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N-Acetyl-*N*′-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]pyrazol-5-yl}-thiourea

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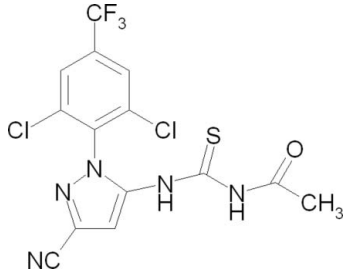
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.078; wR factor = 0.151; data-to-parameter ratio = 13.1.

In the title molecule, $C_{14}H_8Cl_2F_3N_5OS$, all bond lengths and angles are normal. Intramolecular N—H···O hydrogen bonding influences the molecular conformation. The pyrazole and benzene rings make a dihedral angle of 72.5 (1)°. Weak intermolecular N—H···S hydrogen bonds link the molecules into centrosymmetric dimers.

Related literature

For related literature, see: Gong *et al.* (2006); Hatton *et al.* (1993); Guo (2004); Sun *et al.* (2006).



Experimental

Crystal data

$C_{14}H_8Cl_2F_3N_5OS$
M_r = 422.21
Monoclinic, $P2_1/n$
a = 9.0015 (8) Å
b = 14.3443 (13) Å
c = 13.3019 (12) Å
β = 90.803 (2)°
V = 1717.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.55 mm^{-1}
T = 298 (2) K
0.31 × 0.15 × 0.11 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.849, T_{max} = 0.943
8974 measured reflections
3084 independent reflections
2820 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.078
$wR(F^2)$ = 0.151
S = 1.28
3084 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 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
N4—H4···O1	0.86	1.85	2.577 (4)	141
N5—H5···S1^{i}	0.86	2.69	3.524 (3)	164

Symmetry code: (i) $-x+1, -y+1, -z$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2236).

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supplementary materials

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N-Acetyl-*N*'-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]pyrazol-5-yl}thiourea

X.-H. Zhang, P. Zhong and Q.-Y. Lin

Comment

Acyl thiourea derivatives show good bioactivities and may be used in many fields, such as in antimicrobial, sterilization, insecticide and herbicidal (Guo, 2004; Sun *et al.*, 2006). Futhermore, the pyrazoles with the groups of chloride and trifluoromethyl, like 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4- trifluoromethylsulphenylpyrazole, show good bioactivities too (Hatton *et al.*, 1993). Herewith we present the crystal structure of the title compound, (I), synthesized from 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole and acetyl chloride.

The molecular structure of the title compound,(I), is shown in Fig.1, with the atom-numbering scheme. It is an acylthioureas with an overall U-shape. In the crystal structure, the dihedral angle between the pyrazole and attached benzene ring is 72.5 (1)°. There is an intramolecular N4—H4—O1 hydrogen bond with an N4.·O1 separation of 2.577 (4) Å. Besides that, the weak intermolecular N—H···S hydrogen bonds link the molecules into centrosymmetric dimers. The crystal packing is further stabilized by the van der Waals forces.

Experimental

Following the method of Hatton *et al.* (1993), reaction of 2,6-dichloro-4-trifluoromethylamine(0.01 mol) with a suspension of nitrosyl sulfuric acid, followed by reaction with a solution of ethyl 2,3-dicyanopropionate(0.01 mol) in acetic acid, gave 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole (about 0.005 mol) (product 1). Further, in accordance with the method of Gong *et al.* (2006), acetyl chloride (0.007 mol) with dry potassium thiocyanate(0.1 mol)was refluxed in anhydrous CH_3CN for 2 h at the temperature 80, then filtrated to obtain acylisothiocyanate solution (product 2). The obtained products 1 and 2 were then reacted in anhydrous CH_3CN for about 4 h to get the title compound(I). Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solution in acetone (m.p. 473–475 K). IR (KBr, ν cm^{-1}): 3253, 2244, 1698, 1610,1530, 1310; ^{1}H NMR (CD_3COCD_3, δ, p.p.m.): 13.19 (s,1*H*), 10.87 (s, 1H), 8.21 (S, 2H), 7.74(s, 1H), 2.16(s, 3H); ^{13}C NMR (CD_3COCD_3, δ, p.p.m.): 178.0(1 C), 173.9(1 C), 140.2(1 C), 136.1(2 C), 135.9 (1 C, J=28.7 Hz),134.8(1 C), 127.0(1 C), 126.9(2 C),123.2(1 C, J=271 Hz),113.0(1 C), 103.2(1 C),23.0(1 C).

Refinement

The H atoms were positioned geometrically [C—H 0.93–0.97 Å, N—H 0.86 Å] and allowed to ride on their parent atoms with U_{iso}=1.5U_{eq}(parent atom).

Figures

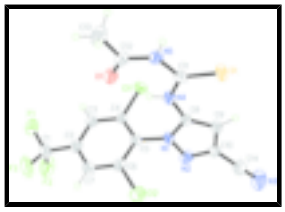


Fig. 1. The molecular structure of (I) showing the atom numbering scheme and displacement ellipsoids at the 50% probability level.

N-Acetyl-*N*'-{3-cyano-1-[2,6-dichloro-4- (trifluoromethyl)phenyl]pyrazol-5-yl}thiourea

Crystal data

$C_{14}H_8Cl_2F_3N_5OS$	F_{000} = 848
M_r = 422.21	D_x = 1.633 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 473 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 9.0015 (8) Å	Cell parameters from 2413 reflections
b = 14.3443 (13) Å	θ = 2.9–24.1º
c = 13.3019 (12) Å	μ = 0.55 mm^{-1}
β = 90.803 (2)º	T = 298 (2) K
V = 1717.4 (3) Å^3	Block, colourless
Z = 4	0.31 × 0.15 × 0.11 mm

Data collection

Bruker APEX area-detector diffractometer	3084 independent reflections
Radiation source: fine-focus sealed tube	2820 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.036
T = 298(2) K	θ_{max} = 25.3º
φ and ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	h = −10→9
T_{min} = 0.849, T_{max} = 0.943	k = −17→17
8974 measured reflections	l = −14→15

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.078	H-atom parameters constrained
$wR(F^2)$ = 0.151	$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 2.7124P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.28	$(\Delta/\sigma)_{max}$ = 0.001

3084 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
236 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Cl1	0.19256 (12)	0.07962 (8)	−0.07071 (9)	0.0462 (3)
Cl2	−0.15095 (15)	0.25247 (10)	0.19982 (9)	0.0594 (4)
S1	0.49154 (13)	0.38450 (9)	0.11126 (9)	0.0471 (3)
F1	−0.3483 (3)	0.1067 (3)	−0.2227 (2)	0.0727 (10)
F2	−0.4383 (4)	0.0369 (3)	−0.0978 (3)	0.1039 (15)
O1	0.1254 (4)	0.3302 (2)	−0.1182 (2)	0.0486 (8)
F3	−0.4768 (4)	0.1812 (3)	−0.1170 (3)	0.0994 (13)
N1	0.1295 (4)	0.1653 (2)	0.1297 (2)	0.0315 (8)
N2	0.1306 (4)	0.1098 (2)	0.2123 (3)	0.0400 (9)
N3	0.3220 (6)	0.0631 (4)	0.4320 (4)	0.095 (2)
N4	0.2570 (4)	0.2851 (2)	0.0481 (2)	0.0356 (8)
H4	0.1922	0.2771	0.0008	0.043*
N5	0.3241 (4)	0.4064 (2)	−0.0514 (2)	0.0361 (8)
H5	0.3856	0.4508	−0.0632	0.043*
C1	−0.3749 (6)	0.1154 (4)	−0.1262 (4)	0.0534 (13)
C2	−0.2382 (5)	0.1359 (3)	−0.0640 (3)	0.0379 (10)
C3	−0.1013 (5)	0.1057 (3)	−0.0955 (3)	0.0353 (10)
H3	−0.0910	0.0777	−0.1581	0.042*
C4	0.0206 (4)	0.1179 (3)	−0.0325 (3)	0.0320 (9)
C5	0.0069 (4)	0.1597 (3)	0.0609 (3)	0.0298 (9)
C6	−0.1312 (5)	0.1933 (3)	0.0876 (3)	0.0360 (10)
C7	−0.2547 (5)	0.1810 (3)	0.0264 (3)	0.0421 (11)
H7	−0.3472	0.2027	0.0459	0.051*
C8	0.2489 (4)	0.2236 (3)	0.1272 (3)	0.0307 (9)
C9	0.3325 (5)	0.2050 (3)	0.2112 (3)	0.0364 (10)
H9	0.4219	0.2324	0.2309	0.044*
C10	0.2538 (5)	0.1357 (3)	0.2605 (3)	0.0366 (10)
C11	0.3520 (4)	0.3560 (3)	0.0346 (3)	0.0329 (9)

C12	0.2119 (5)	0.3956 (3)	−0.1205 (3)	0.0392 (10)
C13	0.2015 (7)	0.4701 (4)	−0.1981 (4)	0.0686 (17)
H13A	0.1269	0.4537	−0.2472	0.103*
H13B	0.2957	0.4766	−0.2304	0.103*
H13C	0.1754	0.5280	−0.1668	0.103*
C14	0.2918 (6)	0.0928 (4)	0.3560 (4)	0.0558 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0337 (6)	0.0556 (7)	0.0495 (7)	0.0009 (5)	0.0069 (5)	−0.0065 (5)
Cl2	0.0590 (8)	0.0703 (9)	0.0489 (7)	0.0053 (7)	0.0012 (6)	−0.0223 (6)
S1	0.0407 (7)	0.0483 (7)	0.0519 (7)	−0.0184 (5)	−0.0136 (5)	0.0133 (6)
F1	0.060 (2)	0.112 (3)	0.0456 (18)	−0.0136 (18)	−0.0190 (14)	−0.0019 (17)
F2	0.080 (3)	0.131 (3)	0.099 (3)	−0.066 (2)	−0.044 (2)	0.046 (2)
O1	0.051 (2)	0.050 (2)	0.0447 (19)	−0.0142 (17)	−0.0137 (15)	0.0100 (15)
F3	0.058 (2)	0.145 (4)	0.094 (3)	0.038 (2)	−0.0370 (19)	−0.022 (2)
N1	0.0293 (18)	0.0338 (18)	0.0315 (18)	−0.0089 (15)	−0.0034 (14)	0.0050 (15)
N2	0.047 (2)	0.037 (2)	0.036 (2)	−0.0092 (17)	0.0003 (17)	0.0122 (16)
N3	0.086 (4)	0.128 (5)	0.069 (3)	−0.039 (4)	−0.028 (3)	0.058 (3)
N4	0.0326 (19)	0.039 (2)	0.0347 (19)	−0.0127 (16)	−0.0074 (15)	0.0060 (16)
N5	0.039 (2)	0.0356 (19)	0.0337 (19)	−0.0106 (16)	−0.0001 (16)	0.0070 (15)
C1	0.042 (3)	0.070 (4)	0.047 (3)	−0.006 (3)	−0.013 (2)	0.012 (3)
C2	0.039 (3)	0.037 (2)	0.038 (2)	−0.0044 (19)	−0.0033 (19)	0.0080 (19)
C3	0.038 (2)	0.037 (2)	0.031 (2)	−0.0028 (19)	−0.0008 (18)	0.0005 (18)
C4	0.030 (2)	0.031 (2)	0.035 (2)	−0.0036 (18)	0.0030 (17)	0.0045 (18)
C5	0.028 (2)	0.029 (2)	0.032 (2)	−0.0095 (17)	−0.0021 (17)	0.0045 (17)
C6	0.041 (2)	0.035 (2)	0.032 (2)	−0.0025 (19)	0.0011 (19)	−0.0019 (18)
C7	0.035 (2)	0.045 (3)	0.046 (3)	0.004 (2)	−0.001 (2)	0.000 (2)
C8	0.030 (2)	0.031 (2)	0.031 (2)	−0.0049 (18)	−0.0015 (17)	0.0004 (18)
C9	0.033 (2)	0.037 (2)	0.039 (2)	−0.0090 (19)	−0.0077 (19)	0.0033 (19)
C10	0.035 (2)	0.041 (2)	0.034 (2)	−0.005 (2)	−0.0062 (18)	0.0048 (19)
C11	0.031 (2)	0.031 (2)	0.036 (2)	−0.0022 (18)	0.0050 (18)	−0.0031 (18)
C12	0.048 (3)	0.038 (2)	0.032 (2)	−0.001 (2)	−0.003 (2)	0.0011 (19)
C13	0.081 (4)	0.065 (4)	0.059 (3)	−0.021 (3)	−0.026 (3)	0.024 (3)
C14	0.050 (3)	0.066 (3)	0.052 (3)	−0.020 (3)	−0.009 (2)	0.022 (3)

Geometric parameters (Å, °)

Cl1—C4	1.726 (4)	C1—C2	1.502 (6)
Cl2—C6	1.729 (4)	C2—C7	1.375 (6)
S1—C11	1.658 (4)	C2—C3	1.376 (6)
F1—C1	1.315 (6)	C3—C4	1.383 (6)
F2—C1	1.320 (6)	C3—H3	0.9300
O1—C12	1.220 (5)	C4—C5	1.387 (6)
F3—C1	1.323 (6)	C5—C6	1.385 (6)
N1—N2	1.356 (4)	C6—C7	1.380 (6)
N1—C8	1.362 (5)	C7—H7	0.9300
N1—C5	1.426 (5)	C8—C9	1.364 (5)

N2—C10	1.327 (5)	C9—C10	1.389 (6)
N3—C14	1.127 (6)	C9—H9	0.9300
N4—C11	1.342 (5)	C10—C14	1.449 (6)
N4—C8	1.377 (5)	C12—C13	1.487 (6)
N4—H4	0.8600	C13—H13A	0.9600
N5—C12	1.365 (5)	C13—H13B	0.9600
N5—C11	1.374 (5)	C13—H13C	0.9600
N5—H5	0.8600		
N2—N1—C8	112.5 (3)	C7—C6—C5	121.5 (4)
N2—N1—C5	118.9 (3)	C7—C6—Cl2	118.8 (3)
C8—N1—C5	128.6 (3)	C5—C6—Cl2	119.7 (3)
C10—N2—N1	102.9 (3)	C2—C7—C6	118.7 (4)
C11—N4—C8	129.0 (3)	C2—C7—H7	120.6
C11—N4—H4	115.5	C6—C7—H7	120.6
C8—N4—H4	115.5	N1—C8—C9	106.7 (3)
C12—N5—C11	128.8 (4)	N1—C8—N4	117.5 (3)
C12—N5—H5	115.6	C9—C8—N4	135.8 (4)
C11—N5—H5	115.6	C8—C9—C10	104.3 (4)
F1—C1—F2	106.5 (5)	C8—C9—H9	127.8
F1—C1—F3	107.1 (4)	C10—C9—H9	127.8
F2—C1—F3	106.2 (5)	N2—C10—C9	113.6 (4)
F1—C1—C2	113.4 (4)	N2—C10—C14	119.4 (4)
F2—C1—C2	111.3 (4)	C9—C10—C14	127.0 (4)
F3—C1—C2	111.9 (4)	N4—C11—N5	113.6 (4)
C7—C2—C3	121.5 (4)	N4—C11—S1	125.7 (3)
C7—C2—C1	118.4 (4)	N5—C11—S1	120.7 (3)
C3—C2—C1	120.1 (4)	O1—C12—N5	122.4 (4)
C2—C3—C4	118.8 (4)	O1—C12—C13	122.4 (4)
C2—C3—H3	120.6	N5—C12—C13	115.1 (4)
C4—C3—H3	120.6	C12—C13—H13A	109.5
C3—C4—C5	121.2 (4)	C12—C13—H13B	109.5
C3—C4—Cl1	119.2 (3)	H13A—C13—H13B	109.5
C5—C4—Cl1	119.5 (3)	C12—C13—H13C	109.5
C6—C5—C4	118.1 (4)	H13A—C13—H13C	109.5
C6—C5—N1	120.4 (4)	H13B—C13—H13C	109.5
C4—C5—N1	121.5 (4)	N3—C14—C10	177.1 (6)
C8—N1—N2—C10	0.1 (5)	C3—C2—C7—C6	−2.0 (7)
C5—N1—N2—C10	−177.3 (4)	C1—C2—C7—C6	174.9 (4)
F1—C1—C2—C7	155.1 (4)	C5—C6—C7—C2	−1.5 (7)
F2—C1—C2—C7	−84.8 (6)	Cl2—C6—C7—C2	178.5 (3)
F3—C1—C2—C7	33.8 (6)	N2—N1—C8—C9	0.5 (5)
F1—C1—C2—C3	−27.9 (6)	C5—N1—C8—C9	177.6 (4)
F2—C1—C2—C3	92.1 (6)	N2—N1—C8—N4	−178.1 (3)
F3—C1—C2—C3	−149.3 (4)	C5—N1—C8—N4	−1.0 (6)
C7—C2—C3—C4	2.7 (6)	C11—N4—C8—N1	171.3 (4)
C1—C2—C3—C4	−174.1 (4)	C11—N4—C8—C9	−6.8 (8)
C2—C3—C4—C5	0.0 (6)	N1—C8—C9—C10	−0.9 (5)
C2—C3—C4—Cl1	179.5 (3)	N4—C8—C9—C10	177.4 (5)

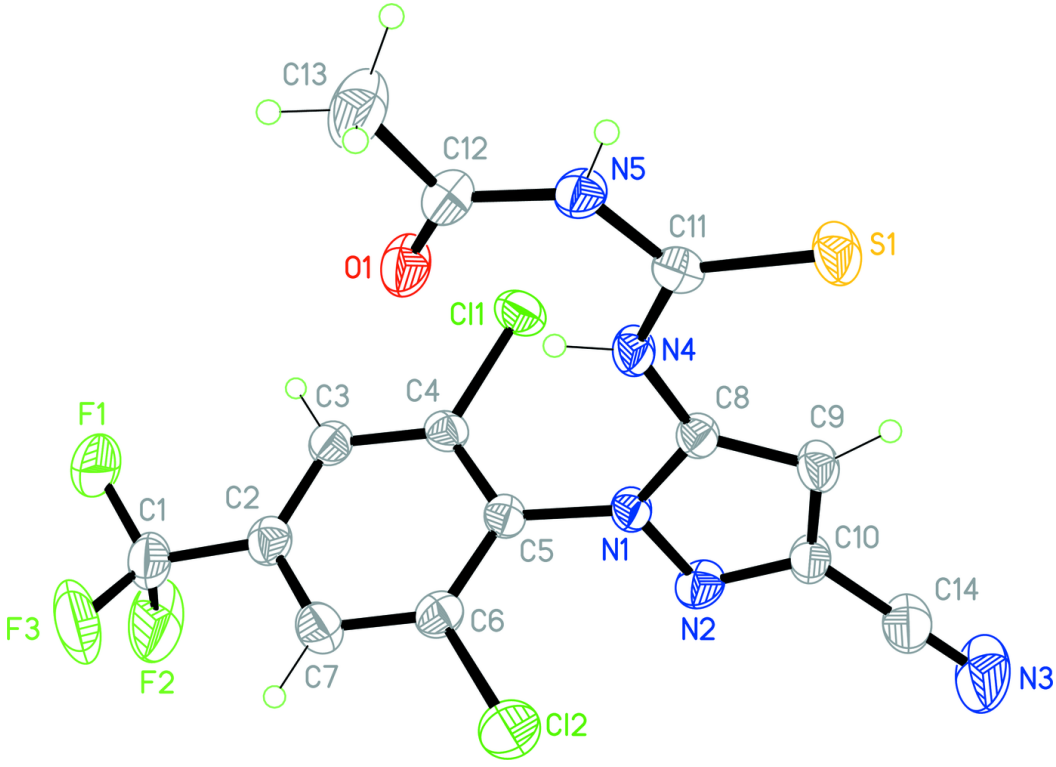
C3—C4—C5—C6	−3.3 (6)	N1—N2—C10—C9	−0.8 (5)
Cl1—C4—C5—C6	177.2 (3)	N1—N2—C10—C14	178.3 (4)
C3—C4—C5—N1	174.6 (4)	C8—C9—C10—N2	1.1 (5)
Cl1—C4—C5—N1	−4.9 (5)	C8—C9—C10—C14	−177.9 (5)
N2—N1—C5—C6	70.7 (5)	C8—N4—C11—N5	−177.1 (4)
C8—N1—C5—C6	−106.3 (5)	C8—N4—C11—S1	2.6 (6)
N2—N1—C5—C4	−107.2 (4)	C12—N5—C11—N4	2.6 (6)
C8—N1—C5—C4	75.9 (5)	C12—N5—C11—S1	−177.2 (4)
C4—C5—C6—C7	4.1 (6)	C11—N5—C12—O1	−7.1 (7)
N1—C5—C6—C7	−173.9 (4)	C11—N5—C12—C13	172.1 (4)
C4—C5—C6—Cl2	−175.9 (3)	N2—C10—C14—N3	−128 (12)
N1—C5—C6—Cl2	6.2 (5)	C9—C10—C14—N3	51 (12)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O1	0.86	1.85	2.577 (4)	141
N5—H5···S1^{i}	0.86	2.69	3.524 (3)	164

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

Fig. 1


C13
C12
N5
C11
S1
O1
Cl1
N4
C3
C4
C8
C9
F1
C1
C2
C5
N1
C10
C14
F3
F2
C6
N2
N3
C7
Cl2