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Crystal structure of 4-amino-3-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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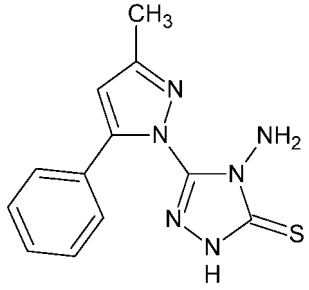
In the title compound, $C_{12}H_{12}N_6S$, the dihedral angles between the central pyrazole ring and the pendant triazole and benzene rings are 68.01 (4) and 59.83 (9)°, respectively. In the crystal, molecules are linked by N—H···N and N—H···S hydrogen bonds, generating $(10\bar{1})$ sheets.

Keywords: crystal structure; aminotriazoles; hydrogen bonding.

CCDC reference: 1401505

1. Related literature

For the bio-activities of aminotriazoles, see: Jin *et al.* (2007); Joung *et al.* (2000). For aminotriazoles as block-building synthons, see: Curtis (2004).



2. Experimental

2.1. Crystal data

$C_{12}H_{12}N_6S$ M_r = 272.34

Monoclinic, $P2_1/n$
a = 11.3278 (4) Å
b = 8.3970 (3) Å
c = 15.4427 (5) Å
β = 109.053 (1)°
V = 1388.43 (8) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 2.04 mm^{-1}
T = 150 K
0.24 × 0.18 × 0.10 mm

2.2. Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.77, T_{max} = 0.82
10355 measured reflections
2683 independent reflections
2515 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.102
S = 1.09
2683 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N1^{i}	0.91	1.94	2.8429 (17)	169
N6—H6A···S1^{ii}	0.91	2.55	3.4157 (13)	159
N6—H6B···N4^{iii}	0.91	2.43	3.0059 (18)	122

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

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7427).

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supporting information

Acta Cryst. (2015). E**71**, o417 [doi:10.1107/S205698901500938X]

Crystal structure of 4-amino-3-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione

Joel T. Mague, Shaaban K. Mohamed, Mehmet Akkurt and Mustafa R. Albayati

S1. Comment

Amino-1,2,4-triazoles are known to be biologically active compounds (Jin *et al*., 2007). For example, the 5-amino-1,2,4-triazole itself has been used as the pesticide Amitrole (Joung *et al.*, 2000) and 3,5-diamino-1,2,4-triazole (Guanazole) is an antitumor drug that inhibits ribonucleotide reductase and DNA synthesis. In addition, they play an important role as amidine type synthons in heterocyclic chemistry (Curtis, 2004) particularly fused ring systems, such as imidazo[1,2-*b*][1,2,4]triazole, imidazo[2,1-*c*][1,2,4]triazole, 1,2,4-triazolo[1,5-*a*]pyrimidine and 1,2,4-traizolo[1,5-*a*][1,3,5]triazine possessing variety of biological effects. In this context, we report in this study the synthesis and crystal structure of the title compound.

In the title compound (Fig. 1), the dihedral angle between the central 5-membered ring and its attached phenyl ring is 59.83 (5)° while the dihedral angle between the two 5-membered rings is 68.01 (4)°. In the crystal, the molecules form sheets lying parallel to $(10\bar{1})$ through N—H···N and N—H···S hydrogen bonds (Fig. 2 and Table 1).

S2. Experimental

A mixture of 1 mmol (258 mg) of 5-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)-1,3,4-oxadiazole-2(3*H*)-thione and 2 ml of hydrazine in 30 ml ethanol was heated at 351 K for 6 h. On cooling, the solid product was filtered off, dried under vacuum and recrystallized from ethanol to afford colorless blocks of the title compound.

S3. Refinement

H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å) while those attached to nitrogen were placed in locations derived from a difference map and their parameters adjusted to give N—H = 0.91 Å. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

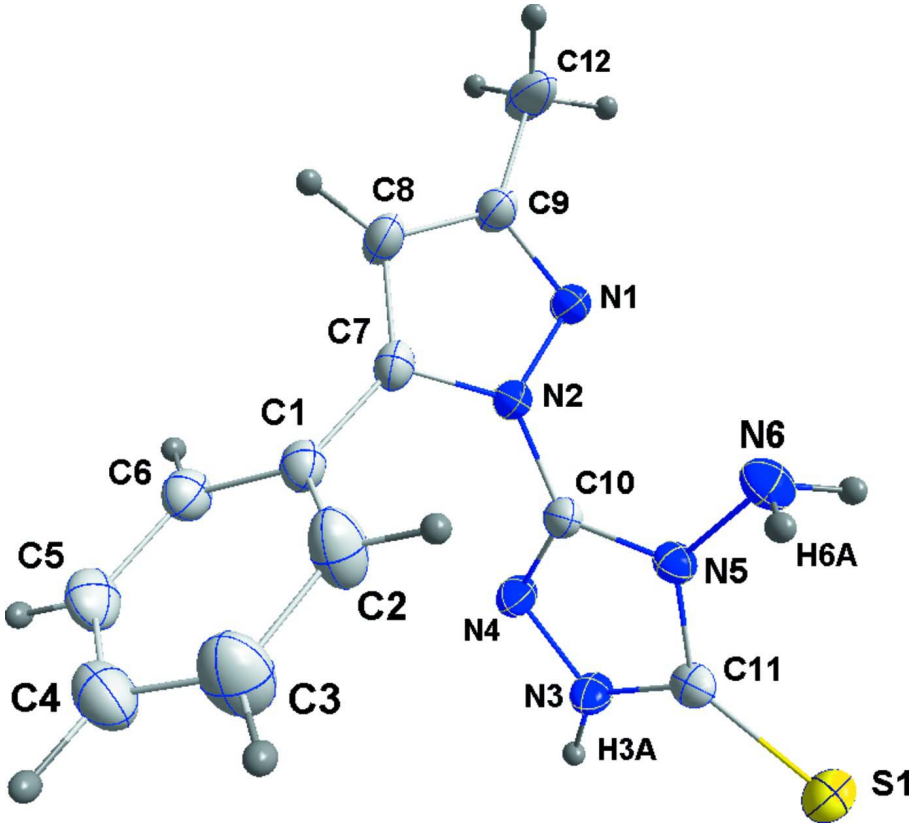

Figure 1

The title molecule showing labeling scheme and 50% probability ellipsoids.

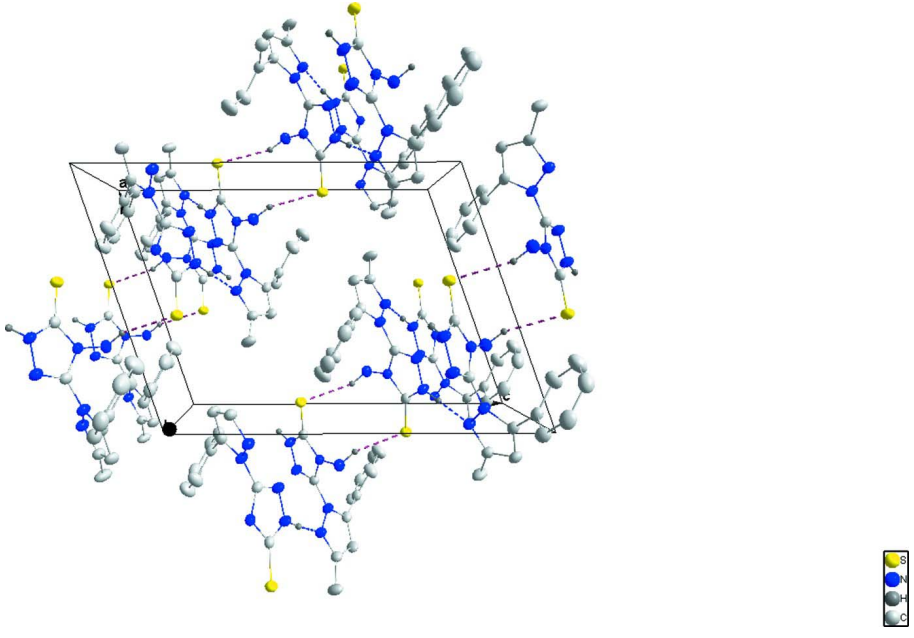

Figure 2

Packing viewed down the *b* axis. N—H···N and N—H···S hydrogen bonds are shown, respectively, as blue and purple dotted lines.

4-Amino-3-(3-methyl-5-phenyl-1*H*-pyrazol-1-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione

Crystal data

$C_{12}H_{12}N_6S$
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$b = 8.3970$ (3) Å
$c = 15.4427$ (5) Å
$\beta = 109.053$ (1)°
$V = 1388.43$ (8) Å^3
$Z = 4$
$F(000) = 568$
$D_x = 1.303$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 8668 reflections
$\theta = 4.3$–$72.3°$
$\mu = 2.04$ mm^{-1}
$T = 150$ K
Block, colourless
0.24 × 0.18 × 0.10 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 (*SADABS*; Bruker, 2014)
$T_{min} = 0.77$, $T_{max} = 0.82$
10355 measured reflections
2683 independent reflections
2515 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 72.3°$, $\theta_{min} = 4.2°$
$h = -13 \rightarrow 13$
$k = -9 \rightarrow 10$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 1.09$
2683 reflections
173 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.5187P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å) while those attached to nitrogen were placed in locations derived from a difference map and their parameters adjusted to give N—H = 0.91 Å. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	1.06212 (3)	0.49379 (4)	0.36297 (2)	0.02864 (14)
N1	0.52909 (11)	0.54447 (14)	0.29113 (8)	0.0249 (3)
N2	0.60148 (11)	0.41615 (13)	0.33081 (8)	0.0235 (3)
N3	0.86566 (11)	0.29657 (15)	0.28254 (8)	0.0263 (3)
H3A	0.9039	0.2256	0.2559	0.032*
N4	0.74091 (11)	0.27516 (15)	0.27154 (9)	0.0273 (3)
N5	0.81912 (11)	0.48358 (13)	0.35855 (8)	0.0205 (3)
N6	0.81859 (11)	0.61690 (14)	0.41236 (8)	0.0262 (3)
H6A	0.8704	0.5948	0.4699	0.031*
H6B	0.8512	0.6973	0.3878	0.031*
C1	0.60875 (14)	0.17810 (17)	0.42641 (9)	0.0251 (3)
C2	0.72215 (17)	0.1972 (2)	0.49645 (11)	0.0399 (4)
H2	0.7559	0.3009	0.5120	0.048*
C3	0.78631 (19)	0.0666 (2)	0.54370 (13)	0.0469 (5)
H3	0.8636	0.0807	0.5914	0.056*
C4	0.73738 (18)	−0.0845 (2)	0.52122 (12)	0.0392 (4)
H4	0.7808	−0.1744	0.5538	0.047*
C5	0.62567 (16)	−0.10472 (18)	0.45161 (11)	0.0344 (4)
H5	0.5927	−0.2088	0.4362	0.041*
C6	0.56078 (15)	0.02533 (18)	0.40384 (11)	0.0292 (3)
H6	0.4839	0.0102	0.3559	0.035*
C7	0.54349 (13)	0.31865 (17)	0.37531 (9)	0.0239 (3)
C8	0.43020 (14)	0.38690 (19)	0.36366 (10)	0.0287 (3)
H8	0.3670	0.3482	0.3862	0.034*
C9	0.42509 (14)	0.52643 (18)	0.31143 (10)	0.0262 (3)
C10	0.71675 (13)	0.39120 (16)	0.31857 (9)	0.0218 (3)
C11	0.91672 (13)	0.42285 (16)	0.33429 (9)	0.0222 (3)
C12	0.32313 (15)	0.6470 (2)	0.28071 (13)	0.0386 (4)
H12A	0.3481	0.7316	0.2466	0.058*
H12B	0.3074	0.6928	0.3343	0.058*
H12C	0.2469	0.5957	0.2411	0.058*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0210 (2)	0.0357 (2)	0.0290 (2)	−0.00344 (13)	0.00779 (15)	−0.00294 (13)
N1	0.0233 (6)	0.0232 (6)	0.0304 (6)	0.0020 (5)	0.0120 (5)	0.0040 (5)
N2	0.0235 (6)	0.0206 (6)	0.0301 (6)	0.0012 (4)	0.0136 (5)	0.0031 (4)
N3	0.0235 (6)	0.0263 (6)	0.0330 (6)	−0.0013 (5)	0.0145 (5)	−0.0075 (5)
N4	0.0242 (6)	0.0270 (6)	0.0340 (6)	−0.0030 (5)	0.0141 (5)	−0.0049 (5)
N5	0.0224 (6)	0.0193 (5)	0.0210 (5)	0.0013 (4)	0.0088 (5)	−0.0009 (4)
N6	0.0311 (7)	0.0225 (6)	0.0248 (6)	0.0018 (5)	0.0089 (5)	−0.0048 (4)
C1	0.0288 (7)	0.0241 (7)	0.0251 (7)	−0.0021 (5)	0.0125 (6)	0.0010 (5)
C2	0.0459 (10)	0.0302 (8)	0.0355 (8)	−0.0082 (7)	0.0019 (7)	0.0026 (6)
C3	0.0468 (11)	0.0443 (10)	0.0382 (9)	−0.0008 (8)	−0.0018 (8)	0.0085 (8)

C4	0.0500 (10)	0.0327 (9)	0.0369 (8)	0.0094 (7)	0.0168 (7)	0.0099 (6)
C5	0.0477 (10)	0.0223 (7)	0.0372 (8)	0.0004 (6)	0.0195 (7)	−0.0018 (6)
C6	0.0316 (8)	0.0262 (7)	0.0313 (8)	−0.0027 (6)	0.0122 (6)	−0.0033 (6)
C7	0.0258 (7)	0.0230 (7)	0.0242 (6)	−0.0061 (5)	0.0101 (5)	−0.0012 (5)
C8	0.0246 (7)	0.0313 (8)	0.0333 (7)	−0.0045 (6)	0.0136 (6)	0.0045 (6)
C9	0.0223 (7)	0.0283 (7)	0.0294 (7)	−0.0019 (5)	0.0104 (6)	0.0014 (6)
C10	0.0217 (7)	0.0208 (6)	0.0242 (6)	0.0001 (5)	0.0094 (5)	0.0018 (5)
C11	0.0244 (7)	0.0229 (7)	0.0207 (6)	0.0014 (5)	0.0091 (5)	0.0014 (5)
C12	0.0262 (8)	0.0422 (9)	0.0521 (10)	0.0079 (7)	0.0193 (7)	0.0143 (8)

Geometric parameters (Å, º)

S1—C11	1.6697 (14)	C2—C3	1.384 (2)
N1—C9	1.3230 (19)	C2—H2	0.9500
N1—N2	1.3714 (16)	C3—C4	1.383 (3)
N2—C7	1.3670 (18)	C3—H3	0.9500
N2—C10	1.3949 (18)	C4—C5	1.377 (3)
N3—C11	1.3401 (18)	C4—H4	0.9500
N3—N4	1.3790 (17)	C5—C6	1.387 (2)
N3—H3A	0.9100	C5—H5	0.9500
N4—C10	1.2968 (18)	C6—H6	0.9500
N5—C10	1.3639 (18)	C7—C8	1.363 (2)
N5—C11	1.3759 (17)	C8—C9	1.413 (2)
N5—N6	1.3953 (15)	C8—H8	0.9500
N6—H6A	0.9101	C9—C12	1.492 (2)
N6—H6B	0.9099	C12—H12A	0.9800
C1—C2	1.392 (2)	C12—H12B	0.9800
C1—C6	1.392 (2)	C12—H12C	0.9800
C1—C7	1.477 (2)		
C9—N1—N2	104.65 (11)	C4—C5—H5	119.6
C7—N2—N1	112.32 (11)	C6—C5—H5	119.6
C7—N2—C10	127.07 (12)	C5—C6—C1	119.77 (15)
N1—N2—C10	120.47 (11)	C5—C6—H6	120.1
C11—N3—N4	113.70 (11)	C1—C6—H6	120.1
C11—N3—H3A	127.7	C8—C7—N2	105.56 (12)
N4—N3—H3A	118.6	C8—C7—C1	133.80 (13)
C10—N4—N3	103.20 (11)	N2—C7—C1	120.55 (12)
C10—N5—C11	107.82 (11)	C7—C8—C9	106.58 (12)
C10—N5—N6	123.89 (11)	C7—C8—H8	126.7
C11—N5—N6	128.28 (12)	C9—C8—H8	126.7
N5—N6—H6A	107.0	N1—C9—C8	110.89 (13)
N5—N6—H6B	105.4	N1—C9—C12	120.25 (13)
H6A—N6—H6B	109.8	C8—C9—C12	128.85 (14)
C2—C1—C6	119.08 (14)	N4—C10—N5	112.16 (12)
C2—C1—C7	119.82 (13)	N4—C10—N2	124.53 (13)
C6—C1—C7	121.07 (13)	N5—C10—N2	123.26 (12)
C3—C2—C1	120.73 (16)	N3—C11—N5	103.12 (11)

C3—C2—H2	119.6	N3—C11—S1	129.55 (11)
C1—C2—H2	119.6	N5—C11—S1	127.32 (11)
C4—C3—C2	119.73 (16)	C9—C12—H12A	109.5
C4—C3—H3	120.1	C9—C12—H12B	109.5
C2—C3—H3	120.1	H12A—C12—H12B	109.5
C5—C4—C3	119.98 (16)	C9—C12—H12C	109.5
C5—C4—H4	120.0	H12A—C12—H12C	109.5
C3—C4—H4	120.0	H12B—C12—H12C	109.5
C4—C5—C6	120.70 (15)		

C9—N1—N2—C7	0.12 (16)	N2—N1—C9—C8	−0.21 (16)
C9—N1—N2—C10	176.19 (12)	N2—N1—C9—C12	178.88 (14)
C11—N3—N4—C10	−0.45 (16)	C7—C8—C9—N1	0.23 (18)
C6—C1—C2—C3	−0.5 (3)	C7—C8—C9—C12	−178.76 (16)
C7—C1—C2—C3	−178.43 (16)	N3—N4—C10—N5	−0.20 (15)
C1—C2—C3—C4	0.0 (3)	N3—N4—C10—N2	−177.56 (12)
C2—C3—C4—C5	0.5 (3)	C11—N5—C10—N4	0.75 (15)
C3—C4—C5—C6	−0.4 (3)	N6—N5—C10—N4	179.53 (12)
C4—C5—C6—C1	−0.1 (2)	C11—N5—C10—N2	178.15 (12)
C2—C1—C6—C5	0.5 (2)	N6—N5—C10—N2	−3.1 (2)
C7—C1—C6—C5	178.45 (13)	C7—N2—C10—N4	64.2 (2)
N1—N2—C7—C8	0.02 (16)	N1—N2—C10—N4	−111.26 (16)
C10—N2—C7—C8	−175.74 (13)	C7—N2—C10—N5	−112.89 (16)
N1—N2—C7—C1	−176.94 (12)	N1—N2—C10—N5	71.66 (18)
C10—N2—C7—C1	7.3 (2)	N4—N3—C11—N5	0.88 (15)
C2—C1—C7—C8	−118.65 (19)	N4—N3—C11—S1	−178.60 (11)
C6—C1—C7—C8	63.4 (2)	C10—N5—C11—N3	−0.94 (14)
C2—C1—C7—N2	57.3 (2)	N6—N5—C11—N3	−179.65 (12)
C6—C1—C7—N2	−120.64 (15)	C10—N5—C11—S1	178.55 (10)
N2—C7—C8—C9	−0.14 (16)	N6—N5—C11—S1	−0.2 (2)
C1—C7—C8—C9	176.23 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N1^{i}	0.91	1.94	2.8429 (17)	169
N6—H6*A*···S1^{ii}	0.91	2.55	3.4157 (13)	159
N6—H6*B*···N4^{iii}	0.91	2.43	3.0059 (18)	122

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