

Crystal structure and Hirshfeld surface analysis of 4-aminopyridinium thiocyanate–4-aminopyridine (1/1)

M. Renugadevi,^a A. Sinthiya,^{a*} Kumaradhas Poomani^b and Suganya Suresh^b

^aDepartment of Physics, St Josephs College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli 620002, Tamil Nadu, India, and ^bLaboratory of Biocrystallography and Computational Molecular Biology, Department of Physics, Periyar University, Salem 636 011, Tamil Nadu, India. *Correspondence e-mail: r.brightson2010@gmail.com

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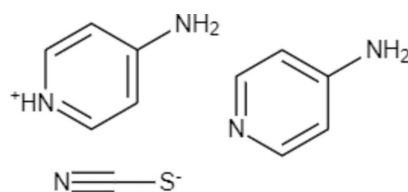
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In the crystals of the title compound, $C_5H_7N_2^+ \cdot CNS^- \cdot C_5H_6N_2$, the components are linked by three $N-H \cdots N$ and two $N-H \cdots S$ hydrogen bonds, resulting in two interpenetrating three-dimensional networks. Hirshfeld surface analysis shows that the most important contributions to the crystal packing are from $H \cdots H$ (36.6%), $C \cdots H/H \cdots C$ (20.4%), $S \cdots H/H \cdots S$ (19.7%) and $N \cdots H/H \cdots N$ (13.4%) interactions.

1. Chemical context

Processes based on metathesis reactions are a greener alternative for the synthesis of organic materials, avoiding hazardous pollution to the environment (Grubbs, 2003). A Nobel prize was awarded for the development of metathesis reactions used for the synthesis of organic molecules. Later, new pharmaceuticals and agrochemical materials were developed using this reaction.



In order to access important sulfur-containing compounds, organic thiocyanates play vital role as synthetic intermediates (Castanheiro *et al.*, 2016). The versatile thiocyanate ion can join to the reaction centre of a suitable cation or neutral molecule through the S or N atom, resulting in the assembly of supramolecular compounds (Lee *et al.*, 2017). For example, the crystal of 2-aminocyclohexan-1-aminium thiocyanate involves $N-H \cdots S$ and $N-H \cdots N$ interactions between the thiocyanate anion and the amine and aminium groups, leading to the formation of a two-dimensional network (Salem *et al.*, 2012). 4-Aminopyridine has many biological applications, especially in treating neurological problems. For example, it acts as a potassium channel blocker (Schwid *et al.*, 1997). With this background, the present work is carried out and the results are reported here.

2. Structural commentary

The asymmetric unit of the title compound is composed of one 4-aminopyridine molecule, one 4-aminopyridinium cation and one thiocyanate anion as shown in Fig. 1. The cation forms

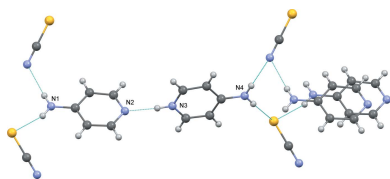


Table 1
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N4-H4A\cdots S^i$	0.86	2.58	3.4222 (17)	165
$N4-H4B\cdots N5$	0.86	2.10	2.952 (2)	168
$N3-H3\cdots N2$	0.86	1.83	2.688 (2)	172
$N1-H1A\cdots S^{ii}$	0.86	2.62	3.4498 (18)	162
$N1-H1B\cdots N5^{iii}$	0.86	2.23	3.083 (3)	172

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

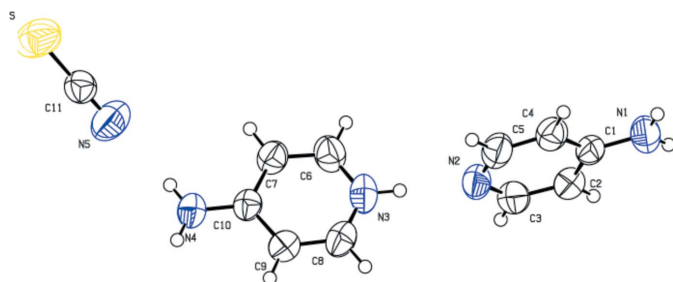
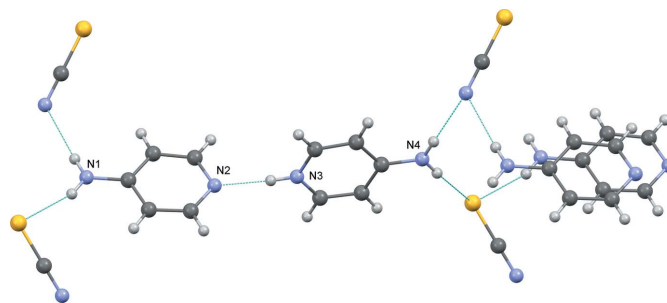
hydrogen bonds with the neutral molecule and with the anion (Table 1). The bond lengths and angles in neutral 4-aminopyridine are similar to those in a previous report (Anderson *et al.*, 2005), but the bond angle at the pyridine N3 atom is increased to 119.47 (14)° due to the hydrogen-bonding interaction. The thiocyanate anion is linear with an N5–C11–S bond of 177.85 (18)°. All bond lengths and angles in the aminopyridinium cation are within the normal ranges (Fun *et al.*, 2010).

3. Supramolecular features

In the crystal, the 4-aminopyridinium cation and 4-aminopyridine molecule are linked by a strong N–H⋯N hydrogen bond (Table 1). The thiocyanate ions act as bridges, each of them forming two N⋯H–N and two S⋯H–N hydrogen bonds (Fig. 2). As a result, two interpenetrating three-dimensional nets of hydrogen bonds are formed, as shown in Fig. 3. The short interplanar distance of 3.3419 (7) Å between the mean planes of two 4-aminopyridine molecules related by an inversion center indicates a π – π interaction [$Cg\cdots Cg(1-x, -y, -z) = 3.7635(13)$ Å where Cg is the centroid of the N2/C1–C5 ring].

4. Hirshfeld surface analysis

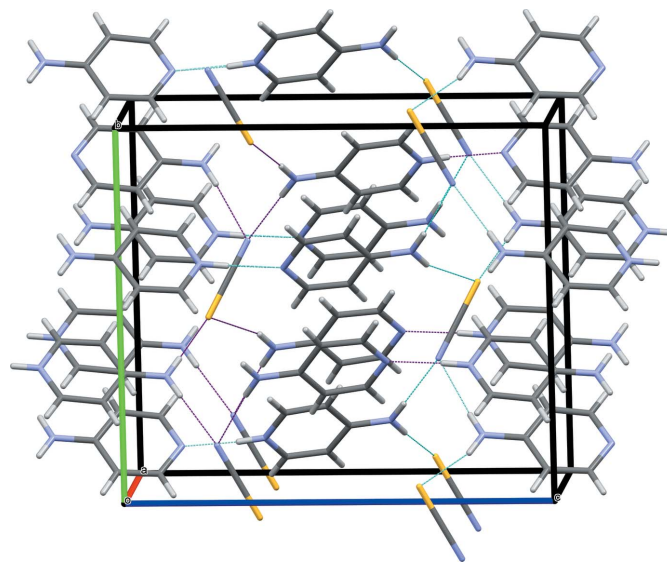
To quantify the intermolecular contacts in the title structure, the Hirshfeld surface and two-dimensional fingerprint plots were calculated using *Crystal Explorer* (Turner *et al.*, 2017). The Hirshfeld surface mapped over d_{norm} is depicted in Fig. 4, where the red regions make apparent hydrogen bonds in this structure. The intensity of the red color is higher for N1–H1A⋯S, indicating the strongest interaction as compared to other red spots on the Hirshfeld surface. The fingerprint plots show that the largest contributions are from H⋯H (36.6%),


Figure 1
 View of the asymmetric unit of the title compound.

Figure 2
 Hydrogen bonds in the crystal of the title compound.

C⋯H/H⋯C (20.4%), S⋯H/H⋯S (19.7%) and N⋯H/H⋯N (13.4%) interactions. Other interactions contributing to the crystal packing are C⋯C (5.8%), N⋯C/C⋯N (2.7%), N⋯N (1.1%), N⋯S/S⋯N (0.2%) and S⋯C/C⋯S (0.2%).

5. Database survey

A search of the Cambridge Crystallographic Database (CSD, version 5.40, update of September 19; Groom *et al.*, 2016) was undertaken for structures containing 4-aminopyridine and for thiocyanate ions in the salts with organic ammonium cations. The room-temperature structure of 4-aminopyridine was reported by Chao & Schempp (1977). Anderson *et al.* (2005) redetermined the structure at 150 K and reported that pyramidalization occurs at the amino N atom, with the N atom displaced from the plane of the three C/H/H atoms to which it is bonded. An N–H⋯N(pyridine) interaction links the molecules in a head-to-tail manner, forming zigzag chains along the c -axis direction. This is in contrast to the structure of the title compound, where N–H⋯N(pyridine) interactions link the molecules in a tail-to-tail manner. van Rooyan & Boeyens (1975) reported the SCH ions in sodium thiocyanate


Figure 3
 Crystal packing diagram of the title compound showing two interpenetrating 3D nets of hydrogen bonds presented as blue and purple dotted lines.

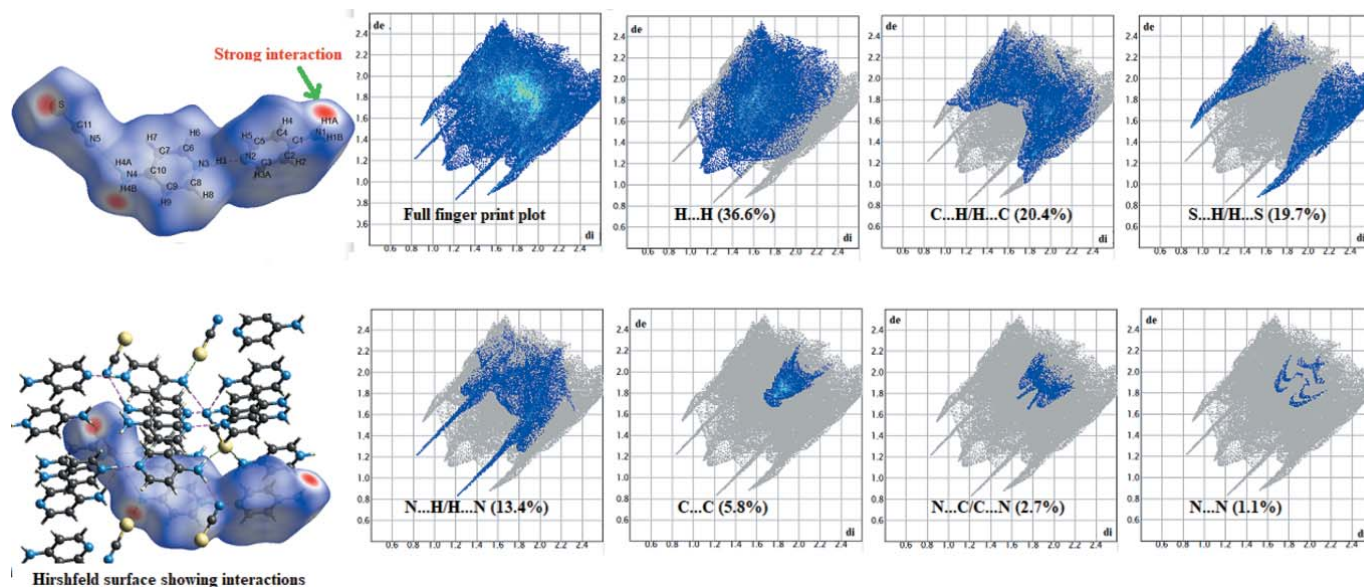


Figure 4
Hirshfeld surface plotted over d_{norm} and two-dimensional fingerprint plots for the title compound.

to be linear within experimental error. reported that in 2-aminocyclohexan-1-aminium thiocyanate (Salem *et al.*, 2012), the thiocyanate anion is involved in $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{N}$ interactions with both the amine and the aminium N atoms. Bagabas *et al.* (2015) reported that cyclohexyl ammonium thiocyanate has slightly a distorted chair conformation

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_5\text{H}_7\text{N}_2^+\text{CNS}^-\text{C}_5\text{H}_6\text{N}_2$
M_r	247.32
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a , b , c (Å)	7.9047 (19), 12.138 (2), 13.959 (3)
β (°)	94.670 (8)
V (Å ³)	1334.9 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.23
Crystal size (mm)	0.70 × 0.44 × 0.34
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2014)
T_{min} , T_{max}	0.86, 0.93
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15272, 3295, 2604
R_{int}	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.148, 1.03
No. of reflections	3295
No. of parameters	154
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.19, -0.27

Computer programs: *APEX2* (Bruker, 2005), *SAINT* (Bruker, 2001), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *ORTEP-3 for Windows* and *WinGX* publication routines (Farrugia, 2012).

and that the molecules are linked by $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen-bonding interactions. In bis[(18-crown-6- $\kappa^6\text{O}$)-sodium] (18-crown-6-1 $\kappa^6\text{O}$)- μ -thiocyanato-1:2 $\kappa^2\text{S}$: N -pentathiocyanato-2 $\kappa^5\text{N}$ -indate(III)sodium 1,2-dichloroethane sesquisolvate (Kong, 2009), the metal atom is in a six-coordinated octahedral environment, bounded to the N atoms of six thiocyanate ions and the crystal packing exhibits no significant short intermolecular contacts. In the title compound the $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds link the molecules into centrosymmetric structure and 4-aminopyridine is connected to the SCN ion by $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds.

6. Synthesis and crystallization

4-Aminopyridine and sodium thiocyanate were purchased from Merck. A solution of equimolar amounts of 4-aminopyridine and sodium thiocyanate in double-distilled water was stirred intensively for nearly 4 h, filtered with Whatman filter paper and allowed to evaporate at room temperature. Colourless needle-like crystals of the title compound were obtained after a period of seven days.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in idealized positions ($\text{C}-\text{H} = 0.93$ Å, $\text{N}-\text{H} = 0.86$ Å) and treated as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_5\text{N})$.

Acknowledgements

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Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

4-Aminopyridinium thiocyanate–4-aminopyridine (1/1)

Crystal data

$C_5H_7N_2^+ \cdot CNS^- \cdot C_5H_6N_2$
 $M_r = 247.32$
 Monoclinic, $P2_1/n$
 $a = 7.9047$ (19) Å
 $b = 12.138$ (2) Å
 $c = 13.959$ (3) Å
 $\beta = 94.670$ (8)°
 $V = 1334.9$ (5) Å³
 $Z = 4$

$F(000) = 520$
 $D_x = 1.231$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
 Cell parameters from 15272 reflections
 $\theta = 3.0$ – 28.0 °
 $\mu = 0.23$ mm⁻¹
 $T = 293$ K
 Needle, colourless
 $0.70 \times 0.44 \times 0.34$ mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2014)
 $T_{\min} = 0.86$, $T_{\max} = 0.93$
 15272 measured reflections

3295 independent reflections
 2604 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 28.3$ °, $\theta_{\min} = 2.9$ °
 $h = -10 \rightarrow 10$
 $k = -16 \rightarrow 14$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.148$
 $S = 1.03$
 3295 reflections
 154 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
 $w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.2492P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19$ 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.53196 (8)	0.54205 (5)	0.81261 (6)	0.1064 (3)
N4	0.60108 (18)	0.16957 (12)	0.60040 (9)	0.0665 (4)
H4A	0.680133	0.129475	0.628322	0.080*
H4B	0.548015	0.216341	0.633239	0.080*
N3	0.47226 (19)	0.13478 (13)	0.31204 (9)	0.0692 (4)
H3	0.444115	0.126754	0.251630	0.083*
N2	0.4113 (2)	0.11863 (13)	0.12028 (10)	0.0723 (4)
N1	0.3084 (2)	0.15215 (13)	−0.17439 (10)	0.0761 (4)
H1A	0.234378	0.110319	−0.204780	0.091*
H1B	0.360945	0.201212	−0.205073	0.091*
C10	0.56072 (18)	0.15921 (12)	0.50609 (10)	0.0513 (3)
C1	0.34225 (19)	0.14074 (13)	−0.07807 (10)	0.0568 (4)
C7	0.4312 (2)	0.22270 (14)	0.45860 (11)	0.0620 (4)
H7	0.373318	0.274750	0.492303	0.074*
C9	0.6444 (2)	0.08397 (13)	0.45041 (11)	0.0599 (4)
H9	0.731830	0.040635	0.478561	0.072*
N5	0.4673 (3)	0.34464 (16)	0.72012 (13)	0.0982 (6)
C8	0.5971 (2)	0.07464 (15)	0.35512 (12)	0.0649 (4)
H8	0.653756	0.024592	0.318724	0.078*
C2	0.2604 (2)	0.06267 (13)	−0.02580 (12)	0.0650 (4)
H2	0.180504	0.015765	−0.056717	0.078*
C11	0.4971 (2)	0.42600 (16)	0.75820 (12)	0.0656 (4)
C4	0.4626 (2)	0.20694 (14)	−0.02711 (12)	0.0638 (4)
H4	0.521971	0.260152	−0.058647	0.077*
C3	0.2976 (2)	0.05505 (15)	0.07087 (12)	0.0713 (5)
H3A	0.240361	0.002503	0.104414	0.086*
C6	0.3912 (2)	0.20756 (16)	0.36331 (13)	0.0718 (5)
H6	0.304243	0.249325	0.332609	0.086*
C5	0.4917 (2)	0.19239 (16)	0.06949 (13)	0.0712 (5)
H5	0.573045	0.236775	0.102281	0.085*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0858 (4)	0.0832 (4)	0.1442 (6)	−0.0020 (3)	−0.0260 (4)	−0.0304 (3)
N4	0.0740 (9)	0.0703 (8)	0.0540 (7)	0.0003 (7)	−0.0030 (6)	−0.0093 (6)
N3	0.0759 (9)	0.0846 (10)	0.0466 (7)	−0.0138 (8)	0.0026 (6)	−0.0061 (6)
N2	0.0837 (10)	0.0825 (10)	0.0502 (7)	0.0200 (8)	0.0031 (7)	−0.0076 (7)
N1	0.0919 (10)	0.0808 (10)	0.0546 (8)	−0.0061 (8)	−0.0003 (7)	−0.0010 (7)

C10	0.0518 (7)	0.0510 (7)	0.0513 (7)	-0.0127 (6)	0.0052 (6)	-0.0041 (6)
C1	0.0602 (8)	0.0580 (8)	0.0524 (8)	0.0128 (6)	0.0052 (6)	-0.0065 (6)
C7	0.0575 (8)	0.0665 (9)	0.0620 (9)	0.0026 (7)	0.0052 (7)	-0.0096 (7)
C9	0.0607 (8)	0.0562 (8)	0.0629 (9)	-0.0008 (7)	0.0065 (7)	-0.0045 (7)
N5	0.1254 (16)	0.0796 (12)	0.0945 (13)	-0.0078 (10)	0.0381 (11)	-0.0197 (10)
C8	0.0708 (10)	0.0654 (9)	0.0606 (9)	-0.0094 (8)	0.0180 (7)	-0.0126 (7)
C2	0.0735 (10)	0.0593 (9)	0.0618 (9)	0.0019 (7)	0.0027 (7)	-0.0071 (7)
C11	0.0665 (9)	0.0691 (10)	0.0618 (9)	0.0046 (8)	0.0096 (7)	0.0052 (8)
C4	0.0604 (9)	0.0683 (9)	0.0630 (9)	0.0036 (7)	0.0075 (7)	-0.0066 (7)
C3	0.0853 (12)	0.0663 (10)	0.0635 (10)	0.0089 (9)	0.0133 (9)	0.0021 (8)
C6	0.0666 (10)	0.0843 (12)	0.0631 (10)	0.0041 (9)	-0.0034 (7)	0.0008 (9)
C5	0.0679 (10)	0.0794 (11)	0.0648 (10)	0.0082 (9)	-0.0028 (8)	-0.0180 (9)

Geometric parameters (Å, °)

S—C11	1.613 (2)	C1—C4	1.395 (2)
N4—C10	1.3351 (19)	C7—C6	1.354 (2)
N4—H4A	0.8600	C7—H7	0.9300
N4—H4B	0.8600	C9—C8	1.357 (2)
N3—C6	1.333 (2)	C9—H9	0.9300
N3—C8	1.331 (2)	N5—C11	1.137 (2)
N3—H3	0.8600	C8—H8	0.9300
N2—C3	1.334 (2)	C2—C3	1.361 (2)
N2—C5	1.335 (2)	C2—H2	0.9300
N1—C1	1.3565 (19)	C4—C5	1.361 (2)
N1—H1A	0.8600	C4—H4	0.9300
N1—H1B	0.8600	C3—H3A	0.9300
C10—C9	1.400 (2)	C6—H6	0.9300
C10—C7	1.404 (2)	C5—H5	0.9300
C1—C2	1.388 (2)		
C10—N4—H4A	120.0	C10—C9—H9	120.2
C10—N4—H4B	120.0	N3—C8—C9	122.14 (15)
H4A—N4—H4B	120.0	N3—C8—H8	118.9
C6—N3—C8	119.47 (14)	C9—C8—H8	118.9
C6—N3—H3	120.3	C3—C2—C1	119.71 (16)
C8—N3—H3	120.3	C3—C2—H2	120.1
C3—N2—C5	116.33 (15)	C1—C2—H2	120.1
C1—N1—H1A	120.0	N5—C11—S	177.85 (18)
C1—N1—H1B	120.0	C5—C4—C1	118.94 (17)
H1A—N1—H1B	120.0	C5—C4—H4	120.5
N4—C10—C9	121.56 (14)	C1—C4—H4	120.5
N4—C10—C7	121.36 (14)	N2—C3—C2	123.74 (17)
C9—C10—C7	117.08 (13)	N2—C3—H3A	118.1
N1—C1—C2	121.87 (15)	C2—C3—H3A	118.1
N1—C1—C4	121.19 (16)	N3—C6—C7	122.20 (16)
C2—C1—C4	116.93 (14)	N3—C6—H6	118.9
C6—C7—C10	119.49 (15)	C7—C6—H6	118.9

C6—C7—H7	120.3	N2—C5—C4	124.33 (17)
C10—C7—H7	120.3	N2—C5—H5	117.8
C8—C9—C10	119.61 (15)	C4—C5—H5	117.8
C8—C9—H9	120.2		
N4—C10—C7—C6	-178.25 (15)	N1—C1—C4—C5	179.89 (15)
C9—C10—C7—C6	1.2 (2)	C2—C1—C4—C5	-0.6 (2)
N4—C10—C9—C8	178.74 (14)	C5—N2—C3—C2	-0.5 (3)
C7—C10—C9—C8	-0.7 (2)	C1—C2—C3—N2	-0.5 (3)
C6—N3—C8—C9	0.6 (3)	C8—N3—C6—C7	-0.1 (3)
C10—C9—C8—N3	-0.2 (2)	C10—C7—C6—N3	-0.8 (3)
N1—C1—C2—C3	-179.40 (15)	C3—N2—C5—C4	1.1 (3)
C4—C1—C2—C3	1.1 (2)	C1—C4—C5—N2	-0.5 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4 <i>A</i> ...S ⁱ	0.86	2.58	3.4222 (17)	165
N4—H4 <i>B</i> ...N5	0.86	2.10	2.952 (2)	168
N3—H3...N2	0.86	1.83	2.688 (2)	172
N1—H1 <i>A</i> ...S ⁱⁱ	0.86	2.62	3.4498 (18)	162
N1—H1 <i>B</i> ...N5 ⁱⁱⁱ	0.86	2.23	3.083 (3)	172

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