Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Amino-1*H*-1,2,4-triazole-5(4*H*)-thione–4,4′-bipyridine (1/1)

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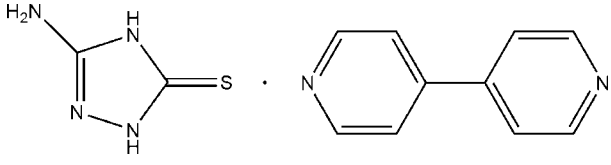
Received 13 August 2012; accepted 1 September 2012

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.114; data-to-parameter ratio = 13.4.

The title two-component molecular crystal, $C_{10}H_8N_2\cdot C_2H_4N_4S$, was obtained unexpectedly by reaction of $Zn(NO_3)_2\cdot 6H_2O$, NH_4BF_4 with 3-amino-1,2,4-triazole-5-thione (3-AMT) and 4,4′-bipyridine in water. The dihedral angle between the pyridine rings in the 4,4′-bipyridine molecule is 17.00 (13)°. In the crystal, N—H···N and N—H···S hydrogen bonds between the components lead to the formation of a three-dimensional network. Furthermore, the structure features face-to-face π–π stacking interactions between the 4,4′-bipyridine and triazole rings, with a centroid–centroid distance of 2.976 (2) Å.

Related literature

For background to the 3-amino-1,2,4-triazole-5-thione ligand, see: Hao *et al.* (2010); Ma *et al.* (2008); Rakova *et al.* (2003). For related structures, see: Deng *et al.* (2005); Downie *et al.* (1972).



Experimental

Crystal data

$C_{10}H_8N_2\cdot C_2H_4N_4S$
M_r = 272.34
Monoclinic, $P2_1/c$
a = 13.5151 (12) Å
b = 6.9680 (5) Å
c = 16.5529 (14) Å
β = 122.385 (2)°
V = 1316.39 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 298 K
0.40 × 0.30 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.910, T_{max} = 0.951
6507 measured reflections
2315 independent reflections
1725 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.114
S = 1.09
2315 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N6^{i}	0.86	1.98	2.828 (3)	171
N2—H2···N5^{ii}	0.86	2.00	2.829 (3)	163
N4—H4*A*···N3^{iii}	0.86	2.33	3.151 (3)	159
N4—H4*B*···S1^{iv}	0.86	2.82	3.424 (2)	129

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China (No.21171119), the National High Technology Research and Development Program 863 of China (2012 A A063201), the Beijing Personnel Bureau, the National Keystone Basic Research Program (973 Program) under grant Nos. 2007CB310408 and 2006CB302901, and the Committee of Education of the Beijing Foundation of China (grant No. KM201210028020.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2081).

References

Bruker (2007). *SMART*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Wisconsin, USA.
Deng, Q.-J., Yao, M.-X. & Zeng, M.-H. (2005). *Acta Cryst.* E**61**, o2239–o2240.
Downie, T. C., Harrison, W., Raper, E. S. & Hepworth, M. A. (1972). *Acta Cryst.* B**28**, 1584–1590.
Hao, Z. M., Guo, C. H., Wu, H. S. & Zhang, X. M. (2010). *CrystEngComm*, **12**, 55–58.
Ma, C., Li, Y., Han, Y. & Zhang, R. (2008). *Inorg. Chim. Acta*, **361**, 380–386.
Rakova, O. A., Sanina, N. A., Aldoshin, S. M., Goncharova, N. V., Shilov, G. V., Shulga, Y. M. & Ovanesyan, N. S. (2003). *Inorg. Chem. Commun.* **6**, 145–148.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2012). E**68**, o2885 [https://doi.org/10.1107/S1600536812037671]

3-Amino-1*H*-1,2,4-triazole-5(4*H*)-thione–4,4′-bipyridine (1/1)

Qi-Ming Qiu, Yu-Han Jiang, Xu Huang, Qiong-Hua Jin and Cun-Lin Zhang

S1. Comment

Supramolecular compounds have received much attention due to their structural diversities and potential applications as new materials. The ligand 3-amino-1,2,4-triazole-5-thione(3-AMT), with one –SH, one –NH_2 group and three potential coordination nitrogen atoms of triazole, is excellent in building metal-organic supramolecular structures (Hao *et al.*, 2010; Ma *et al.*, 2008; Rakova *et al.*, 2003). Moreover, its nitrogen atom and sulfur atom may be involved in hydrogen bonding (Deng *et al.*, 2005; Downie *et al.*, 1972).

The title compound was unexpectedly obtained in the course of synthesizing 3-AMT-Zn(II) complexes. The molecular structure of the title compound is shown in Fig.1. The crystal structure of $C_2H_2N_4S.C_{10}H_8N_2$ has been determined at room temperature. The compound has the space group P2(1)/c, with a = 13.5151 (12), b = 6.9680 (5), c = 16.5529 (14) Å and beta = 122.385 (2)°. The hydrogen bonds are formed between the N—H donors of 3-AMT and the nitrogen atoms from 4,4′-bipyridine and 3-AMT, and the atoms N6, N5 and N3 act as acceptors with d(N1···O6) = 2.828 (3) Å, d(N2···N5) = 2.829 (3) Å, d(N4···N3) = 3.151 (3) Å, N1—H1···N6 =171°, N2—H2···N5 =163° and N4—H4A···N3 =159°, which are just similar to the corresponding distances and angles in the compound of $C_{10}H_8N_2.2C_2H_3N_3S_2$ (Deng *et al.*, 2005). Intermolecular hydrogen bonds N—H···N and N—H···S between the components lead to the formation of a three-dimensional network (Fig.2). Furthermore, the structure is stabilized by the face to face π-π stacking interactions between 4,4′-bipyridine and triazole ring, with the centroid-centroid distance of 2.976 (2) Å.

S2. Experimental

A mixture of 3-AMT (0.6 mmol), NaOH (0.6 mmol), NH_4BF_4 (0.6 mmol), $Zn(NO_3)_2.6H_2O$ (0.3 mmol), 4,4′-bipyridine (0.3 mmol) and water (10 mL) was placed in a Teflon-lined stainless steel vessel (20 mL) and heated at 150°C for 72 h and then cooled to room temperature at a rate of 5°C/h.The filtrate was evaporated slowly at room temperature for 2 weeks to yield yellow crystalline products.

S3. Refinement

The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. All hydrogen atoms were located in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded (U_{iso}(H) = 1.2Ueq).

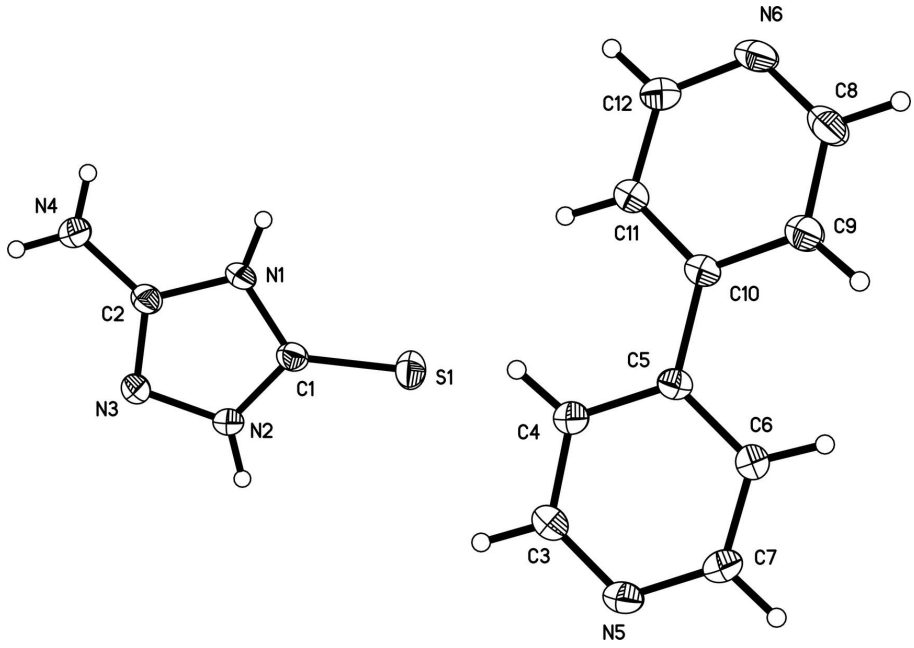


Figure 1

The molecular entities of the title compound, showing the atom-numbering scheme and with displacement ellipsoids drawn at the 50% probability level.

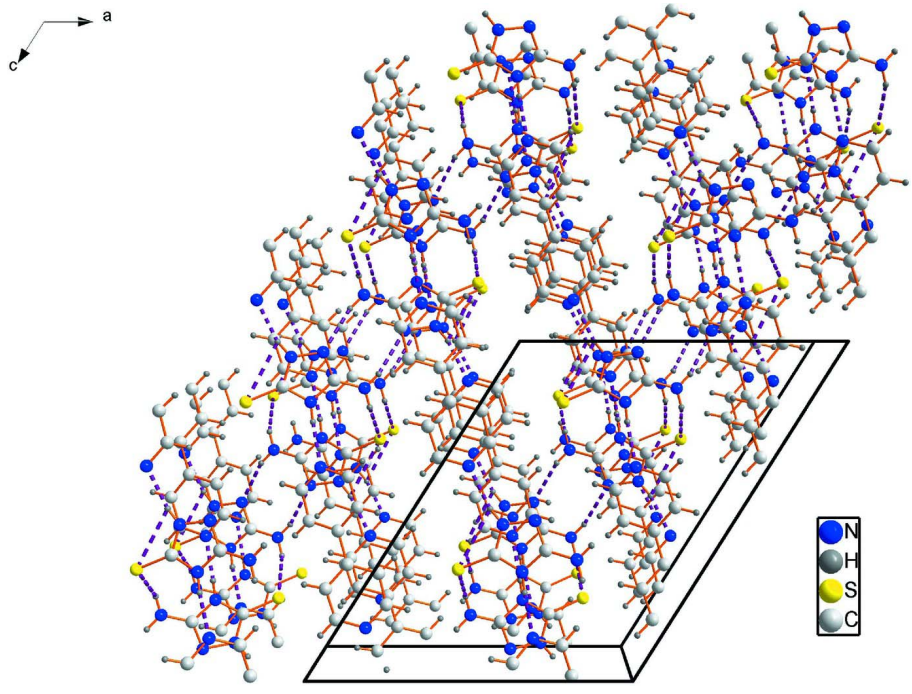


Figure 2

Three-dimensional structure formed by Intermolecular N—H···N and N—H···S hydrogen bonds.

3-Amino-1*H*-1,2,4-triazole-5(4*H*)-thione–4,4′-bipyridine (1/1)

Crystal data

$C_{10}H_8N_2·C_2H_4N_4S$
$M_r = 272.34$
Monoclinic, $P2_1/c$
$a = 13.5151$ (12) Å
$b = 6.9680$ (5) Å
$c = 16.5529$ (14) Å
$\beta = 122.385$ (2)°
$V = 1316.39$ (19) Å^3
$Z = 4$
$F(000) = 568$
$D_x = 1.374$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2519 reflections
$\theta = 2.9$–$27.9°$
$\mu = 0.24$ mm^{-1}
$T = 298$ K
Block, yellow
0.40 × 0.30 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
$T_{min} = 0.910$, $T_{max} = 0.951$
6507 measured reflections
2315 independent reflections
1725 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.2°$
$h = -16\rightarrow16$
$k = -8\rightarrow6$
$l = -19\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.114$
$S = 1.09$
2315 reflections
173 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.5763P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.028 (2)

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.

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

	x	y	z	U_{iso}*/U_{eq}
N1	0.54234 (15)	0.3890 (3)	0.81338 (12)	0.0356 (5)
H1	0.4953	0.3948	0.7523	0.043*
N2	0.69266 (15)	0.3516 (3)	0.95219 (12)	0.0377 (5)

H2	0.7632	0.3273	0.9982	0.045*
N3	0.60324 (16)	0.3979 (3)	0.96667 (13)	0.0377 (5)
N4	0.40154 (16)	0.4607 (3)	0.85462 (14)	0.0487 (6)
H4A	0.3859	0.4756	0.8982	0.058*
H4B	0.3469	0.4722	0.7953	0.058*
N5	1.08698 (16)	0.6753 (3)	0.87403 (13)	0.0420 (5)
N6	0.62173 (17)	0.6303 (3)	0.38615 (13)	0.0451 (5)
S1	0.74194 (6)	0.31020 (11)	0.81472 (5)	0.0535 (3)
C1	0.65892 (18)	0.3483 (3)	0.86103 (15)	0.0345 (5)
C2	0.51320 (19)	0.4188 (3)	0.87965 (15)	0.0342 (5)
C3	0.9754 (2)	0.6751 (4)	0.84854 (17)	0.0480 (6)
H3	0.9595	0.6770	0.8967	0.058*
C4	0.8821 (2)	0.6721 (4)	0.75504 (16)	0.0438 (6)
H4	0.8058	0.6755	0.7414	0.053*
C5	0.90223 (18)	0.6640 (3)	0.68118 (15)	0.0310 (5)
C6	1.01851 (19)	0.6645 (4)	0.70791 (16)	0.0417 (6)
H6	1.0375	0.6606	0.6616	0.050*
C7	1.1056 (2)	0.6709 (4)	0.80326 (17)	0.0460 (6)
H7	1.1828	0.6721	0.8191	0.055*
C8	0.7294 (2)	0.6805 (4)	0.41216 (18)	0.0546 (7)
H8	0.7437	0.7076	0.3643	0.065*
C9	0.8213 (2)	0.6949 (4)	0.50561 (17)	0.0509 (7)
H9	0.8948	0.7324	0.5193	0.061*
C10	0.80481 (18)	0.6537 (3)	0.57918 (15)	0.0328 (5)
C11	0.6921 (2)	0.6022 (4)	0.55197 (16)	0.0444 (6)
H11	0.6752	0.5737	0.5982	0.053*
C12	0.6055 (2)	0.5932 (4)	0.45693 (17)	0.0495 (6)
H12	0.5306	0.5589	0.4410	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0317 (10)	0.0518 (12)	0.0198 (9)	−0.0015 (8)	0.0114 (8)	−0.0012 (8)
N2	0.0271 (10)	0.0541 (12)	0.0266 (10)	0.0016 (8)	0.0109 (8)	−0.0015 (8)
N3	0.0343 (10)	0.0523 (12)	0.0273 (10)	0.0052 (9)	0.0170 (9)	0.0023 (9)
N4	0.0319 (11)	0.0795 (16)	0.0330 (11)	0.0092 (10)	0.0162 (9)	0.0050 (10)
N5	0.0352 (11)	0.0506 (13)	0.0296 (10)	−0.0007 (9)	0.0102 (9)	0.0000 (9)
N6	0.0417 (12)	0.0526 (13)	0.0265 (10)	0.0024 (9)	0.0086 (9)	−0.0008 (9)
S1	0.0467 (4)	0.0750 (5)	0.0509 (4)	−0.0104 (3)	0.0342 (4)	−0.0130 (3)
C1	0.0324 (12)	0.0398 (13)	0.0284 (12)	−0.0063 (10)	0.0145 (10)	−0.0040 (9)
C2	0.0344 (12)	0.0412 (13)	0.0264 (12)	−0.0010 (10)	0.0157 (10)	0.0019 (10)
C3	0.0418 (14)	0.0716 (18)	0.0290 (13)	−0.0008 (12)	0.0178 (11)	−0.0008 (12)
C4	0.0313 (12)	0.0660 (17)	0.0316 (13)	−0.0017 (11)	0.0152 (11)	0.0021 (11)
C5	0.0308 (11)	0.0312 (12)	0.0268 (11)	−0.0009 (9)	0.0125 (9)	0.0011 (9)
C6	0.0348 (13)	0.0588 (16)	0.0328 (13)	−0.0009 (11)	0.0190 (11)	−0.0007 (11)
C7	0.0275 (12)	0.0640 (17)	0.0391 (14)	−0.0004 (11)	0.0129 (11)	0.0008 (12)
C8	0.0579 (17)	0.0742 (19)	0.0285 (13)	−0.0081 (14)	0.0211 (13)	0.0033 (12)
C9	0.0401 (14)	0.0761 (19)	0.0322 (13)	−0.0137 (13)	0.0165 (12)	0.0004 (12)

C10	0.0333 (12)	0.0336 (12)	0.0266 (11)	0.0004 (9)	0.0128 (10)	−0.0005 (9)
C11	0.0353 (13)	0.0659 (17)	0.0298 (12)	−0.0015 (11)	0.0160 (11)	−0.0011 (11)
C12	0.0324 (13)	0.0705 (18)	0.0352 (14)	−0.0017 (12)	0.0113 (11)	−0.0038 (12)

Geometric parameters (Å, º)

N1—C1	1.362 (3)	C3—H3	0.9300
N1—C2	1.365 (3)	C4—C5	1.388 (3)
N1—H1	0.8600	C4—H4	0.9300
N2—C1	1.322 (3)	C5—C6	1.386 (3)
N2—N3	1.390 (2)	C5—C10	1.486 (3)
N2—H2	0.8600	C6—C7	1.374 (3)
N3—C2	1.304 (3)	C6—H6	0.9300
N4—C2	1.365 (3)	C7—H7	0.9300
N4—H4A	0.8600	C8—C9	1.374 (3)
N4—H4B	0.8600	C8—H8	0.9300
N5—C7	1.323 (3)	C9—C10	1.380 (3)
N5—C3	1.331 (3)	C9—H9	0.9300
N6—C8	1.324 (3)	C10—C11	1.384 (3)
N6—C12	1.328 (3)	C11—C12	1.370 (3)
S1—C1	1.685 (2)	C11—H11	0.9300
C3—C4	1.376 (3)	C12—H12	0.9300
C1—N1—C2	107.97 (17)	C6—C5—C4	116.2 (2)
C1—N1—H1	126.0	C6—C5—C10	121.74 (19)
C2—N1—H1	126.0	C4—C5—C10	122.03 (19)
C1—N2—N3	113.61 (18)	C7—C6—C5	119.6 (2)
C1—N2—H2	123.2	C7—C6—H6	120.2
N3—N2—H2	123.2	C5—C6—H6	120.2
C2—N3—N2	102.64 (17)	N5—C7—C6	124.5 (2)
C2—N4—H4A	120.0	N5—C7—H7	117.8
C2—N4—H4B	120.0	C6—C7—H7	117.8
H4A—N4—H4B	120.0	N6—C8—C9	123.9 (2)
C7—N5—C3	116.07 (19)	N6—C8—H8	118.0
C8—N6—C12	115.9 (2)	C9—C8—H8	118.0
N2—C1—N1	104.02 (18)	C8—C9—C10	120.2 (2)
N2—C1—S1	127.97 (17)	C8—C9—H9	119.9
N1—C1—S1	127.98 (16)	C10—C9—H9	119.9
N3—C2—N1	111.74 (18)	C9—C10—C11	115.8 (2)
N3—C2—N4	125.82 (19)	C9—C10—C5	121.9 (2)
N1—C2—N4	122.42 (19)	C11—C10—C5	122.21 (19)
N5—C3—C4	123.8 (2)	C12—C11—C10	120.0 (2)
N5—C3—H3	118.1	C12—C11—H11	120.0
C4—C3—H3	118.1	C10—C11—H11	120.0
C3—C4—C5	119.8 (2)	N6—C12—C11	124.1 (2)
C3—C4—H4	120.1	N6—C12—H12	117.9
C5—C4—H4	120.1	C11—C12—H12	117.9

C1—N2—N3—C2	1.2 (3)	C3—N5—C7—C6	−0.6 (4)
N3—N2—C1—N1	−1.6 (2)	C5—C6—C7—N5	0.5 (4)
N3—N2—C1—S1	176.54 (17)	C12—N6—C8—C9	0.1 (4)
C2—N1—C1—N2	1.4 (2)	N6—C8—C9—C10	0.8 (4)
C2—N1—C1—S1	−176.79 (18)	C8—C9—C10—C11	−1.0 (4)
N2—N3—C2—N1	−0.3 (2)	C8—C9—C10—C5	178.9 (2)
N2—N3—C2—N4	178.2 (2)	C6—C5—C10—C9	−17.5 (3)
C1—N1—C2—N3	−0.7 (3)	C4—C5—C10—C9	163.0 (2)
C1—N1—C2—N4	−179.3 (2)	C6—C5—C10—C11	162.4 (2)
C7—N5—C3—C4	−0.6 (4)	C4—C5—C10—C11	−17.1 (3)
N5—C3—C4—C5	1.7 (4)	C9—C10—C11—C12	0.5 (4)
C3—C4—C5—C6	−1.6 (3)	C5—C10—C11—C12	−179.4 (2)
C3—C4—C5—C10	177.8 (2)	C8—N6—C12—C11	−0.7 (4)
C4—C5—C6—C7	0.6 (3)	C10—C11—C12—N6	0.4 (4)
C10—C5—C6—C7	−178.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N6^{i}	0.86	1.98	2.828 (3)	171
N2—H2···N5^{ii}	0.86	2.00	2.829 (3)	163
N4—H4*A*···N3^{iii}	0.86	2.33	3.151 (3)	159
N4—H4*B*···S1^{iv}	0.86	2.82	3.424 (2)	129

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