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Isomorphous methyl- and chloro-substituted small heterocyclic analogues obeying the chlorine–methyl (Cl–Me) exchange rule[1]

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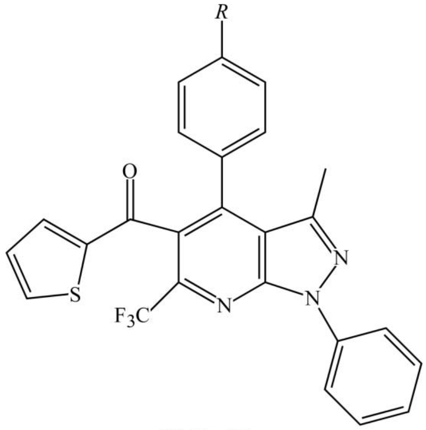
The two new isomorphous structures [3-methyl-4-(4-methylphenyl)-1-phenyl-6-trifluoromethyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl](thiophen-2-yl)methanone, $C_{26}H_{18}F_3N_3OS$, (I), and [4-(4-chlorophenyl)-3-methyl-1-phenyl-6-trifluoromethyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl](thiophen-2-yl)methanone, $C_{25}H_{15}ClF_3N_3OS$, (II), are shown to obey the chlorine–methyl exchange rule. Both structures show extensive disorder, treatment of which greatly improves the quality of the description of the structures. In addition, it is worth noting that the presence of extensive disorder may make it difficult to detect the isomorphism automatically during data-mining procedures (such as searches of the Cambridge Structural Database).

Comment

The prediction of crystal structures is still a major challenge for crystallographers owing to the complex nature of molecular interactions that range from the robust to the weak. Hence, reliable crystallographic studies of the effect of substituents on the packing of molecules in crystals are essential for understanding the nature and strength of intermolecular interactions with the goal of classifying and ultimately predicting them. Since the first use of the term 'crystal engineering' by G. M. J. Schmidt (1971), the close-packing model for organic molecules based on pure geometrical considerations (Kitaigorodskii, 1973) that led to the chlorine–methyl (Cl–Me) exchange rule may well be considered a significant first step towards crystal-structure prediction. Subsequently, crystal-engineering studies on selected photodimerizable cyclopentanones (Jones *et al.*, 1981) and certain coumarins (Gnanaguru *et al.*, 1984) showed that the Cl–Me exchange rule, based solely on the size of the substituent, need not always be valid. Desiraju & Sarma (1986) observed that this rule is a valid proposition only for large irregularly shaped molecules, preferably with one Cl atom; however, it is not necessarily true for more planar and regular-shaped molecules where short Cl$\cdots$Cl contacts, which may be incompatible with the geometrical model, influence the molecular interactions. The crystal structures analysed in the present study, namely [3-methyl-4-(4-methylphenyl)-1-phenyl-6-trifluoromethyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl](thiophen-2-yl)methanone, (I), and [4-(4-chlorophenyl)-3-methyl-1-phenyl-6-trifluoromethyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl](thiophen-2-yl)methanone, (II), are good examples of a case where the Cl–Me exchange rule holds. In addition, the reported crystal structures are potential candidates for remaining unnoticed for their isomorphism in the Cambridge Structural Database (Allen, 2002) due to the extensive disorder observed in both of them.



(I) *R* = Me
(II) *R* = Cl

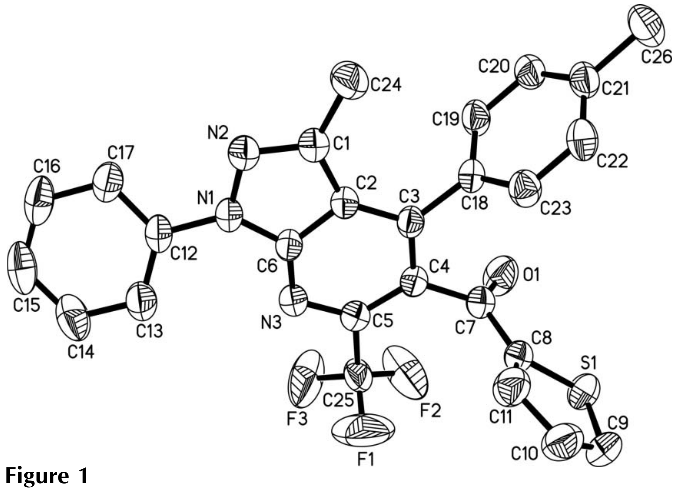


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms and atoms of the minor disorder components have been omitted for clarity.

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[1] This paper is dedicated to the memory of Professor M. A. Viswamitra on the occasion of the 12th anniversary of his death.

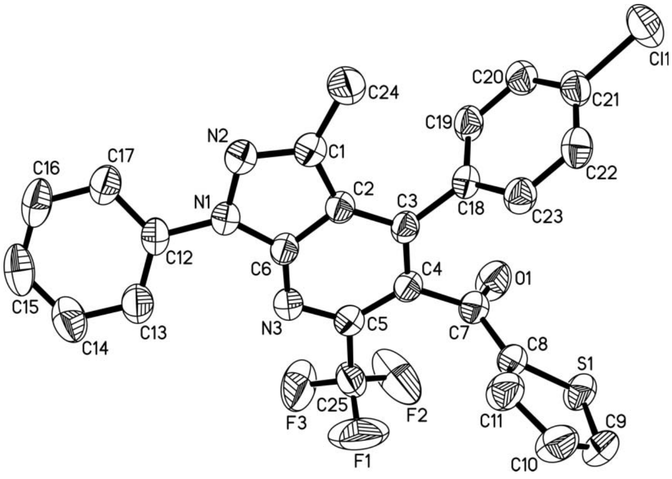

Figure 2
The molecular structure of (II), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms and atoms of the minor disorder components have been omitted for clarity.

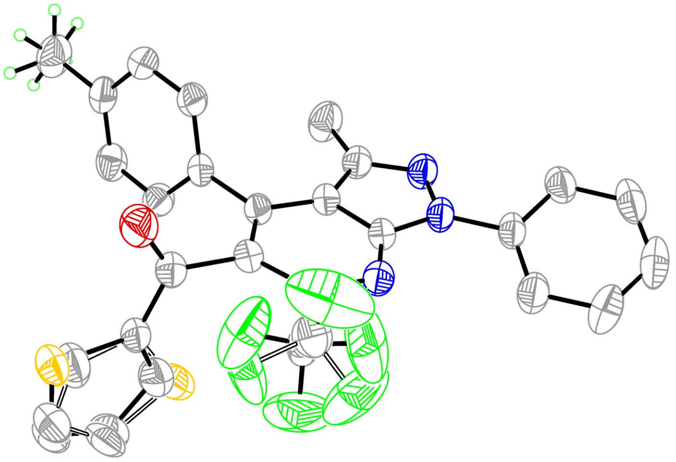

Figure 3
The molecular structure of (I), showing the disordered components of the thiophene ring, the –CF_3 group and the benzyl methyl group. The disorder observed in (II) is nearly identical to that in (I).

The crystal structures of compounds (I) and (II) (Figs. 1 and 2) are relevant in the above context since they differ from each other only by a methyl group in (I) being replaced by a Cl atom in (II). The replacement of Me by Cl has not caused any significant change in their unit-cell parameters, lattice type, space group and intermolecular interaction pattern, *i.e.* (I) and (II) are isomorphous and isostructural. Interestingly, the –CF_3 groups and the thiophene rings in both (I) and (II) exhibit disorder, the proper treatment of which significantly improved the crystal structures (see *Refinement*; Fig. 3). For example, residual electron density between the methyl H atoms became apparent only after the –CF_3 group disorder had been addressed appropriately; the initial model corresponding to a simple rotation about the C5—C25 bond was not sufficient to reveal the methyl-group disorder. This example underlines the importance of refining disorder carefully and accurately, because even though the simpler disorder model would have been considered acceptable by most standards, only the improved model paved the way for further improvement.

The weak noncovalent crystal-packing interactions are similar in both (I) and (II) (Tables 1 and 2).

There are two C—H$\cdots$O hydrogen bonds, one leading to the formation of centrosymmetric dimers and the other linking these pairs into double chains along [011] (Fig. 4). There is a significant π–π interaction [$Cg1\cdots Cg2^{ii}$; $Cg1$ is the centroid of the pyrazole ring and $Cg2$ that of the phenyl ring attached to the pyrazole ring; symmetry code: (ii) $-x+1, -y+1, -z+1$] between centrosymmetric pairs within the chain (Fig. 5), with $Cg1\cdots Cg2^{ii}$ values of 3.9140 (9) and 3.9319 (10) Å in (I) and (II), respectively. The C15$\cdots$O1^{i} and H15$\cdots$O1^{i} distances in (II) [symmetry code: (i) $x, y-1, z-1$] are noticeably lengthened, with values of 3.610 (2) and 2.74 Å, respectively, compared with values of 3.531 (2) and 2.66 Å in (I). However, the geometries of these bonds remain essentially identical, as can be seen from the C—H$\cdots$O angle of 156° in both structures. The longer C$\cdots$O contact in (II) is recognized as a hydrogen bond since the angle tends towards linearity and asserts the need to inspect the intermolecular contacts more

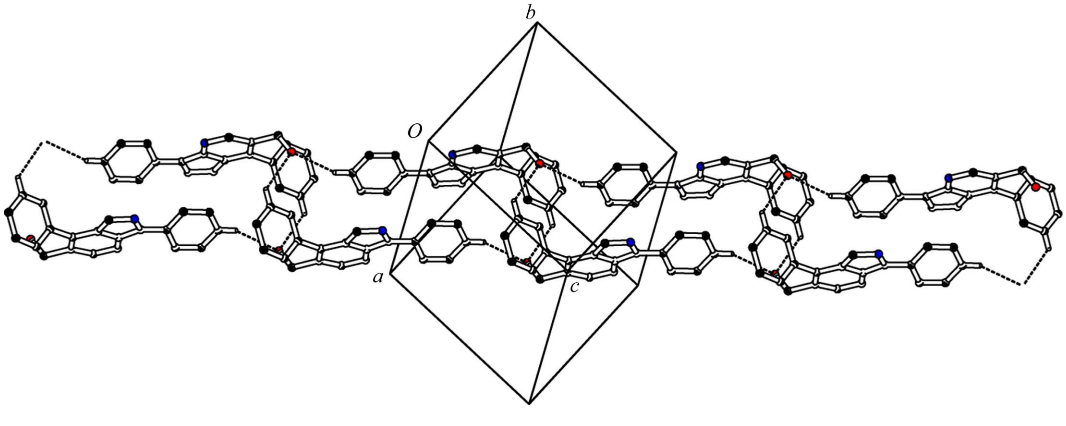

Figure 4
The role of C—H$\cdots$O hydrogen bonds leading to the formation of double chains along [011] in (I). Nonparticipating H atoms, methyl C atoms, thiophene rings and the minor component of the disordered –CF_3 group have been omitted for clarity. The corresponding figure for (II) is identical.

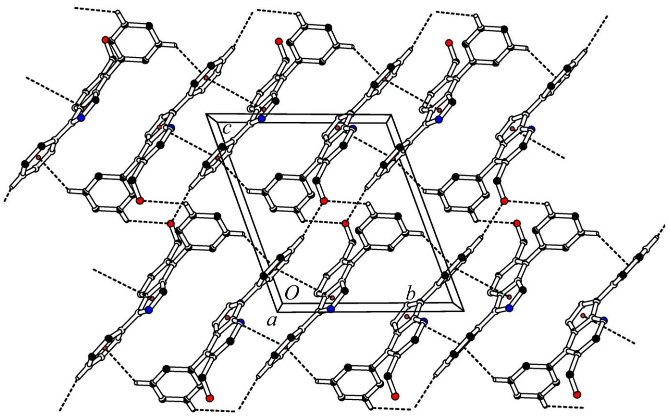

Figure 5
A layer of molecules of (I) with C—H···O, C—H···π and π–π interactions between them. Nonparticipating H atoms, methyl C atoms, thiophene rings and the minor component of the disordered thiophene and –CF_3 groups have been omitted for clarity. The corresponding figure for (II) is identical to that of (I).

carefully. Further, a C22—H22···$Cg2^{iii}$ interaction, with H···$Cg2^{iii}$ distances [symmetry code: (iii) $-x+1, -y+1, -z$] of 2.76 and 2.74 Å in (I) and (II), respectively, links these chains into sheets parallel to the *bc* plane and may well be regarded as the weakest interaction and yet is crucial in the crystal structure. Thus, the structures of (I) and (II) serve as good examples of the importance of C—H···π and π–π interactions amidst extensive disorder in molecules in the crystalline state.

Experimental

For the preparation of compound (I), a mixture of 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dione (1 mmol), 2-methylbenzaldehyde (1 mmol) and 3-methyl-1-phenyl-1*H*-pyrazol-5-amine (1 mmol) in the presence of L-proline (50 mol%) in ethanol (15 ml) was stirred at 333 K for 7 h. After completion of the reaction [monitored by thin-layer chromatography (TLC)], the reaction mixture was extracted with ethyl acetate (2 × 40 ml). After removal of the solvent, the residue was chromatographed over silica gel (230–400 mesh) using a petroleum ether–ethyl acetate mixture (4:1 *v*/*v*), which afforded the pure compound.

Compound (II) was prepared by the same method using 4-chlorobenzaldehyde in place of 2-methylbenzaldehyde and with a stirring time of 6 h.

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

*Cg*2 is the centroid of the C12–C17 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···$O1^{i}$	0.93	2.66	3.531 (2)	156
C20—H20···$O1^{ii}$	0.93	2.65	3.2769 (18)	126
C22—H22···$Cg2^{iii}$	0.93	2.76	3.4509 (17)	132

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

*Cg*2 is the centroid of the C12–C17 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···$O1^{i}$	0.93	2.74	3.610 (2)	156
C20—H20···$O1^{ii}$	0.93	2.57	3.209 (2)	127
C22—H22···$Cg2^{iii}$	0.93	2.74	3.4075 (18)	129

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

Compound (I)

Crystal data

$C_{26}H_{18}F_3N_3OS$
M_r = 477.49
Triclinic, $P\overline{1}$
a = 10.0323 (4) Å
b = 10.3715 (5) Å
c = 11.7411 (5) Å
α = 109.211 (2)°
β = 96.105 (2)°
γ = 95.676 (2)°
V = 1135.36 (9) Å^3
Z = 2
Mo *K*α radiation
μ = 0.19 mm^{-1}
T = 298 K
0.28 × 0.18 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.900, T_{max} = 0.989
25018 measured reflections
6692 independent reflections
4773 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.126
S = 1.02
6692 reflections
382 parameters
345 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Compound (II)

Crystal data

$C_{25}H_{15}ClF_3N_3OS$
M_r = 497.91
Triclinic, $P\overline{1}$
a = 10.0018 (7) Å
b = 10.3503 (8) Å
c = 11.6309 (10) Å
α = 108.607 (4)°
β = 95.295 (4)°
γ = 95.628 (4)°
V = 1125.82 (15) Å^3
Z = 2
Mo *K*α radiation
μ = 0.31 mm^{-1}
T = 298 K
0.30 × 0.14 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.890, T_{max} = 0.978
22298 measured reflections
5407 independent reflections
3912 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.097
S = 1.03
5407 reflections
382 parameters
345 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

The structures were refined against F^2 on all data by full-matrix least-squares with *SHELXL97* (Sheldrick, 2008), following established refinement strategies (Müller, 2009). All H atoms were included in the model at geometrically calculated positions (C—H target distance = 0.96 Å for methyl H atoms and 0.93 Å for all others) and refined using a riding model. Except for one methyl group (defined by C26), which was refined as disordered (see below), the torsion angles of the methyl groups were allowed to refine. The U_{iso} values of all H atoms were constrained to 1.2 times U_{eq} (1.5 times for methyl H atoms) of the respective atom to which the H atom binds.

As mentioned above, both structures display disorder of the $-CF_3$ and thiophene groups. This disorder was treated identically in both structures and this refinement is explained only once (the atom names are the same in both structures, see Figs. 1 and 2). Disorder was refined with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters, as well as rigid bond restraints (*viz*. Hirshfeld restraints) for anisotropic displacement parameters.

The first approach to the $-CF_3$ disorder was to refine the $-CF_3$ group as freely rotating about the C5—C25 bond [typical similarity restraints and equal anisotropic displacement constraints for this model are explained in detail in Müller (2009)]. While this approach was partially successful, the displacement ellipsoids of the six F atoms do not form a circular toroid as expected for a pure rotation about the C—C bond, but rather an oval elongated in a direction approximately perpendicular to the aromatic ring plane to which the $-CF_3$ group binds. In addition, there is still appreciable residual electron density around the $-CF_3$ group and the displacement ellipsoid of C25, the C atom in the $-CF_3$ group carrying the F atoms, is elongated in a direction perpendicular to the plane of the aromatic system to which the $-CF_3$ group binds. Therefore, the position of C25 was split as well, thus describing the $-CF_3$ group as being slightly above or below the aromatic system to which it is bound. This approach does not require the use of constraints and gives rise to an improved model. Even though the anisotropic displacement ellipsoids of C25 and C25*A* are still elongated, the residual electron density is much lower and the residual values of the refinement are significantly better. It should be noted that in the first model, Hirshfeld restraints applied to the six C25—F bonds (unsuccessfully) pushed the ellipsoid of atom C25 to be almost perfectly round. This effect is much weaker in the second model, which may explain why the ellipsoids for C25 and C25*A* are still elongated. This elongation should not be considered a problem, however, as the displacement ellipsoids of C25 and C25*A* are elongated along the direction of the motion suggested in the disorder model (the entire $-CF_3$ group is moving slightly up and down perpendicular to the aromatic plane while rotating). The occupancy ratios of the two components were refined freely and converged at 0.569 (7) for (I) and at 0.577 (9) for (II).

Both structures show disorder of the thiophene ring, corresponding to an approximate 180° rotation about the C7—C8 bond, leading the ring systems of the two disorder components to be approximately coplanar. In addition to the types of similarity restraints mentioned above, the thiophene rings were restrained to be approximately planar, yet no coplanarity of the disorder components was assumed. The occupancy ratios of the two components were refined freely and converged at 0.845 (2) for (I) and at 0.860 (2) for (II).

In addition to the disorder described above, the methyl group defined by C26 in (I) was refined as rotating about the C21—C26 bond with six half-occupied H atoms 60° apart. This disorder was introduced because there was significant residual electron density between the three H atoms of this methyl group when the torsion angle of this methyl group was refined. Introducing this third disordered assembly in (I) further improves the model significantly.

Both data sets contain reflections partially obscured by the primary beam stop [one reflection for the data of (I) and three reflections for the data of (II)]. These reflections were omitted from the refinements.

For both compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TP3020). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Isomorphous methyl- and chloro-substituted small heterocyclic analogues obeying the chlorine–methyl (Cl–Me) exchange rule

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(I) [3-Methyl-4-(4-methylphenyl)-1-phenyl-6-trifluoromethyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl](thiophen-2-yl)methanone

Crystal data

$C_{26}H_{18}F_3N_3OS$
$M_r = 477.49$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 10.0323\ (4)$ Å
$b = 10.3715\ (5)$ Å
$c = 11.7411\ (5)$ Å
$\alpha = 109.211\ (2)°$
$\beta = 96.105\ (2)°$
$\gamma = 95.676\ (2)°$
$V = 1135.36\ (9)$ Å^3
$Z = 2$
$F(000) = 492$
$D_x = 1.397$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 10124 reflections
$\theta = 2.1–28.0°$
$\mu = 0.19$ mm^{-1}
$T = 298$ K
Needle, yellow
0.28 × 0.18 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.900$, $T_{max} = 0.989$
25018 measured reflections
6692 independent reflections
4773 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30.4°$, $\theta_{min} = 2.1°$
$h = -14 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.126$
$S = 1.02$
6692 reflections
382 parameters
345 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
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.2446P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.22031 (13)	0.53727 (13)	0.43932 (10)	0.0649 (3)	
N1	0.45272 (11)	0.20561 (11)	−0.02588 (10)	0.0423 (3)	
N2	0.57941 (12)	0.28107 (12)	−0.00452 (11)	0.0469 (3)	
N3	0.24775 (11)	0.23106 (11)	0.06404 (10)	0.0438 (3)	
C1	0.58186 (13)	0.39452 (14)	0.08892 (12)	0.0436 (3)	
C2	0.45472 (12)	0.39688 (12)	0.13287 (11)	0.0376 (3)	
C3	0.39830 (13)	0.48555 (12)	0.22745 (11)	0.0368 (3)	
C4	0.26395 (13)	0.44530 (13)	0.23546 (12)	0.0401 (3)	
C5	0.19596 (13)	0.31823 (14)	0.15358 (12)	0.0436 (3)	
C25	0.0502 (6)	0.2683 (7)	0.1625 (6)	0.0624 (15)	0.569 (7)
F1	−0.0332 (3)	0.3069 (8)	0.0918 (5)	0.1235 (18)	0.569 (7)
F2	0.0218 (5)	0.3180 (6)	0.2697 (3)	0.1110 (19)	0.569 (7)
F3	0.0284 (4)	0.1350 (3)	0.1241 (7)	0.132 (3)	0.569 (7)
C25A	0.0600 (8)	0.2512 (9)	0.1634 (7)	0.0580 (18)	0.431 (7)
F1A	0.0660 (5)	0.1633 (9)	0.2197 (9)	0.133 (3)	0.431 (7)
F2A	−0.0196 (6)	0.1901 (10)	0.0643 (4)	0.125 (3)	0.431 (7)
F3A	−0.0148 (6)	0.3372 (5)	0.2272 (9)	0.129 (3)	0.431 (7)
C6	0.37445 (13)	0.27416 (13)	0.05595 (11)	0.0383 (3)	
C7	0.19828 (13)	0.53776 (14)	0.33622 (12)	0.0431 (3)	
C8	0.11091 (13)	0.62838 (14)	0.30385 (12)	0.0423 (3)	
S1	0.00886 (7)	0.71013 (8)	0.40507 (6)	0.05390 (18)	0.845 (2)
C9	−0.0533 (5)	0.7880 (5)	0.3084 (4)	0.0586 (7)	0.845 (2)
H9	−0.1191	0.8461	0.3248	0.070*	0.845 (2)
C10	0.0032 (6)	0.7563 (7)	0.2051 (5)	0.0626 (9)	0.845 (2)
H10	−0.0168	0.7917	0.1431	0.075*	0.845 (2)
C11	0.0958 (6)	0.6631 (6)	0.2031 (3)	0.0589 (9)	0.845 (2)
H11	0.1426	0.6285	0.1378	0.071*	0.845 (2)
S1A	0.1045 (8)	0.6501 (9)	0.1657 (5)	0.0652 (13)	0.155 (2)
C9A	−0.012 (3)	0.761 (3)	0.203 (3)	0.064 (3)	0.155 (2)
H9A	−0.0535	0.8001	0.1510	0.077*	0.155 (2)
C10A	−0.036 (3)	0.783 (3)	0.318 (3)	0.074 (4)	0.155 (2)
H10A	−0.0898	0.8463	0.3581	0.089*	0.155 (2)
C11A	0.0292 (16)	0.7016 (18)	0.3688 (14)	0.064 (3)	0.155 (2)
H11A	0.0163	0.6982	0.4451	0.077*	0.155 (2)
C12	0.42500 (14)	0.07335 (13)	−0.11801 (11)	0.0420 (3)	
C13	0.29410 (17)	0.01699 (15)	−0.17233 (14)	0.0551 (4)	
H13	0.2222	0.0638	−0.1471	0.066*	

C14	0.2707 (2)	−0.11019 (17)	−0.26499 (16)	0.0665 (5)	
H14	0.1825	−0.1488	−0.3020	0.080*	
C15	0.3765 (2)	−0.17989 (16)	−0.30278 (15)	0.0665 (5)	
H15	0.3603	−0.2645	−0.3660	0.080*	
C16	0.5059 (2)	−0.12383 (16)	−0.24672 (14)	0.0606 (4)	
H16	0.5773	−0.1716	−0.2716	0.073*	
C17	0.53208 (17)	0.00274 (15)	−0.15371 (13)	0.0502 (3)	
H17	0.6202	0.0398	−0.1158	0.060*	
C18	0.48269 (13)	0.61143 (12)	0.31676 (11)	0.0370 (3)	
C19	0.57813 (15)	0.59816 (14)	0.40508 (12)	0.0459 (3)	
H19	0.5852	0.5115	0.4104	0.055*	
C20	0.66267 (15)	0.71197 (14)	0.48505 (13)	0.0477 (3)	
H20	0.7261	0.7010	0.5437	0.057*	
C21	0.65478 (14)	0.84204 (14)	0.47957 (13)	0.0454 (3)	
C22	0.55912 (16)	0.85475 (14)	0.39198 (13)	0.0488 (3)	
H22	0.5521	0.9416	0.3871	0.059*	
C23	0.47327 (15)	0.74156 (13)	0.31123 (13)	0.0447 (3)	
H23	0.4092	0.7529	0.2532	0.054*	
C24	0.70538 (16)	0.49990 (18)	0.13200 (16)	0.0614 (4)	
H24A	0.7675	0.4777	0.0739	0.092*	
H24B	0.7477	0.5006	0.2095	0.092*	
H24C	0.6805	0.5892	0.1403	0.092*	
C26	0.74974 (18)	0.96556 (17)	0.56560 (17)	0.0671 (5)	
H26A	0.8087	0.9370	0.6198	0.101*	0.50
H26B	0.6982	1.0319	0.6121	0.101*	0.50
H26C	0.8028	1.0065	0.5196	0.101*	0.50
H26D	0.7311	1.0466	0.5479	0.101*	0.50
H26E	0.8416	0.9517	0.5556	0.101*	0.50
H26F	0.7370	0.9771	0.6481	0.101*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0818 (8)	0.0745 (8)	0.0431 (6)	0.0340 (6)	0.0136 (5)	0.0184 (5)
N1	0.0433 (6)	0.0362 (6)	0.0394 (6)	0.0070 (4)	0.0074 (4)	0.0017 (4)
N2	0.0434 (6)	0.0457 (6)	0.0437 (6)	0.0061 (5)	0.0088 (5)	0.0043 (5)
N3	0.0417 (6)	0.0390 (6)	0.0431 (6)	0.0055 (4)	0.0048 (5)	0.0044 (5)
C1	0.0422 (6)	0.0417 (7)	0.0412 (7)	0.0068 (5)	0.0063 (5)	0.0063 (6)
C2	0.0399 (6)	0.0324 (6)	0.0371 (6)	0.0071 (5)	0.0050 (5)	0.0072 (5)
C3	0.0434 (6)	0.0307 (6)	0.0346 (6)	0.0098 (5)	0.0042 (5)	0.0081 (5)
C4	0.0414 (6)	0.0378 (6)	0.0378 (6)	0.0113 (5)	0.0055 (5)	0.0071 (5)
C5	0.0393 (6)	0.0443 (7)	0.0422 (7)	0.0079 (5)	0.0057 (5)	0.0078 (6)
C25	0.037 (2)	0.051 (2)	0.070 (3)	−0.0051 (17)	0.0084 (19)	−0.014 (2)
F1	0.0400 (11)	0.197 (5)	0.130 (3)	0.0192 (19)	0.0018 (15)	0.054 (3)
F2	0.091 (3)	0.135 (3)	0.0646 (15)	−0.050 (2)	0.0421 (15)	−0.0126 (15)
F3	0.084 (3)	0.0425 (15)	0.227 (6)	−0.0171 (13)	0.076 (4)	−0.018 (2)
C25A	0.053 (3)	0.072 (5)	0.048 (3)	0.017 (3)	0.018 (2)	0.014 (3)
F1A	0.073 (2)	0.155 (5)	0.231 (7)	0.007 (3)	0.034 (3)	0.144 (5)
F2A	0.070 (3)	0.187 (8)	0.070 (2)	−0.054 (4)	0.0078 (16)	0.000 (3)

F3A	0.064 (3)	0.058 (2)	0.225 (7)	0.0022 (16)	0.076 (4)	−0.020 (3)
C6	0.0417 (6)	0.0338 (6)	0.0354 (6)	0.0103 (5)	0.0046 (5)	0.0054 (5)
C7	0.0435 (7)	0.0422 (7)	0.0392 (7)	0.0089 (5)	0.0075 (5)	0.0069 (5)
C8	0.0389 (6)	0.0419 (7)	0.0402 (7)	0.0090 (5)	0.0079 (5)	0.0047 (5)
S1	0.0491 (3)	0.0574 (3)	0.0532 (3)	0.0188 (2)	0.0195 (2)	0.0095 (3)
C9	0.0450 (15)	0.0563 (14)	0.0718 (16)	0.0218 (11)	0.0097 (12)	0.0140 (12)
C10	0.059 (2)	0.0703 (19)	0.0619 (14)	0.0234 (14)	0.0057 (13)	0.0246 (13)
C11	0.0599 (15)	0.0662 (16)	0.0500 (19)	0.0214 (11)	0.0140 (15)	0.0138 (17)
S1A	0.062 (2)	0.081 (3)	0.060 (3)	0.0340 (18)	0.011 (2)	0.027 (3)
C9A	0.044 (6)	0.058 (7)	0.089 (7)	0.028 (5)	0.006 (6)	0.019 (6)
C10A	0.053 (7)	0.069 (7)	0.084 (6)	0.026 (5)	0.005 (5)	0.000 (6)
C11A	0.056 (6)	0.063 (6)	0.066 (6)	0.015 (4)	0.021 (5)	0.005 (5)
C12	0.0571 (8)	0.0333 (6)	0.0335 (6)	0.0109 (5)	0.0091 (5)	0.0068 (5)
C13	0.0578 (9)	0.0455 (8)	0.0509 (8)	0.0054 (6)	0.0099 (7)	0.0018 (7)
C14	0.0796 (12)	0.0485 (9)	0.0542 (9)	−0.0112 (8)	0.0098 (8)	0.0005 (7)
C15	0.1101 (15)	0.0331 (7)	0.0490 (9)	0.0069 (8)	0.0196 (9)	0.0031 (6)
C16	0.0974 (13)	0.0447 (8)	0.0466 (8)	0.0328 (8)	0.0240 (8)	0.0144 (7)
C17	0.0648 (9)	0.0473 (8)	0.0405 (7)	0.0220 (7)	0.0118 (6)	0.0123 (6)
C18	0.0431 (6)	0.0309 (6)	0.0346 (6)	0.0079 (5)	0.0088 (5)	0.0062 (5)
C19	0.0577 (8)	0.0319 (6)	0.0439 (7)	0.0113 (6)	0.0002 (6)	0.0082 (5)
C20	0.0510 (7)	0.0434 (7)	0.0413 (7)	0.0101 (6)	−0.0014 (6)	0.0062 (6)
C21	0.0474 (7)	0.0386 (7)	0.0422 (7)	0.0020 (5)	0.0113 (6)	0.0032 (6)
C22	0.0629 (9)	0.0305 (6)	0.0516 (8)	0.0041 (6)	0.0099 (7)	0.0124 (6)
C23	0.0540 (8)	0.0371 (7)	0.0424 (7)	0.0077 (6)	0.0029 (6)	0.0137 (6)
C24	0.0469 (8)	0.0621 (10)	0.0588 (9)	−0.0044 (7)	0.0119 (7)	0.0013 (8)
C26	0.0645 (10)	0.0500 (9)	0.0660 (11)	−0.0093 (7)	0.0033 (8)	−0.0007 (8)

Geometric parameters (Å, º)

O1—C7	1.2090 (17)	C9A—H9A	0.9300
N1—C6	1.3662 (15)	C10A—C11A	1.360 (18)
N1—N2	1.3773 (16)	C10A—H10A	0.9300
N1—C12	1.4188 (16)	C11A—H11A	0.9300
N2—C1	1.3145 (17)	C12—C13	1.378 (2)
N3—C6	1.3288 (17)	C12—C17	1.3840 (19)
N3—C5	1.3327 (16)	C13—C14	1.385 (2)
C1—C2	1.4254 (18)	C13—H13	0.9300
C1—C24	1.490 (2)	C14—C15	1.374 (3)
C2—C3	1.4014 (16)	C14—H14	0.9300
C2—C6	1.4036 (17)	C15—C16	1.369 (3)
C3—C4	1.3933 (18)	C15—H15	0.9300
C3—C18	1.4874 (17)	C16—C17	1.383 (2)
C4—C5	1.4055 (19)	C16—H16	0.9300
C4—C7	1.5157 (17)	C17—H17	0.9300
C5—C25A	1.502 (8)	C18—C23	1.3843 (18)
C5—C25	1.529 (6)	C18—C19	1.3857 (18)
C25—F2	1.268 (7)	C19—C20	1.3775 (19)
C25—F3	1.293 (7)	C19—H19	0.9300
C25—F1	1.298 (7)	C20—C21	1.381 (2)
C25A—F2A	1.270 (8)	C20—H20	0.9300

C25A—F1A	1.293 (9)	C21—C22	1.378 (2)
C25A—F3A	1.316 (9)	C21—C26	1.507 (2)
C7—C8	1.4572 (19)	C22—C23	1.3830 (19)
C8—C11A	1.306 (12)	C22—H22	0.9300
C8—C11	1.344 (4)	C23—H23	0.9300
C8—S1A	1.705 (6)	C24—H24A	0.9600
C8—S1	1.7166 (13)	C24—H24B	0.9600
S1—C9	1.698 (3)	C24—H24C	0.9600
C9—C10	1.349 (4)	C26—H26A	0.9600
C9—H9	0.9300	C26—H26B	0.9600
C10—C11	1.402 (6)	C26—H26C	0.9600
C10—H10	0.9300	C26—H26D	0.9600
C11—H11	0.9300	C26—H26E	0.9600
S1A—C9A	1.706 (19)	C26—H26F	0.9600
C9A—C10A	1.344 (17)		

C6—N1—N2	110.02 (10)	C8—C11A—H11A	122.0
C6—N1—C12	130.48 (11)	C10A—C11A—H11A	122.0
N2—N1—C12	119.38 (10)	C13—C12—C17	120.52 (13)
C1—N2—N1	107.65 (11)	C13—C12—N1	120.67 (12)
C6—N3—C5	114.01 (11)	C17—C12—N1	118.81 (13)
N2—C1—C2	110.33 (12)	C12—C13—C14	119.32 (15)
N2—C1—C24	120.30 (12)	C12—C13—H13	120.3
C2—C1—C24	129.36 (12)	C14—C13—H13	120.3
C3—C2—C6	118.43 (12)	C15—C14—C13	120.63 (17)
C3—C2—C1	136.61 (12)	C15—C14—H14	119.7
C6—C2—C1	104.96 (11)	C13—C14—H14	119.7
C4—C3—C2	116.51 (11)	C16—C15—C14	119.48 (14)
C4—C3—C18	123.14 (11)	C16—C15—H15	120.3
C2—C3—C18	120.27 (11)	C14—C15—H15	120.3
C3—C4—C5	119.12 (11)	C15—C16—C17	121.10 (15)
C3—C4—C7	118.53 (11)	C15—C16—H16	119.5
C5—C4—C7	122.29 (12)	C17—C16—H16	119.5
N3—C5—C4	125.57 (12)	C16—C17—C12	118.93 (16)
N3—C5—C25A	109.0 (4)	C16—C17—H17	120.5
C4—C5—C25A	125.0 (3)	C12—C17—H17	120.5
N3—C5—C25	113.8 (3)	C23—C18—C19	118.63 (12)
C4—C5—C25	120.6 (3)	C23—C18—C3	122.02 (11)
F2—C25—F3	110.8 (6)	C19—C18—C3	119.28 (11)
F2—C25—F1	107.1 (6)	C20—C19—C18	120.67 (12)
F3—C25—F1	106.6 (5)	C20—C19—H19	119.7
F2—C25—C5	112.3 (4)	C18—C19—H19	119.7
F3—C25—C5	110.1 (5)	C19—C20—C21	121.11 (13)
F1—C25—C5	109.7 (5)	C19—C20—H20	119.4
F2A—C25A—F1A	106.1 (8)	C21—C20—H20	119.4
F2A—C25A—F3A	101.9 (7)	C22—C21—C20	117.98 (12)
F1A—C25A—F3A	102.2 (6)	C22—C21—C26	121.25 (14)
F2A—C25A—C5	116.6 (6)	C20—C21—C26	120.76 (14)
F1A—C25A—C5	114.0 (6)	C21—C22—C23	121.62 (13)

F3A—C25A—C5	114.3 (7)	C21—C22—H22	119.2
N3—C6—N1	126.63 (11)	C23—C22—H22	119.2
N3—C6—C2	126.30 (11)	C22—C23—C18	119.99 (13)
N1—C6—C2	107.04 (11)	C22—C23—H23	120.0
O1—C7—C8	121.97 (12)	C18—C23—H23	120.0
O1—C7—C4	120.76 (12)	C1—C24—H24A	109.5
C8—C7—C4	117.25 (12)	C1—C24—H24B	109.5
C11A—C8—C11	101.5 (8)	H24A—C24—H24B	109.5
C11A—C8—C7	128.4 (7)	C1—C24—H24C	109.5
C11—C8—C7	130.1 (2)	H24A—C24—H24C	109.5
C11A—C8—S1A	110.5 (7)	H24B—C24—H24C	109.5
C7—C8—S1A	121.2 (2)	C21—C26—H26A	109.5
C11—C8—S1	110.73 (19)	C21—C26—H26B	109.5
C7—C8—S1	119.16 (11)	H26A—C26—H26B	109.5
S1A—C8—S1	119.6 (2)	C21—C26—H26C	109.5
C9—S1—C8	91.27 (14)	H26A—C26—H26C	109.5
C10—C9—S1	112.5 (3)	H26B—C26—H26C	109.5
C10—C9—H9	123.7	C21—C26—H26D	109.5
S1—C9—H9	123.7	H26A—C26—H26D	141.1
C9—C10—C11	111.5 (3)	H26B—C26—H26D	56.3
C9—C10—H10	124.3	H26C—C26—H26D	56.3
C11—C10—H10	124.3	C21—C26—H26E	109.5
C8—C11—C10	114.0 (3)	H26A—C26—H26E	56.3
C8—C11—H11	123.0	H26B—C26—H26E	141.1
C10—C11—H11	123.0	H26C—C26—H26E	56.3
C8—S1A—C9A	90.6 (9)	H26D—C26—H26E	109.5
C10A—C9A—S1A	111.3 (17)	C21—C26—H26F	109.5
C10A—C9A—H9A	124.4	H26A—C26—H26F	56.3
S1A—C9A—H9A	124.4	H26B—C26—H26F	56.3
C9A—C10A—C11A	111.3 (19)	H26C—C26—H26F	141.1
C9A—C10A—H10A	124.3	H26D—C26—H26F	109.5
C11A—C10A—H10A	124.3	H26E—C26—H26F	109.5
C8—C11A—C10A	116.0 (14)		

Hydrogen-bond geometry (Å, º)

*Cg*2 is the centroid of the C12–C17 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···O1^{i}	0.93	2.66	3.531 (2)	156
C20—H20···O1^{ii}	0.93	2.65	3.2769 (18)	126
C22—H22···*Cg*2^{iii}	0.93	2.76	3.4509 (17)	132

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

(II) [4-(4-Chlorophenyl)-3-methyl-1-phenyl-6-trifluoromethyl-1*H*-pyrazolo[3,4-*b*]pyridin-5-yl](thiophen-2-yl)methanone

Crystal data

$C_{25}H_{15}ClF_3N_3OS$
$M_r = 497.91$

Triclinic, $P\overline{1}$
Hall symbol: -P 1

$a = 10.0018$ (7) Å
$b = 10.3503$ (8) Å
$c = 11.6309$ (10) Å
$\alpha = 108.607$ (4)°
$\beta = 95.295$ (4)°
$\gamma = 95.628$ (4)°
$V = 1125.82$ (15) Å^3
$Z = 2$
$F(000) = 508$

$D_x = 1.469$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1226 reflections
$\theta = 2.3$–28.0°
$\mu = 0.31$ mm^{-1}
$T = 298$ K
Needle, yellow
0.30 × 0.14 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{\min} = 0.890$, $T_{\max} = 0.978$

22298 measured reflections
5407 independent reflections
3912 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.027$
$\theta_{\max} = 28.1°$, $\theta_{\min} = 2.3°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.097$
$S = 1.03$
5407 reflections
382 parameters
345 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
$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 0.2614P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.75890 (5)	0.97291 (5)	1.07183 (5)	0.07168 (16)	
O1	0.21636 (14)	0.53523 (13)	0.94144 (11)	0.0652 (3)	
N1	0.45432 (12)	0.20812 (12)	0.47402 (11)	0.0433 (3)	
N2	0.58047 (13)	0.28291 (13)	0.49460 (12)	0.0474 (3)	
N3	0.24730 (12)	0.23298 (12)	0.56487 (12)	0.0447 (3)	
C1	0.58184 (15)	0.39550 (15)	0.58813 (14)	0.0439 (3)	
C2	0.45390 (14)	0.39739 (14)	0.63292 (13)	0.0385 (3)	
C3	0.39551 (14)	0.48487 (13)	0.72757 (13)	0.0380 (3)	
C4	0.26054 (15)	0.44524 (14)	0.73639 (13)	0.0408 (3)	

C5	0.19383 (15)	0.31888 (16)	0.65423 (14)	0.0447 (3)	
C25	0.0486 (7)	0.2706 (7)	0.6617 (7)	0.0635 (17)	0.577 (9)
F1	−0.0340 (3)	0.3145 (7)	0.5947 (5)	0.1198 (17)	0.577 (9)
F2	0.0183 (6)	0.3142 (7)	0.7715 (4)	0.122 (2)	0.577 (9)
F3	0.0232 (4)	0.1376 (4)	0.6197 (7)	0.115 (2)	0.577 (9)
C25A	0.0556 (9)	0.2528 (10)	0.6666 (9)	0.058 (2)	0.423 (9)
F1A	0.0618 (6)	0.1588 (9)	0.7157 (12)	0.138 (3)	0.423 (9)
F2A	−0.0234 (7)	0.2003 (14)	0.5664 (4)	0.143 (4)	0.423 (9)
F3A	−0.0143 (8)	0.3372 (6)	0.7361 (10)	0.122 (3)	0.423 (9)
C6	0.37455 (14)	0.27573 (14)	0.55613 (13)	0.0393 (3)	
C7	0.19409 (15)	0.53713 (15)	0.83811 (14)	0.0447 (3)	
C8	0.10869 (15)	0.63006 (15)	0.80710 (14)	0.0435 (3)	
S1	0.01384 (8)	0.72012 (8)	0.91303 (6)	0.0549 (2)	0.860 (2)
C9	−0.0460 (5)	0.7999 (5)	0.8160 (5)	0.0601 (8)	0.860 (2)
H9	−0.1075	0.8631	0.8348	0.072*	0.860 (2)
C10	0.0049 (6)	0.7621 (6)	0.7093 (5)	0.0638 (8)	0.860 (2)
H10	−0.0156	0.7967	0.6461	0.077*	0.860 (2)
C11	0.0923 (6)	0.6643 (6)	0.7051 (3)	0.0595 (9)	0.860 (2)
H11	0.1356	0.6259	0.6373	0.071*	0.860 (2)
S1A	0.0992 (11)	0.6482 (11)	0.6658 (6)	0.0630 (16)	0.140 (2)
C9A	−0.011 (4)	0.765 (4)	0.708 (3)	0.066 (4)	0.140 (2)
H9A	−0.0521	0.8055	0.6563	0.079*	0.140 (2)
C10A	−0.033 (4)	0.791 (3)	0.826 (3)	0.069 (4)	0.140 (2)
H10A	−0.0853	0.8560	0.8663	0.083*	0.140 (2)
C11A	0.033 (2)	0.707 (2)	0.8773 (16)	0.065 (3)	0.140 (2)
H11A	0.0240	0.7057	0.9559	0.078*	0.140 (2)
C12	0.42790 (16)	0.07661 (14)	0.38187 (13)	0.0426 (3)	
C13	0.29746 (18)	0.02172 (17)	0.32764 (16)	0.0562 (4)	
H13	0.2251	0.0689	0.3528	0.067*	
C14	0.2754 (2)	−0.10428 (18)	0.23531 (17)	0.0676 (5)	
H14	0.1876	−0.1420	0.1984	0.081*	
C15	0.3813 (2)	−0.17437 (17)	0.19751 (17)	0.0659 (5)	
H15	0.3657	−0.2584	0.1343	0.079*	
C16	0.5103 (2)	−0.11993 (17)	0.25340 (16)	0.0610 (5)	
H16	0.5822	−0.1681	0.2286	0.073*	
C17	0.53523 (18)	0.00572 (16)	0.34624 (14)	0.0504 (4)	
H17	0.6230	0.0420	0.3842	0.061*	
C18	0.47870 (14)	0.60931 (14)	0.81689 (13)	0.0380 (3)	
C19	0.57629 (16)	0.59314 (15)	0.90202 (14)	0.0459 (4)	
H19	0.5845	0.5057	0.9055	0.055*	
C20	0.66101 (16)	0.70477 (16)	0.98134 (14)	0.0483 (4)	
H20	0.7261	0.6935	1.0386	0.058*	
C21	0.64805 (16)	0.83317 (15)	0.97480 (14)	0.0452 (4)	
C22	0.55173 (17)	0.85244 (15)	0.89245 (15)	0.0483 (4)	
H22	0.5440	0.9403	0.8899	0.058*	
C23	0.46635 (16)	0.74027 (14)	0.81336 (14)	0.0443 (3)	
H23	0.4003	0.7525	0.7575	0.053*	
C24	0.70480 (17)	0.49984 (19)	0.63054 (17)	0.0612 (5)	
H24A	0.7464	0.4992	0.7081	0.092*	

H24B	0.6797	0.5893	0.6391	0.092*
H24C	0.7677	0.4784	0.5718	0.092*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0683 (3)	0.0525 (3)	0.0723 (3)	−0.0107 (2)	0.0014 (2)	−0.0019 (2)
O1	0.0821 (9)	0.0753 (8)	0.0450 (7)	0.0340 (7)	0.0143 (6)	0.0207 (6)
N1	0.0422 (7)	0.0404 (6)	0.0417 (7)	0.0089 (5)	0.0075 (5)	0.0043 (5)
N2	0.0430 (7)	0.0486 (7)	0.0455 (7)	0.0083 (6)	0.0091 (6)	0.0068 (6)
N3	0.0430 (7)	0.0412 (7)	0.0441 (7)	0.0059 (5)	0.0052 (5)	0.0063 (5)
C1	0.0417 (8)	0.0450 (8)	0.0428 (8)	0.0079 (6)	0.0073 (6)	0.0101 (7)
C2	0.0405 (8)	0.0353 (7)	0.0388 (8)	0.0087 (6)	0.0052 (6)	0.0101 (6)
C3	0.0440 (8)	0.0326 (7)	0.0377 (7)	0.0108 (6)	0.0052 (6)	0.0107 (6)
C4	0.0418 (8)	0.0398 (7)	0.0404 (8)	0.0129 (6)	0.0057 (6)	0.0102 (6)
C5	0.0400 (8)	0.0464 (8)	0.0441 (8)	0.0086 (6)	0.0064 (6)	0.0088 (7)
C25	0.047 (3)	0.058 (3)	0.061 (3)	−0.004 (2)	0.006 (3)	−0.010 (3)
F1	0.0395 (13)	0.172 (4)	0.146 (3)	0.020 (2)	−0.0024 (17)	0.052 (3)
F2	0.098 (3)	0.159 (5)	0.0644 (18)	−0.060 (3)	0.0409 (16)	−0.0118 (19)
F3	0.071 (3)	0.0492 (17)	0.184 (6)	−0.0163 (13)	0.050 (3)	−0.017 (2)
C25A	0.045 (4)	0.068 (5)	0.063 (4)	0.014 (3)	0.019 (3)	0.018 (4)
F1A	0.075 (3)	0.142 (5)	0.260 (9)	0.013 (3)	0.043 (4)	0.147 (6)
F2A	0.069 (4)	0.241 (11)	0.071 (3)	−0.059 (5)	0.0060 (19)	0.010 (4)
F3A	0.071 (3)	0.058 (2)	0.201 (7)	0.0016 (19)	0.080 (5)	−0.020 (4)
C6	0.0422 (8)	0.0361 (7)	0.0381 (8)	0.0108 (6)	0.0065 (6)	0.0083 (6)
C7	0.0450 (8)	0.0457 (8)	0.0417 (9)	0.0101 (6)	0.0089 (6)	0.0100 (7)
C8	0.0392 (8)	0.0455 (8)	0.0419 (8)	0.0104 (6)	0.0087 (6)	0.0067 (6)
S1	0.0520 (3)	0.0591 (4)	0.0539 (4)	0.0211 (2)	0.0210 (3)	0.0110 (3)
C9	0.0496 (17)	0.0575 (16)	0.0739 (18)	0.0240 (12)	0.0110 (13)	0.0171 (13)
C10	0.059 (2)	0.0739 (19)	0.0658 (16)	0.0250 (14)	0.0066 (15)	0.0286 (14)
C11	0.0586 (17)	0.0710 (19)	0.049 (2)	0.0238 (13)	0.0129 (18)	0.0140 (19)
S1A	0.065 (3)	0.078 (3)	0.056 (3)	0.036 (2)	0.013 (3)	0.026 (3)
C9A	0.056 (8)	0.065 (8)	0.074 (7)	0.032 (6)	0.003 (7)	0.015 (6)
C10A	0.058 (8)	0.064 (7)	0.080 (7)	0.026 (5)	0.015 (6)	0.008 (6)
C11A	0.065 (8)	0.066 (7)	0.057 (6)	0.024 (5)	0.017 (5)	0.004 (6)
C12	0.0563 (9)	0.0355 (7)	0.0347 (8)	0.0111 (6)	0.0089 (6)	0.0076 (6)
C13	0.0586 (10)	0.0484 (9)	0.0526 (10)	0.0061 (8)	0.0113 (8)	0.0036 (8)
C14	0.0782 (13)	0.0525 (10)	0.0573 (11)	−0.0086 (9)	0.0095 (9)	0.0025 (8)
C15	0.1069 (16)	0.0345 (8)	0.0506 (10)	0.0066 (9)	0.0181 (10)	0.0051 (7)
C16	0.0960 (15)	0.0470 (9)	0.0481 (10)	0.0339 (10)	0.0234 (10)	0.0161 (8)
C17	0.0639 (10)	0.0494 (9)	0.0413 (9)	0.0225 (8)	0.0107 (7)	0.0142 (7)
C18	0.0434 (8)	0.0335 (7)	0.0362 (7)	0.0088 (6)	0.0100 (6)	0.0081 (6)
C19	0.0566 (9)	0.0342 (7)	0.0457 (9)	0.0131 (7)	0.0028 (7)	0.0108 (6)
C20	0.0507 (9)	0.0466 (8)	0.0433 (9)	0.0112 (7)	0.0008 (7)	0.0090 (7)
C21	0.0468 (8)	0.0395 (8)	0.0429 (8)	0.0015 (6)	0.0114 (7)	0.0043 (6)
C22	0.0611 (10)	0.0332 (7)	0.0512 (9)	0.0076 (7)	0.0121 (8)	0.0131 (7)
C23	0.0510 (9)	0.0393 (8)	0.0442 (8)	0.0109 (6)	0.0053 (7)	0.0148 (6)
C24	0.0468 (9)	0.0633 (11)	0.0608 (11)	−0.0017 (8)	0.0137 (8)	0.0039 (9)

Geometric parameters (Å, º)

Cl1—C21	1.7342 (15)	C10—H10	0.9300
O1—C7	1.2087 (19)	C11—H11	0.9300
N1—C6	1.3645 (17)	S1A—C9A	1.703 (19)
N1—N2	1.3722 (18)	C9A—C10A	1.346 (17)
N1—C12	1.4204 (18)	C9A—H9A	0.9300
N2—C1	1.3140 (18)	C10A—C11A	1.387 (19)
N3—C5	1.3277 (18)	C10A—H10A	0.9300
N3—C6	1.3297 (19)	C11A—H11A	0.9300
C1—C2	1.425 (2)	C12—C13	1.377 (2)
C1—C24	1.486 (2)	C12—C17	1.380 (2)
C2—C3	1.3997 (19)	C13—C14	1.382 (2)
C2—C6	1.403 (2)	C13—H13	0.9300
C3—C4	1.395 (2)	C14—C15	1.369 (3)
C3—C18	1.4855 (19)	C14—H14	0.9300
C4—C5	1.408 (2)	C15—C16	1.369 (3)
C4—C7	1.516 (2)	C15—H15	0.9300
C5—C25	1.509 (7)	C16—C17	1.382 (2)
C5—C25A	1.522 (9)	C16—H16	0.9300
C25—F2	1.287 (7)	C17—H17	0.9300
C25—F1	1.295 (8)	C18—C19	1.386 (2)
C25—F3	1.295 (7)	C18—C23	1.3863 (19)
C25A—F2A	1.272 (10)	C19—C20	1.374 (2)
C25A—F1A	1.279 (10)	C19—H19	0.9300
C25A—F3A	1.296 (10)	C20—C21	1.373 (2)
C7—C8	1.453 (2)	C20—H20	0.9300
C8—C11A	1.300 (13)	C21—C22	1.369 (2)
C8—C11	1.343 (4)	C22—C23	1.379 (2)
C8—S1A	1.708 (6)	C22—H22	0.9300
C8—S1	1.7155 (15)	C23—H23	0.9300
S1—C9	1.698 (4)	C24—H24A	0.9600
C9—C10	1.341 (4)	C24—H24B	0.9600
C9—H9	0.9300	C24—H24C	0.9600
C10—C11	1.393 (5)		
C6—N1—N2	110.16 (11)	C8—C11—C10	114.4 (3)
C6—N1—C12	130.36 (13)	C8—C11—H11	122.8
N2—N1—C12	119.37 (12)	C10—C11—H11	122.8
C1—N2—N1	107.76 (12)	C9A—S1A—C8	89.8 (10)
C5—N3—C6	114.27 (12)	C10A—C9A—S1A	112.5 (18)
N2—C1—C2	110.16 (13)	C10A—C9A—H9A	123.7
N2—C1—C24	120.38 (14)	S1A—C9A—H9A	123.7
C2—C1—C24	129.45 (14)	C9A—C10A—C11A	111 (2)
C3—C2—C6	118.22 (13)	C9A—C10A—H10A	124.6
C3—C2—C1	136.80 (14)	C11A—C10A—H10A	124.6
C6—C2—C1	104.98 (12)	C8—C11A—C10A	114.5 (15)
C4—C3—C2	116.91 (13)	C8—C11A—H11A	122.7
C4—C3—C18	122.91 (12)	C10A—C11A—H11A	122.7
C2—C3—C18	120.10 (13)	C13—C12—C17	120.56 (14)

C3—C4—C5	118.74 (13)	C13—C12—N1	120.49 (13)
C3—C4—C7	118.39 (13)	C17—C12—N1	118.94 (14)
C5—C4—C7	122.80 (13)	C12—C13—C14	119.17 (16)
N3—C5—C4	125.59 (14)	C12—C13—H13	120.4
N3—C5—C25	113.8 (3)	C14—C13—H13	120.4
C4—C5—C25	120.6 (3)	C15—C14—C13	120.81 (19)
N3—C5—C25A	110.0 (4)	C15—C14—H14	119.6
C4—C5—C25A	123.9 (4)	C13—C14—H14	119.6
F2—C25—F1	107.0 (6)	C16—C15—C14	119.53 (16)
F2—C25—F3	109.3 (6)	C16—C15—H15	120.2
F1—C25—F3	106.0 (5)	C14—C15—H15	120.2
F2—C25—C5	112.4 (5)	C15—C16—C17	120.85 (16)
F1—C25—C5	110.8 (5)	C15—C16—H16	119.6
F3—C25—C5	111.0 (5)	C17—C16—H16	119.6
F2A—C25A—F1A	106.9 (9)	C12—C17—C16	119.05 (17)
F2A—C25A—F3A	103.5 (8)	C12—C17—H17	120.5
F1A—C25A—F3A	103.3 (8)	C16—C17—H17	120.5
F2A—C25A—C5	114.4 (7)	C19—C18—C23	119.13 (14)
F1A—C25A—C5	113.5 (7)	C19—C18—C3	118.89 (12)
F3A—C25A—C5	114.1 (8)	C23—C18—C3	121.89 (13)
N3—C6—N1	126.82 (13)	C20—C19—C18	120.78 (14)
N3—C6—C2	126.21 (13)	C20—C19—H19	119.6
N1—C6—C2	106.93 (12)	C18—C19—H19	119.6
O1—C7—C8	122.15 (14)	C21—C20—C19	118.96 (15)
O1—C7—C4	120.33 (14)	C21—C20—H20	120.5
C8—C7—C4	117.47 (13)	C19—C20—H20	120.5
C11A—C8—C11	102.8 (9)	C22—C21—C20	121.55 (14)
C11A—C8—C7	126.9 (9)	C22—C21—Cl1	119.71 (12)
C11—C8—C7	130.2 (2)	C20—C21—Cl1	118.73 (13)
C11A—C8—S1A	112.2 (9)	C21—C22—C23	119.35 (14)
C7—C8—S1A	120.8 (3)	C21—C22—H22	120.3
C11—C8—S1	110.3 (2)	C23—C22—H22	120.3
C7—C8—S1	119.44 (12)	C22—C23—C18	120.21 (15)
S1A—C8—S1	119.7 (3)	C22—C23—H23	119.9
C9—S1—C8	91.16 (16)	C18—C23—H23	119.9
C10—C9—S1	112.7 (3)	C1—C24—H24A	109.5
C10—C9—H9	123.6	C1—C24—H24B	109.5
S1—C9—H9	123.6	H24A—C24—H24B	109.5
C9—C10—C11	111.4 (4)	C1—C24—H24C	109.5
C9—C10—H10	124.3	H24A—C24—H24C	109.5
C11—C10—H10	124.3	H24B—C24—H24C	109.5

Hydrogen-bond geometry (Å, º)

*Cg*2 is the centroid of the C12–C17 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···O1[i]	0.93	2.74	3.610 (2)	156

C20—H20···O1^{ii}	0.93	2.57	3.209 (2)	127
C22—H22···*Cg*2^{iii}	0.93	2.74	3.4075 (18)	129

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