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3-(4-Chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

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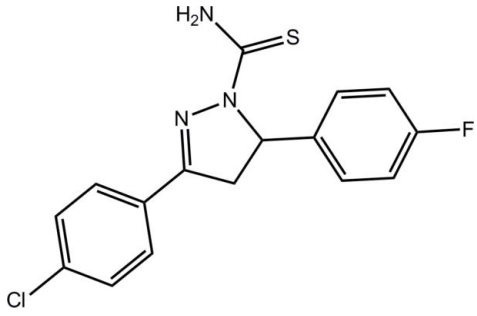
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.111; data-to-parameter ratio = 17.5.

In the title compound, $C_{16}H_{13}ClFN_3S$, the pyrazole ring adopts an envelope conformation with the methine C atom being the flap atom. The chloro- and fluorobenzene rings are twisted out of the plane of the pyrazole ring [dihedral angles = 15.12 (11) and 80.55 (10)°, respectively]. The amine group is orientated towards a ring N atom, forming an intramolecular N—H···N hydrogen bond. This H atom also forms a hydrogen bond to the F atom, which along with N—H···S hydrogen bonding leads to a supramolecular chain along the c axis. Connections between chains of the type Cl···π lead to a layer in the bc plane.

Related literature

For the biological activity of pyrazolin-1-ylthiazoles, see: Abdel-Wahab *et al.* (2009, 2012); Chimenti *et al.* (2010). For related structures, see: Chantrapromma *et al.* (2012); Abdel-Wahab *et al.* (2013).



Experimental

Crystal data

$C_{16}H_{13}ClFN_3S$
M_r = 333.80
Monoclinic, $P2_1/c$
a = 14.5402 (9) Å
b = 11.2700 (8) Å
c = 9.5169 (6) Å
β = 103.850 (6)°
V = 1514.17 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 295 K
0.40 × 0.30 × 0.20 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.898, T_{max} = 1.000
10191 measured reflections
3478 independent reflections
2570 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.111
S = 1.01
3478 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31···N1	0.88	2.24	2.617 (2)	106
N3—H31···F1^{i}	0.88	2.41	3.257 (2)	163
N3—H32···S1^{ii}	0.88	2.81	3.5203 (19)	139
C4—Cl1···*Cg*1^{iii}	1.735 (2)	3.9240 (12)	4.183 (2)	86.17 (17)

Symmetry codes: (i) $x, y, z+1$; (ii) $x, -y+\frac{5}{2}, z+\frac{1}{2}$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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, 2012) 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: HG5293).

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supporting information

Acta Cryst. (2013). E**69**, o414–o415 [doi:10.1107/S1600536813004492]

3-(4-Chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

Bakr F. Abdel-Wahab, Hanan A. Mohamed, Seik Weng Ng and Edward R. T. Tiekink

S1. Comment

Pyrazolin-1-ylthiazole derivatives are known to exhibit biological potential (Abdel-Wahab *et al.*, 2012; Abdel-Wahab *et al.*, 2009; Chimenti *et al.*, 2010) and motivated the investigation of the title compound, (I).

The central pyrazolyl ring in (I), Fig. 1, adopts an envelope conformation with the methine-C9 atom being the flap atom. The amine group is orientated towards the ring-N2 atom, forming a hydrogen bond, Table 1, assisted by the near co-planar relationship between the thioamide group and the pyrazolyl ring with the N1—N2—C16—N3 torsion angle being -0.7 (2)°. Both the chloro- and fluoro-benzene rings are twisted out of the least-squares plane through the five-membered ring, forming dihedral angles of 15.12 (11) and 80.55 (10)°, respectively. Quite similar conformations have been observed in related structures bearing two six-membered rings (Chantrapromma *et al.*, 2012; Abdel-Wahab *et al.*, 2013).

In the crystal packing, the amine-H31 atom participating in the intramolecular N—H···N hydrogen bond also forms a hydrogen bond to the F1 atom, Table 1. This interaction along with an N—H···S hydrogen bond leads to a supramolecular chain along the *c* axis, Table 1. Chains are connected into a layer in the *bc* plane by Cl···π interactions, Fig. 2 and Table 1. Layers stack along the *a* axis without specific interactions between them, Fig. 3.

S2. Experimental

To a suspension of (*E*)-1-(4-chlorophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (1 mmol, 0.26 g) and sodium hydroxide (2.5 mmol, 1.0 g) in ethanol (20 ml), thiosemicarbazide (1.2 mmol, 0.11 g) was added. The mixture was refluxed for 12 h, then left to cool. The solid product was filtered off, washed with ethanol and dried. Recrystallization was by slow evaporation of its DMF solution.

S3. Refinement

Nitrogen- and carbon-bound H-atoms were placed in calculated positions (N—H = 0.88 Å, and C—H 0.93 to 0.98 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) = 1.2–1.5U_{equiv}(N,*C*).

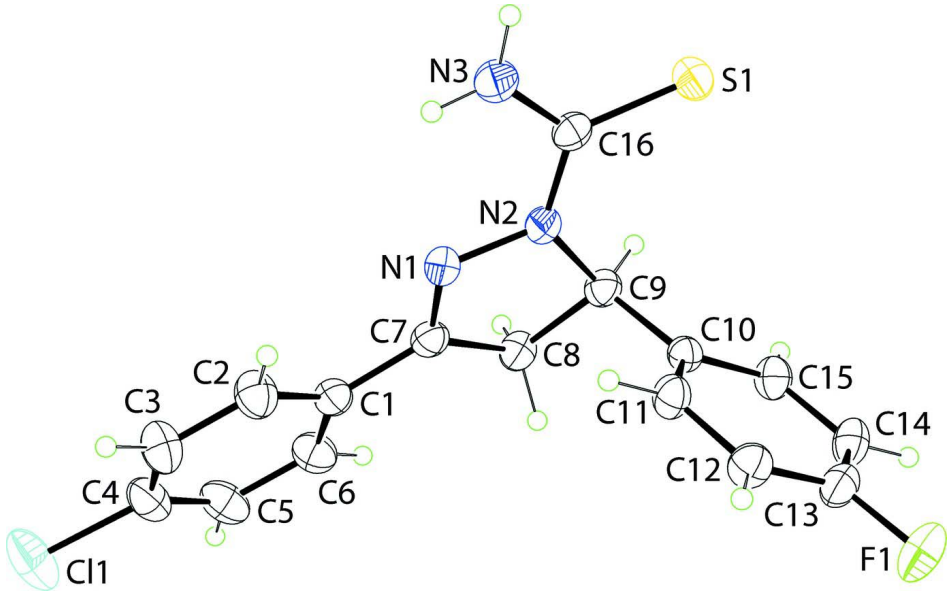

Figure 1

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level.

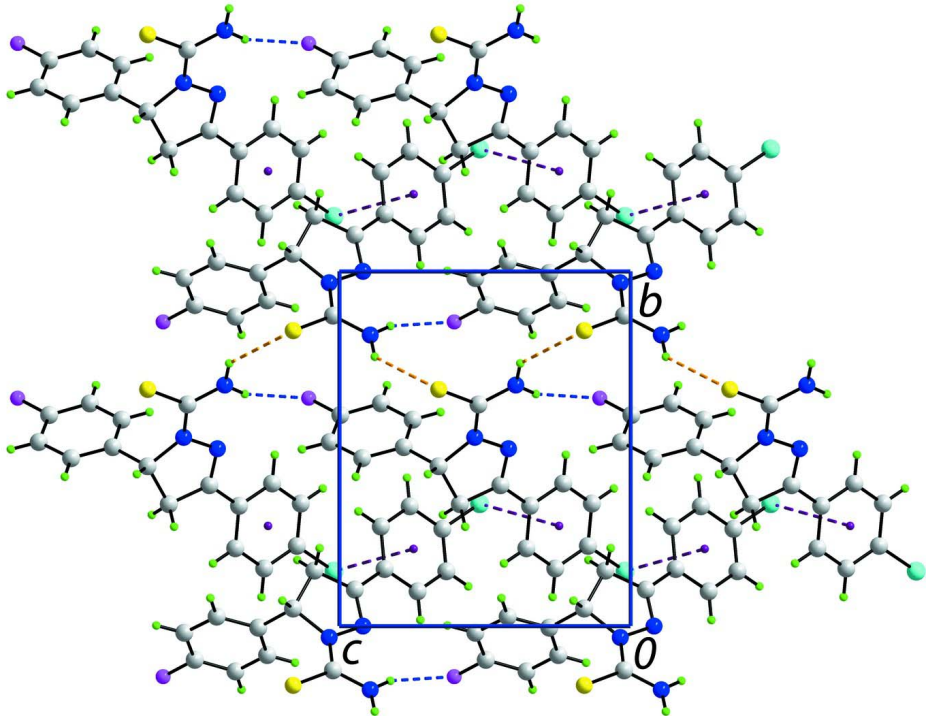

Figure 2

A view of the supramolecular layer in the *bc* plane in (I) mediated by N—H···S, N—H···F and Cl···π interactions, shown as orange, blue and purple dashed lines, respectively.

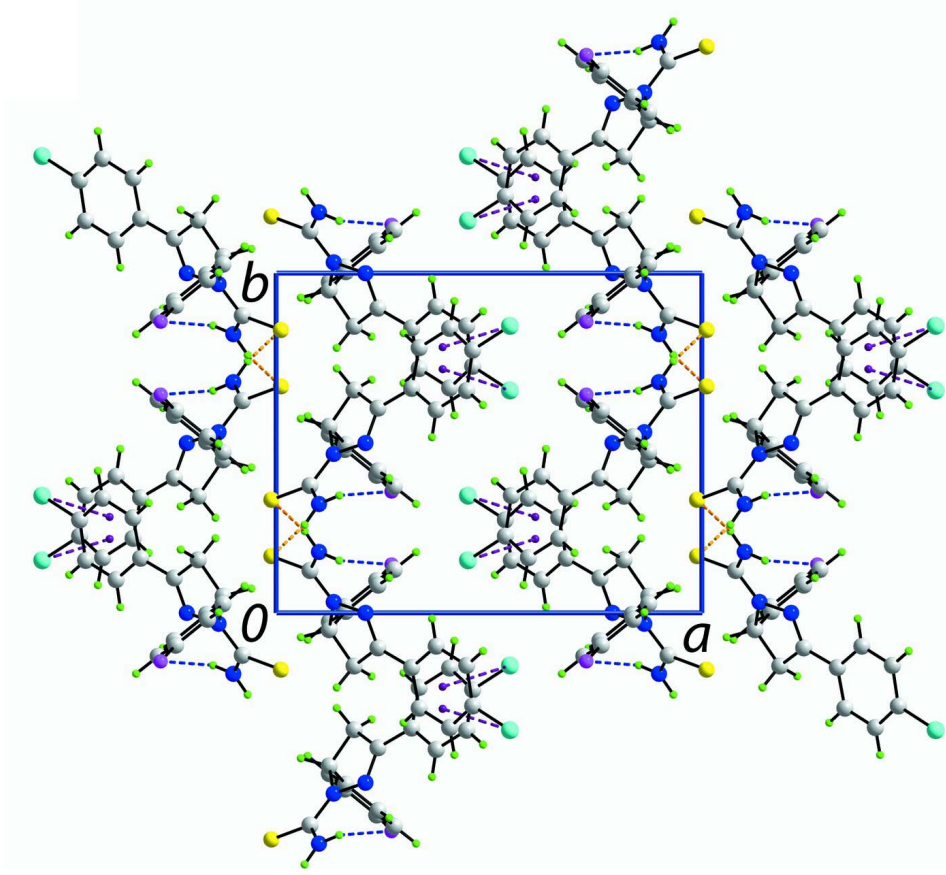

Figure 3

A view of the crystal packing in projection down the *c* axis. The N—H···S, N—H···F and Cl···π interactions are shown as orange, blue and purple dashed lines, respectively.

3-(4-Chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide

Crystal data

$C_{16}H_{13}ClFN_3S$
$M_r = 333.80$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 14.5402\ (9)$ Å
$b = 11.2700\ (8)$ Å
$c = 9.5169\ (6)$ Å
$\beta = 103.850\ (6)°$
$V = 1514.17\ (17)$ Å^3
$Z = 4$
$F(000) = 688$
$D_x = 1.464$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2717 reflections
$\theta = 2.9–27.5°$
$\mu = 0.40$ mm^{-1}
$T = 295$ K
Prism, colourless
0.40 × 0.30 × 0.20 mm

Data collection

Agilent SuperNova Dual diffractometer with an Atlas detector
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.4041 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{min} = 0.898$, $T_{max} = 1.000$
10191 measured reflections
3478 independent reflections
2570 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$

θ_{max} = 27.5°, θ_{min} = 2.9°
h = −15→18
k = −14→11
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.111
S = 1.01
3478 reflections
199 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
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.4541P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.54931 (5)	0.65490 (7)	0.48095 (8)	0.0811 (3)
S1	−0.01110 (4)	1.16708 (5)	−0.15948 (5)	0.04527 (17)
F1	0.27125 (11)	1.14248 (13)	−0.60633 (13)	0.0658 (4)
N1	0.20984 (11)	1.00001 (15)	0.08010 (15)	0.0379 (4)
N2	0.13525 (11)	1.03202 (14)	−0.03592 (15)	0.0368 (4)
N3	0.10065 (13)	1.17944 (16)	0.10514 (17)	0.0463 (4)
H31	0.1483	1.1542	0.1741	0.056*
H32	0.0669	1.2407	0.1207	0.056*
C1	0.31834 (13)	0.83907 (18)	0.1544 (2)	0.0381 (4)
C2	0.37595 (15)	0.9020 (2)	0.2678 (2)	0.0498 (5)
H2	0.3661	0.9829	0.2772	0.060*
C3	0.44754 (16)	0.8454 (2)	0.3665 (2)	0.0559 (6)
H3	0.4860	0.8879	0.4419	0.067*
C4	0.46163 (14)	0.7261 (2)	0.3529 (2)	0.0505 (6)
C5	0.40755 (15)	0.6624 (2)	0.2408 (3)	0.0533 (6)
H5	0.4187	0.5819	0.2314	0.064*
C6	0.33602 (14)	0.7194 (2)	0.1414 (2)	0.0476 (5)
H6	0.2993	0.6766	0.0647	0.057*
C7	0.23925 (13)	0.89711 (18)	0.05223 (19)	0.0366 (4)
C8	0.18302 (14)	0.84371 (17)	−0.08689 (19)	0.0394 (4)
H8A	0.1424	0.7802	−0.0687	0.047*
H8B	0.2242	0.8136	−0.1452	0.047*
C9	0.12464 (13)	0.95057 (17)	−0.15998 (18)	0.0365 (4)

H9	0.0581	0.9282	−0.1966	0.044*
C10	0.16342 (12)	1.00448 (17)	−0.27969 (17)	0.0330 (4)
C11	0.23938 (13)	1.08168 (18)	−0.24895 (19)	0.0403 (5)
H11	0.2656	1.1032	−0.1534	0.048*
C12	0.27723 (14)	1.12774 (19)	−0.3580 (2)	0.0442 (5)
H12	0.3288	1.1791	−0.3370	0.053*
C13	0.23618 (15)	1.09503 (19)	−0.4978 (2)	0.0430 (5)
C14	0.16111 (15)	1.01890 (19)	−0.53370 (19)	0.0463 (5)
H14	0.1350	0.9983	−0.6296	0.056*
C15	0.12497 (14)	0.97331 (18)	−0.42252 (19)	0.0400 (4)
H15	0.0741	0.9210	−0.4442	0.048*
C16	0.07946 (13)	1.12480 (17)	−0.02300 (19)	0.0352 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0556 (4)	0.0764 (5)	0.0967 (5)	0.0061 (3)	−0.0106 (3)	0.0318 (4)
S1	0.0410 (3)	0.0485 (4)	0.0446 (3)	0.0047 (2)	0.0067 (2)	0.0045 (2)
F1	0.0922 (10)	0.0679 (10)	0.0444 (7)	−0.0139 (8)	0.0304 (7)	0.0066 (6)
N1	0.0384 (8)	0.0440 (10)	0.0306 (7)	0.0025 (7)	0.0068 (6)	0.0007 (7)
N2	0.0406 (8)	0.0402 (10)	0.0295 (7)	0.0046 (7)	0.0080 (6)	−0.0024 (6)
N3	0.0537 (10)	0.0438 (10)	0.0409 (9)	0.0073 (8)	0.0106 (7)	−0.0069 (7)
C1	0.0368 (10)	0.0409 (12)	0.0380 (9)	0.0007 (8)	0.0116 (7)	0.0033 (8)
C2	0.0544 (13)	0.0427 (13)	0.0485 (12)	0.0034 (10)	0.0045 (9)	−0.0004 (9)
C3	0.0520 (13)	0.0587 (16)	0.0488 (12)	−0.0014 (11)	−0.0041 (10)	0.0004 (10)
C4	0.0349 (10)	0.0542 (15)	0.0606 (13)	0.0006 (10)	0.0078 (9)	0.0182 (11)
C5	0.0412 (11)	0.0397 (13)	0.0768 (15)	0.0024 (10)	0.0094 (10)	0.0066 (11)
C6	0.0400 (11)	0.0449 (13)	0.0565 (12)	−0.0026 (9)	0.0091 (9)	−0.0029 (10)
C7	0.0360 (10)	0.0397 (12)	0.0361 (9)	−0.0015 (8)	0.0129 (7)	0.0007 (8)
C8	0.0462 (11)	0.0372 (11)	0.0355 (9)	−0.0004 (9)	0.0111 (8)	−0.0002 (8)
C9	0.0364 (9)	0.0401 (11)	0.0324 (9)	−0.0022 (8)	0.0074 (7)	−0.0048 (8)
C10	0.0329 (9)	0.0343 (10)	0.0307 (8)	0.0027 (8)	0.0056 (7)	−0.0015 (7)
C11	0.0412 (10)	0.0458 (12)	0.0313 (9)	−0.0044 (9)	0.0033 (7)	−0.0028 (8)
C12	0.0431 (11)	0.0462 (13)	0.0437 (11)	−0.0074 (9)	0.0114 (8)	−0.0010 (9)
C13	0.0575 (12)	0.0397 (12)	0.0354 (10)	0.0030 (10)	0.0181 (9)	0.0038 (8)
C14	0.0605 (13)	0.0466 (13)	0.0289 (9)	−0.0014 (10)	0.0053 (8)	−0.0020 (8)
C15	0.0440 (11)	0.0380 (11)	0.0350 (9)	−0.0046 (9)	0.0037 (8)	−0.0030 (8)
C16	0.0378 (9)	0.0351 (11)	0.0358 (9)	−0.0042 (8)	0.0148 (7)	0.0024 (8)

Geometric parameters (Å, º)

Cl1—C4	1.735 (2)	C5—H5	0.9300
S1—C16	1.6821 (19)	C6—H6	0.9300
F1—C13	1.365 (2)	C7—C8	1.505 (2)
N1—C7	1.285 (2)	C8—C9	1.540 (3)
N1—N2	1.397 (2)	C8—H8A	0.9700
N2—C16	1.347 (2)	C8—H8B	0.9700
N2—C9	1.474 (2)	C9—C10	1.514 (3)

N3—C16	1.335 (2)	C9—H9	0.9800
N3—H31	0.8800	C10—C11	1.381 (3)
N3—H32	0.8800	C10—C15	1.386 (2)
C1—C6	1.384 (3)	C11—C12	1.386 (3)
C1—C2	1.392 (3)	C11—H11	0.9300
C1—C7	1.470 (3)	C12—C13	1.373 (3)
C2—C3	1.380 (3)	C12—H12	0.9300
C2—H2	0.9300	C13—C14	1.366 (3)
C3—C4	1.371 (3)	C14—C15	1.388 (3)
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.367 (3)	C15—H15	0.9300
C5—C6	1.385 (3)		

C7—N1—N2	107.67 (15)	C7—C8—H8B	111.4
C16—N2—N1	119.92 (15)	C9—C8—H8B	111.4
C16—N2—C9	127.35 (15)	H8A—C8—H8B	109.2
N1—N2—C9	112.63 (14)	N2—C9—C10	111.49 (15)
C16—N3—H31	120.0	N2—C9—C8	100.63 (13)
C16—N3—H32	120.0	C10—C9—C8	112.91 (15)
H31—N3—H32	120.0	N2—C9—H9	110.5
C6—C1—C2	118.41 (18)	C10—C9—H9	110.5
C6—C1—C7	120.48 (18)	C8—C9—H9	110.5
C2—C1—C7	121.10 (19)	C11—C10—C15	118.82 (17)
C3—C2—C1	120.5 (2)	C11—C10—C9	121.08 (15)
C3—C2—H2	119.7	C15—C10—C9	120.06 (17)
C1—C2—H2	119.7	C10—C11—C12	121.19 (17)
C4—C3—C2	119.7 (2)	C10—C11—H11	119.4
C4—C3—H3	120.2	C12—C11—H11	119.4
C2—C3—H3	120.2	C13—C12—C11	117.83 (19)
C3—C4—C5	121.16 (19)	C13—C12—H12	121.1
C3—C4—Cl1	119.23 (17)	C11—C12—H12	121.1
C5—C4—Cl1	119.61 (19)	C14—C13—F1	118.55 (17)
C4—C5—C6	119.1 (2)	C14—C13—C12	123.16 (18)
C4—C5—H5	120.4	F1—C13—C12	118.28 (19)
C6—C5—H5	120.4	C13—C14—C15	117.89 (17)
C5—C6—C1	121.1 (2)	C13—C14—H14	121.1
C5—C6—H6	119.5	C15—C14—H14	121.1
C1—C6—H6	119.5	C10—C15—C14	121.10 (18)
N1—C7—C1	120.74 (17)	C10—C15—H15	119.4
N1—C7—C8	113.88 (16)	C14—C15—H15	119.4
C1—C7—C8	125.33 (18)	N3—C16—N2	115.42 (16)
C7—C8—C9	102.08 (15)	N3—C16—S1	122.79 (16)
C7—C8—H8A	111.4	N2—C16—S1	121.78 (14)
C9—C8—H8A	111.4		

C7—N1—N2—C16	167.15 (16)	C16—N2—C9—C8	−159.69 (18)
C7—N1—N2—C9	−9.4 (2)	N1—N2—C9—C8	16.59 (19)
C6—C1—C2—C3	−1.4 (3)	C7—C8—C9—N2	−16.22 (18)

C7—C1—C2—C3	177.32 (19)	C7—C8—C9—C10	102.72 (17)
C1—C2—C3—C4	−0.3 (3)	N2—C9—C10—C11	31.9 (2)
C2—C3—C4—C5	1.8 (4)	C8—C9—C10—C11	−80.5 (2)
C2—C3—C4—Cl1	−177.91 (17)	N2—C9—C10—C15	−150.42 (17)
C3—C4—C5—C6	−1.4 (4)	C8—C9—C10—C15	97.1 (2)
Cl1—C4—C5—C6	178.23 (17)	C15—C10—C11—C12	−0.1 (3)
C4—C5—C6—C1	−0.3 (3)	C9—C10—C11—C12	177.60 (18)
C2—C1—C6—C5	1.7 (3)	C10—C11—C12—C13	0.6 (3)
C7—C1—C6—C5	−177.00 (19)	C11—C12—C13—C14	−0.7 (3)
N2—N1—C7—C1	179.67 (16)	C11—C12—C13—F1	178.21 (18)
N2—N1—C7—C8	−2.9 (2)	F1—C13—C14—C15	−178.68 (19)
C6—C1—C7—N1	165.27 (18)	C12—C13—C14—C15	0.2 (3)
C2—C1—C7—N1	−13.4 (3)	C11—C10—C15—C14	−0.4 (3)
C6—C1—C7—C8	−11.9 (3)	C9—C10—C15—C14	−178.12 (18)
C2—C1—C7—C8	169.41 (19)	C13—C14—C15—C10	0.3 (3)
N1—C7—C8—C9	12.9 (2)	N1—N2—C16—N3	−0.7 (2)
C1—C7—C8—C9	−169.76 (17)	C9—N2—C16—N3	175.38 (17)
C16—N2—C9—C10	80.3 (2)	N1—N2—C16—S1	179.89 (13)
N1—N2—C9—C10	−103.38 (17)	C9—N2—C16—S1	−4.1 (3)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H31···N1	0.88	2.24	2.617 (2)	106
N3—H31···F1^{i}	0.88	2.41	3.257 (2)	163
N3—H32···S1^{ii}	0.88	2.81	3.5203 (19)	139
C4—Cl1···*Cg*1^{iii}	1.74 (1)	3.92 (1)	4.183 (2)	86 (1)

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*, −*y*+5/2, *z*+1/2; (iii) *x*, −*y*+1/2, *z*−1/2.