IUCrData

ISSN 2414-3146

4-(Prop-2-yn-1-ylsulfanyl)-1*H*-pyrazolo[3,4-*d*]-pyrimidine

Mohamed El Hafi,[a]* Mohammed Boulhaoua,[a] Youssef Ramli,[b] Mohammed Benchidmi,[a] El Mokhtar Essassi[a] and Joel T. Mague[c]

[a]Laboratoire de Chimie Organique Hétérocyclique, Centre de Recherche Des Sciences des Médicaments, Pôle de Compétence Pharmacochimie, Av Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco, [b]Laboratory of Medicinal Chemistry, Faculty of Medicine and Pharmacy, Mohammed V University, Rabat, Morocco, and [c]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. *Correspondence e-mail: elhafi.mohamed1@gmail.com

Received 24 August 2017
Accepted 19 October 2017

Edited by S. Bernès, Benemérita Universidad Autónoma de Puebla, México

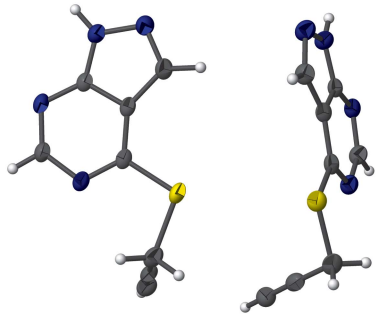
Keywords: crystal structure; hydrogen bond; π-stacking; pyrimidine.

CCDC reference: 1581006

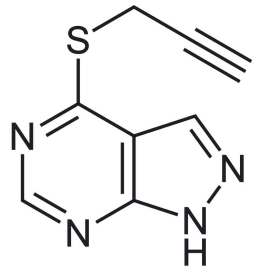
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $C_8H_6N_4S$, consists of two independent molecules differing in the orientation of the side chain. In the crystal, molecules form dimers through N—H···N hydrogen bonds. The dimers stack along the *a*-axis direction with weak π–π stacking interactions [centroid–centroid distances of 3.898 (2) and 3.908 (2) Å]. The crystal studied was refined as a two-component twin.

3D view



Chemical scheme



Structure description

As a continuation of our research work devoted to the development of S-substituted pyrazolo[3,4-*d*]pyrimidine derivatives (El Fal *et al.*, 2014), we have studied the action of propargyl bromide towards 1*H*-pyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione, using ethanol as solvent and potassium hydroxide as base. The title compound was isolated and its structure was established.

The asymmetric unit of the title compound consists of two independent molecules differing to a small extent in the orientation of the side chain with respect to the bicyclic core (Fig. 1). Thus, the dihedral angle between the mean plane of the N1–N4/C1–C5 unit and that defined by S1/C6–C8 is 79.3 (2)°, while the corresponding angle in the second molecule is 76.4 (2)°. The bicyclic cores are planar with the maximum deviation from the mean plane being 0.016 (3) Å (C5) in the first molecule (r.m.s. deviation = 0.0094 Å) and −0.015 (3) Å (C13) in the second (r.m.s. deviation = 0.0086 Å). The dihedral angle between the bicyclic units is 76.42 (7)°.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N2^{i}	0.90 (6)	2.10 (6)	2.972 (4)	165 (5)
N7—H7···N6^{ii}	0.81 (6)	2.18 (6)	2.965 (5)	163 (5)

Symmetry codes: (i) $-x+3, -y, -z+1$; (ii) $-x+2, -y, -z$.

In the crystal, each independent molecule forms a dimer with an inversion-related counterpart through pairwise N—H···N hydrogen bonds (Table 1). The dimers stack along the *a*-axis direction with the aid of head-to-tail π–π-stacking interactions (Fig. 2). For the molecules containing S1, the centroid–centroid distance is 3.898 (2) Å, while for those containing S2, the distance is 3.908 (2) Å. In both instances, the dihedral angle between the associated planes is 1.2 (2)°.

Synthesis and crystallization

To a solution of 1*H*-pyrazolo[3,4-*d*]pyrimidine-4-thione (0.5 g, 3.3 mmol) in EtOH (15 ml) was added propargyl bromide (0.25 ml, 3.3 mmol) and potassium hydroxide (0.19 g, 3.3 mmol). The mixture was refluxed for 8 h, and after cooling, the reaction mixture was poured slowly into an ice bath under stirring to homogenize the whole. The solid product was precipitated and filtered. The residue was purified by recrystallization from ethanol to afford the title compound as colourless crystals (65% yield; m.p. 398–400 K).

Refinement

Crystal data, data collection and structure refinement details are summarize in Table 2. The studied crystal was found to be twinned by a 180° rotation about the *b** axis, and the model was refined as a two-component twin using *CELL_NOW* (Sheldrick, 2008*b*).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_6N_4S$
M_r	190.23
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	4.8851 (1), 9.8472 (3), 17.4428 (5)
α, β, γ (°)	86.380 (1), 89.606 (1), 81.027 (1)
V (Å^3)	827.15 (4)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.09
Crystal size (mm)	0.29 × 0.09 × 0.03
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.46, 0.91
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11085, 11079, 9249
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.163, 1.09
No. of reflections	11079
No. of parameters	284
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, −0.31

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008*a*).

Acknowledgements

The support of NSF–MRI Grant No. 1228232 for the purchase of the diffractometer and Tulane University for support of the Tulane Crystallography Laboratory are gratefully acknowledged.

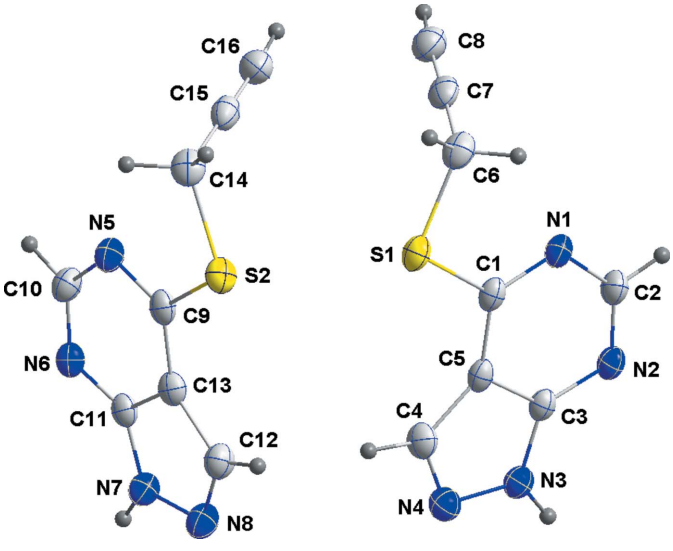


Figure 1
The asymmetric unit with the atom-labelling scheme and 50% probability ellipsoids for non-H atoms

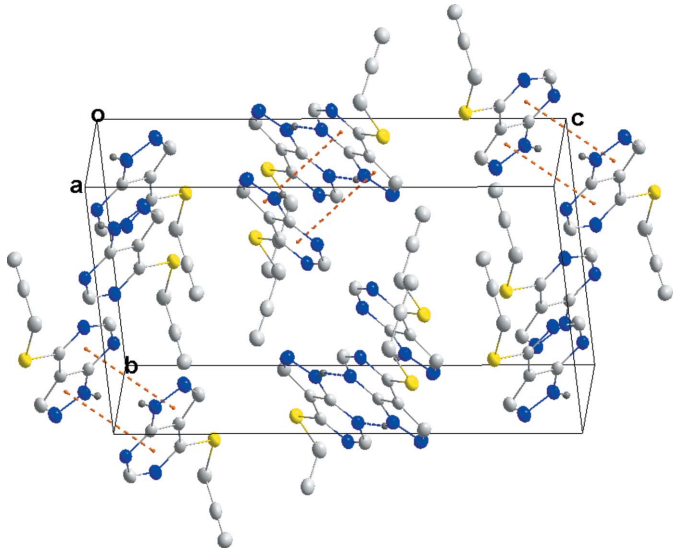


Figure 2
Oblique view of the packing with N—H···N hydrogen bonds and π–π-stacking interactions shown, respectively, as blue and orange dashed lines.

References

Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2016). *APEX3*, *SAINT* and *TWINABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

El Fal, M., Ramli, Y., Essassi, E. M., Saadi, M. & El Ammari, L. (2014). *Acta Cryst.* E**70**, o1038.

Sheldrick, G. M. (2008*a*). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2008*b*). *CELL_NOW*. University of Göttingen, Göttingen, Germany.

Sheldrick, G. M. (2009). *TWINABS*. University of Göttingen, Göttingen, Germany.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2017). **2**, x171526 [https://doi.org/10.1107/S2414314617015267]

4-(Prop-2-yn-1-ylsulfanyl)-1*H*-pyrazolo[3,4-*d*]pyrimidine

Mohamed El Hafi, Mohammed Boulhaoua, Youssef Ramli, Mohammed Benchidmi, El Mokhtar Essassi and Joel T. Mague

4-(Prop-2-yn-1-ylsulfanyl)-1*H*-pyrazolo[3,4-*d*]pyrimidine

Crystal data

$C_8H_6N_4S$
M_r = 190.23
Triclinic, $P\overline{1}$
a = 4.8851 (1) Å
b = 9.8472 (3) Å
c = 17.4428 (5) Å
α = 86.380 (1)°
β = 89.606 (1)°
γ = 81.027 (1)°
V = 827.15 (4) Å^3
Z = 4
$F(000)$ = 392
D_x = 1.528 Mg m^{-3}
Melting point: 398 K
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 7441 reflections
θ = 5.1–72.4°
μ = 3.09 mm^{-1}
T = 150 K
Plate, colourless
0.29 × 0.09 × 0.03 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min} = 0.46, T_{max} = 0.91
11085 measured reflections
11079 independent reflections
9249 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 72.4°, θ_{min} = 2.5°
h = −6→6
k = −12→11
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.163
S = 1.09
11079 reflections
284 parameters
0 restraints
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 0.6596P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Special details

Experimental. Analysis of 887 reflections having I/σ(I) > 12 and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008) showed the crystal to belong to the triclinic system and to be twinned by a 180° rotation about the *b** axis. The raw data were processed using the multi-component version of*SAINT* under control of the two-component orientation file generated by *CELL_NOW*.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.5206 (2)	0.33776 (10)	0.33099 (5)	0.0286 (3)
N1	0.8655 (7)	0.3466 (3)	0.44900 (18)	0.0270 (7)
N2	1.2403 (7)	0.1661 (3)	0.49127 (18)	0.0263 (7)
N3	1.2790 (7)	−0.0317 (3)	0.41350 (19)	0.0272 (7)
H3	1.421 (13)	−0.086 (6)	0.438 (3)	0.054 (16)*
N4	1.1421 (7)	−0.0703 (4)	0.3524 (2)	0.0304 (8)
C1	0.7945 (8)	0.2734 (4)	0.3936 (2)	0.0233 (8)
C2	1.0831 (8)	0.2892 (4)	0.4948 (2)	0.0274 (9)
H2	1.127 (9)	0.343 (4)	0.534 (3)	0.026 (11)*
C3	1.1622 (8)	0.0951 (4)	0.4342 (2)	0.0223 (8)
C4	0.9406 (8)	0.0320 (4)	0.3344 (2)	0.0294 (9)
H4	0.814 (11)	0.013 (5)	0.291 (3)	0.046 (14)*
C5	0.9395 (8)	0.1406 (4)	0.3835 (2)	0.0230 (8)
C6	0.4067 (9)	0.5068 (4)	0.3667 (2)	0.0315 (9)
H6A	0.398 (9)	0.498 (4)	0.423 (3)	0.027 (11)*
H6B	0.212 (11)	0.525 (5)	0.347 (3)	0.042 (13)*
C7	0.5835 (9)	0.6066 (4)	0.3404 (2)	0.0308 (9)
C8	0.7249 (10)	0.6887 (5)	0.3172 (3)	0.0363 (10)
H8	0.851 (11)	0.744 (5)	0.304 (3)	0.039 (14)*
S2	0.0250 (2)	0.29312 (10)	0.17167 (5)	0.0281 (3)
N5	0.3598 (7)	0.3327 (3)	0.05226 (18)	0.0287 (7)
N6	0.7361 (7)	0.1642 (3)	0.00878 (18)	0.0265 (7)
N7	0.7867 (7)	−0.0506 (4)	0.08603 (19)	0.0272 (7)
H7	0.910 (12)	−0.098 (5)	0.064 (3)	0.044 (15)*
N8	0.6605 (7)	−0.1054 (4)	0.1483 (2)	0.0321 (8)
C9	0.2964 (8)	0.2445 (4)	0.1088 (2)	0.0249 (8)
C10	0.5752 (8)	0.2867 (4)	0.0059 (2)	0.0289 (9)
H10	0.620 (9)	0.355 (4)	−0.034 (3)	0.027 (11)*
C11	0.6642 (8)	0.0790 (4)	0.0663 (2)	0.0237 (8)
C12	0.4571 (9)	−0.0095 (4)	0.1677 (2)	0.0294 (9)
H12	0.336 (11)	−0.019 (5)	0.209 (3)	0.038 (13)*
C13	0.4474 (8)	0.1111 (4)	0.1182 (2)	0.0238 (8)
C14	−0.0920 (9)	0.4710 (5)	0.1372 (3)	0.0310 (9)
H14A	−0.112 (12)	0.476 (5)	0.080 (3)	0.051 (15)*
H14B	−0.260 (11)	0.490 (5)	0.160 (3)	0.039 (13)*
C15	0.0894 (9)	0.5647 (4)	0.1597 (2)	0.0313 (9)
C16	0.2341 (10)	0.6432 (5)	0.1784 (3)	0.0357 (10)
H16	0.356 (13)	0.705 (6)	0.189 (4)	0.060 (17)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0232 (5)	0.0360 (6)	0.0253 (5)	−0.0025 (4)	−0.0072 (3)	0.0030 (4)
N1	0.0268 (17)	0.0316 (17)	0.0214 (16)	−0.0022 (14)	−0.0024 (12)	0.0023 (13)
N2	0.0234 (17)	0.0315 (18)	0.0235 (16)	−0.0043 (14)	−0.0059 (12)	0.0021 (13)
N3	0.0244 (17)	0.0297 (18)	0.0267 (17)	−0.0026 (15)	−0.0030 (13)	0.0011 (14)
N4	0.0275 (18)	0.0326 (18)	0.0310 (18)	−0.0032 (15)	−0.0040 (14)	−0.0034 (14)
C1	0.0187 (18)	0.031 (2)	0.0200 (18)	−0.0064 (16)	−0.0005 (13)	0.0033 (15)
C2	0.026 (2)	0.033 (2)	0.0231 (19)	−0.0034 (17)	−0.0054 (15)	−0.0001 (16)
C3	0.0193 (18)	0.0276 (19)	0.0202 (17)	−0.0059 (16)	−0.0001 (13)	0.0025 (15)
C4	0.025 (2)	0.036 (2)	0.028 (2)	−0.0055 (18)	−0.0035 (15)	−0.0031 (17)
C5	0.0206 (19)	0.0297 (19)	0.0189 (18)	−0.0066 (16)	−0.0008 (13)	0.0031 (14)
C6	0.022 (2)	0.039 (2)	0.030 (2)	0.0018 (18)	−0.0016 (15)	0.0022 (18)
C7	0.030 (2)	0.032 (2)	0.027 (2)	0.0064 (19)	−0.0069 (16)	0.0002 (17)
C8	0.038 (3)	0.035 (2)	0.034 (2)	−0.001 (2)	−0.0024 (18)	0.0028 (19)
S2	0.0228 (5)	0.0348 (5)	0.0265 (5)	−0.0032 (4)	0.0031 (3)	−0.0024 (4)
N5	0.0277 (18)	0.0336 (18)	0.0238 (16)	−0.0024 (15)	0.0009 (13)	0.0002 (14)
N6	0.0227 (17)	0.0336 (18)	0.0236 (16)	−0.0058 (14)	0.0002 (12)	−0.0021 (13)
N7	0.0226 (17)	0.0315 (18)	0.0263 (17)	−0.0009 (15)	0.0033 (13)	0.0002 (14)
N8	0.0298 (19)	0.0361 (19)	0.0286 (18)	−0.0011 (16)	0.0017 (13)	0.0023 (14)
C9	0.0211 (19)	0.034 (2)	0.0209 (18)	−0.0072 (16)	−0.0016 (14)	−0.0046 (15)
C10	0.028 (2)	0.033 (2)	0.025 (2)	−0.0047 (18)	0.0021 (15)	0.0029 (17)
C11	0.0201 (18)	0.031 (2)	0.0213 (18)	−0.0057 (16)	−0.0013 (14)	−0.0047 (15)
C12	0.027 (2)	0.035 (2)	0.026 (2)	−0.0049 (18)	0.0033 (16)	−0.0009 (17)
C13	0.0183 (18)	0.031 (2)	0.0233 (18)	−0.0063 (16)	−0.0008 (14)	−0.0037 (15)
C14	0.019 (2)	0.040 (2)	0.032 (2)	0.0006 (18)	0.0009 (16)	−0.0032 (18)
C15	0.033 (2)	0.034 (2)	0.0223 (19)	0.0065 (19)	0.0027 (15)	−0.0002 (16)
C16	0.041 (3)	0.032 (2)	0.033 (2)	−0.003 (2)	−0.0040 (19)	−0.0017 (18)

Geometric parameters (Å, º)

S1—C1	1.747 (4)	S2—C9	1.743 (4)
S1—C6	1.818 (4)	S2—C14	1.821 (4)
N1—C1	1.322 (5)	N5—C9	1.339 (5)
N1—C2	1.362 (5)	N5—C10	1.361 (5)
N2—C2	1.334 (5)	N6—C10	1.331 (5)
N2—C3	1.343 (5)	N6—C11	1.348 (5)
N3—C3	1.359 (5)	N7—C11	1.347 (5)
N3—N4	1.366 (5)	N7—N8	1.368 (5)
N3—H3	0.90 (6)	N7—H7	0.81 (6)
N4—C4	1.318 (5)	N8—C12	1.317 (6)
C1—C5	1.407 (5)	C9—C13	1.403 (5)
C2—H2	0.95 (5)	C10—H10	0.98 (5)
C3—C5	1.406 (5)	C11—C13	1.399 (5)
C4—C5	1.411 (6)	C12—C13	1.418 (6)
C4—H4	1.03 (6)	C12—H12	0.93 (6)
C6—C7	1.457 (6)	C14—C15	1.448 (6)

C6—H6A	0.98 (5)	C14—H14A	1.00 (6)
C6—H6B	1.00 (5)	C14—H14B	0.91 (5)
C7—C8	1.194 (7)	C15—C16	1.187 (7)
C8—H8	0.90 (5)	C16—H16	0.94 (6)

C1—S1—C6	101.40 (19)	C9—S2—C14	101.5 (2)
C1—N1—C2	117.5 (3)	C9—N5—C10	116.9 (3)
C2—N2—C3	112.2 (3)	C10—N6—C11	112.1 (3)
C3—N3—N4	110.9 (3)	C11—N7—N8	111.3 (3)
C3—N3—H3	125 (4)	C11—N7—H7	128 (4)
N4—N3—H3	124 (4)	N8—N7—H7	120 (4)
C4—N4—N3	106.5 (3)	C12—N8—N7	106.3 (3)
N1—C1—C5	120.4 (3)	N5—C9—C13	120.4 (4)
N1—C1—S1	121.3 (3)	N5—C9—S2	120.7 (3)
C5—C1—S1	118.2 (3)	C13—C9—S2	118.9 (3)
N2—C2—N1	128.4 (4)	N6—C10—N5	128.8 (4)
N2—C2—H2	116 (3)	N6—C10—H10	116 (3)
N1—C2—H2	116 (3)	N5—C10—H10	115 (3)
N2—C3—N3	127.8 (3)	N7—C11—N6	127.4 (4)
N2—C3—C5	125.4 (3)	N7—C11—C13	107.0 (3)
N3—C3—C5	106.8 (3)	N6—C11—C13	125.6 (4)
N4—C4—C5	111.3 (3)	N8—C12—C13	110.9 (4)
N4—C4—H4	114 (3)	N8—C12—H12	125 (3)
C5—C4—H4	134 (3)	C13—C12—H12	124 (3)
C3—C5—C1	115.9 (3)	C11—C13—C9	116.1 (3)
C3—C5—C4	104.4 (3)	C11—C13—C12	104.5 (3)
C1—C5—C4	139.6 (3)	C9—C13—C12	139.4 (4)
C7—C6—S1	112.2 (3)	C15—C14—S2	113.1 (3)
C7—C6—H6A	112 (3)	C15—C14—H14A	110 (3)
S1—C6—H6A	109 (2)	S2—C14—H14A	109 (3)
C7—C6—H6B	116 (3)	C15—C14—H14B	111 (3)
S1—C6—H6B	100 (3)	S2—C14—H14B	103 (3)
H6A—C6—H6B	108 (4)	H14A—C14—H14B	110 (4)
C8—C7—C6	178.5 (4)	C16—C15—C14	178.8 (5)
C7—C8—H8	172 (3)	C15—C16—H16	175 (4)

C3—N3—N4—C4	0.2 (4)	C11—N7—N8—C12	0.1 (4)
C2—N1—C1—C5	0.5 (6)	C10—N5—C9—C13	−0.4 (5)
C2—N1—C1—S1	−179.4 (3)	C10—N5—C9—S2	179.8 (3)
C6—S1—C1—N1	0.1 (4)	C14—S2—C9—N5	−1.6 (3)
C6—S1—C1—C5	−179.8 (3)	C14—S2—C9—C13	178.6 (3)
C3—N2—C2—N1	−0.2 (6)	C11—N6—C10—N5	0.4 (6)
C1—N1—C2—N2	0.4 (6)	C9—N5—C10—N6	−0.2 (6)
C2—N2—C3—N3	178.8 (4)	N8—N7—C11—N6	179.0 (3)
C2—N2—C3—C5	−0.9 (5)	N8—N7—C11—C13	0.1 (4)
N4—N3—C3—N2	−180.0 (4)	C10—N6—C11—N7	−178.7 (4)
N4—N3—C3—C5	−0.3 (4)	C10—N6—C11—C13	0.1 (5)
N3—N4—C4—C5	−0.1 (5)	N7—N8—C12—C13	−0.3 (4)

N2—C3—C5—C1	1.7 (6)	N7—C11—C13—C9	178.3 (3)
N3—C3—C5—C1	−178.0 (3)	N6—C11—C13—C9	−0.7 (5)
N2—C3—C5—C4	179.9 (4)	N7—C11—C13—C12	−0.3 (4)
N3—C3—C5—C4	0.2 (4)	N6—C11—C13—C12	−179.2 (3)
N1—C1—C5—C3	−1.4 (5)	N5—C9—C13—C11	0.8 (5)
S1—C1—C5—C3	178.5 (3)	S2—C9—C13—C11	−179.4 (3)
N1—C1—C5—C4	−178.7 (5)	N5—C9—C13—C12	178.7 (4)
S1—C1—C5—C4	1.1 (7)	S2—C9—C13—C12	−1.5 (6)
N4—C4—C5—C3	−0.1 (5)	N8—C12—C13—C11	0.4 (4)
N4—C4—C5—C1	177.5 (5)	N8—C12—C13—C9	−177.7 (4)
C1—S1—C6—C7	79.3 (3)	C9—S2—C14—C15	−76.1 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···N2^{i}	0.90 (6)	2.10 (6)	2.972 (4)	165 (5)
N7—H7···N6^{ii}	0.81 (6)	2.18 (6)	2.965 (5)	163 (5)

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