2 (2)	C7—C2—O2—C1	5.7 (3)
N1—C11—C12—C13	174.4 (2)	C3—C2—O2—C1	−174.8 (2)
N4—C11—C12—C13	−4.0 (3)	N3—C10—S1—C9	15.55 (19)
C11—C12—C13—N2	−174.90 (19)	N4—C10—S1—C9	−166.19 (14)
C11—C12—C13—N3	6.7 (3)	C8—C9—S1—C10	−86.82 (15)
N4—C10—N3—C13	−2.8 (3)		

Hydrogen-bond geometry (Å, º)

*Cg*1 and *Cg*2 are the centroids of the N3/C10/N4/C11–C13 and C2–C7 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*D*···N4^{i}	0.91 (2)	2.17 (2)	3.048 (2)	164.2 (2)
N2—H2*B*···O1^{ii}	0.87 (2)	2.08 (2)	2.922 (2)	163.1 (2)
N5—H5···N3	0.84 (2)	2.06 (2)	2.863 (2)	160.3 (2)

N2—H2*A*···*Cg*1[iii]	0.91 (2)	2.62 (1)	3.533 (2)	156.7 (2)
C4—H4···*Cg*2[iv]	0.93	2.76	3.623 (2)	134

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