IUCrData

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3-{2-[3-(4-Chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-1-yl]thiazol-4-yl}-3,8a-dihydro-2*H*-chromen-2-one

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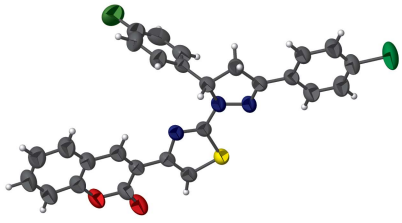
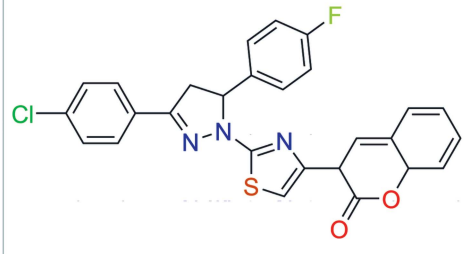
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{27}H_{17}ClFN_3O_2S$, comprises chromonyl (*A*), thiazolyl (*B*), pyrazolyl (*C*), chlorophenyl (*D*) and fluorophenyl (*E*) rings with twist angles between the planes of adjacent rings pairs *A*/*B*, *B*/*C*, *C*/*D* and *C*/*E* of 14.1 (1), 18.2 (2), 1.3 (1) and 4.9 (1)°, respectively. The crystal structure is characterized by a range of intermolecular interactions including C—H···F, C—H···Cl and C—H···O contacts. Aromatic π–π stacking between chromonyl groups and chlorophenyl groups [centroid–centroid separations = 3.7170 (16) and 4.017 (2) Å, respectively] lead to columns of molecules propagating parallel to the [100] direction.

3D view



Chemical scheme



Structure description

Coumarins act as anticoagulant drugs (O'Reilly & Aggeler, 1968). Thiazoles are an essential core scaffold in many natural products (Chhabria *et al.*, 2016) and pyrazoles have a broad spectrum of biological activities (Faria *et al.*, 2017). We now describe the synthesis and structure of the title compound.

The asymmetric unit consists of one molecule, which comprises chromonyl (*A*), thiazolyl (*B*), pyrazolyl (*C*), chlorophenyl (*D*) and fluorophenyl (*E*) rings (Fig. 1). The twist angles between the planes through neighbouring rings pairs *A*/*B*, *B*/*C*, *C*/*D* and *C*/*E* are 14.1 (1), 18.2 (2), 1.3 (1) and 4.9 (1)°, respectively. The stereogenic centre C13 has an *S*

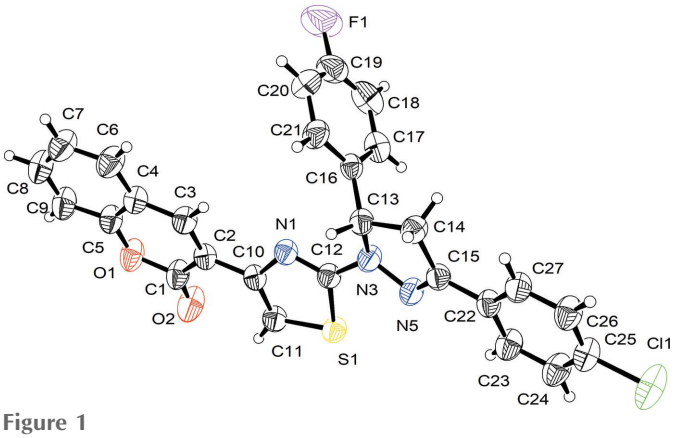


Figure 1
The molecular structure of the title compound showing 50% displacement ellipsoids.

configuration in the arbitrarily chosen asymmetric unit, but the crystal symmetry generates a racemic mixture.

The extended structure is characterized by a range of intermolecular interactions including C—H···F, C—H···Cl and C—H···O contacts (Table 1, Fig. 2). Aromatic π–π stacking between chromonyl groups [with centroid-to-centroid distances of 3.7170 (16) Å] and between chlorophenyl groups [with ring-centroid separations of 4.017 (2) Å] lead to the formation of columns propagating in the [100] direction (Fig. 3).

Synthesis and crystallization

The title compound was synthesized from the condensation of 3-(4-chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide (0.67 g, 2.0 mmol) with 3-(2-bromoacetyl)-3,8a-dihydro-2*H*-chromen-2-one (0.54 g, 2.0 mmol) in anhydrous ethanol (20 ml) under reflux for 2 h. The formed solid was recrystallized from dimethylformamide solution to give colourless blocks (83%), m.p. 228–230°C.

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

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···F1^{i}	0.98	2.47	3.372 (4)	154
C20—H20···Cl1^{ii}	0.93	2.98	3.829 (4)	153
C26—H26···O2^{iii}	0.93	2.54	3.282 (4)	137

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{27}H_{17}ClFN_3O_2S$
M_r	501.95
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	296
a, b, c (Å)	7.9243 (5), 23.7112 (9), 24.9270 (15)
V (Å^3)	4683.7 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.29
Crystal size (mm)	0.31 × 0.18 × 0.14
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.997, 0.998
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21351, 5809, 3055
R_{int}	0.044
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.702
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.184, 1.04
No. of reflections	5809
No. of parameters	317
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.64, −0.58

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *CHEMDRAW Ultra* (Cambridge Soft, 2001).

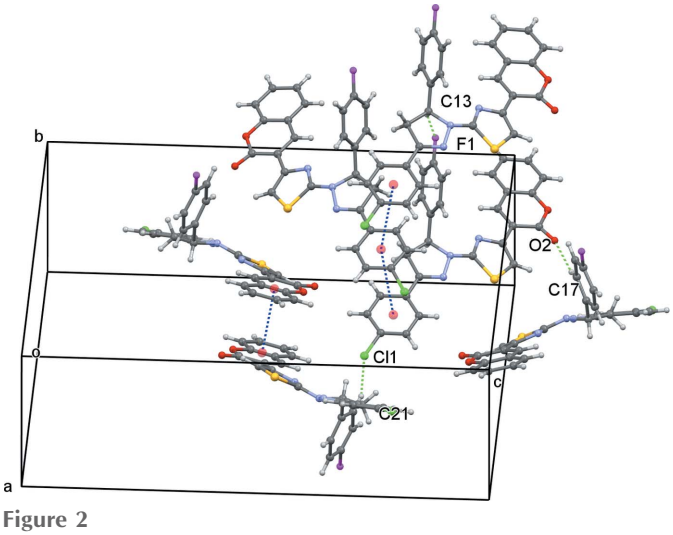


Figure 2
A segment of the crystal structure showing intermolecular contacts as dotted lines.

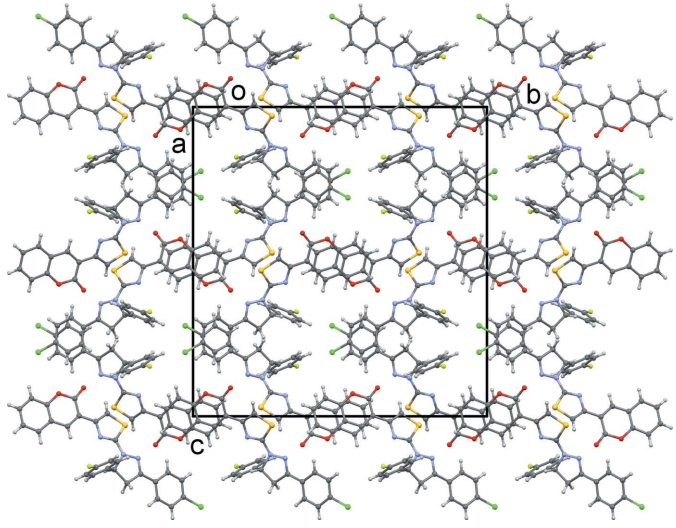


Figure 3
The crystal structure viewed down the *a*-axis direction.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2019). **4**, x190170 [https://doi.org/10.1107/S2414314619001706]

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Crystal data

$C_{27}H_{17}ClFN_3O_2S$
M_r = 501.95
Orthorhombic, *Pbca*
a = 7.9243 (5) Å
b = 23.7112 (9) Å
c = 24.9270 (15) Å
V = 4683.7 (4) Å^3
Z = 8
$F(000)$ = 2064
D_x = 1.424 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3797 reflections
θ = 4.0–25.8°
μ = 0.29 mm^{-1}
T = 296 K
Block, colourless
0.31 × 0.18 × 0.14 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas diffractometer
ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.997, T_{max} = 0.998
21351 measured reflections
5809 independent reflections
3055 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 29.9°, θ_{min} = 3.4°
h = −10→11
k = −32→24
l = −28→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.184
S = 1.04
5809 reflections
317 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0699P)^2 + 1.7487P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}
Extinction correction: SHELXL-2018/1 (Sheldrick 2018), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0020 (4)

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.

Refinement. All hydrogen atoms were placed in calculated positions and refined using a riding model. Bond distances for sp^2 C—H hydrogen atoms were set to 0.93 Å and their U_{iso} set to 1.2 times U_{eq}(C). Bond distances for methine and methylene C—H hydrogen atoms were set to 0.98 Å and 0.97 Å respectively and their U_{iso} set to 1.2 times U_{eq}(C).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6165 (5)	0.40241 (12)	0.44274 (13)	0.0673 (9)
C2	0.6420 (3)	0.38786 (11)	0.49852 (12)	0.0527 (7)
C3	0.7055 (4)	0.42696 (11)	0.53236 (13)	0.0599 (8)
H3	0.723831	0.417008	0.567977	0.072*
C4	0.7455 (4)	0.48295 (11)	0.51563 (13)	0.0606 (8)
C5	0.7184 (4)	0.49645 (12)	0.46241 (13)	0.0630 (8)
C6	0.8068 (5)	0.52546 (13)	0.54907 (16)	0.0795 (10)
H6	0.826003	0.517879	0.585166	0.095*
C7	0.8392 (5)	0.57845 (14)	0.52916 (17)	0.0845 (11)
H7	0.880402	0.606465	0.551749	0.101*
C8	0.8110 (5)	0.58998 (14)	0.47617 (17)	0.0843 (11)
H8	0.833890	0.625898	0.463070	0.101*
C9	0.7497 (5)	0.54977 (13)	0.44212 (16)	0.0811 (10)
H9	0.729519	0.557999	0.406213	0.097*
C10	0.5992 (4)	0.33085 (11)	0.51677 (11)	0.0512 (7)
C11	0.5060 (4)	0.29166 (12)	0.49111 (13)	0.0590 (7)
H11	0.458704	0.296635	0.457296	0.071*
C12	0.6074 (4)	0.26392 (11)	0.57715 (12)	0.0527 (7)
C13	0.6996 (4)	0.26833 (11)	0.67224 (12)	0.0543 (7)
H13	0.622678	0.300241	0.677451	0.065*
C14	0.6679 (4)	0.22431 (12)	0.71584 (13)	0.0623 (8)
H14A	0.773301	0.210687	0.730791	0.075*
H14B	0.599109	0.239701	0.744513	0.075*
C15	0.5765 (4)	0.17823 (11)	0.68671 (12)	0.0549 (7)
C16	0.8778 (3)	0.28972 (10)	0.66887 (11)	0.0484 (6)
C17	1.0059 (4)	0.25844 (13)	0.64682 (13)	0.0647 (8)
H17	0.982862	0.222720	0.633272	0.078*
C18	1.1688 (5)	0.27924 (19)	0.64442 (16)	0.0850 (11)
H18	1.255418	0.258144	0.629208	0.102*
C19	1.1984 (5)	0.3308 (2)	0.66472 (18)	0.0861 (11)
C20	1.0797 (5)	0.36238 (15)	0.68832 (17)	0.0872 (11)
H20	1.106018	0.397365	0.702961	0.105*
C21	0.9171 (4)	0.34161 (11)	0.69032 (14)	0.0676 (9)
H21	0.832787	0.362996	0.706419	0.081*
C22	0.5073 (4)	0.12765 (11)	0.71181 (12)	0.0539 (7)
C23	0.4302 (4)	0.08538 (12)	0.68196 (14)	0.0683 (8)

H23	0.422286	0.088981	0.644896	0.082*
C24	0.3655 (5)	0.03834 (13)	0.70667 (15)	0.0751 (10)
H24	0.314270	0.010204	0.686412	0.090*
C25	0.3768 (5)	0.03306 (11)	0.76113 (15)	0.0700 (9)
C26	0.4514 (5)	0.07388 (12)	0.79203 (14)	0.0706 (9)
H26	0.458289	0.069842	0.829072	0.085*
C27	0.5162 (4)	0.12107 (12)	0.76704 (13)	0.0637 (8)
H27	0.566947	0.149040	0.787635	0.076*
N1	0.6574 (3)	0.31478 (9)	0.56682 (9)	0.0545 (6)
N3	0.6491 (3)	0.23679 (9)	0.62379 (10)	0.0629 (7)
N5	0.5655 (3)	0.18683 (9)	0.63576 (11)	0.0607 (6)
O1	0.6566 (3)	0.45689 (8)	0.42704 (9)	0.0774 (7)
O2	0.5641 (4)	0.37238 (9)	0.40796 (10)	0.0963 (9)
S1	0.48577 (10)	0.23142 (3)	0.52875 (3)	0.0601 (3)
Cl1	0.29654 (18)	−0.02666 (4)	0.79278 (5)	0.1103 (4)
F1	1.3583 (3)	0.35259 (13)	0.66200 (13)	0.1451 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.101 (2)	0.0501 (15)	0.051 (2)	−0.0008 (16)	−0.0030 (17)	0.0017 (14)
C2	0.0635 (16)	0.0520 (14)	0.0427 (18)	0.0052 (13)	0.0025 (13)	0.0007 (12)
C3	0.078 (2)	0.0568 (15)	0.0448 (18)	−0.0010 (15)	−0.0017 (15)	−0.0005 (13)
C4	0.0722 (19)	0.0532 (15)	0.057 (2)	0.0002 (14)	0.0046 (16)	0.0007 (14)
C5	0.081 (2)	0.0504 (15)	0.057 (2)	0.0040 (15)	0.0025 (16)	−0.0009 (14)
C6	0.109 (3)	0.0625 (19)	0.067 (2)	−0.0128 (18)	−0.001 (2)	−0.0054 (16)
C7	0.109 (3)	0.0623 (19)	0.082 (3)	−0.0137 (19)	−0.001 (2)	−0.0077 (18)
C8	0.112 (3)	0.0541 (17)	0.087 (3)	−0.0056 (18)	0.008 (2)	0.0085 (18)
C9	0.115 (3)	0.0567 (17)	0.071 (3)	−0.0001 (19)	−0.001 (2)	0.0081 (16)
C10	0.0621 (17)	0.0509 (13)	0.0404 (17)	0.0058 (13)	−0.0005 (13)	−0.0007 (12)
C11	0.0741 (19)	0.0576 (16)	0.0453 (18)	−0.0008 (14)	−0.0093 (14)	−0.0016 (13)
C12	0.0600 (16)	0.0534 (15)	0.0447 (17)	−0.0003 (13)	−0.0018 (13)	0.0017 (12)
C13	0.0659 (17)	0.0482 (13)	0.0488 (18)	0.0010 (13)	−0.0046 (13)	−0.0015 (12)
C14	0.074 (2)	0.0609 (16)	0.052 (2)	−0.0109 (15)	−0.0033 (15)	0.0034 (14)
C15	0.0635 (17)	0.0495 (14)	0.052 (2)	−0.0002 (13)	−0.0052 (14)	0.0013 (13)
C16	0.0613 (16)	0.0444 (13)	0.0397 (16)	0.0052 (12)	−0.0026 (12)	0.0008 (11)
C17	0.084 (2)	0.0634 (17)	0.0468 (19)	0.0155 (16)	0.0023 (15)	−0.0049 (14)
C18	0.071 (2)	0.119 (3)	0.065 (3)	0.031 (2)	0.0178 (18)	0.014 (2)
C19	0.059 (2)	0.111 (3)	0.088 (3)	−0.009 (2)	−0.0010 (19)	0.033 (2)
C20	0.087 (3)	0.068 (2)	0.106 (3)	−0.022 (2)	−0.012 (2)	0.003 (2)
C21	0.071 (2)	0.0489 (15)	0.083 (3)	0.0014 (15)	0.0023 (18)	−0.0112 (14)
C22	0.0671 (18)	0.0478 (14)	0.0468 (18)	0.0010 (13)	−0.0023 (13)	0.0013 (12)
C23	0.095 (2)	0.0564 (16)	0.053 (2)	−0.0090 (17)	−0.0010 (17)	−0.0058 (14)
C24	0.106 (3)	0.0536 (16)	0.066 (3)	−0.0150 (17)	0.0013 (19)	−0.0111 (15)
C25	0.092 (2)	0.0509 (15)	0.067 (2)	−0.0062 (16)	0.0103 (18)	0.0031 (15)
C26	0.099 (2)	0.0604 (17)	0.052 (2)	−0.0064 (17)	0.0027 (17)	0.0030 (15)
C27	0.081 (2)	0.0543 (15)	0.056 (2)	−0.0049 (14)	−0.0059 (16)	0.0016 (14)
N1	0.0670 (14)	0.0523 (12)	0.0442 (15)	−0.0023 (11)	−0.0048 (11)	0.0024 (10)

N3	0.0846 (17)	0.0538 (13)	0.0503 (16)	−0.0152 (12)	−0.0163 (13)	0.0064 (11)
N5	0.0790 (17)	0.0497 (12)	0.0534 (17)	−0.0092 (12)	−0.0080 (13)	0.0029 (11)
O1	0.125 (2)	0.0554 (11)	0.0522 (14)	−0.0044 (12)	−0.0058 (13)	0.0056 (10)
O2	0.172 (3)	0.0663 (13)	0.0507 (15)	−0.0200 (16)	−0.0255 (16)	0.0004 (11)
S1	0.0744 (5)	0.0541 (4)	0.0517 (5)	−0.0075 (3)	−0.0083 (4)	−0.0012 (3)
Cl1	0.1708 (11)	0.0635 (5)	0.0965 (9)	−0.0316 (6)	0.0262 (7)	0.0075 (5)
F1	0.0697 (14)	0.196 (3)	0.170 (3)	−0.0305 (16)	−0.0078 (16)	0.066 (2)

Geometric parameters (Å, º)

C1—O2	1.196 (4)	C14—C15	1.499 (4)
C1—O1	1.386 (3)	C14—H14A	0.9700
C1—C2	1.447 (4)	C14—H14B	0.9700
C2—C3	1.351 (4)	C15—N5	1.289 (4)
C2—C10	1.466 (4)	C15—C22	1.459 (4)
C3—C4	1.427 (4)	C16—C17	1.372 (4)
C3—H3	0.9300	C16—C21	1.377 (4)
C4—C5	1.381 (4)	C17—C18	1.383 (5)
C4—C6	1.395 (4)	C17—H17	0.9300
C5—O1	1.377 (4)	C18—C19	1.344 (5)
C5—C9	1.384 (4)	C18—H18	0.9300
C6—C7	1.375 (4)	C19—C20	1.338 (6)
C6—H6	0.9300	C19—F1	1.370 (4)
C7—C8	1.367 (5)	C20—C21	1.380 (5)
C7—H7	0.9300	C20—H20	0.9300
C8—C9	1.366 (5)	C21—H21	0.9300
C8—H8	0.9300	C22—C27	1.387 (4)
C9—H9	0.9300	C22—C23	1.390 (4)
C10—C11	1.348 (4)	C23—C24	1.373 (4)
C10—N1	1.384 (3)	C23—H23	0.9300
C11—S1	1.716 (3)	C24—C25	1.366 (5)
C11—H11	0.9300	C24—H24	0.9300
C12—N1	1.295 (3)	C25—C26	1.371 (4)
C12—N3	1.369 (4)	C25—Cl1	1.741 (3)
C12—S1	1.726 (3)	C26—C27	1.380 (4)
C13—N3	1.476 (4)	C26—H26	0.9300
C13—C16	1.503 (4)	C27—H27	0.9300
C13—C14	1.528 (4)	N3—N5	1.389 (3)
C13—H13	0.9800		
O2—C1—O1	115.4 (3)	H14A—C14—H14B	109.0
O2—C1—C2	127.1 (3)	N5—C15—C22	121.8 (3)
O1—C1—C2	117.5 (3)	N5—C15—C14	113.2 (2)
C3—C2—C1	119.2 (3)	C22—C15—C14	125.0 (3)
C3—C2—C10	121.7 (3)	C17—C16—C21	118.1 (3)
C1—C2—C10	119.1 (2)	C17—C16—C13	122.4 (3)
C2—C3—C4	122.6 (3)	C21—C16—C13	119.5 (3)
C2—C3—H3	118.7	C16—C17—C18	121.0 (3)

C4—C3—H3	118.7	C16—C17—H17	119.5
C5—C4—C6	117.4 (3)	C18—C17—H17	119.5
C5—C4—C3	117.5 (3)	C19—C18—C17	118.1 (3)
C6—C4—C3	125.1 (3)	C19—C18—H18	121.0
O1—C5—C4	120.8 (3)	C17—C18—H18	121.0
O1—C5—C9	116.9 (3)	C20—C19—C18	123.5 (3)
C4—C5—C9	122.3 (3)	C20—C19—F1	117.5 (4)
C7—C6—C4	120.6 (3)	C18—C19—F1	119.0 (4)
C7—C6—H6	119.7	C19—C20—C21	118.2 (3)
C4—C6—H6	119.7	C19—C20—H20	120.9
C8—C7—C6	120.1 (3)	C21—C20—H20	120.9
C8—C7—H7	120.0	C16—C21—C20	121.1 (3)
C6—C7—H7	120.0	C16—C21—H21	119.5
C9—C8—C7	121.3 (3)	C20—C21—H21	119.5
C9—C8—H8	119.4	C27—C22—C23	118.2 (3)
C7—C8—H8	119.4	C27—C22—C15	119.9 (3)
C8—C9—C5	118.3 (3)	C23—C22—C15	121.9 (3)
C8—C9—H9	120.8	C24—C23—C22	120.7 (3)
C5—C9—H9	120.8	C24—C23—H23	119.7
C11—C10—N1	114.9 (2)	C22—C23—H23	119.7
C11—C10—C2	127.9 (3)	C25—C24—C23	119.7 (3)
N1—C10—C2	117.2 (2)	C25—C24—H24	120.1
C10—C11—S1	111.4 (2)	C23—C24—H24	120.1
C10—C11—H11	124.3	C24—C25—C26	121.4 (3)
S1—C11—H11	124.3	C24—C25—Cl1	120.1 (3)
N1—C12—N3	122.2 (3)	C26—C25—Cl1	118.5 (3)
N1—C12—S1	116.6 (2)	C25—C26—C27	118.7 (3)
N3—C12—S1	121.2 (2)	C25—C26—H26	120.7
N3—C13—C16	112.3 (2)	C27—C26—H26	120.7
N3—C13—C14	101.0 (2)	C26—C27—C22	121.3 (3)
C16—C13—C14	115.1 (2)	C26—C27—H27	119.3
N3—C13—H13	109.3	C22—C27—H27	119.3
C16—C13—H13	109.3	C12—N1—C10	109.5 (2)
C14—C13—H13	109.3	C12—N3—N5	117.9 (2)
C15—C14—C13	103.5 (2)	C12—N3—C13	121.5 (2)
C15—C14—H14A	111.1	N5—N3—C13	112.7 (2)
C13—C14—H14A	111.1	C15—N5—N3	108.3 (2)
C15—C14—H14B	111.1	C5—O1—C1	122.3 (3)
C13—C14—H14B	111.1	C11—S1—C12	87.62 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···F1^{i}	0.98	2.47	3.372 (4)	154
C20—H20···Cl1^{ii}	0.93	2.98	3.829 (4)	153
C26—H26···O2^{iii}	0.93	2.54	3.282 (4)	137

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