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5-(3-Chlorophenylsulfanyl)-1-methyl-3-trifluoromethyl-1*H*-pyrazole-4-carbaldehyde *O*-[(2-chloro-1,3-thiazol-5-yl)-methyl]oxime

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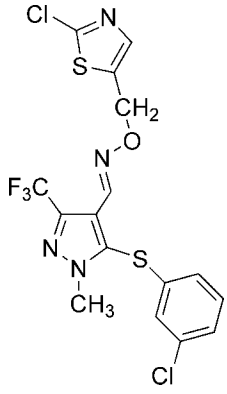
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.006 Å; R factor = 0.088; wR factor = 0.273; data-to-parameter ratio = 13.0.

In the title compound, $C_{16}H_{11}Cl_2F_3N_4OS_2$, the benzene ring and the thiazole ring make dihedral angles of 83.2 (3) and 78.3 (3)°, respectively, with the pyrazole ring. The crystal packing shows S···N contacts of 3.309 (2) Å.

Related literature

For the bioactivity of pyrazole oxime derivatives, see: Takao *et al.* (1994); Watanabe *et al.* (2001). For the biological activity of thiazole derivatives, see: Fahmy & Bekhit (2002); Sidoova *et al.* (1999); Zhang *et al.* (2000).



Experimental

Crystal data

$C_{16}H_{11}Cl_2F_3N_4OS_2$
M_r = 467.31
Monoclinic, $P2_1/n$
a = 12.328 (3) Å
b = 12.787 (3) Å
c = 13.139 (3) Å
β = 110.16 (3)°
V = 1944.3 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 113 K
0.20 × 0.16 × 0.10 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min} = 0.891, T_{max} = 0.943
9881 measured reflections
3309 independent reflections
2725 reflections with $I > 2\sigma(I)$
R_{int} = 0.116

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.088
$wR(F^2)$ = 0.273
S = 1.10
3309 reflections
254 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.94 e Å^{-3}

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AA2035).

References

Fahmy, H. Y. T. & Bekhit, A. A. (2002). *Pharmazie*, **57**, 800–803.
Rigaku (2008). *CrystalClear*. Rigaku Corporation, Toyko, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sidoova, E., Kralova, K. & Loos, D. (1999). *Molecules*, **4**, 73–80.
Takao, H., Wakisaka, S. & Murai, K. (1994). Jpn Patent No. 06329633.
Watanabe, M., Kuwata, T., Okada, T., Ohita, S., Asahara, T., Noritake, T. & Fukuda, Y. (2001). Jpn Patent No. 2001233861.
Zhang, A. G., Kayser, H., Maienfisch, P. & Casida, J. E. (2000). *J. Neurochem.* **75**, 1294–1303.

supplementary materials

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5-(3-Chlorophenylsulfanyl)-1-methyl-3-trifluoromethyl-1*H*-pyrazole-4-carbaldehyde *O*-[(2-chloro-1,3-thiazol-5-yl)methyl]oxime

H. Dai, S. Li, K.-P. Luo, J.-X. Fang and Y.-J. Shi

Comment

Recently, pyrazole oximes are reported to possess diverse biological activities, such as fungicidal, insecticidal, and acaricidal activities (Takao *et al.*, 1994; Watanabe *et al.*, 2001). On the other hand, many thiazole derivatives have been found to show insecticidal, herbicidal, and anticancer activities (Sidoova *et al.*, 1999; Zhang *et al.*, 2000; Fahmy & Bekhit, 2002). In search of novel pyrazole oxime derivatives with good bioactivities, we have sought to synthesize new pyrazole oxime ethers containing thiazole units. We report here the crystal structure of the target compound, (I). It contains three planes, the pyrazole ring (C2/C3/C4/N1/N2), the substituted phenyl ring (C6/C7/C8/C9/C10/C11) and the thiazole ring (C15/C14/S2/C16/N4) (Fig. 1). The dihedral angles between the the phenyl ring and the pyrazole ring and between the thiazole ring and the pyrazole ring are 83.2 (3)° and 78.3 (3)°, respectively. The crystal structure of (I) is stabilized by S···N contacts.

Experimental

To a violently stirred solution of 1-methyl-3-trifluoromethyl-5- (3-chlorophenylthio)-1*H*-pyrazole-4-carbaldehyde oxime (3 mmol) and potassium carbonate (9 mmol) in 20 ml of anhydrous *N*,*N*-dimethylformamide, was added dropwise a solution of 2-chloro-5-chloromethylthiazole (3.6 mmol) in 10 ml of anhydrous *N*,*N*-dimethylformamide. Then, to the above mixture was added a catalytic amount of caesium chloride at room temperature. The resulting solution was heated to 373 K for 6 h. After cooling to room temperature, the mixture was poured into water (200 ml) and extracted with ethyl acetate (3 × 50 ml). The organic layer was washed with 10% sodium carbonate solution (3 × 30 ml) and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was separated by column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate to obtain colourless crystals.

Refinement

Although all H atoms were visible in difference maps, they were placed in geometrically calculated positions and included in the final refinement in the riding-model approximation with C—H distances of 0.93–0.97 ° A, and U_{iso}(H) = 1.2U_{eq}(C).

Figures

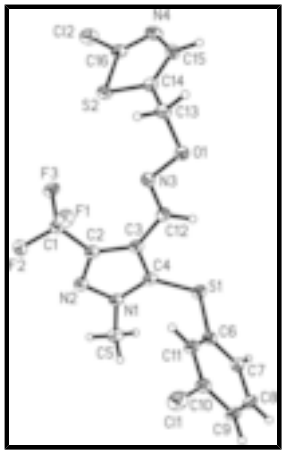


Fig. 1. View of the title compound (I), with displacement ellipsoids drawn at the 30% probability level.

5-(3-Chlorophenylsulfanyl)-1-methyl-3-trifluoromethyl-1*H*-pyrazole-4- carbaldehyde *O*-[(2-chloro-1,3-thiazol-5-yl)methyl]oxime

Crystal data

$C_{16}H_{11}Cl_2F_3N_4OS_2$	$F(000) = 944$
$M_r = 467.31$	$D_x = 1.597$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5433 reflections
$a = 12.328$ (3) Å	$\theta = 1.6$–$27.2°$
$b = 12.787$ (3) Å	$\mu = 0.59$ mm^{-1}
$c = 13.139$ (3) Å	$T = 113$ K
$\beta = 110.16$ (3)°	Prism, colourless
$V = 1944.3$ (9) Å^3	0.20 × 0.16 × 0.10 mm
$Z = 4$	

Data collection

Rigaku Saturn diffractometer	3309 independent reflections
Radiation source: rotating anode	2725 reflections with $I > 2\sigma(I)$
confocal	$R_{int} = 0.116$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)	$h = -11 \rightarrow 14$
$T_{min} = 0.891$, $T_{max} = 0.943$	$k = -15 \rightarrow 14$
9881 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.088$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.273$	H-atom parameters constrained
$S = 1.10$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3309 reflections	$(\Delta/\sigma)_{max} = 0.001$
254 parameters	$\Delta\rho_{max} = 0.81$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.94$ 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 $F^2 > \sigma(F^2)$ 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	0.01343 (10)	0.94499 (10)	0.66778 (11)	0.0519 (5)
Cl2	0.57227 (10)	0.80206 (10)	0.00569 (10)	0.0483 (4)
S1	0.36532 (9)	1.11017 (8)	0.55348 (9)	0.0348 (4)
S2	0.38132 (9)	0.80301 (8)	0.09658 (8)	0.0334 (4)
F1	0.2428 (2)	0.69627 (18)	0.3650 (2)	0.0403 (7)
F2	0.3861 (2)	0.62954 (18)	0.49260 (18)	0.0396 (7)
F3	0.4134 (2)	0.70073 (18)	0.3550 (2)	0.0388 (7)
O1	0.1746 (3)	0.9511 (2)	0.1630 (2)	0.0351 (7)
N1	0.4428 (3)	0.9119 (3)	0.6202 (2)	0.0280 (7)
N2	0.4393 (3)	0.8114 (2)	0.5871 (3)	0.0293 (8)
N3	0.2447 (3)	0.8956 (2)	0.2545 (3)	0.0312 (8)
N4	0.3842 (3)	0.9182 (3)	−0.0643 (3)	0.0402 (9)
C1	0.3548 (3)	0.7100 (3)	0.4235 (3)	0.0305 (9)
C2	0.3752 (3)	0.8122 (3)	0.4828 (3)	0.0283 (9)
C3	0.3354 (3)	0.9140 (3)	0.4454 (3)	0.0279 (8)
C4	0.3791 (3)	0.9760 (3)	0.5370 (3)	0.0285 (8)
C5	0.5030 (4)	0.9391 (3)	0.7338 (3)	0.0381 (10)
H5A	0.4487	0.9410	0.7714	0.057*
H5B	0.5386	1.0065	0.7379	0.057*
H5C	0.5613	0.8876	0.7666	0.057*
C6	0.2689 (3)	1.1125 (3)	0.6278 (3)	0.0310 (9)
C7	0.2734 (4)	1.2006 (3)	0.6906 (3)	0.0348 (10)
H7	0.3280	1.2526	0.6967	0.042*

C8	0.1934 (4)	1.2099 (3)	0.7451 (4)	0.0405 (11)
H8	0.1950	1.2690	0.7869	0.049*
C9	0.1125 (4)	1.1326 (3)	0.7376 (3)	0.0397 (10)
H9	0.0596	1.1389	0.7734	0.048*
C10	0.1127 (4)	1.0458 (3)	0.6753 (3)	0.0345 (9)
C11	0.1877 (3)	1.0346 (3)	0.6185 (3)	0.0328 (9)
H11	0.1839	0.9763	0.5750	0.039*
C12	0.2648 (3)	0.9524 (3)	0.3388 (3)	0.0308 (9)
H12	0.2339	1.0195	0.3321	0.037*
C13	0.1586 (4)	0.8867 (3)	0.0688 (3)	0.0351 (10)
H13A	0.0938	0.9134	0.0089	0.042*
H13B	0.1397	0.8161	0.0841	0.042*
C14	0.2639 (3)	0.8834 (3)	0.0357 (3)	0.0302 (9)
C15	0.2824 (4)	0.9380 (3)	−0.0462 (3)	0.0360 (10)
H15	0.2288	0.9862	−0.0877	0.043*
C16	0.4424 (4)	0.8484 (3)	0.0046 (3)	0.0355 (10)

Atomic displacement parameters (Å^2)

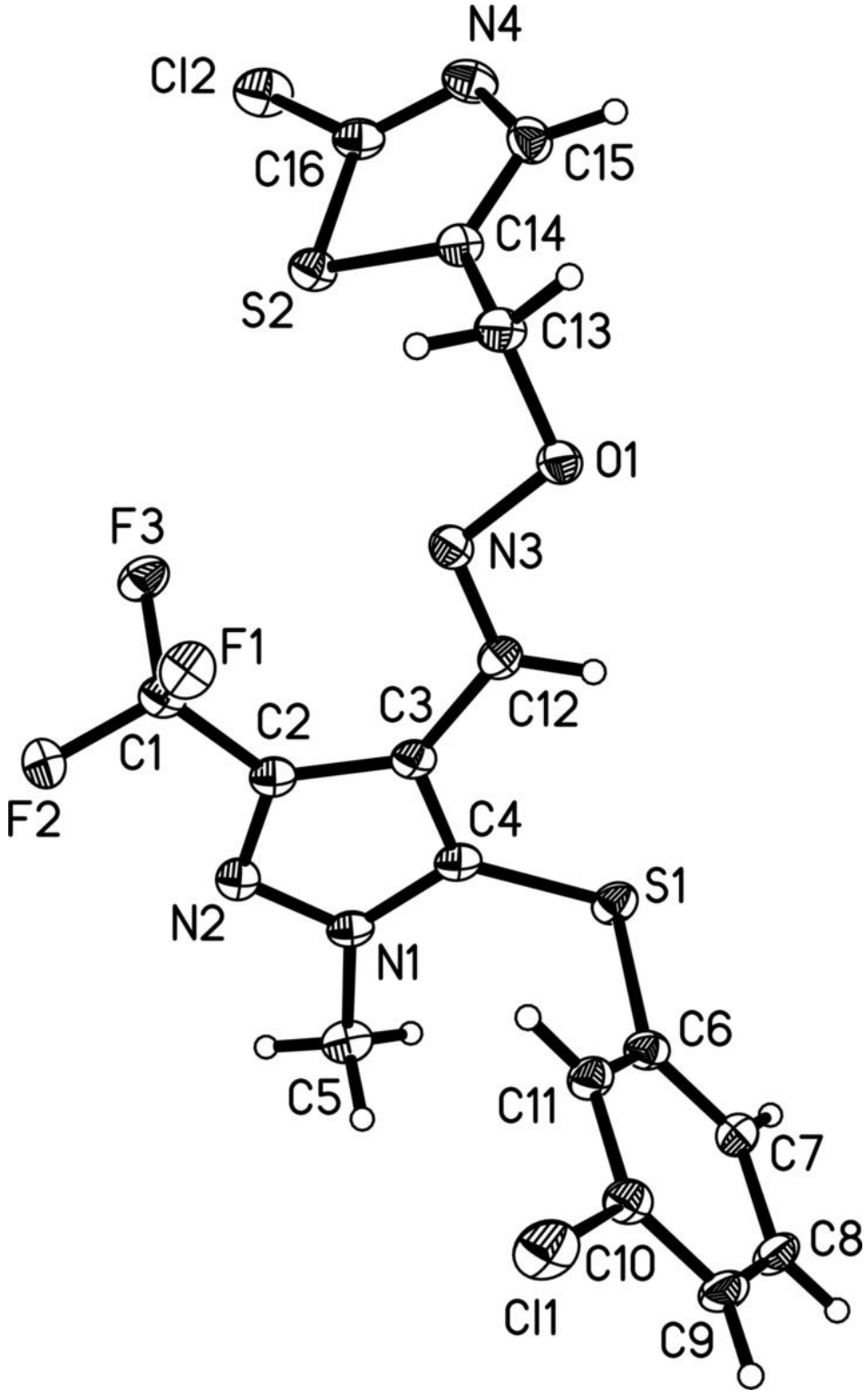
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0347 (7)	0.0614 (8)	0.0707 (9)	−0.0063 (5)	0.0322 (6)	−0.0026 (5)
Cl2	0.0299 (7)	0.0728 (9)	0.0460 (7)	0.0030 (5)	0.0179 (5)	−0.0001 (5)
S1	0.0347 (7)	0.0345 (6)	0.0437 (7)	−0.0039 (4)	0.0244 (5)	−0.0030 (4)
S2	0.0270 (7)	0.0436 (7)	0.0312 (7)	0.0031 (4)	0.0119 (5)	0.0028 (4)
F1	0.0242 (13)	0.0447 (14)	0.0503 (15)	−0.0077 (9)	0.0109 (11)	−0.0058 (10)
F2	0.0461 (16)	0.0323 (12)	0.0411 (14)	0.0024 (10)	0.0161 (12)	0.0052 (9)
F3	0.0392 (15)	0.0408 (13)	0.0442 (14)	−0.0027 (10)	0.0244 (12)	−0.0076 (10)
O1	0.0342 (16)	0.0420 (15)	0.0284 (14)	0.0115 (11)	0.0100 (12)	0.0036 (11)
N1	0.0197 (16)	0.0392 (17)	0.0297 (17)	−0.0036 (13)	0.0143 (13)	−0.0025 (13)
N2	0.0219 (17)	0.0339 (17)	0.0336 (18)	−0.0021 (12)	0.0115 (14)	−0.0001 (13)
N3	0.0263 (18)	0.0370 (18)	0.0319 (17)	0.0058 (13)	0.0120 (14)	0.0054 (13)
N4	0.036 (2)	0.054 (2)	0.0329 (19)	−0.0050 (17)	0.0147 (16)	0.0029 (17)
C1	0.022 (2)	0.040 (2)	0.033 (2)	0.0003 (15)	0.0145 (16)	0.0024 (16)
C2	0.0200 (19)	0.037 (2)	0.032 (2)	−0.0028 (14)	0.0142 (16)	−0.0006 (15)
C3	0.0203 (19)	0.0370 (19)	0.032 (2)	−0.0006 (14)	0.0160 (16)	0.0011 (15)
C4	0.0191 (18)	0.040 (2)	0.034 (2)	−0.0026 (15)	0.0190 (16)	−0.0001 (15)
C5	0.031 (2)	0.048 (2)	0.035 (2)	−0.0055 (17)	0.0110 (18)	−0.0068 (18)
C6	0.026 (2)	0.040 (2)	0.0281 (19)	0.0018 (15)	0.0111 (16)	0.0017 (15)
C7	0.036 (2)	0.035 (2)	0.036 (2)	0.0047 (15)	0.016 (2)	0.0016 (15)
C8	0.042 (3)	0.047 (2)	0.036 (2)	0.0157 (19)	0.019 (2)	−0.0039 (18)
C9	0.033 (2)	0.056 (3)	0.035 (2)	0.0158 (19)	0.0181 (19)	0.0011 (19)
C10	0.024 (2)	0.046 (2)	0.036 (2)	0.0040 (16)	0.0134 (17)	0.0046 (17)
C11	0.026 (2)	0.041 (2)	0.033 (2)	0.0066 (16)	0.0125 (17)	0.0007 (16)
C12	0.025 (2)	0.036 (2)	0.035 (2)	0.0039 (15)	0.0158 (17)	0.0010 (15)
C13	0.029 (2)	0.047 (2)	0.029 (2)	0.0040 (16)	0.0098 (17)	0.0009 (16)
C14	0.0233 (19)	0.038 (2)	0.0286 (19)	0.0009 (15)	0.0077 (16)	−0.0017 (15)
C15	0.033 (2)	0.040 (2)	0.034 (2)	0.0066 (16)	0.0105 (18)	0.0056 (16)
C16	0.030 (2)	0.047 (2)	0.031 (2)	−0.0041 (17)	0.0120 (17)	−0.0030 (17)

Geometric parameters (Å, °)

Cl1—C10	1.756 (4)	C3—C12	1.456 (5)
Cl2—C16	1.703 (4)	C5—H5A	0.9600
S1—C4	1.744 (4)	C5—H5B	0.9600
S1—C6	1.780 (4)	C5—H5C	0.9600
S2—C16	1.729 (4)	C6—C7	1.386 (6)
S2—C14	1.730 (4)	C6—C11	1.387 (6)
F1—C1	1.341 (5)	C7—C8	1.409 (6)
F2—C1	1.338 (5)	C7—H7	0.9300
F3—C1	1.339 (5)	C8—C9	1.383 (7)
O1—N3	1.407 (4)	C8—H8	0.9300
O1—C13	1.442 (5)	C9—C10	1.380 (6)
N1—N2	1.352 (5)	C9—H9	0.9300
N1—C4	1.376 (5)	C10—C11	1.382 (6)
N1—C5	1.461 (5)	C11—H11	0.9300
N2—C2	1.325 (5)	C12—H12	0.9300
N3—C12	1.275 (5)	C13—C14	1.505 (6)
N4—C16	1.298 (6)	C13—H13A	0.9700
N4—C15	1.379 (6)	C13—H13B	0.9700
C1—C2	1.497 (5)	C14—C15	1.366 (6)
C2—C3	1.418 (5)	C15—H15	0.9300
C3—C4	1.386 (5)		
C4—S1—C6	101.37 (18)	C6—C7—C8	118.7 (4)
C16—S2—C14	88.5 (2)	C6—C7—H7	120.7
N3—O1—C13	107.9 (3)	C8—C7—H7	120.7
N2—N1—C4	111.4 (3)	C9—C8—C7	121.1 (4)
N2—N1—C5	120.2 (3)	C9—C8—H8	119.4
C4—N1—C5	128.3 (3)	C7—C8—H8	119.4
C2—N2—N1	105.5 (3)	C10—C9—C8	117.9 (4)
C12—N3—O1	109.5 (3)	C10—C9—H9	121.0
C16—N4—C15	108.8 (4)	C8—C9—H9	121.0
F2—C1—F3	107.0 (3)	C9—C10—C11	122.8 (4)
F2—C1—F1	106.7 (3)	C9—C10—Cl1	118.7 (3)
F3—C1—F1	106.9 (3)	C11—C10—Cl1	118.5 (3)
F2—C1—C2	111.1 (3)	C10—C11—C6	118.4 (4)
F3—C1—C2	113.3 (3)	C10—C11—H11	120.8
F1—C1—C2	111.6 (3)	C6—C11—H11	120.8
N2—C2—C3	112.2 (3)	N3—C12—C3	121.1 (4)
N2—C2—C1	117.7 (3)	N3—C12—H12	119.5
C3—C2—C1	130.1 (4)	C3—C12—H12	119.5
C4—C3—C2	103.9 (3)	O1—C13—C14	112.8 (3)
C4—C3—C12	124.5 (4)	O1—C13—H13A	109.0
C2—C3—C12	131.6 (3)	C14—C13—H13A	109.0
N1—C4—C3	107.0 (3)	O1—C13—H13B	109.0
N1—C4—S1	122.7 (3)	C14—C13—H13B	109.0
C3—C4—S1	130.2 (3)	H13A—C13—H13B	107.8
N1—C5—H5A	109.5	C15—C14—C13	127.5 (4)

N1—C5—H5B	109.5	C15—C14—S2	109.1 (3)
H5A—C5—H5B	109.5	C13—C14—S2	123.4 (3)
N1—C5—H5C	109.5	C14—C15—N4	116.8 (4)
H5A—C5—H5C	109.5	C14—C15—H15	121.6
H5B—C5—H5C	109.5	N4—C15—H15	121.6
C7—C6—C11	121.0 (4)	N4—C16—Cl2	122.5 (3)
C7—C6—S1	116.3 (3)	N4—C16—S2	116.7 (3)
C11—C6—S1	122.5 (3)	Cl2—C16—S2	120.8 (3)
C4—N1—N2—C2	1.0 (4)	C4—S1—C6—C11	−28.8 (4)
C5—N1—N2—C2	177.4 (3)	C11—C6—C7—C8	0.0 (6)
C13—O1—N3—C12	177.1 (3)	S1—C6—C7—C8	175.6 (3)
N1—N2—C2—C3	0.1 (4)	C6—C7—C8—C9	0.7 (6)
N1—N2—C2—C1	−179.5 (3)	C7—C8—C9—C10	0.2 (6)
F2—C1—C2—N2	13.1 (5)	C8—C9—C10—C11	−1.8 (6)
F3—C1—C2—N2	−107.4 (4)	C8—C9—C10—Cl1	178.2 (3)
F1—C1—C2—N2	131.9 (4)	C9—C10—C11—C6	2.4 (6)
F2—C1—C2—C3	−166.4 (4)	Cl1—C10—C11—C6	−177.6 (3)
F3—C1—C2—C3	73.2 (5)	C7—C6—C11—C10	−1.4 (6)
F1—C1—C2—C3	−47.5 (5)	S1—C6—C11—C10	−176.8 (3)
N2—C2—C3—C4	−1.1 (4)	O1—N3—C12—C3	179.8 (3)
C1—C2—C3—C4	178.4 (4)	C4—C3—C12—N3	167.3 (4)
N2—C2—C3—C12	179.3 (4)	C2—C3—C12—N3	−13.1 (7)
C1—C2—C3—C12	−1.3 (7)	N3—O1—C13—C14	−75.3 (4)
N2—N1—C4—C3	−1.7 (4)	O1—C13—C14—C15	−100.8 (5)
C5—N1—C4—C3	−177.7 (4)	O1—C13—C14—S2	81.4 (4)
N2—N1—C4—S1	179.5 (3)	C16—S2—C14—C15	−1.1 (3)
C5—N1—C4—S1	3.5 (5)	C16—S2—C14—C13	177.0 (4)
C2—C3—C4—N1	1.6 (4)	C13—C14—C15—N4	−177.1 (4)
C12—C3—C4—N1	−178.7 (3)	S2—C14—C15—N4	0.9 (5)
C2—C3—C4—S1	−179.7 (3)	C16—N4—C15—C14	−0.1 (5)
C12—C3—C4—S1	0.0 (6)	C15—N4—C16—Cl2	178.8 (3)
C6—S1—C4—N1	−74.0 (3)	C15—N4—C16—S2	−0.9 (5)
C6—S1—C4—C3	107.5 (4)	C14—S2—C16—N4	1.2 (3)
C4—S1—C6—C7	155.6 (3)	C14—S2—C16—Cl2	−178.5 (3)

Fig. 1


N4
Cl2
C16
C15
C14
S2
C13
O1
F3
N3
F1
C12
C3
C2
C1
F2
C4
S1
N2
N1
C6
C5
C11
C7
C10
C8
Cl1
C9