Crystal structure and Hirshfeld surface analysis of rac-2-[2-(4-chlorophenyl)-3,4-dihydro-2H-1-benzopyran-4-ylidene]hydrazine-1-carbothioamide

Ruokuosenuo Zatsu,a Prabhakar Maddela,a* M. Indira Devi,a Ranjit Singhb and Chullikkattil P. Pradeepb

aDepartment of Chemistry, Nagaland University, Hqtrs: Lumami, Nagaland-798627, India, and bSchool of Basic Sciences, Indian Institute of Technology Mandi, Mandi-175005, Himachal Pradesh, India. *Correspondence e-mail: prabha7chem@gmail.com

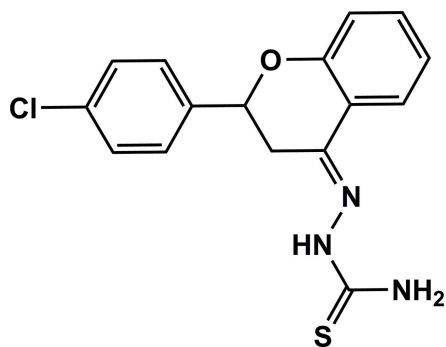In the title compound, $C_{16}H_{14}N_3OSCl$, a Schiff base derivative of a thiosemicarbazide with a flavanone, the 4-chlorophenyl ring is inclined to the benzene ring of the chromane ring system by 30.72 (12)°. The pyran ring has an envelope conformation with the methine C atom as the flap. The mean plane of the thiourea unit is twisted with respect to the benzene ring of the chromanone ring system, subtending a dihedral angle of 19.78 (19)°. In the crystal, molecules are linked by two pairs of N—H···S hydrogen bonds, forming inversion dimers enclosing $R_2^2(8)$ ring motifs, which are linked to form ribbons propagating along the b-axis direction. The intermolecular contacts in the crystal have been analysed using Hirshfeld surface analysis.

1. Chemical context

Flavanones, a subclass of flavonoids, are widely recognized for their nutraceutical values (Testai & Calderone, 2017). Flavanones are also known for their potential bioactivities against cancer (Bauvois et al., 2003). Thiosemicarbazides are a class of versatile ligands exhibiting important physicochemical properties due to their π-delocalization and flexibility of coordination modes. Therefore, a combination of flavanones and thiosemicarbazides may lead to compounds having synergistic properties of both classes of compounds. Schiff base derivatives of thiosemicarbazides have been studied for their biological and pharmacological properties (Bai et al., 2017). However, Schiff base derivatives of flavanones with thiosemicarbazides have not been explored extensively (Brodowska et al., 2016; Bargujar et al., 2018). In particular, structurally characterized flavanone–thiosemicarbazone Schiff bases are rare in the literature. The presence of NH and S moieties in such compounds opens up the possibility of studying the role of the comparatively less explored class of N—H···S interactions in building supramolecular architectures. This is of interest as hydrogen bonding to sulfur is known to play an important role in biological systems (Andersen et al., 2014; Walters et al., 2005). Considering the above, we have synthesized the title compound through a Schiff base condensation reaction, and report herein on its crystal structure and the Hirshfeld surface analysis.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$N\cdots$S1$^{\text{i}}$	0.85 (3)	2.65 (3)	3.480 (2)	167 (2)
N3—H3$BN\cdots$S1$^{\text{ii}}$	0.88 (3)	2.52 (3)	3.392 (2)	171 (2)

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

enclosing $R_2^2(8)$ ring motifs, which are linked to form ribbons propagating along the b-axis direction (Table 1 and Fig. 2). In the crystal, there are no other significant short intermolecular interactions present.

2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The 4-chlorophenyl ring (C11–C16) is inclined to the benzene ring (C5–C10) of the chromanone ring system by 30.72 (12)°. The pyran ring (O1/C2–C5/C10) has an envelope conformation with atom C2 as the flap, being displaced by 0.655 (2) Å from the mean plane through the other five atoms of the ring. The mean plane of the thiourea unit (N2/C17/S1/N3) is twisted with respect to benzene ring (C5-C10) of the chromane ring system, forming a dihedral angle of 19.78 (19)°.

3. Supramolecular features

A strong hydrogen bond often involves highly electronegative second row elements such as N, O and F. However, the less electronegative third row elements (P, S and Cl) are also known to take part in hydrogen-bonding interactions. In the crystal of the title compound, molecules are linked by two pairs of N—H$\cdots$S hydrogen bonds, forming inversion dimers

4. Hirshfeld surface analysis and two-dimensional fingerprint plots for the title compound

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017). A recent article by Tiekink and collaborators (Tan *et al.*, 2019) 'outlines the various procedures and what can be learned by using *CrystalExplorer*'.

The Hirshfeld surface of the title compound mapped over d_{norm} is given in Fig. 3a. The red spots indicate specific points of contact in the crystal. The Hirshfeld surface mapped over the shape-index is given in Fig. 3b, showing red spots and blue regions indicative of possible C$\cdots$H/H$\cdots$C (*i.e.* C—H$\cdots\pi$) contacts. The Hirshfeld surface mapped over the curvedness is given in Fig. 3c. Here the region around the chromane ring system is fairly flat, indicative of possible π–π interactions. However, these interactions must be extremely weak as analysis of the structure using *PLATON* (Spek, 2009) did not
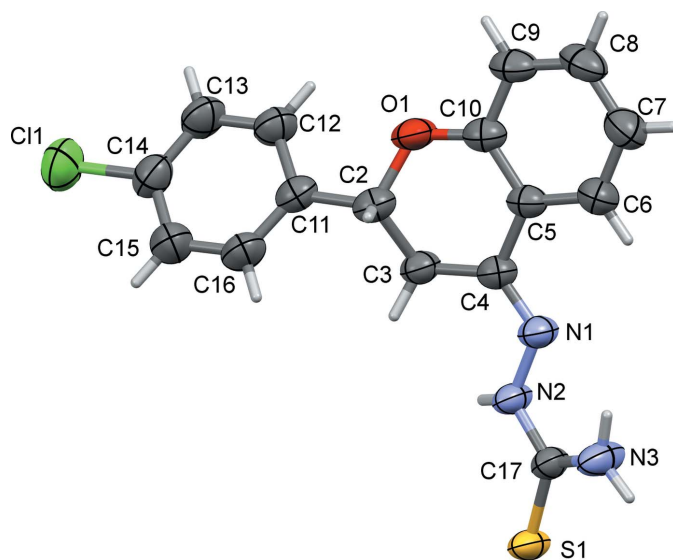

Figure 1
A view of the molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The orientation of the fiigure means that one of the two H atoms on C3 is not shown.
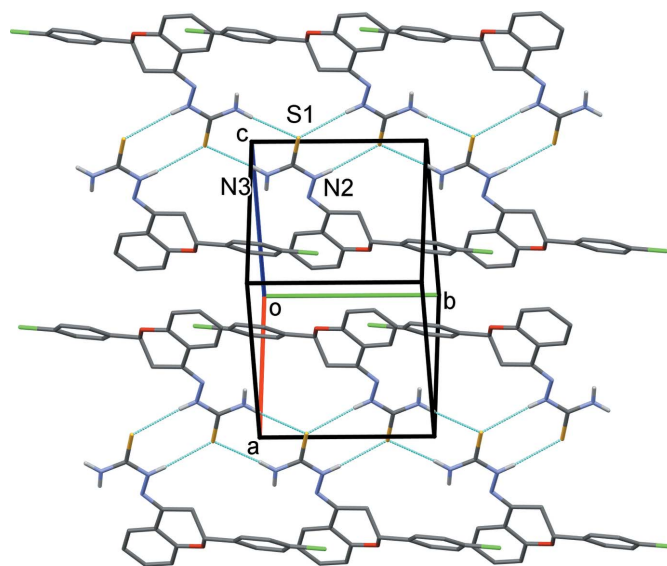

Figure 2
A view normal to plane (101) of the crystal packing of the title compound. The N—H$\cdots$S hydrogen bonds are shown as dashed lines (Table 1). For clarity, C-bound H atoms have been omitted.
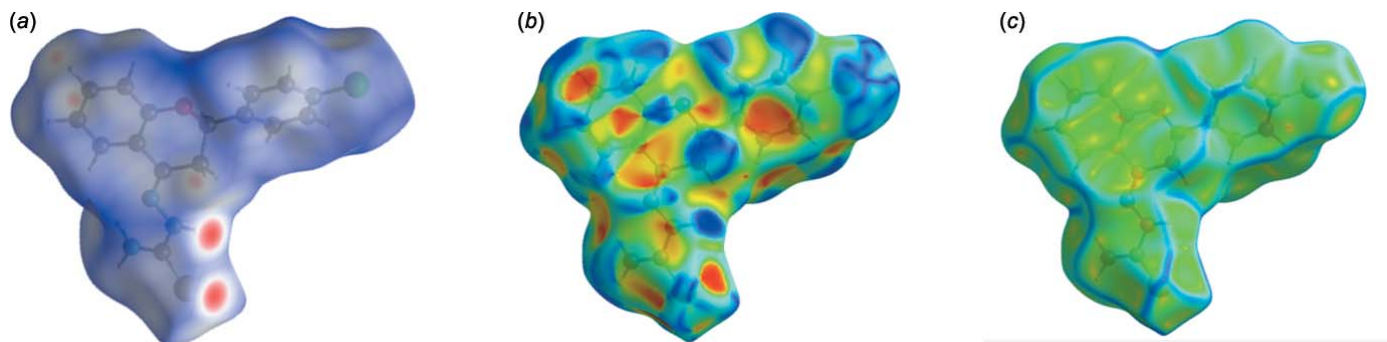
Figure 3
The Hirshfeld surface of the title compound mapped over (*a*) d_{norm}, −0.3525 to 1.4929 arbitrary units, (*b*) shape-index and (*c*) curvedness.

indicate the presence of any significant C—H⋯π or offset π–π interactions in the crystal.

The full two-dimensional fingerprint plot for the title compound is given in Fig. 4*a*. The principal intermolecular interactions (Fig. 4*b*–4*f*) are delineated into H⋯H (38.9%), C⋯H/H⋯C (20.3%), S⋯H/H⋯S (13.1%), Cl⋯H/H⋯Cl (12.0%) and N⋯H/H⋯N (3.0%) contacts. Note that only for the H⋯H, C⋯H/H⋯C and S⋯H/H⋯S contacts is $d_e + d_i$ (where d_e and d_i are the distances from a given point on the surface to the nearest atom outside and inside, respectively), less than the sum of the van der Waals radii of the individual atoms.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, update February 2019; Groom *et al.*, 2016) for a similar structure gave one hit, the compound 2′[(2-(4-fluoro-phenyl)chroman-4-ylidene]isonicotinohydrazide (CSD refcode TEJQUV; Nie *et al.*, 2006). Here, the pyran ring has an envelope conformation and the 4-fluorophenyl ring is inclined to the benzene ring of the chromane ring system by 66.57 (11)°. In the title compound, the pyran ring also has an envelope conformation and the 4-chloropheny ring is inclined

to the benzene ring of the chromane ring system by only 30.72 (12)°.

A search for the 2-(tetrahydro-4*H*-pyran-4-ylidene)-hydrazine-1-carbothioamide skeleton gave one hit, *viz.* (*E*)-2-[2,6-bis(4-chlorophenyl)-3,5-dimethyltetrahydro-4*H*-pyran-4-ylidene]hydrazinecarbothioamide (UQAWAL; Umamathes-wari *et al.*, 2011). Here, the pyran ring has a chair conforma-tion and the bond lengths and angles of the hydrazinecarbothioamide unit are similar to those in the title compound.

6. Synthesis and crystallization

The synthesis of the title compound was achieved by following a reported procedure with some modifications (Bargale *et al.*, 1988). Conc. H_2SO_4 (10 mol %) in ethanol (5 ml) was added to a stirred solution of 2-(4-chlorophenyl)-chroman-4-one (0.258 g, 1 mmol) (Zheng *et al.*, 2013) and thiosemicarbazide (0.091 g, 1 mmol). The mixture was refluxed for 96 h with continuous stirring. After completion of the reaction, as monitored by TLC, the solvent was removed under reduce pressure and then ice-cold water was added. The resulting solid product was collected by filtration, washed with water (3–4 times) and finally with hexane and then dried at room temperature. Pale-yellow plate-like crystals of the title compound were obtained by slow evaporation at room temperature of a solution in acetonitrile (yield 90%, m.p. 483-486 K). IR (KBr, cm^{-1}): 3417, 3245, 3152, 2984, 2888, 2790, 1598, 1512, 1454, 1298, 1250, 1089, 1077, 883, 766, 507, 498. ^{1}H NMR (400 MHz, DMSO-d_6), δ ppm: 10.47 (*s*, 1H, NH), 8.32 (*d*, 2H, *J* = 6.50 Hz, NH$_2$); 8.13 (*s*, 1H, Ar-H); 7.54 (*dd*, 4H, *J* = 8.41 Hz, Ar-H); 7.35–7.31 (*m*, 1H, Ar-H); 7.02–6.97 (*m*, 2H, Ar-H); 5.25 (*dd*, 1H, *J* = 2.36, 2.40 Hz, CH); 2.79 (*dd*, 1H, *J* = 12.10, 12.0 Hz, CH$_2$); 2.51 (*s*, 1H, CH$_2$). ^{13}C NMR (300 MHz, DMSO-d_6), δ ppm: 178.84; 156.71; 141.71; 138.79; 132.76; 131.24; 128.44; 128.27; 125.49; 121.48; 120.10; 117.47; 75.41; 31.83. Analysis calculated for $C_{16}H_{14}N_3OSCl$: C, 57.91; H, 4.25; N, 12.66; S, 9.66. Found: C, 57.85; H, 4.28; N, 12.61; S, 9.59.

Figure 4
(*a*) The full two-dimensional fingerprint plot for the title compound and fingerprint plots delineated into (*b*) H⋯H, (*c*) C⋯H/H⋯C, (*d*) S⋯H/H⋯S, (*e*) Cl⋯H/H⋯Cl and (*f*) N⋯H/H⋯N contacts.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH and NH$_2$ H atoms were
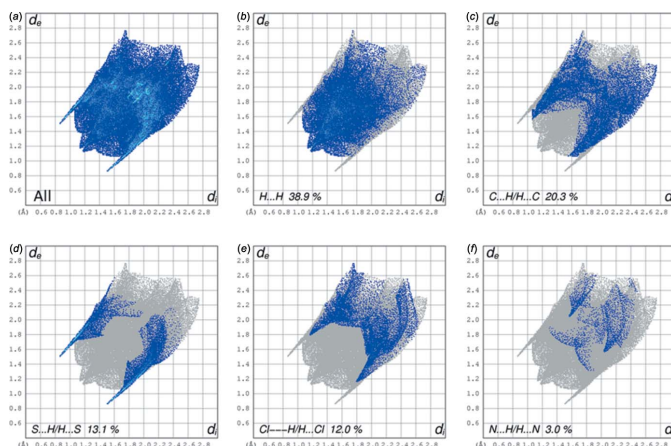
located in a difference-Fourier map and refined freely. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.93–0.98 Å with $U_{iso}(H) = 1.2U_{eq}(C)$.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{14}ClN_3OS$
M_r	331.81
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	7.8218 (7), 8.4207 (6), 12.3402 (11)
α, β, γ (°)	99.838 (7), 95.771 (7), 96.515 (7)
V (Å^3)	789.66 (12)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.41
Crystal size (mm)	$0.50 \times 0.17 \times 0.10$
Data collection	
Diffractometer	Rigaku OD, SuperNova, Dual, Cu at zero, Eos
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.464, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	4478, 2766, 2346
R_{int}	0.019
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.121, 1.05
No. of reflections	2766
No. of parameters	211
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.51, −0.41

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/03* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2008), *SHELXL2018/03* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/03* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009), *SHELXL2018/03* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

rac-2-[2-(4-Chlorophenyl)-3,4-dihydro-2*H*-1-benzopyran-4-ylidene]hydrazine-1-carbothioamide

Crystal data

$C_{16}H_{14}ClN_3OS$	$Z = 2$
$M_r = 331.81$	$F(000) = 344$
Triclinic, $P\bar{1}$	$D_x = 1.395$ Mg m^{-3}
$a = 7.8218$ (7) Å	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$b = 8.4207$ (6) Å	Cell parameters from 2014 reflections
$c = 12.3402$ (11) Å	$\theta = 3.7$–66.5°
$\alpha = 99.838$ (7)°	$\mu = 3.41$ mm^{-1}
$\beta = 95.771$ (7)°	$T = 293$ K
$\gamma = 96.515$ (7)°	Plate, yellow
$V = 789.66$ (12) Å^3	$0.50 \times 0.17 \times 0.10$ mm

Data collection

Rigaku OD, SuperNova, Dual, Cu at zero, Eos diffractometer	2766 independent reflections
	2346 reflections with $I > 2\sigma(I)$
Radiation source: micro-focus sealed X-ray tube	$R_{int} = 0.019$
ω scans	$\theta_{max} = 66.7°$, $\theta_{min} = 3.7°$
Absorption correction: gaussian	$h = -9 \rightarrow 9$
(CrysAlis PRO; Rigaku OD, 2015)	$k = -10 \rightarrow 7$
$T_{min} = 0.464$, $T_{max} = 1.000$	$l = -14 \rightarrow 14$
4478 measured reflections	

Refinement

Refinement on F^2	211 parameters
Least-squares matrix: full	0 restraints
$R[F^2 > 2\sigma(F^2)] = 0.042$	Primary atom site location: structure-invariant direct methods
$wR(F^2) = 0.121$	
$S = 1.05$	Secondary atom site location: difference Fourier map
2766 reflections	

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 0.1825P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.03040 (9)	0.27189 (6)	1.04983 (4)	0.0560 (2)
Cl1	0.63580 (11)	1.37767 (8)	0.85742 (7)	0.0909 (3)
O1	0.2996 (2)	0.65276 (19)	0.57103 (12)	0.0597 (4)
N1	0.1205 (2)	0.3125 (2)	0.75055 (14)	0.0492 (4)
N2	0.1066 (3)	0.3537 (2)	0.86177 (14)	0.0492 (4)
H2N	0.089 (3)	0.448 (3)	0.892 (2)	0.061 (7)*
N3	0.0872 (4)	0.0835 (2)	0.86608 (18)	0.0689 (6)
H3AN	0.115 (4)	0.073 (3)	0.800 (3)	0.076 (9)*
H3BN	0.062 (3)	−0.002 (3)	0.896 (2)	0.074 (8)*
C2	0.3685 (3)	0.6714 (3)	0.68520 (18)	0.0499 (5)
H2	0.467722	0.610398	0.689533	0.060*
C3	0.2332 (3)	0.6009 (3)	0.74971 (17)	0.0493 (5)
H3A	0.281782	0.610110	0.826354	0.059*
H3B	0.134816	0.661355	0.748204	0.059*
C4	0.1747 (3)	0.4250 (2)	0.69944 (17)	0.0450 (4)
C5	0.1826 (3)	0.3784 (3)	0.58006 (16)	0.0474 (5)
C6	0.1305 (3)	0.2204 (3)	0.52088 (19)	0.0606 (6)
H6	0.091678	0.139229	0.558488	0.073*
C7	0.1353 (3)	0.1822 (3)	0.4087 (2)	0.0681 (7)
H7	0.104231	0.075412	0.371456	0.082*
C8	0.1866 (3)	0.3031 (4)	0.35112 (19)	0.0650 (7)
H8	0.186752	0.278143	0.274751	0.078*
C9	0.2373 (3)	0.4599 (3)	0.40644 (19)	0.0607 (6)
H9	0.269457	0.541354	0.367367	0.073*
C10	0.2406 (3)	0.4967 (3)	0.52061 (17)	0.0500 (5)
C11	0.4330 (3)	0.8494 (3)	0.72737 (18)	0.0506 (5)
C12	0.4111 (3)	0.9656 (3)	0.6620 (2)	0.0604 (6)
H12	0.352887	0.934776	0.590588	0.073*
C13	0.4752 (3)	1.1273 (3)	0.7020 (2)	0.0668 (7)
H13	0.460876	1.204685	0.657535	0.080*
C14	0.5595 (3)	1.1727 (3)	0.8070 (2)	0.0624 (6)
C15	0.5862 (4)	1.0597 (3)	0.8729 (2)	0.0719 (7)
H15	0.645873	1.091518	0.943806	0.086*
C16	0.5233 (4)	0.8983 (3)	0.8325 (2)	0.0682 (7)

H16	0.541890	0.821123	0.876540	0.082*
C17	0.0759 (3)	0.2312 (2)	0.91799 (17)	0.0470 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0973 (4)	0.0372 (3)	0.0360 (3)	0.0047 (3)	0.0169 (3)	0.0114 (2)
Cl1	0.1088 (6)	0.0550 (4)	0.1009 (6)	−0.0103 (4)	−0.0092 (4)	0.0184 (4)
O1	0.0846 (11)	0.0556 (9)	0.0446 (8)	0.0059 (8)	0.0172 (7)	0.0219 (7)
N1	0.0673 (11)	0.0448 (9)	0.0385 (9)	0.0057 (8)	0.0134 (8)	0.0132 (7)
N2	0.0761 (12)	0.0362 (9)	0.0386 (9)	0.0049 (8)	0.0174 (8)	0.0121 (7)
N3	0.127 (2)	0.0374 (10)	0.0482 (12)	0.0088 (11)	0.0328 (12)	0.0121 (9)
C2	0.0547 (11)	0.0521 (12)	0.0491 (12)	0.0100 (9)	0.0147 (9)	0.0200 (9)
C3	0.0593 (12)	0.0485 (11)	0.0438 (11)	0.0050 (9)	0.0130 (9)	0.0163 (9)
C4	0.0498 (11)	0.0480 (11)	0.0406 (10)	0.0083 (8)	0.0092 (8)	0.0143 (8)
C5	0.0500 (11)	0.0577 (12)	0.0380 (10)	0.0090 (9)	0.0085 (8)	0.0154 (9)
C6	0.0730 (15)	0.0630 (14)	0.0427 (12)	−0.0017 (11)	0.0043 (10)	0.0101 (10)
C7	0.0738 (16)	0.0771 (17)	0.0467 (13)	0.0005 (13)	0.0025 (11)	0.0017 (12)
C8	0.0578 (13)	0.101 (2)	0.0356 (11)	0.0103 (13)	0.0068 (9)	0.0095 (12)
C9	0.0627 (13)	0.0833 (17)	0.0434 (12)	0.0128 (12)	0.0161 (10)	0.0244 (11)
C10	0.0519 (11)	0.0594 (13)	0.0440 (11)	0.0128 (9)	0.0121 (9)	0.0173 (9)
C11	0.0518 (11)	0.0508 (12)	0.0546 (12)	0.0066 (9)	0.0154 (9)	0.0198 (10)
C12	0.0671 (14)	0.0556 (13)	0.0624 (14)	0.0069 (10)	0.0047 (11)	0.0241 (11)
C13	0.0729 (15)	0.0549 (14)	0.0773 (17)	0.0061 (11)	0.0021 (13)	0.0305 (12)
C14	0.0617 (13)	0.0518 (13)	0.0755 (16)	0.0005 (10)	0.0090 (12)	0.0208 (11)
C15	0.0828 (17)	0.0661 (16)	0.0636 (15)	−0.0061 (13)	−0.0029 (13)	0.0199 (12)
C16	0.0828 (17)	0.0581 (14)	0.0663 (16)	0.0004 (12)	0.0026 (13)	0.0283 (12)
C17	0.0642 (12)	0.0382 (10)	0.0407 (10)	0.0027 (9)	0.0109 (9)	0.0129 (8)

Geometric parameters (Å, º)

S1—C17	1.687 (2)	C5—C6	1.398 (3)
Cl1—C14	1.746 (2)	C6—C7	1.372 (3)
O1—C10	1.361 (3)	C6—H6	0.9300
O1—C2	1.433 (3)	C7—C8	1.383 (4)
N1—C4	1.281 (3)	C7—H7	0.9300
N1—N2	1.375 (2)	C8—C9	1.373 (4)
N2—C17	1.351 (3)	C8—H8	0.9300
N2—H2N	0.85 (3)	C9—C10	1.387 (3)
N3—C17	1.315 (3)	C9—H9	0.9300
N3—H3AN	0.85 (3)	C11—C16	1.385 (3)
N3—H3BN	0.88 (3)	C11—C12	1.385 (3)
C2—C11	1.511 (3)	C12—C13	1.383 (3)
C2—C3	1.514 (3)	C12—H12	0.9300
C2—H2	0.9800	C13—C14	1.364 (4)
C3—C4	1.505 (3)	C13—H13	0.9300
C3—H3A	0.9700	C14—C15	1.374 (4)
C3—H3B	0.9700	C15—C16	1.381 (4)

C4—C5	1.468 (3)	C15—H15	0.9300
C5—C10	1.396 (3)	C16—H16	0.9300
C10—O1—C2	114.56 (16)	C8—C7—H7	120.1
C4—N1—N2	118.41 (17)	C9—C8—C7	120.2 (2)
C17—N2—N1	117.54 (17)	C9—C8—H8	119.9
C17—N2—H2N	117.8 (17)	C7—C8—H8	119.9
N1—N2—H2N	122.4 (17)	C8—C9—C10	120.0 (2)
C17—N3—H3AN	117 (2)	C8—C9—H9	120.0
C17—N3—H3BN	121.9 (18)	C10—C9—H9	120.0
H3AN—N3—H3BN	121 (3)	O1—C10—C9	117.1 (2)
O1—C2—C11	107.89 (17)	O1—C10—C5	121.98 (19)
O1—C2—C3	110.01 (18)	C9—C10—C5	120.9 (2)
C11—C2—C3	114.02 (18)	C16—C11—C12	118.5 (2)
O1—C2—H2	108.3	C16—C11—C2	119.6 (2)
C11—C2—H2	108.3	C12—C11—C2	121.8 (2)
C3—C2—H2	108.3	C13—C12—C11	120.5 (2)
C4—C3—C2	109.75 (17)	C13—C12—H12	119.7
C4—C3—H3A	109.7	C11—C12—H12	119.7
C2—C3—H3A	109.7	C14—C13—C12	119.7 (2)
C4—C3—H3B	109.7	C14—C13—H13	120.1
C2—C3—H3B	109.7	C12—C13—H13	120.1
H3A—C3—H3B	108.2	C13—C14—C15	121.0 (2)
N1—C4—C5	117.19 (19)	C13—C14—Cl1	119.26 (19)
N1—C4—C3	126.53 (19)	C15—C14—Cl1	119.7 (2)
C5—C4—C3	116.28 (17)	C14—C15—C16	119.1 (3)
C10—C5—C6	117.4 (2)	C14—C15—H15	120.4
C10—C5—C4	119.36 (19)	C16—C15—H15	120.4
C6—C5—C4	123.21 (19)	C15—C16—C11	121.0 (2)
C7—C6—C5	121.6 (2)	C15—C16—H16	119.5
C7—C6—H6	119.2	C11—C16—H16	119.5
C5—C6—H6	119.2	N3—C17—N2	117.00 (19)
C6—C7—C8	119.7 (2)	N3—C17—S1	122.99 (17)
C6—C7—H7	120.1	N2—C17—S1	120.00 (16)
C4—N1—N2—C17	−169.8 (2)	C8—C9—C10—C5	−4.0 (3)
C10—O1—C2—C11	178.22 (17)	C6—C5—C10—O1	−177.7 (2)
C10—O1—C2—C3	−56.8 (2)	C4—C5—C10—O1	3.8 (3)
O1—C2—C3—C4	57.2 (2)	C6—C5—C10—C9	3.4 (3)
C11—C2—C3—C4	178.59 (17)	C4—C5—C10—C9	−175.0 (2)
N2—N1—C4—C5	−178.00 (17)	O1—C2—C11—C16	−173.0 (2)
N2—N1—C4—C3	2.7 (3)	C3—C2—C11—C16	64.5 (3)
C2—C3—C4—N1	150.2 (2)	O1—C2—C11—C12	4.2 (3)
C2—C3—C4—C5	−29.1 (2)	C3—C2—C11—C12	−118.3 (2)
N1—C4—C5—C10	179.93 (19)	C16—C11—C12—C13	−1.3 (4)
C3—C4—C5—C10	−0.7 (3)	C2—C11—C12—C13	−178.5 (2)
N1—C4—C5—C6	1.6 (3)	C11—C12—C13—C14	−0.5 (4)
C3—C4—C5—C6	−179.1 (2)	C12—C13—C14—C15	1.8 (4)

C10—C5—C6—C7	−0.2 (4)	C12—C13—C14—Cl1	−178.7 (2)
C4—C5—C6—C7	178.2 (2)	C13—C14—C15—C16	−1.3 (4)
C5—C6—C7—C8	−2.4 (4)	Cl1—C14—C15—C16	179.2 (2)
C6—C7—C8—C9	1.9 (4)	C14—C15—C16—C11	−0.5 (4)
C7—C8—C9—C10	1.3 (4)	C12—C11—C16—C15	1.8 (4)
C2—O1—C10—C9	−155.12 (19)	C2—C11—C16—C15	179.1 (2)
C2—O1—C10—C5	26.0 (3)	N1—N2—C17—N3	9.8 (3)
C8—C9—C10—O1	177.1 (2)	N1—N2—C17—S1	−171.68 (15)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2N⋯S1[i]	0.85 (3)	2.65 (3)	3.480 (2)	167 (2)
N3—H3BN⋯S1[ii]	0.88 (3)	2.52 (3)	3.392 (2)	171 (2)

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