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N-(4-Chlorophenyl)-5-(4,5-dihydro-1*H*-imidazol-2-yl)thieno[2,3-*b*]pyridin-4-amine

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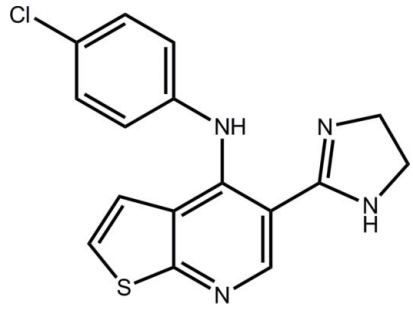
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.008 Å; disorder in main residue; R factor = 0.079; wR factor = 0.217; data-to-parameter ratio = 13.6.

In the title compound, $C_{16}H_{13}ClN_4S$, the thienopyridine fused-ring system is nearly planar (r.m.s. deviation = 0.0333 Å) and forms a dihedral angle of 4.4 (3)° with the attached dihydroimidazole ring (r.m.s. deviation = 0.0429 Å) allowing for the formation of an intramolecular (exocyclic amine)N—H···N(imine) hydrogen bond. The benzene rings of the disordered (50:50) –N(H)—C_6H_4Cl residue form dihedral angles of 59.1 (3) and 50.59 (15)° with the fused ring system. In the crystal, (imidazole amine)N—H···N(pyridine) hydrogen bonds lead to a supramolecular helical chain along the *b* axis. The chains assemble into layers (*ab* plane) with interdigitation of the chlorobenzene rings which results in weak C—H···Cl interactions in the *c*-axis direction.

Related literature

For the synthesis and biological activity of thienopyridine derivatives, see: Kaigorodova *et al.* (2000); Moloney (2001); Bernardino *et al.* (2004, 2006); Leal *et al.* (2008); Pinheiro *et al.* (2008*a*); El-Kashef *et al.* (2010); Testa *et al.* (2010); Panchamukhi *et al.* (2011). For the anti-leishmanial activity of 5-(4,5-dihydro-1*H*-imidazol-2-yl)-4-(arylamino)thieno[2,3-*b*]pyridine, see: Pinheiro *et al.* (2012).



Experimental

Crystal data

$C_{16}H_{13}ClN_4S$
M_r = 328.81
Monoclinic, $P2_1/c$
a = 17.784 (3) Å
b = 6.2264 (4) Å
c = 13.6226 (18) Å
β = 102.700 (4)°
V = 1471.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 120 K
0.25 × 0.15 × 0.03 mm

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.639, T_{max} = 1.000
9375 measured reflections
2591 independent reflections
1106 reflections with $I > 2\sigma(I)$
R_{int} = 0.138

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.079
$wR(F^2)$ = 0.217
S = 0.99
2591 reflections
191 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2n···N3	0.88 (10)	1.87 (11)	2.578 (18)	136 (10)
N2′—H2n'···N3	0.88 (10)	2.04 (11)	2.740 (15)	135 (7)
N4—H4n···N1^{i}	0.88 (3)	2.10 (3)	2.956 (8)	167 (5)
C6—H6···Cl1′^{ii}	0.95	2.74	3.559 (10)	146

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows*(Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5563).

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supplementary materials

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N-(4-Chlorophenyl)-5-(4,5-dihydro-1*H*-imidazol-2-yl)thieno[2,3-*b*]pyridin-4-amine

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Comment

Thienopyridine derivatives have been synthesized by a variety of routes (Kaigorodova *et al.*, 2000; Bernardino *et al.*, 2006; Pinheiro *et al.*, 2008; El-Kashef *et al.*, 2010; Testa *et al.*, 2010). A primary motivation for the preparation of these compounds is their biological activity, *viz*. anti-viral (Bernardino *et al.*, 2004), anti-inflammatory (Moloney, 2001), anti-bacterial (Leal *et al.*, 2008; Pinheiro *et al.*, 2008; Panchamukhi *et al.*, 2011) and anti-parasitic (Bernardino *et al.*, 2006). Recently, the anti-leishmanial activity of a family of 5-(4,5-dihydro-1*H*-imidazol-2-yl)-4-(arylamino)thieno[2,3-*b*]pyridine derivatives was reported (Pinheiro *et al.*, 2012). We now wish to report the crystal structure determination of a related derivative, namely 5-(4,5-dihydro-1*H*-imidazol-2-yl)-4-(4′-chlorophenylamino)-thieno[2,3-*b*]pyridine, (I).

In (I), Fig. 1, the nine non-hydrogen atoms of the thienopyridine ring are planar, having a r.m.s. deviation = 0.0333 Å and maximum deviations of 0.051 (5) Å [for the C7 atom] and -0.038 (5) Å [C6]. The imidazolyl ring is approximately planar [r.m.s. deviation = 0.0429 Å] and is co-planar with the fused ring system forming a dihedral angle of 4.4 (3)°. The imine-N3 atom of the imidazolyl ring is orientated towards the exocyclic amine so that an intramolecular hydrogen bond is formed, Table 1. There are two orientations for the disordered —N(H)—C_6H_4Cl residue of equal weight. The benzene rings of this residue are approximately co-planar (dihedral angle = 8.7 (5)°) and slightly displaced from each other. The dihedral angles between each orientation and the fused ring system are 59.1 (3) and 50.59 (15)°.

The most prominent feature of the crystal packing is the formation of N—H···N hydrogen bonds between the imidazolyl-amine and the pyridyl-N atom which lead to supramolecular helical chains along the *b* axis, Fig. 2 and Table 1. These assemble into layers in the *ab* plane allowing for inter-digitation of the chlorobenzene rings which in turn, allows for the formation of weak C—H···Cl interactions, Table 1. For the illustrated orientation of disordered benzene ring, Fig. 3, the H6···Cl1 separation is 2.95 Å.

Experimental

Following general procedures (Bernardino *et al.*, 2006; Pinheiro *et al.*, 2012), a solution of 4-(4′-chlorophenylamino)-thieno[2,3-*b*]pyridine-5-carbonitrile (1.5 mmol) in ethylenediamine (5 ml) was cooled at 273 K, carbon disulfide (8 drops) was added and the reaction mixture heated at 373 for 24 h. The resulting mixture was cooled, treated with water and filtered to give a brown crystalline solid, which was collected and dried. The sample used in the structure determination was grown from $CHCl_3$ solution. IR (KBr, cm^{-1}): *v* NH 3225, *v* C═N 1591). ^{1}H NMR (300 MHz, $CDCl_3$, TMS, δ in p.p.m.) 7.09 (d, 6.0, 1H, H2); 6.50 (d, 6.0, 1H, H3); 8.51 (s, 1H, H6); 7.29 (d, 8.7, 2H, Ar—H); 7.09 (d, 8.7, 2H, Ar—H); 3.83 (s, 4H, CH_2). ^{13}C NMR (75 MHz, DMSO-d6, TMS, δ in p.p.m.) 164.4; 164.1; 146.9; 146.6; 140.0; 129.3; 128.8; 125.4; 123.6; 121.3; 119.4; 105.4. ESI-(+)-MS [*M*+H]+ - 329.051 (100).

Refinement

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The N-bound H atoms were located from a difference map and refined with a distance restraint of N—H = 0.88±0.01 Å, and with U_{iso}(H) = 1.2U_{eq}(carrier atom). The —N(H)—C_6H_4Cl residue was disordered over two position. From anisotropic refinement (equivalent pairs of atoms were tied, and C_6 rings were idealized) the orientations were equal and so in the final refinement the site occupancies factors were fixed at 0.5. Several reflections, *i.e.* (1 0 0), (2 0 0), (0 0 2) and (-1 0 2), were affected by the beam-stop and were omitted from the final refinement.

Computing details

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows*(Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

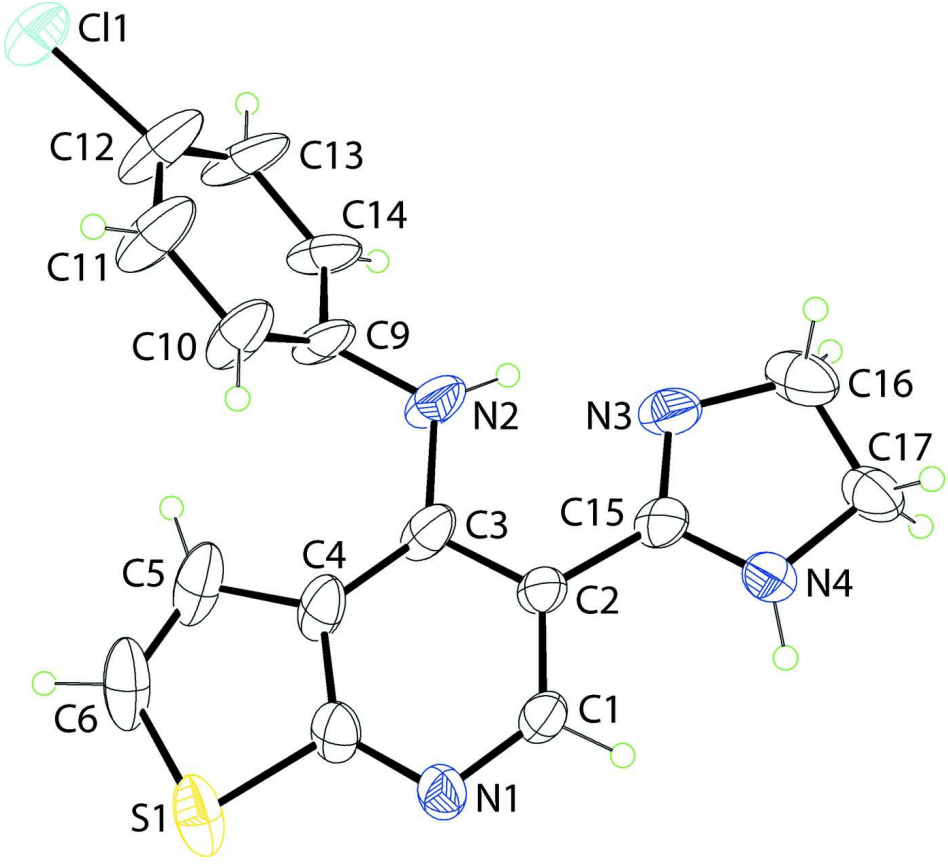

Figure 1

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level. Only one orientation of the disordered —N(H)—C_6H_4Cl residue is shown.

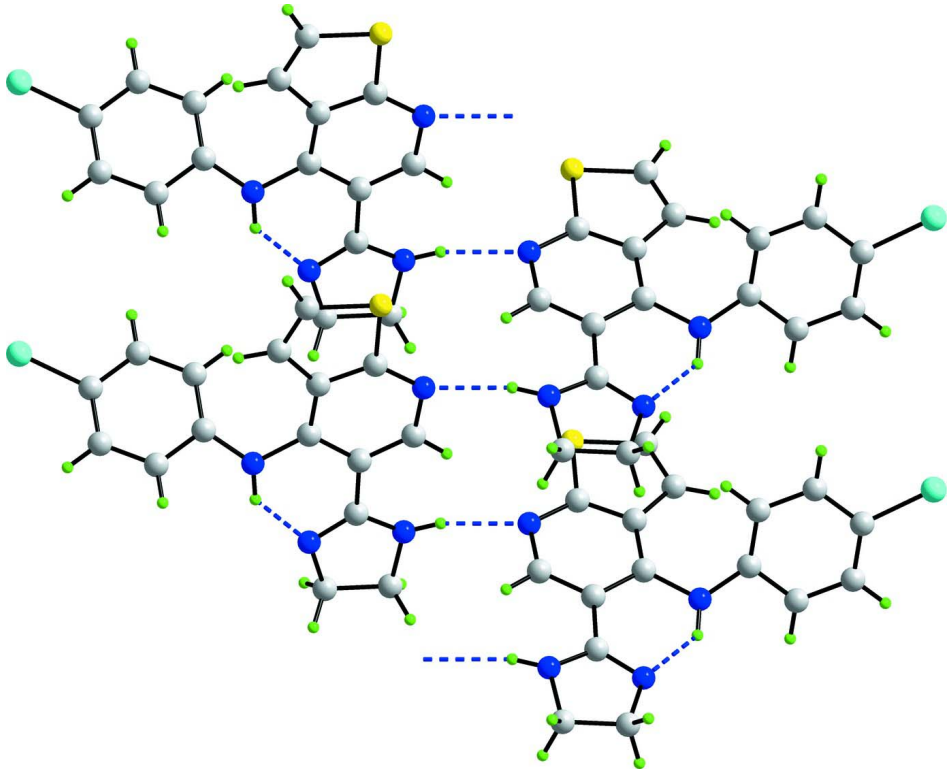

Figure 2

A view of the supramolecular helical chain propagated along [010] in (I) showing intra- and inter-molecular N—H···N (blue dashed lines) hydrogen bonds.

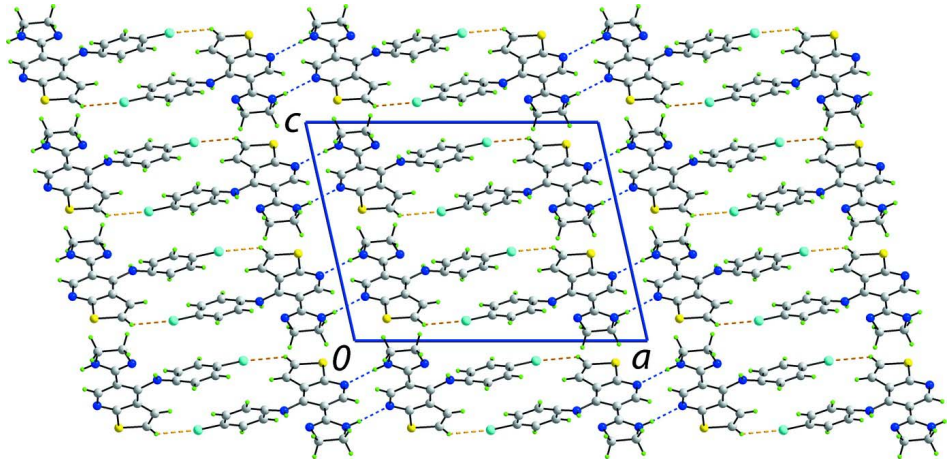

Figure 3

A view in projection down the *b* axis of the unit-cell contents for (I). The N—H···N and C—H···Cl interactions are shown as blue and orange dashed lines, respectively.

N-(4-Chlorophenyl)-5-(4,5-dihydro-1*H*-imidazol- 2-yl)thieno[2,3-*b*]pyridin-4-amine

Crystal data

$C_{16}H_{13}ClN_4S$
$M_r = 328.81$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 17.784$ (3) Å
$b = 6.2264$ (4) Å
$c = 13.6226$ (18) Å
$\beta = 102.700$ (4)°
$V = 1471.5$ (3) Å^3
$Z = 4$
$F(000) = 680$
$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5430 reflections
$\theta = 1.0$–$26.4°$
$\mu = 0.40$ mm^{-1}
$T = 120$ K
Plate, colourless
0.25 × 0.15 × 0.03 mm

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{min} = 0.639$, $T_{max} = 1.000$
9375 measured reflections
2591 independent reflections
1106 reflections with $I > 2\sigma(I)$
$R_{int} = 0.138$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.4°$
$h = -21 \rightarrow 21$
$k = -7 \rightarrow 7$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.079$
$wR(F^2) = 0.217$
$S = 0.99$
2591 reflections
191 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.088P)^2 + 1.3236P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}	Occ. (<1)
S1	0.12641 (12)	0.5151 (2)	0.60112 (15)	0.0763 (7)	
N1	0.0697 (3)	0.2115 (6)	0.7026 (4)	0.0512 (13)	

N3	0.2209 (3)	−0.3570 (7)	0.8955 (4)	0.0739 (18)	
N4	0.0959 (3)	−0.3191 (7)	0.8940 (4)	0.0549 (14)	
H4N	0.0473 (11)	−0.288 (8)	0.869 (4)	0.066*	
C1	0.0829 (3)	0.0361 (8)	0.7610 (4)	0.0462 (14)	
H1	0.0394	−0.0312	0.7777	0.055*	
C2	0.1545 (3)	−0.0563 (7)	0.7995 (4)	0.0464 (15)	
C3	0.2210 (3)	0.0395 (8)	0.7765 (5)	0.0601 (18)	
C4	0.2088 (4)	0.2238 (8)	0.7136 (5)	0.0592 (18)	
C5	0.2606 (4)	0.3478 (10)	0.6675 (6)	0.081 (2)	
H5	0.3144	0.3211	0.6777	0.097*	
C6	0.2236 (5)	0.5055 (10)	0.6084 (6)	0.087 (2)	
H6	0.2493	0.6035	0.5736	0.104*	
C7	0.1334 (4)	0.2970 (8)	0.6822 (5)	0.0526 (16)	
Cl1	0.6039 (3)	0.3366 (8)	0.9082 (4)	0.0739 (13)	0.50
N2	0.2952 (7)	−0.067 (3)	0.8204 (17)	0.074 (3)	0.50
H2N	0.292 (7)	−0.200 (8)	0.842 (9)	0.089*	0.50
C8	0.3602 (3)	0.0556 (17)	0.8170 (11)	0.066 (3)	0.50
C9	0.3724 (3)	0.2610 (16)	0.8574 (12)	0.083 (3)	0.50
H9	0.3297	0.3483	0.8629	0.099*	0.50
C10	0.4470 (3)	0.3387 (12)	0.8896 (11)	0.093 (3)	0.50
H10	0.4554	0.4790	0.9172	0.111*	0.50
C11	0.5095 (3)	0.2109 (10)	0.8815 (5)	0.100 (3)	0.50
C12	0.4973 (4)	0.0056 (14)	0.8411 (8)	0.095 (4)	0.50
H12	0.5400	−0.0817	0.8356	0.113*	0.50
C13	0.4227 (4)	−0.0721 (16)	0.8089 (10)	0.071 (4)	0.50
H13	0.4143	−0.2124	0.7813	0.085*	0.50
Cl1′	0.6109 (3)	0.2495 (8)	0.9508 (4)	0.0739 (13)	0.50
N2′	0.2871 (4)	−0.045 (2)	0.8004 (14)	0.074 (3)	0.50
H2N′	0.2828	−0.1058	0.8574	0.089*	0.50
C8′	0.3706 (3)	0.0220 (11)	0.8521 (6)	0.066 (3)	0.50
C9′	0.3835 (4)	0.2370 (11)	0.8780 (8)	0.083 (3)	0.50
H9′	0.3412	0.3287	0.8805	0.099*	0.50
C10′	0.4582 (4)	0.3178 (14)	0.9004 (9)	0.093 (3)	0.50
H10′	0.4670	0.4647	0.9181	0.111*	0.50
C11′	0.5200 (4)	0.1836 (17)	0.8968 (9)	0.100 (3)	0.50
C12′	0.5071 (3)	−0.0313 (16)	0.8709 (9)	0.095 (4)	0.50
H12′	0.5494	−0.1230	0.8685	0.113*	0.50
C13′	0.4325 (3)	−0.1121 (14)	0.8486 (7)	0.071 (4)	0.50
H13′	0.4237	−0.2590	0.8309	0.085*	0.50
C14	0.1587 (2)	−0.2514 (6)	0.8627 (3)	0.0494 (15)	
C15	0.2003 (2)	−0.5287 (6)	0.9594 (4)	0.079 (2)	
H15A	0.2272	−0.5067	1.0304	0.094*	
H15B	0.2153	−0.6706	0.9371	0.094*	
C16	0.1138 (3)	−0.5183 (6)	0.9492 (3)	0.0678 (19)	
H16A	0.0875	−0.6421	0.9108	0.081*	
H16B	0.1000	−0.5117	1.0157	0.081*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.1145 (17)	0.0388 (9)	0.0898 (14)	0.0007 (9)	0.0533 (12)	0.0066 (8)
N1	0.051 (3)	0.038 (3)	0.068 (4)	0.004 (2)	0.020 (3)	0.007 (2)
N3	0.048 (3)	0.035 (3)	0.121 (5)	−0.001 (2)	−0.019 (3)	0.006 (3)
N4	0.051 (3)	0.048 (3)	0.060 (4)	0.000 (3)	0.000 (3)	0.011 (2)
C1	0.037 (4)	0.043 (3)	0.059 (4)	−0.007 (3)	0.012 (3)	−0.004 (3)
C2	0.037 (4)	0.032 (3)	0.066 (4)	−0.002 (2)	0.003 (3)	−0.002 (3)
C3	0.035 (4)	0.033 (3)	0.113 (6)	−0.002 (3)	0.018 (4)	−0.016 (3)
C4	0.055 (4)	0.031 (3)	0.100 (5)	−0.007 (3)	0.034 (4)	−0.013 (3)
C5	0.082 (5)	0.050 (4)	0.129 (7)	−0.024 (4)	0.061 (5)	−0.024 (4)
C6	0.129 (7)	0.041 (4)	0.113 (6)	−0.019 (4)	0.077 (5)	−0.011 (4)
C7	0.060 (4)	0.032 (3)	0.071 (5)	0.002 (3)	0.027 (3)	−0.005 (3)
Cl1	0.0423 (14)	0.087 (4)	0.094 (4)	−0.012 (2)	0.019 (2)	−0.012 (2)
N2	0.031 (4)	0.041 (4)	0.144 (8)	0.002 (3)	0.004 (4)	−0.005 (4)
C8	0.022 (4)	0.043 (4)	0.126 (11)	0.008 (3)	−0.004 (5)	−0.012 (5)
C9	0.036 (4)	0.048 (4)	0.166 (9)	−0.002 (3)	0.028 (5)	−0.035 (5)
C10	0.038 (5)	0.083 (5)	0.162 (8)	−0.011 (4)	0.029 (5)	−0.061 (5)
C11	0.034 (5)	0.112 (6)	0.154 (8)	−0.021 (5)	0.022 (5)	−0.075 (6)
C12	0.022 (4)	0.102 (7)	0.147 (11)	0.013 (4)	−0.009 (5)	−0.057 (7)
C13	0.040 (5)	0.059 (5)	0.097 (12)	0.020 (4)	−0.020 (6)	−0.024 (7)
Cl1′	0.0423 (14)	0.087 (4)	0.094 (4)	−0.012 (2)	0.019 (2)	−0.012 (2)
N2′	0.031 (4)	0.041 (4)	0.144 (8)	0.002 (3)	0.004 (4)	−0.005 (4)
C8′	0.022 (4)	0.043 (4)	0.126 (11)	0.008 (3)	−0.004 (5)	−0.012 (5)
C9′	0.036 (4)	0.048 (4)	0.166 (9)	−0.002 (3)	0.028 (5)	−0.035 (5)
C10′	0.038 (5)	0.083 (5)	0.162 (8)	−0.011 (4)	0.029 (5)	−0.061 (5)
C11′	0.034 (5)	0.112 (6)	0.154 (8)	−0.021 (5)	0.022 (5)	−0.075 (6)
C12′	0.022 (4)	0.102 (7)	0.147 (11)	0.013 (4)	−0.009 (5)	−0.057 (7)
C13′	0.040 (5)	0.059 (5)	0.097 (12)	0.020 (4)	−0.020 (6)	−0.024 (7)
C14	0.045 (4)	0.035 (3)	0.061 (4)	−0.009 (3)	−0.003 (3)	−0.011 (3)
C15	0.091 (6)	0.042 (4)	0.082 (5)	0.002 (3)	−0.026 (4)	−0.001 (3)
C16	0.077 (5)	0.044 (3)	0.068 (5)	−0.007 (3)	−0.015 (4)	0.010 (3)

Geometric parameters (Å, º)

S1—C6	1.710 (8)	C9—C10	1.3900
S1—C7	1.738 (6)	C9—H9	0.9500
N1—C7	1.336 (7)	C10—C11	1.3900
N1—C1	1.341 (6)	C10—H10	0.9500
N3—C14	1.281 (6)	C11—C12	1.3900
N3—C15	1.474 (6)	C12—C13	1.3900
N4—C14	1.348 (6)	C12—H12	0.9500
N4—C16	1.449 (6)	C13—H13	0.9500
N4—H4N	0.877 (10)	Cl1′—C11′	1.674 (10)
C1—C2	1.390 (7)	N2′—C8′	1.556 (10)
C1—H1	0.9500	N2′—H2N′	0.88 (1)
C2—C3	1.421 (8)	C8′—C9′	1.3900
C2—C14	1.481 (6)	C8′—C13′	1.3900
C3—N2′	1.263 (12)	C9′—C10′	1.3900

C3—C4	1.420 (8)	C9′—H9′	0.9500
C3—N2	1.479 (16)	C10′—C11′	1.3900
C4—C7	1.391 (8)	C10′—H10′	0.9500
C4—C5	1.447 (8)	C11′—C12′	1.3900
C5—C6	1.347 (10)	C12′—C13′	1.3900
C5—H5	0.9500	C12′—H12′	0.9500
C6—H6	0.9500	C13′—H13′	0.9500
Cl1—C11	1.815 (9)	C15—C16	1.5151
N2—C8	1.394 (17)	C15—H15A	0.9900
N2—H2N	0.88 (1)	C15—H15B	0.9900
C8—C9	1.3900	C16—H16A	0.9900
C8—C13	1.3900	C16—H16B	0.9900
C6—S1—C7	90.3 (3)	C13—C12—C11	120.0
C7—N1—C1	113.7 (5)	C13—C12—H12	120.0
C14—N3—C15	105.7 (4)	C11—C12—H12	120.0
C14—N4—C16	109.2 (4)	C12—C13—C8	120.0
C14—N4—H4N	128 (4)	C12—C13—H13	120.0
C16—N4—H4N	119 (4)	C8—C13—H13	120.0
N1—C1—C2	126.0 (5)	C3—N2′—C8′	138.2 (13)
N1—C1—H1	117.0	C3—N2′—H2N	118 (6)
C2—C1—H1	117.0	C8′—N2′—H2N	92 (6)
C1—C2—C3	118.8 (5)	C3—N2′—H2N′	98.6
C1—C2—C14	118.9 (5)	C8′—N2′—H2N′	88.6
C3—C2—C14	122.3 (5)	C9′—C8′—C13′	120.0
N2′—C3—C4	120.3 (8)	C9′—C8′—N2′	117.5 (7)
N2′—C3—C2	122.7 (8)	C13′—C8′—N2′	120.4 (8)
C4—C3—C2	116.6 (5)	C8′—C9′—C10′	120.0
C4—C3—N2	127.6 (8)	C8′—C9′—H9′	120.0
C2—C3—N2	115.8 (8)	C10′—C9′—H9′	120.0
C7—C4—C3	117.4 (5)	C11′—C10′—C9′	120.0
C7—C4—C5	110.8 (6)	C11′—C10′—H10′	120.0
C3—C4—C5	131.6 (6)	C9′—C10′—H10′	120.0
C6—C5—C4	111.9 (7)	C10′—C11′—C12′	120.0
C6—C5—H5	124.0	C10′—C11′—Cl1′	122.2 (6)
C4—C5—H5	124.0	C12′—C11′—Cl1′	115.9 (6)
C5—C6—S1	114.6 (5)	C13′—C12′—C11′	120.0
C5—C6—H6	122.7	C13′—C12′—H12′	120.0
S1—C6—H6	122.7	C11′—C12′—H12′	120.0
N1—C7—C4	127.6 (5)	C12′—C13′—C8′	120.0
N1—C7—S1	119.9 (5)	C12′—C13′—H13′	120.0
C4—C7—S1	112.4 (4)	C8′—C13′—H13′	120.0
C8—N2—C3	114.5 (16)	N3—C14—N4	116.2 (4)
C8—N2—H2N	129 (8)	N3—C14—C2	123.6 (4)
C3—N2—H2N	116 (8)	N4—C14—C2	120.1 (4)
C3—N2—H2N′	93.2	N3—C15—C16	107.1 (2)
C9—C8—C13	120.0	N3—C15—H15A	110.3
C9—C8—N2	123.2 (15)	C16—C15—H15A	110.3
C13—C8—N2	111.9 (13)	N3—C15—H15B	110.3

C10—C9—C8	120.0	C16—C15—H15B	110.3
C10—C9—H9	120.0	H15A—C15—H15B	108.6
C8—C9—H9	120.0	N4—C16—C15	100.8 (2)
C11—C10—C9	120.0	N4—C16—H16A	111.6
C11—C10—H10	120.0	C15—C16—H16A	111.6
C9—C10—H10	120.0	N4—C16—H16B	111.6
C10—C11—C12	120.0	C15—C16—H16B	111.6
C10—C11—Cl1	117.2 (4)	H16A—C16—H16B	109.4
C12—C11—Cl1	122.2 (4)		

C7—N1—C1—C2	0.1 (8)	C8—C9—C10—C11	0.0
N1—C1—C2—C3	0.1 (8)	C9—C10—C11—C12	0.0
N1—C1—C2—C14	−179.7 (5)	C9—C10—C11—Cl1	171.4 (3)
C1—C2—C3—N2′	−173.2 (10)	C10—C11—C12—C13	0.0
C14—C2—C3—N2′	6.6 (13)	Cl1—C11—C12—C13	−170.9 (3)
C1—C2—C3—C4	−0.9 (8)	C11—C12—C13—C8	0.0
C14—C2—C3—C4	178.9 (5)	C9—C8—C13—C12	0.0
C1—C2—C3—N2	179.7 (10)	N2—C8—C13—C12	−156.1 (17)
C14—C2—C3—N2	−0.5 (11)	C4—C3—N2′—C8′	57 (3)
N2′—C3—C4—C7	174.0 (10)	C2—C3—N2′—C8′	−131.2 (19)
C2—C3—C4—C7	1.5 (8)	N2—C3—N2′—C8′	−87 (7)
N2—C3—C4—C7	−179.2 (11)	C3—N2′—C8′—C9′	−4 (3)
N2′—C3—C4—C5	−0.7 (13)	C3—N2′—C8′—C13′	−168.0 (18)
C2—C3—C4—C5	−173.2 (6)	C13′—C8′—C9′—C10′	0.0
N2—C3—C4—C5	6.1 (15)	N2′—C8′—C9′—C10′	−163.7 (10)
C7—C4—C5—C6	1.7 (8)	C8′—C9′—C10′—C11′	0.0
C3—C4—C5—C6	176.6 (6)	C9′—C10′—C11′—C12′	0.0
C4—C5—C6—S1	−1.2 (8)	C9′—C10′—C11′—Cl1′	−163.6 (6)
C7—S1—C6—C5	0.4 (5)	C10′—C11′—C12′—C13′	0.0
C1—N1—C7—C4	0.6 (8)	Cl1′—C11′—C12′—C13′	164.6 (6)
C1—N1—C7—S1	176.0 (4)	C11′—C12′—C13′—C8′	0.0
C3—C4—C7—N1	−1.5 (9)	C9′—C8′—C13′—C12′	0.0
C5—C4—C7—N1	174.3 (6)	N2′—C8′—C13′—C12′	163.2 (9)
C3—C4—C7—S1	−177.2 (4)	C15—N3—C14—N4	0.7 (6)
C5—C4—C7—S1	−1.4 (6)	C15—N3—C14—C2	176.6 (5)
C6—S1—C7—N1	−175.4 (5)	C16—N4—C14—N3	−7.2 (7)
C6—S1—C7—C4	0.6 (5)	C16—N4—C14—C2	176.7 (4)
N2′—C3—N2—C8	55 (5)	C1—C2—C14—N3	174.8 (5)
C4—C3—N2—C8	15 (3)	C3—C2—C14—N3	−5.0 (8)
C2—C3—N2—C8	−165.7 (17)	C1—C2—C14—N4	−9.4 (8)
C3—N2—C8—C9	55 (2)	C3—C2—C14—N4	170.8 (5)
C3—N2—C8—C13	−149.3 (11)	C14—N3—C15—C16	5.8 (4)
C13—C8—C9—C10	0.0	C14—N4—C16—C15	9.7 (5)
N2—C8—C9—C10	153.3 (17)	N3—C15—C16—N4	−9.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2n···N3	0.88 (10)	1.87 (11)	2.578 (18)	136 (10)

N2′—H2n′···N3	0.88 (10)	2.04 (11)	2.740 (15)	135 (7)
N4—H4n···N1^{i}	0.88 (3)	2.10 (3)	2.956 (8)	167 (5)
C6—H6···Cl1′^{ii}	0.95	2.74	3.559 (10)	146

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