research papers

Three closely related 4,5,6,7-tetrahydro-1H-pyrazolo[4,3-c]pyridines: synthesis, molecular conformations and hydrogen bonding in zero, one and two dimensions

Belakavadi K. Sagar,[a] Kachigere B. Harsha,[a] Hemmige S. Yathirajan,[a] Kanchugarakoppal S. Rangappa,[a] Ravindranath S. Rathore[b] and Christopher Glidewell[c]*

[a]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysuru 570 006, India, [b]Centre for Biological Sciences (Bioinformatics), School of Earth, Biological and Environmental Sciences, Central University of South Bihar, Patna 800 014, India, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland. *Correspondence e-mail: cg@st-andrews.ac.uk

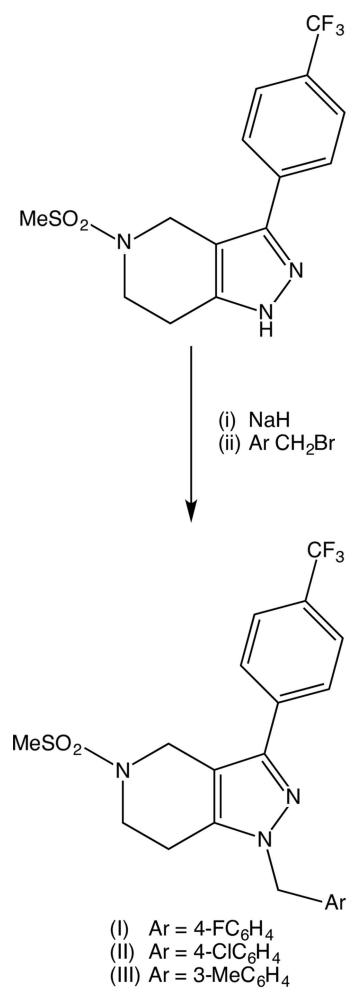In each of 1-(4-fluorophenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1H-pyrazolo[4,3-c]pyridine, $C_{21}H_{19}F_4N_3O_2S$, (I), 1-(4-chlorophenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1H-pyrazolo[4,3-c]pyridine, $C_{21}H_{19}ClF_3N_3O_2S$, (II), and 1-(3-methylphenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1H-pyrazolo-[4,3-c]pyridine, $C_{22}H_{22}F_3N_3O_2S$, (III), the reduced pyridine ring adopts a half-chair conformation with the methylsulfonyl substituent occupying an equatorial site. Although compounds (I) and (II) are not isostructural, having the space groups Pbca and $P2_12_12_1$, respectively, their molecular conformations are very similar, but the conformation of compound (III) differs from those of (I) and (II) in the relative orientation of the N-benzyl and methylsulfonyl substituents. In compounds (II) and (III), but not in (I), the trifluoromethyl groups are disordered over two sets of atomic sites. Molecules of (I) are linked into centrosymmetric dimers by C—H···π(arene) hydrogen bonds, molecules of (II) are linked by two C—H···O hydrogen bonds to form ribbons of $R_3^3(18)$ rings, which are themselves further linked by a C—Cl···π(arene) interaction, and a combination of C—H···O and C—H···π(arene) hydrogen bonds links the molecules of (III) into sheets. Comparisons are made with the structures of some related compounds.

1. Introduction

3-Aryl-4,5,6,7-tetrahydropyrazolo[4,3-c]pyridines were first synthesized as a new class of antihypertensive agent (Winters et al., 1985) and compounds of this type have subsequently been used for the treatment of neuropathic pain (Yogeeswari et al., 2013). 5-Arylsulfonyl-4,5,6,7-tetrahydropyrazolo[4,3-c]-pyridines have been shown (Ye et al., 2010) to act as potent inhibitors of γ-secretase, an intramembrane protease. Structural studies of tetrahydropyrazolo[4,3-c]pyridines are rather few in number (Smith et al., 2007; Ye et al., 2010; Guo, 2011; Petersen et al., 2013), although the structure of a hexahydro derivative has been reported (Shahani et al., 2010) and, prompted by this comparative paucity of structural data, we now report the molecular and supramolecular structures of three closely related compounds of this class, namely 1-(4-fluorophenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1H-pyrazolo[4,3-c]pyridine, (I), 1-(4-chloro-phenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-
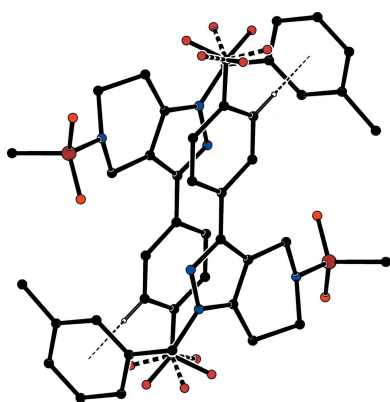
tetrahydro-1*H*-pyrazolo[4,3-*c*]pyridine, (II), and 1-(3-methyl-phenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1*H*-pyrazolo[4,3-*c*]pyridine, (III) (see Scheme 1). Pyrazoles are readily synthesized by condensation of 1,3-diketones with monosubstituted hydrazines (Wiley & Hexner, 1963) and similar reactions using 3-acylpiperidine-4-ones lead directly to 3-aryl-4,5,6,7-tetrahydropyrazolo[4,3-*c*]pyridines (Winters *et al.*, 1985). Compounds (I)–(III) were synthesized using as the common precursor 5-methylsulfonyl-3-[4-(tri-fluoromethyl)phenyl]-4,5,6,7-tetrahydro-1*H*-pyrazolo[4,3-*c*]-pyridine (Scheme 1), which had itself been prepared by the hydrazine/1,3-diketone condensation method, *viz.* deprotonation of this precursor using sodium hydride, followed by reaction of the resulting anion with an appropriately substituted benzyl bromide gave compounds (I)–(III) in yields of around 90%.

Scheme 1

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of compounds (I)–(III), a solution of 5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetra-hydro-1*H*-pyrazolo[4,3-*c*]pyridine (1 mmol) in *N,N*-dimethyl-formamide (20 ml) was added to sodium hydride (1 mmol) at 273 K. The appropriately substituted benzyl bromide

[4-fluorobenzyl bromide for (I), 4-chlorobenzylbromide for (II) or 3-methylbenzyl bromide for (III)] (1 mmol) was then added dropwise and the mixtures were stirred at ambient temperature for 6–8 h, with thin-layer chromatography (TLC) monitoring of the progress of the reactions. When the reactions were judged to be complete, an excess of crushed ice was added to each mixture, and the resulting solid products were collected by filtration, and then dried in air; the yield was 90% for (I), 92% for (II) and 94% for (III). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in the presence of air, of solutions in *N,N*-dimethylformamide [m.p. 441 K for (I), 433 K for (II) and 443 K for (III)].

2.2. Refinement

Crystal data, data collection and structure refinement details for (I)–(III) are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.93 (aromatic), 0.96 (CH$_3$) or 0.97 Å (CH$_2$) and with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for the methyl groups, which were allowed to rotate but not to tilt, and 1.2 for all other H atoms. For compound (II), the correct absolute configuration of the molecules in the crystal selected for data collection was established by means of the Flack x parameter (Flack, 1983), x = 0.03 (3), calculated (Parsons *et al.*, 2013) by the use of 1208 quotients of the type $[(I^+) - (I^-)]/[(I^+) + (I^-)]$, and by the use of the Hooft y parameter (Hooft *et al.*, 2008), y = 0.02 (3), calculated using 2053 Bijvoet pairs (100% coverage). The reference molecules in compounds (I) and (III) were selected to have the same absolute configuration as found for compound (II). In each of compounds (II) and (III), the F atoms of the CF$_3$ group were disordered over two sets of atomic sites, with occupancies of 0.51 (2) and 0.49 (2) in (II), and 0.579 (19) and 0.421 (19) in (III). In the final analysis of variance for each of compounds (I) and (III), there was a negative value of K = mean(F_o^2)/mean(F_c^2) for the groups of the very weakest reflections: for (I), K = −7.571 for the 451 reflections having F_c/F_c(max) in the range 0.000 < F_c/F_c(max) < 0.005, and for (III), K = −0.828 for the 447 reflections having F_c/F_c(max) in the range 0.000 < F_c/F_c(max) < 0.005.

3. Results and discussion

The constitutions of compounds (I)–(III) differ only in the identity and location of a single simple substituent in the *N*-benzyl ring, *i.e.* 4-fluoro in (I), 4-chloro in (II) and 3-methyl in (III). Despite this, the three compounds all crystallize in different space groups, *i.e. Pbca* for (I), $P2_12_12_1$ for (II) and $P2_1/n$ for (III); thus, the 4-halogeno compounds (I) and (II) are far from being isomorphous.

In compound (I), the CF$_3$ group is fully ordered, but in each of (II) and (III), the F atoms of this group are disordered over two sets of atomic sites having occupancies of 0.51 (2) and 0.49 (2) in (II), and of 0.579 (19) and 0.421 (19) in (III) (Figs. 1–3).

Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_{21}H_{19}F_4N_3O_2S$	$C_{21}H_{19}ClF_3N_3O_2S$	$C_{22}H_{22}F_3N_3O_2S$
M_r	453.45	469.90	449.48
Crystal system, space group	Orthorhombic, $Pbca$	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/n$
Temperature (K)	296	296	296
a, b, c (Å)	19.7282 (6), 9.7644 (3), 20.7157 (7)	5.4468 (2), 11.4102 (4), 34.3009 (9)	13.8408 (10), 8.7145 (6), 18.0898 (13)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 106.470 (2), 90
V (Å^3)	3990.5 (2)	2131.77 (12)	2092.4 (3)
Z	8	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.22	0.33	0.21
Crystal size (mm)	$0.31 \times 0.29 \times 0.28$	$0.40 \times 0.30 \times 0.30$	$0.34 \times 0.24 \times 0.22$
Data collection			
Diffractometer	Bruker Kappa APEXII	Bruker Kappa APEXII	Bruker Kappa APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 20012)	Multi-scan (*SADABS*; Bruker, 2012)	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.926, 0.939	0.879, 0.907	0.946, 0.956
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	50117, 4148, 2738	15002, 4920, 3587	33310, 4391, 2953
R_{int}	0.039	0.032	0.045
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.629	0.651	0.632
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.058, 0.210, 1.12	0.039, 0.093, 1.03	0.044, 0.112, 1.04
No. of reflections	4148	4920	4391
No. of parameters	282	309	310
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.35, −0.53	0.16, −0.22	0.33, −0.29
Absolute structure	–	See §2.2, *Refinement*	–

Computer programs: *APEX2* (Bruker, 2012), *SAINT-Plus* (Bruker, 2012), *SHELXS86* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009).
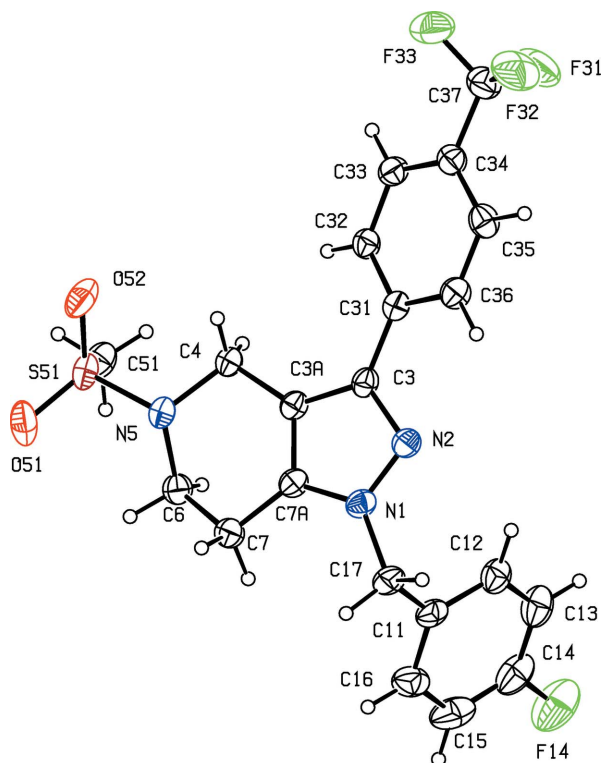

Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
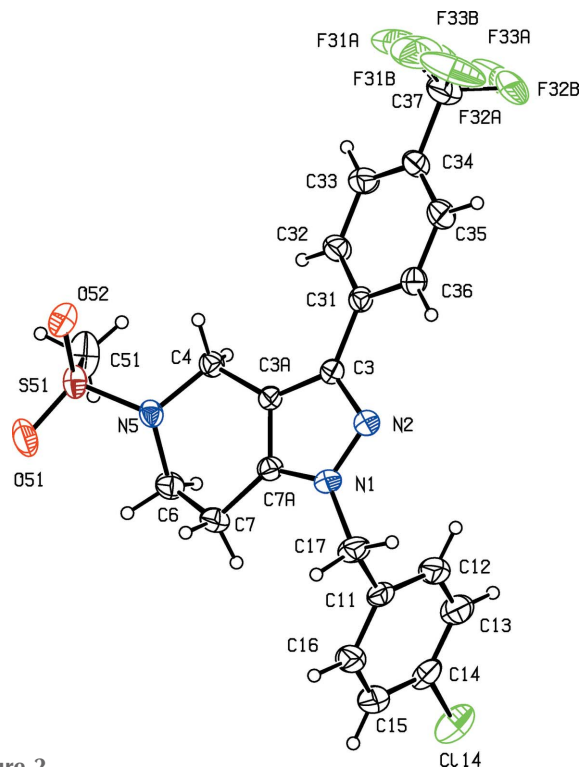

Figure 2
The molecular structure of compound (II), showing the atom-labelling scheme and both orientations of the disordered –CF$_3$ group. Displacement ellipsoids are drawn at the 30% probability level.

Figure 3
The molecular structure of compound (III), showing the atom-labelling scheme and both orientations of the disordered –CF₃ group. Displacement ellipsoids are drawn at the 30% probability level.
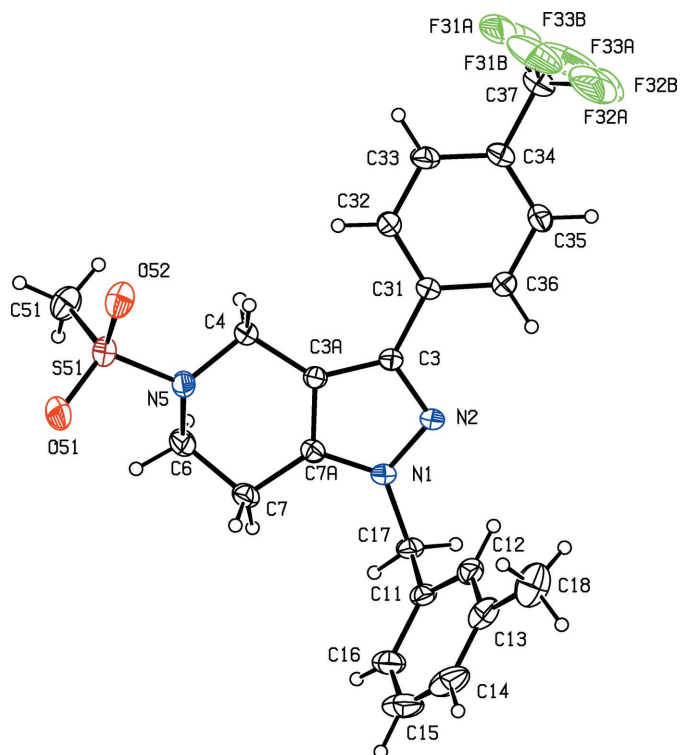
For the reduced pyridine ring in each of compounds (I)–(III), the ring-puckering parameters (Cremer & Pople, 1975) show (Table 2) that this ring (Fig. 4) adopts a half-chair conformation (Evans & Boeyens, 1989); for an idealized half chair form, the puckering angles are $\theta = 50.8°$ and $\varphi = (60k + 30)°$, where k represents an integer. The displacements of atom N5 from the C4/C3A/C7A/C7 plane are 0.289 (5), 0.409 (5) and 0.288 (4) Å, respectively, for compounds (I)–(III), and the corresponding displacements of atom C6 to the opposite side of this plane are 0.439 (6), 0.373 (6) and 0.463 (4) Å. In each case, the methylsulfonyl group occupies an equatorial site.

In addition to these very similar ring conformations in (I)–(III), the torsion angles defining the orientation of the methylsulfonyl and 4-trifluoromethylphenyl substituents relative to the fused-ring system are also very similar (Table 2).
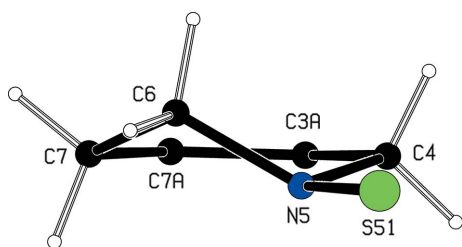

Figure 4
The reduced pyridine ring in compound (I), showing the half-chair conformation. For the sake of clarity, the majority of the other atoms in the molecule have been omitted.

Table 2
Selected geometrical parameters (Å) for compounds (I)–(III).

Ring-puckering angles are calculated for the atom sequence N5–C4–C3A–C7A–C7–C6.

	(I)	(II)	(III)
Ring-puckering parameters			
Q	0.481 (3)	0.517 (3)	0.498 (2)
θ	48.0 (4)	50.4 (3)	52.6 (2)
φ	322.9 (5)	331.6 (5)	322.4 (3)
Torsion angles			
N2—N1—C17—C11	−87.2 (3)	−105.1 (3)	89.5 (2)
N1—C17—C11—C12	58.1 (4)	59.0 (4)	−56.3 (3)
N2—C3—C31—C32	162.9 (3)	164.3 (3)	178.9 (2)
C4—C5—S51—O51	−171.2 (2)	179.7 (2)	−167.12 (16)
C4—C5—S51—O52	−42.6 (3)	−51.9 (2)	−37.73 (19)
C4—C5—S51—C51	73.2 (2)	62.8 (3)	77.85 (19)

Table 3
Hydrogen bonds and short intermolecular contacts (Å, °) for compounds (I)–(III).

$Cg1$ and $Cg2$ represent the centroids of the C11–C16 and C31–C36 rings, respectively.

	D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
(I)	C6—H6⋯$Cg2$ⁱ	0.97	2.76	3.694 (4)	161
	C33—H33⋯$Cg1$ⁱ	0.03	2.73	3.595 (3)	154
	C51—H51A⋯N2ⁱⁱ	0.96	2.55	3.483 (4)	165
(II)	C15—H15⋯O52ⁱⁱⁱ	0.93	2.44	3.339 (4)	163
	C17—H17A⋯O51ⁱᵛ	0.97	2.57	3.487 (4)	158
(III)	C17—H17A⋯O51ᵛ	0.97	2.52	3.426 (3)	155
	C33—H33⋯$Cg2$ⁱ	0.93	2.70	3.488 (3)	144

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

However, the torsion angles defining the orientation of the N-benzyl unit relative to the pyrazole ring, while similar in the 4-halogeno compounds (I) and (II), differ from those in compound (III). In each of (I) and (II), the N-benzyl unit lies on the same side of the fused-ring system as the methyl group of the MeSO₂ unit, whereas in (III), it lies on the opposite side (Figs. 1–3).

All of the molecules are conformationally chiral and for each of (I) and (III), the centrosymmetric space group confirms that equal numbers of the two conformational enantiomers are present, but in compound (II), there is only one enantiomer present in each crystal. The correct enantiomorph in the crystal of (II) selected for data collection was established by means of the Flack x parameter (Flack, 1983) and the Hooft y parameter (Hooft et al., 2008); $x = 0.03$ (3) and $y = 0.02$ (3). The reference molecules for (I) and (III) were selected to have the same hand for the reduced-ring conformation as that found for (II).

The supramolecular assembly in compound (I) is quite simple: the combined action of two independent C—H⋯π(arene) hydrogen bonds (Table 3) links inversion-related pairs of molecules into centrosymmetric dimers (Fig. 5). The only other short direction-specific contact between the molecules of compound (I) is a C—H⋯N contact (Table 3) which involves a methyl C—H bond and is therefore

Table 4
C—Cl···π(arene) contacts (Å, °) in compound (II).

Cg1 and Cg2 represent the centroids of the C11–C16 and C31–C36 rings, respectively.

C—Cl···Cg	C—Cl	Cl···Cg	C···Cg	C—Cl···Cg
C14—Cl14···$Cg1^i$	1.736 (4)	3.839 (2)	4.559 (4)	103.13 (13)
C14—Cl14···$Cg2^{ii}$	1.736 (4)	3.4292 (18)	5.031 (4)	152.23 (14)

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

unlikely to be of structural significance (Riddell & Rogerson, 1996, 1997).

In the crystal structure of compound (II), molecules related by translation are linked by a C—H···O hydrogen bond to form a $C(12)$ (Bernstein et al., 1995) chain running parallel to the [010] direction, while a second, longer, C—H···O hydrogen bond links molecules related by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ to form a $C(9)$ chain along [010]; the combination of these two chain motifs generates a ribbon running parallel to the [010] direction and characterized by a $C(9)C(12)$-$[R_3^3(18)]$ motif (Fig. 6). In addition, the crystal structure of compound (II) contains two short intermolecular C—Cl···π(arene) contacts (Table 4), and the contact involving the C31–C36 ring has a C···(ring centroid) distance slightly shorter than the mean distance of 3.6 Å deduced from a database study (Imai et al., 2008) for attractive contacts of this type. In compound (II), this interaction links molecules related by translation to form a chain running parallel to the [110] direction (Fig. 7). The ribbon along [010] and the chain along [110] combine to form a complex sheet lying parallel to (001).

For compound (III), the supramolecular assembly depends upon a combination of one C—H···O hydrogen bond and one

Figure 6
A stereoview of part of the crystal structure of compound (II), showing the formation of a $C(9)C(12)[R_3^3(18)]$ ribbon running parallel to the [010] direction. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted.

C—H···π(arene) hydrogen bond (Table 3). Molecules related by inversion are linked by the symmetry-related pairs of C—H···π(arene) hydrogen bonds to form cyclic centrosymmetric dimers (Fig. 8), somewhat reminiscent of the dimer formation in compound (I). The C—H···O hydrogen bond links molecules related by the n-glide plane at $y = \frac{3}{4}$ to form a $C(9)$ chain running parallel to the [101] direction (Fig. 9), and the combination of these two motifs generates a sheet lying parallel to $(10\bar{1})$.

Hence, the patterns of supramolecular assembly in compounds (I)–(III) depend on a different range of hydrogen bonds in each case, namely C—H···π(arene) in compound (I), C—H···O in compound (II) and a combination of these two types in compound (III), which lead in turn to a hydrogen-

Figure 5
Part of the crystal structure of compound (I), showing the formation of a centrosymmetric dimer. For the sake of clarity, the unit-cell outline and H atoms bonded to C atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x + 1, -y + 1, -z + 1)$.
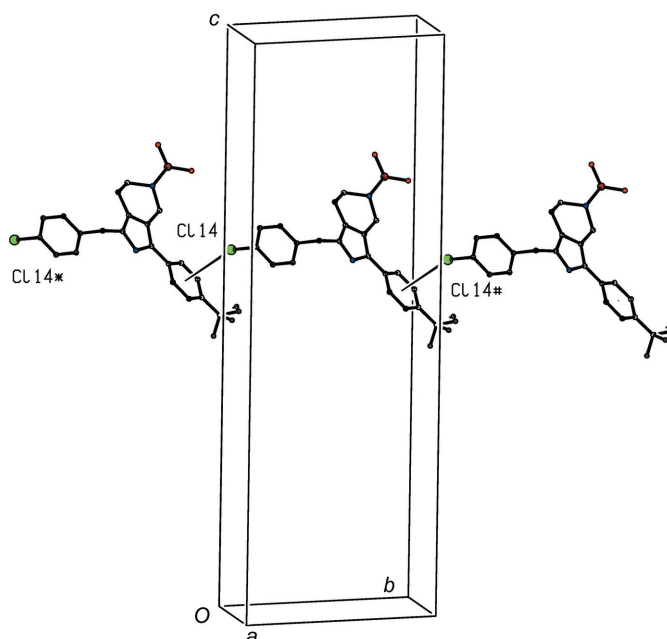
Figure 7
Part of the crystal structure of compound (II), showing the formation of a chain along the [110] direction built from C—Cl···π(arene) interactions. For the sake of clarity, all H atoms have been omitted. Cl atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x - 1, y - 1, z)$ and $(x + 1, y + 1, z)$, respectively.

bonded assembly which is finite, or zero-dimensional, in (I), one-dimensional in (II) and two-dimensional in (III), with that in (II) being amplified by an C—Cl···π(arene) interaction to form a sheet structure entirely different from that formed in (III).
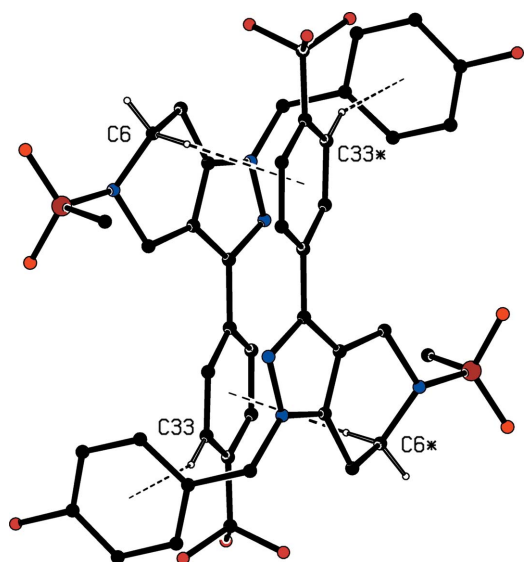
Scheme 2

Figure 8
Part of the crystal structure of compound (III), showing the formation of a cyclic centrosymmetric dimer. For the sake of clarity, the unit-cell outline and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($-x + 1$, $-y + 1$, $-z + 1$).
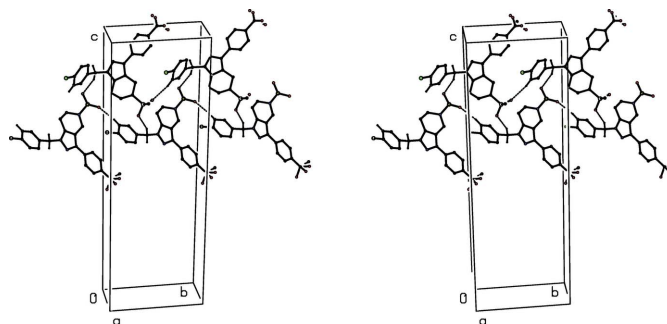
chain by N—H···N hydrogen bonds (Ye *et al.*, 2010). In the crystal structure of hexahydro compound (VI), molecules are linked by two independent N—H···O hydrogen bonds to form ribbons containing alternating rings of $R_2^2(8)$ and $R_4^2(10)$ types, although this was not pointed out in the original report (Shahani *et al.*, 2010). Finally, we note unreduced derivative

It is of interest briefly to compare the structures of compounds (I)–(III) with those of the related compounds (IV)–(VIII) (see Scheme 2). In each of (IV) (Guo, 2011), (V) (Ye *et al.*, 2010) and (VI) (Shahani *et al.*, 2010), the reduced pyridine ring adopts a half-chair conformation, as found here for (I)–(III), although for (VI) this was described in the original report as half-boat. Although in each of compounds (I)–(III), the methylsulfonyl substituent occupies an equatorial site, in diester (IV), the *N*-alkoxycarbonyl substituent occupies an axial site on the reduced pyridine ring, and in arylsulfonyl compound (V), all three substituents on this ring adopt axial sites, so that the aryl sulfonyl unit is *trans* to both of the ethyl substituents, which are themselves mutually *cis*; in hexahydro compound (VI), the N atom of the reduced pyridine ring has planar geometry. Inversion-related pairs of molecules of (IV) are linked by C—H···O hydrogen bonds to form cyclic centrosymmetric $R_2^2(16)$ dimers (Guo, 2011), while in the crystal structure of compound (V), which crystallizes as a single enantiomer in the Sohncke space group $P2_12_12_1$, molecules related by a 2_1 screw axis are linked into a $C(8)$

Figure 9
Part of the crystal structure of compound (III), showing the formation of a $C(9)$ chain parallel to [101] built from C—H···O hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z + \frac{1}{2}$) and ($x - \frac{1}{2}$, $-y + \frac{3}{2}$, $z - \frac{1}{2}$), respectively.

(VII) (Commeiras *et al.*, 2004) and dione (VIII) (Smith *et al.*, 2007), in both of which the fused bicyclic ring system is planar. Inversion-related pairs of molecules of (VII) are linked into centrosymmetric dimers by a combination of C—H···π(arene) hydrogen bonds and a π–π stacking interaction, while the molecules of (VIII) are linked into sheets containing $S(6)$, $R_2^2(10)$ and $R_5^4(19)$ rings by the action of four independent N—H···O hydrogen bonds.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2012). *APEX2, SADABS* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.

Commeiras, E., Woodcock, S. C., Baldwin, J. E., Adlington, R. M., Cowley, A. R. & Wilkinson, P. J. (2004). *Tetrahedron*, **60**, 933–938.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Evans, D. G. & Boeyens, J. C. A. (1989). *Acta Cryst.* B**45**, 581–590.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Guo, H.-M. (2011). *Acta Cryst.* E**67**, o3239.

Hooft, R. W. W., Straver, L. H. & Spek, A. L. (2008). *J. Appl. Cryst.* **41**, 96–103.

Imai, Y. N., Inoue, Y., Nakanishi, I. & Kitaura, K. (2008). *Protein Sci.* **17**, 1129–1137.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Petersen, J. G., Bergmann, R., Møller, H. A., Jørgensen, C. G., Nielsen, B., Kehler, J., Frydenvang, K., Kristensen, J., Balle, T., Jensen, A. A., Kristiansen, U. & Frølund, B. (2013). *J. Med. Chem.* **56**, 993–1006.

Riddell, F. G. & Rogerson, M. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 493–504.

Riddell, F. G. & Rogerson, M. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 249–256.

Shahani, T., Fun, H.-K., Ragavan, R. V., Vijayakumar, V. & Sarveswari, S. (2010). *Acta Cryst.* E**66**, o142–o143.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Smith, L. A., Matthews, T. P., Horton, P. N., Hursthouse, M. B. & Collins, I. (2007). *Tetrahedron*, **63**, 9627–9634.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Wiley, R. H. & Hexner, P. E. (1963). *Org. Synth.* Coll. Vol. 4, pp. 351–352.

Winters, G., Sala, A., Barone, D. & Baldoni, E. (1985). *J. Med. Chem.* **28**, 934–940.

Ye, X. M., Konradi, A. W., Smith, J., Xu, Y.-Z., Dressen, D., Garofalo, A. W., Marugg, J., Sham, H. L., Troung, A. P. T., Jagodzinski, J., Pleiss, M., Zhang, H., Goldbach, E., Sauer, J.-M., Brigham, E., Bova, M. & Basi, G. S. (2010). *Bioorg. Med. Chem. Lett.* **20**, 2195–2199.

Yogeeswari, P., Sharma, M., Samala, G., Gangadhar, M., Karthick, S., Mallipeddi, S., Semwai, A. & Sriram, D. (2013). *Eur. J. Med. Chem.* **66**, 211–220.

supporting information

Three closely related 4,5,6,7-tetrahydro-1*H*-pyrazolo[4,3-*c*]pyridines: synthesis, molecular conformations and hydrogen bonding in zero, one and two dimensions

Belakavadi K. Sagar, Kachigere B. Harsha, Hemmige S. Yathirajan, Kanchugarakoppal S. Rangappa, Ravindranath S. Rathore and Christopher Glidewell

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2012); cell refinement: *APEX2* (Bruker, 2012); data reduction: *SAINT-Plus* (Bruker, 2012); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009). Software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009) for (I), (III); *SHELXL2014* (Sheldrick, 2015 and *PLATON* (Spek, 2009) for (II).

(I) 1-(4-Fluorophenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1*H*-pyrazolo[4,3-*c*]pyridine

Crystal data

$C_{21}H_{19}F_4N_3O_2S$	$D_x = 1.510$ Mg m^{-3}
$M_r = 453.45$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 4704 reflections
$a = 19.7282$ (6) Å	$\theta = 2.1–27.8°$
$b = 9.7644$ (3) Å	$\mu = 0.22$ mm^{-1}
$c = 20.7157$ (7) Å	$T = 296$ K
$V = 3990.5$ (2) Å^3	Block, colourless
$Z = 8$	$0.31 \times 0.29 \times 0.28$ mm
$F(000) = 1872$	

Data collection

Bruker Kappa APEXII diffractometer	4148 independent reflections
	2738 reflections with $I > 2\sigma(I)$
Radiation source: fine focus sealed tube	$R_{int} = 0.039$
φ and ω scans	$\theta_{max} = 26.6°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan	$h = -22 \rightarrow 24$
(SADABS; Bruker, 20012)	$k = -12 \rightarrow 12$
$T_{min} = 0.926$, $T_{max} = 0.939$	$l = -25 \rightarrow 26$
50117 measured reflections	

Refinement

Refinement on F^2	$S = 1.12$
Least-squares matrix: full	4148 reflections
$R[F^2 > 2\sigma(F^2)] = 0.058$	282 parameters
$wR(F^2) = 0.210$	0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1039P)^2 + 2.7804P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.35$ e Å^{-3}

$\Delta\rho_{min} = -0.53$ e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0032 (8)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.38650 (11)	0.7471 (3)	0.45255 (12)	0.0452 (6)
N2	0.37282 (12)	0.6640 (3)	0.50338 (13)	0.0464 (6)
C3	0.43251 (13)	0.6512 (3)	0.53422 (14)	0.0412 (7)
C3A	0.48364 (14)	0.7256 (3)	0.50227 (14)	0.0402 (6)
C4	0.55757 (14)	0.7426 (3)	0.51515 (15)	0.0435 (7)
H4A	0.5649	0.7621	0.5605	0.052*
H4B	0.5815	0.6588	0.5044	0.052*
N5	0.58350 (12)	0.8571 (3)	0.47532 (12)	0.0450 (6)
C6	0.56076 (15)	0.8565 (4)	0.40750 (15)	0.0498 (7)
H6A	0.5721	0.7694	0.3877	0.060*
H6B	0.5839	0.9283	0.3838	0.060*
C7	0.48439 (16)	0.8792 (3)	0.40391 (16)	0.0492 (7)
H7A	0.4736	0.9736	0.4143	0.059*
H7B	0.4681	0.8599	0.3607	0.059*
C7A	0.45184 (14)	0.7861 (3)	0.45089 (14)	0.0430 (7)
C17	0.33306 (15)	0.7798 (3)	0.40629 (16)	0.0512 (8)
H17A	0.3421	0.8691	0.3876	0.061*
H17B	0.2901	0.7850	0.4289	0.061*
C11	0.32736 (14)	0.6760 (4)	0.35284 (15)	0.0482 (8)
C12	0.31506 (16)	0.5384 (4)	0.36714 (18)	0.0562 (8)
H12	0.3117	0.5110	0.4100	0.067*
C13	0.30780 (18)	0.4429 (4)	0.3189 (2)	0.0704 (11)
H13	0.3004	0.3512	0.3288	0.084*
C14	0.31172 (19)	0.4851 (6)	0.2564 (2)	0.0766 (12)
F14	0.30351 (16)	0.3926 (4)	0.20841 (14)	0.1188 (11)
C15	0.3238 (2)	0.6185 (6)	0.2395 (2)	0.0806 (13)
H15	0.3265	0.6444	0.1964	0.097*
C16	0.33188 (17)	0.7143 (4)	0.28874 (18)	0.0650 (10)
H16	0.3404	0.8053	0.2783	0.078*
C31	0.43545 (14)	0.5722 (3)	0.59446 (14)	0.0413 (7)
C32	0.49679 (14)	0.5259 (3)	0.61880 (14)	0.0452 (7)
H32	0.5364	0.5422	0.5957	0.054*
C33	0.50019 (16)	0.4561 (3)	0.67656 (15)	0.0484 (7)

H33	0.5419	0.4273	0.6926	0.058*
C34	0.44176 (16)	0.4290 (3)	0.71045 (15)	0.0480 (7)
C35	0.37958 (16)	0.4711 (3)	0.68658 (16)	0.0531 (8)
H35	0.3400	0.4507	0.7089	0.064*
C36	0.37683 (15)	0.5435 (3)	0.62941 (16)	0.0506 (8)
H36	0.3351	0.5736	0.6140	0.061*
C37	0.4453 (2)	0.3459 (4)	0.76991 (18)	0.0622 (9)
F31	0.44298 (18)	0.2127 (2)	0.75781 (13)	0.1069 (10)
F32	0.39575 (15)	0.3710 (3)	0.81152 (12)	0.1023 (9)
F33	0.50207 (14)	0.3661 (3)	0.80380 (11)	0.0960 (8)
S51	0.66482 (4)	0.88817 (9)	0.48509 (4)	0.0538 (3)
O51	0.67969 (14)	1.0121 (3)	0.45186 (16)	0.0803 (8)
O52	0.67724 (13)	0.8798 (3)	0.55280 (13)	0.0733 (8)
C51	0.70896 (16)	0.7557 (4)	0.44678 (18)	0.0609 (9)
H51A	0.7567	0.7676	0.4536	0.091*
H51B	0.6994	0.7576	0.4013	0.091*
H51C	0.6949	0.6694	0.4644	0.091*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0343 (12)	0.0517 (14)	0.0497 (14)	0.0055 (10)	−0.0031 (10)	0.0008 (12)
N2	0.0351 (12)	0.0520 (15)	0.0521 (15)	0.0015 (11)	−0.0016 (10)	0.0044 (12)
C3	0.0310 (13)	0.0428 (15)	0.0499 (17)	0.0013 (11)	0.0000 (11)	−0.0025 (13)
C3A	0.0331 (14)	0.0419 (16)	0.0458 (15)	0.0040 (11)	0.0001 (11)	−0.0036 (12)
C4	0.0348 (14)	0.0476 (16)	0.0481 (17)	−0.0029 (12)	−0.0013 (11)	0.0006 (13)
N5	0.0363 (13)	0.0474 (14)	0.0513 (15)	−0.0052 (11)	−0.0002 (10)	−0.0043 (11)
C6	0.0439 (16)	0.0561 (18)	0.0495 (18)	−0.0020 (14)	0.0024 (13)	0.0025 (14)
C7	0.0453 (17)	0.0516 (18)	0.0508 (18)	0.0004 (13)	0.0006 (13)	0.0051 (14)
C7A	0.0358 (14)	0.0469 (16)	0.0462 (16)	0.0041 (12)	−0.0003 (12)	−0.0023 (13)
C17	0.0357 (15)	0.0591 (19)	0.059 (2)	0.0086 (13)	−0.0078 (13)	0.0046 (15)
C11	0.0294 (14)	0.067 (2)	0.0482 (18)	0.0074 (13)	−0.0031 (12)	0.0018 (15)
C12	0.0427 (17)	0.068 (2)	0.058 (2)	−0.0061 (15)	0.0052 (14)	−0.0056 (17)
C13	0.052 (2)	0.081 (3)	0.078 (3)	−0.0109 (19)	0.0098 (18)	−0.015 (2)
C14	0.049 (2)	0.112 (4)	0.068 (3)	−0.003 (2)	0.0007 (17)	−0.029 (3)
F14	0.103 (2)	0.166 (3)	0.088 (2)	−0.0128 (19)	−0.0001 (15)	−0.062 (2)
C15	0.065 (3)	0.129 (4)	0.047 (2)	0.016 (3)	−0.0060 (17)	−0.005 (2)
C16	0.053 (2)	0.079 (3)	0.062 (2)	0.0121 (17)	−0.0017 (16)	0.014 (2)
C31	0.0370 (14)	0.0416 (15)	0.0455 (16)	−0.0011 (12)	−0.0004 (11)	−0.0043 (13)
C32	0.0358 (14)	0.0487 (16)	0.0511 (17)	−0.0020 (12)	0.0021 (12)	0.0038 (14)
C33	0.0461 (16)	0.0489 (17)	0.0503 (17)	0.0006 (13)	−0.0069 (13)	−0.0001 (14)
C34	0.0543 (18)	0.0451 (16)	0.0445 (17)	−0.0033 (13)	0.0017 (13)	−0.0016 (13)
C35	0.0470 (17)	0.0554 (19)	0.057 (2)	−0.0004 (14)	0.0135 (14)	0.0025 (16)
C36	0.0364 (15)	0.0564 (19)	0.059 (2)	0.0045 (13)	0.0035 (13)	0.0036 (16)
C37	0.077 (2)	0.059 (2)	0.050 (2)	−0.0042 (18)	0.0008 (17)	0.0042 (17)
F31	0.181 (3)	0.0580 (14)	0.0817 (17)	−0.0065 (16)	−0.0127 (17)	0.0183 (13)
F32	0.108 (2)	0.137 (2)	0.0623 (15)	0.0034 (17)	0.0266 (14)	0.0241 (15)
F33	0.0966 (19)	0.130 (2)	0.0617 (14)	−0.0050 (16)	−0.0185 (13)	0.0194 (14)

S51	0.0414 (5)	0.0556 (5)	0.0644 (6)	−0.0143 (3)	0.0013 (3)	−0.0099 (4)
O51	0.0717 (17)	0.0566 (15)	0.113 (2)	−0.0264 (13)	0.0075 (15)	0.0034 (15)
O52	0.0542 (15)	0.107 (2)	0.0590 (15)	−0.0233 (13)	−0.0064 (11)	−0.0212 (14)
C51	0.0395 (16)	0.075 (2)	0.068 (2)	−0.0023 (16)	0.0020 (15)	−0.0066 (18)

Geometric parameters (Å, º)

N1—C7A	1.344 (4)	C13—H13	0.9300
N1—N2	1.356 (4)	C14—F14	1.353 (5)
N1—C17	1.460 (4)	C14—C15	1.369 (7)
N2—C3	1.345 (4)	C15—C16	1.392 (6)
C3—C3A	1.408 (4)	C15—H15	0.9300
C3—C31	1.468 (4)	C16—H16	0.9300
C3A—C7A	1.369 (4)	C31—C32	1.387 (4)
C3A—C4	1.492 (4)	C31—C36	1.393 (4)
C4—N5	1.480 (4)	C32—C33	1.379 (4)
C4—H4A	0.9700	C32—H32	0.9300
C4—H4B	0.9700	C33—C34	1.375 (4)
N5—C6	1.475 (4)	C33—H33	0.9300
N5—S51	1.645 (2)	C34—C35	1.385 (4)
C6—C7	1.525 (4)	C34—C37	1.477 (5)
C6—H6A	0.9700	C35—C36	1.380 (5)
C6—H6B	0.9700	C35—H35	0.9300
C7—C7A	1.479 (4)	C36—H36	0.9300
C7—H7A	0.9700	C37—F31	1.325 (4)
C7—H7B	0.9700	C37—F32	1.326 (5)
C17—C11	1.505 (5)	C37—F33	1.337 (4)
C17—H17A	0.9700	S51—O51	1.423 (3)
C17—H17B	0.9700	S51—O52	1.426 (3)
C11—C16	1.383 (5)	S51—C51	1.749 (4)
C11—C12	1.397 (5)	C51—H51A	0.9600
C12—C13	1.374 (5)	C51—H51B	0.9600
C12—H12	0.9300	C51—H51C	0.9600
C13—C14	1.361 (6)		
C7A—N1—N2	112.3 (2)	C14—C13—H13	120.7
C7A—N1—C17	127.8 (3)	C12—C13—H13	120.7
N2—N1—C17	119.8 (2)	F14—C14—C13	119.4 (5)
C3—N2—N1	104.5 (2)	F14—C14—C15	117.9 (4)
N2—C3—C3A	110.9 (3)	C13—C14—C15	122.7 (4)
N2—C3—C31	119.1 (2)	C14—C15—C16	118.2 (4)
C3A—C3—C31	130.0 (3)	C14—C15—H15	120.9
C7A—C3A—C3	105.0 (2)	C16—C15—H15	120.9
C7A—C3A—C4	122.6 (3)	C11—C16—C15	120.9 (4)
C3—C3A—C4	132.4 (3)	C11—C16—H16	119.5
N5—C4—C3A	108.8 (2)	C15—C16—H16	119.5
N5—C4—H4A	109.9	C32—C31—C36	118.0 (3)
C3A—C4—H4A	109.9	C32—C31—C3	121.0 (3)

N5—C4—H4B	109.9	C36—C31—C3	121.0 (3)
C3A—C4—H4B	109.9	C33—C32—C31	121.3 (3)
H4A—C4—H4B	108.3	C33—C32—H32	119.4
C6—N5—C4	115.0 (2)	C31—C32—H32	119.4
C6—N5—S51	114.5 (2)	C34—C33—C32	119.8 (3)
C4—N5—S51	114.06 (19)	C34—C33—H33	120.1
N5—C6—C7	110.3 (3)	C32—C33—H33	120.1
N5—C6—H6A	109.6	C33—C34—C35	120.2 (3)
C7—C6—H6A	109.6	C33—C34—C37	119.5 (3)
N5—C6—H6B	109.6	C35—C34—C37	120.2 (3)
C7—C6—H6B	109.6	C36—C35—C34	119.5 (3)
H6A—C6—H6B	108.1	C36—C35—H35	120.2
C7A—C7—C6	107.9 (3)	C34—C35—H35	120.2
C7A—C7—H7A	110.1	C35—C36—C31	121.1 (3)
C6—C7—H7A	110.1	C35—C36—H36	119.5
C7A—C7—H7B	110.1	C31—C36—H36	119.5
C6—C7—H7B	110.1	F31—C37—F32	106.2 (3)
H7A—C7—H7B	108.4	F31—C37—F33	105.9 (3)
N1—C7A—C3A	107.3 (3)	F32—C37—F33	104.4 (3)
N1—C7A—C7	127.4 (3)	F31—C37—C34	112.4 (3)
C3A—C7A—C7	125.3 (3)	F32—C37—C34	113.9 (3)
N1—C17—C11	112.9 (2)	F33—C37—C34	113.3 (3)
N1—C17—H17A	109.0	O51—S51—O52	119.30 (18)
C11—C17—H17A	109.0	O51—S51—N5	107.37 (16)
N1—C17—H17B	109.0	O52—S51—N5	106.14 (14)
C11—C17—H17B	109.0	O51—S51—C51	107.85 (19)
H17A—C17—H17B	107.8	O52—S51—C51	108.55 (18)
C16—C11—C12	118.4 (3)	N5—S51—C51	107.04 (15)
C16—C11—C17	121.3 (3)	S51—C51—H51A	109.5
C12—C11—C17	120.3 (3)	S51—C51—H51B	109.5
C13—C12—C11	121.1 (4)	H51A—C51—H51B	109.5
C13—C12—H12	119.4	S51—C51—H51C	109.5
C11—C12—H12	119.4	H51A—C51—H51C	109.5
C14—C13—C12	118.7 (4)	H51B—C51—H51C	109.5
C7A—N1—N2—C3	−0.1 (3)	C12—C13—C14—C15	1.2 (6)
C17—N1—N2—C3	177.8 (3)	F14—C14—C15—C16	179.6 (3)
N1—N2—C3—C3A	−0.5 (3)	C13—C14—C15—C16	−0.4 (6)
N1—N2—C3—C31	176.9 (3)	C12—C11—C16—C15	0.5 (5)
N2—C3—C3A—C7A	0.9 (3)	C17—C11—C16—C15	−177.4 (3)
C31—C3—C3A—C7A	−176.2 (3)	C14—C15—C16—C11	−0.4 (6)
N2—C3—C3A—C4	−178.3 (3)	N2—C3—C31—C32	162.9 (3)
C31—C3—C3A—C4	4.6 (5)	C3A—C3—C31—C32	−20.2 (5)
C7A—C3A—C4—N5	13.9 (4)	N2—C3—C31—C36	−18.1 (4)
C3—C3A—C4—N5	−167.0 (3)	C3A—C3—C31—C36	158.7 (3)
C3A—C4—N5—C6	−45.2 (3)	C36—C31—C32—C33	−1.4 (5)
C3A—C4—N5—S51	179.6 (2)	C3—C31—C32—C33	177.5 (3)
C4—N5—C6—C7	65.6 (3)	C31—C32—C33—C34	1.3 (5)

S51—N5—C6—C7	−159.4 (2)	C32—C33—C34—C35	0.3 (5)
N5—C6—C7—C7A	−47.9 (3)	C32—C33—C34—C37	175.7 (3)
N2—N1—C7A—C3A	0.7 (3)	C33—C34—C35—C36	−1.7 (5)
C17—N1—C7A—C3A	−177.0 (3)	C37—C34—C35—C36	−177.1 (3)
N2—N1—C7A—C7	−178.0 (3)	C34—C35—C36—C31	1.5 (5)
C17—N1—C7A—C7	4.3 (5)	C32—C31—C36—C35	0.0 (5)
C3—C3A—C7A—N1	−0.9 (3)	C3—C31—C36—C35	−178.9 (3)
C4—C3A—C7A—N1	178.4 (3)	C33—C34—C37—F31	−85.3 (4)
C3—C3A—C7A—C7	177.8 (3)	C35—C34—C37—F31	90.1 (4)
C4—C3A—C7A—C7	−2.9 (5)	C33—C34—C37—F32	153.9 (3)
C6—C7—C7A—N1	−161.8 (3)	C35—C34—C37—F32	−30.7 (5)
C6—C7—C7A—C3A	19.7 (4)	C33—C34—C37—F33	34.7 (5)
C7A—N1—C17—C11	90.4 (4)	C35—C34—C37—F33	−149.9 (3)
N2—N1—C17—C11	−87.2 (3)	C6—N5—S51—O51	53.3 (3)
N1—C17—C11—C16	−124.1 (3)	C4—N5—S51—O51	−171.2 (2)
N1—C17—C11—C12	58.1 (4)	C6—N5—S51—O52	−178.0 (2)
C16—C11—C12—C13	0.2 (5)	C4—N5—S51—O52	−42.6 (3)
C17—C11—C12—C13	178.1 (3)	C6—N5—S51—C51	−62.2 (3)
C11—C12—C13—C14	−1.1 (5)	C4—N5—S51—C51	73.2 (2)
C12—C13—C14—F14	−178.9 (3)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C6—H6A⋯$Cg2^{i}$	0.97	2.76	3.694 (4)	161
C33—H33⋯$Cg1^{i}$	0.93	2.73	3.595 (3)	154
C51—H51A⋯N2^{ii}	0.96	2.55	3.483 (4)	165

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

(II) 1-(4-Chlorophenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1H-pyrazolo[4,3-c]pyridine

Crystal data

$C_{21}H_{19}ClF_3N_3O_2S$
$M_r = 469.90$
Orthorhombic, $P2_12_12_1$
$a = 5.4468 (2)$ Å
$b = 11.4102 (4)$ Å
$c = 34.3009 (9)$ Å
$V = 2131.77 (12)$ Å^3
$Z = 4$
$F(000) = 968$

$D_x = 1.464$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5856 reflections
$\theta = 1.2$–$29.3°$
$\mu = 0.33$ mm^{-1}
$T = 296$ K
Block, colourless
$0.40 \times 0.30 \times 0.30$ mm

Data collection

Bruker Kappa APEXII
   diffractometer
Radiation source: fine focus sealed tube
φ and ω scans
Absorption correction: multi-scan
   (SADABS; Bruker, 2012)

$T_{min} = 0.879$, $T_{max} = 0.907$
15002 measured reflections
4920 independent reflections
3587 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.1°$

$h = -3 \rightarrow 7$

$k = -14 \rightarrow 14$

$l = -44 \rightarrow 29$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.0545P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
4920 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
309 parameters	Absolute structure: Flack x determined using
0 restraints	1208 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et*
Hydrogen site location: inferred from	*al.*, 2013)
neighbouring sites	Absolute structure parameter: 0.03 (3)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.6422 (4)	0.5128 (2)	0.64083 (7)	0.0435 (6)	
N2	0.7153 (4)	0.5746 (2)	0.60944 (7)	0.0430 (6)	
C3	0.5874 (5)	0.6739 (3)	0.61079 (7)	0.0363 (6)	
C3A	0.4302 (5)	0.6749 (3)	0.64357 (7)	0.0355 (6)	
C4	0.2561 (5)	0.7637 (3)	0.65979 (8)	0.0393 (7)	
H4A	0.3280	0.8414	0.6585	0.047*	
H4B	0.1045	0.7639	0.6450	0.047*	
N5	0.2071 (4)	0.7314 (2)	0.70082 (7)	0.0401 (6)	
C6	0.1312 (6)	0.6083 (3)	0.70578 (9)	0.0506 (8)	
H6A	−0.0004	0.5900	0.6877	0.061*	
H6B	0.0712	0.5961	0.7321	0.061*	
C7	0.3479 (6)	0.5294 (3)	0.69817 (9)	0.0502 (8)	
H7A	0.4623	0.5333	0.7198	0.060*	
H7B	0.2934	0.4489	0.6953	0.060*	
C7A	0.4698 (5)	0.5696 (3)	0.66161 (8)	0.0395 (7)	
C17	0.7330 (6)	0.3936 (3)	0.64656 (10)	0.0556 (9)	
H17A	0.7849	0.3841	0.6734	0.067*	
H17B	0.8748	0.3808	0.6300	0.067*	
C11	0.5399 (6)	0.3036 (3)	0.63724 (9)	0.0497 (8)	
C12	0.4368 (8)	0.2988 (3)	0.60081 (10)	0.0666 (10)	
H12	0.4922	0.3496	0.5815	0.080*	
C13	0.2532 (9)	0.2204 (3)	0.59234 (11)	0.0733 (12)	
H13	0.1822	0.2191	0.5677	0.088*	
C14	0.1756 (7)	0.1438 (3)	0.62071 (11)	0.0611 (10)	
Cl14	−0.0571 (2)	0.04450 (10)	0.61044 (4)	0.0892 (4)	
C15	0.2776 (8)	0.1455 (3)	0.65713 (11)	0.0694 (11)	

H15	0.2257	0.0930	0.6762	0.083*	
C16	0.4585 (8)	0.2263 (3)	0.66515 (10)	0.0646 (10)	
H16	0.5270	0.2286	0.6900	0.078*	
C31	0.6213 (5)	0.7627 (3)	0.58017 (8)	0.0377 (7)	
C32	0.4564 (6)	0.8528 (3)	0.57475 (9)	0.0494 (8)	
H32	0.3189	0.8575	0.5908	0.059*	
C33	0.4902 (6)	0.9359 (3)	0.54621 (9)	0.0549 (9)	
H33	0.3775	0.9964	0.5432	0.066*	
C34	0.6925 (7)	0.9287 (3)	0.52216 (9)	0.0529 (9)	
C35	0.8556 (6)	0.8382 (3)	0.52649 (9)	0.0575 (9)	
H35	0.9899	0.8323	0.5099	0.069*	
C36	0.8215 (6)	0.7563 (3)	0.55522 (9)	0.0485 (8)	
H36	0.9341	0.6957	0.5580	0.058*	
C37	0.7371 (10)	1.0200 (5)	0.49169 (13)	0.0752 (12)	
F31A	0.875 (5)	1.0995 (15)	0.5014 (5)	0.134 (7)	0.51 (2)
F32A	0.812 (4)	0.9771 (12)	0.4588 (4)	0.143 (9)	0.51 (2)
F33A	0.537 (3)	1.073 (2)	0.4812 (5)	0.129 (6)	0.51 (2)
F31B	0.974 (3)	1.050 (2)	0.4901 (7)	0.147 (9)	0.49 (2)
F32B	0.680 (6)	0.995 (2)	0.4590 (4)	0.183 (10)	0.49 (2)
F33B	0.635 (7)	1.1226 (14)	0.5013 (9)	0.188 (11)	0.49 (2)
S51	0.07584 (13)	0.83056 (8)	0.72794 (2)	0.0464 (2)	
O51	0.0454 (5)	0.7815 (3)	0.76567 (6)	0.0724 (8)	
O52	0.2154 (4)	0.9352 (2)	0.72410 (7)	0.0565 (6)	
C51	−0.2150 (6)	0.8583 (4)	0.70770 (11)	0.0795 (14)	
H51A	−0.2939	0.9200	0.7220	0.119*	
H51B	−0.3132	0.7885	0.7091	0.119*	
H51C	−0.1967	0.8815	0.6810	0.119*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0500 (15)	0.0338 (15)	0.0467 (14)	0.0050 (12)	0.0004 (12)	0.0033 (11)
N2	0.0479 (14)	0.0397 (15)	0.0415 (13)	0.0025 (12)	0.0018 (11)	0.0005 (11)
C3	0.0369 (13)	0.0354 (16)	0.0367 (14)	0.0011 (14)	−0.0013 (12)	−0.0024 (12)
C3A	0.0378 (13)	0.0335 (16)	0.0351 (13)	−0.0019 (14)	0.0004 (12)	−0.0016 (12)
C4	0.0377 (14)	0.0417 (18)	0.0386 (15)	0.0010 (14)	0.0025 (12)	0.0002 (13)
N5	0.0378 (12)	0.0459 (16)	0.0367 (12)	−0.0060 (12)	0.0070 (10)	−0.0030 (11)
C6	0.053 (2)	0.049 (2)	0.0502 (18)	−0.0140 (16)	0.0085 (15)	0.0020 (15)
C7	0.059 (2)	0.044 (2)	0.0474 (18)	−0.0066 (16)	0.0040 (15)	0.0090 (15)
C7A	0.0430 (16)	0.0348 (17)	0.0406 (15)	−0.0022 (13)	−0.0013 (13)	0.0005 (13)
C17	0.061 (2)	0.039 (2)	0.066 (2)	0.0127 (17)	−0.0060 (18)	0.0059 (16)
C11	0.069 (2)	0.0321 (17)	0.0482 (17)	0.0109 (16)	−0.0067 (16)	−0.0002 (14)
C12	0.103 (3)	0.046 (2)	0.0510 (19)	0.001 (2)	−0.014 (2)	0.0062 (16)
C13	0.113 (3)	0.048 (2)	0.059 (2)	0.005 (2)	−0.033 (2)	−0.0026 (18)
C14	0.073 (2)	0.037 (2)	0.073 (2)	0.0063 (18)	−0.0073 (19)	−0.0168 (18)
Cl14	0.0822 (7)	0.0607 (7)	0.1248 (9)	−0.0037 (6)	−0.0140 (7)	−0.0279 (7)
C15	0.099 (3)	0.047 (2)	0.062 (2)	−0.013 (2)	0.004 (2)	0.0018 (18)
C16	0.098 (3)	0.049 (2)	0.0466 (18)	−0.006 (2)	−0.0124 (19)	0.0037 (16)

C31	0.0379 (15)	0.0381 (17)	0.0370 (14)	−0.0030 (13)	0.0011 (12)	−0.0026 (13)
C32	0.0515 (18)	0.050 (2)	0.0467 (17)	0.0068 (17)	0.0100 (14)	0.0082 (15)
C33	0.063 (2)	0.046 (2)	0.055 (2)	0.0091 (17)	0.0020 (16)	0.0097 (16)
C34	0.069 (2)	0.051 (2)	0.0389 (17)	−0.0099 (19)	0.0052 (16)	0.0052 (15)
C35	0.061 (2)	0.059 (2)	0.0528 (19)	−0.0081 (19)	0.0214 (15)	0.0021 (17)
C36	0.0509 (17)	0.046 (2)	0.0482 (17)	0.0046 (16)	0.0109 (14)	−0.0010 (15)
C37	0.096 (3)	0.066 (3)	0.064 (3)	−0.016 (3)	0.009 (3)	0.017 (2)
F31A	0.19 (2)	0.084 (9)	0.130 (9)	−0.075 (11)	−0.025 (11)	0.029 (7)
F32A	0.260 (19)	0.093 (7)	0.077 (8)	0.022 (10)	0.103 (12)	0.025 (6)
F33A	0.144 (8)	0.141 (13)	0.101 (8)	0.046 (8)	0.029 (6)	0.081 (8)
F31B	0.102 (8)	0.172 (18)	0.165 (16)	−0.057 (8)	−0.009 (6)	0.120 (14)
F32B	0.290 (19)	0.193 (19)	0.065 (9)	−0.167 (16)	−0.075 (11)	0.069 (9)
F33B	0.32 (3)	0.081 (8)	0.166 (15)	0.041 (12)	0.110 (19)	0.069 (8)
S51	0.0359 (4)	0.0627 (5)	0.0406 (4)	−0.0030 (4)	0.0025 (3)	−0.0132 (4)
O51	0.0878 (16)	0.092 (2)	0.0379 (12)	−0.0073 (16)	0.0147 (12)	−0.0082 (12)
O52	0.0480 (12)	0.0539 (16)	0.0676 (14)	−0.0022 (11)	0.0040 (11)	−0.0185 (12)
C51	0.0346 (17)	0.123 (4)	0.080 (3)	0.011 (2)	−0.0040 (17)	−0.034 (3)

Geometric parameters (Å, º)

N1—C7A	1.346 (4)	C14—C15	1.367 (5)
N1—N2	1.347 (3)	C14—Cl14	1.736 (4)
N1—C17	1.461 (4)	C15—C16	1.377 (5)
N2—C3	1.332 (4)	C15—H15	0.9300
C3—C3A	1.413 (4)	C16—H16	0.9300
C3—C31	1.471 (4)	C31—C32	1.378 (4)
C3A—C7A	1.368 (4)	C31—C36	1.388 (4)
C3A—C4	1.496 (4)	C32—C33	1.375 (4)
C4—N5	1.479 (4)	C32—H32	0.9300
C4—H4A	0.9700	C33—C34	1.379 (5)
C4—H4B	0.9700	C33—H33	0.9300
N5—C6	1.473 (4)	C34—C35	1.370 (5)
N5—S51	1.630 (3)	C34—C37	1.495 (5)
C6—C7	1.507 (4)	C35—C36	1.371 (5)
C6—H6A	0.9700	C35—H35	0.9300
C6—H6B	0.9700	C36—H36	0.9300
C7—C7A	1.491 (4)	C37—F32B	1.199 (12)
C7—H7A	0.9700	C37—F31A	1.224 (15)
C7—H7B	0.9700	C37—F32A	1.297 (10)
C17—C11	1.504 (5)	C37—F33A	1.302 (13)
C17—H17A	0.9700	C37—F31B	1.336 (15)
C17—H17B	0.9700	C37—F33B	1.338 (16)
C11—C12	1.371 (5)	S51—O51	1.420 (2)
C11—C16	1.375 (5)	S51—O52	1.421 (2)
C12—C13	1.373 (6)	S51—C51	1.758 (3)
C12—H12	0.9300	C51—H51A	0.9600
C13—C14	1.374 (5)	C51—H51B	0.9600
C13—H13	0.9300	C51—H51C	0.9600

C7A—N1—N2	112.2 (2)	C15—C14—Cl14	119.4 (3)
C7A—N1—C17	127.9 (3)	C13—C14—Cl14	119.7 (3)
N2—N1—C17	119.7 (3)	C14—C15—C16	118.8 (4)
C3—N2—N1	105.3 (2)	C14—C15—H15	120.6
N2—C3—C3A	110.5 (3)	C16—C15—H15	120.6
N2—C3—C31	119.7 (2)	C11—C16—C15	121.4 (3)
C3A—C3—C31	129.7 (3)	C11—C16—H16	119.3
C7A—C3A—C3	104.9 (2)	C15—C16—H16	119.3
C7A—C3A—C4	121.8 (2)	C32—C31—C36	117.9 (3)
C3—C3A—C4	133.3 (3)	C32—C31—C3	121.9 (2)
N5—C4—C3A	107.4 (2)	C36—C31—C3	120.2 (3)
N5—C4—H4A	110.2	C33—C32—C31	121.5 (3)
C3A—C4—H4A	110.2	C33—C32—H32	119.2
N5—C4—H4B	110.2	C31—C32—H32	119.2
C3A—C4—H4B	110.2	C32—C33—C34	119.5 (3)
H4A—C4—H4B	108.5	C32—C33—H33	120.3
C6—N5—C4	113.5 (2)	C34—C33—H33	120.3
C6—N5—S51	118.21 (19)	C35—C34—C33	119.9 (3)
C4—N5—S51	116.6 (2)	C35—C34—C37	119.7 (3)
N5—C6—C7	109.2 (2)	C33—C34—C37	120.4 (4)
N5—C6—H6A	109.8	C34—C35—C36	120.2 (3)
C7—C6—H6A	109.8	C34—C35—H35	119.9
N5—C6—H6B	109.8	C36—C35—H35	119.9
C7—C6—H6B	109.8	C35—C36—C31	120.9 (3)
H6A—C6—H6B	108.3	C35—C36—H36	119.5
C7A—C7—C6	108.1 (3)	C31—C36—H36	119.5
C7A—C7—H7A	110.1	F31A—C37—F32A	108.8 (10)
C6—C7—H7A	110.1	F31A—C37—F33A	104.0 (10)
C7A—C7—H7B	110.1	F32A—C37—F33A	101.6 (9)
C6—C7—H7B	110.1	F32B—C37—F31B	105.9 (11)
H7A—C7—H7B	108.4	F32B—C37—F33B	109.3 (13)
N1—C7A—C3A	107.1 (2)	F31B—C37—F33B	100.7 (12)
N1—C7A—C7	127.4 (3)	F32B—C37—C34	116.4 (8)
C3A—C7A—C7	125.5 (3)	F31A—C37—C34	115.2 (8)
N1—C17—C11	111.7 (3)	F32A—C37—C34	113.4 (7)
N1—C17—H17A	109.3	F33A—C37—C34	112.6 (7)
C11—C17—H17A	109.3	F31B—C37—C34	111.5 (7)
N1—C17—H17B	109.3	F33B—C37—C34	111.7 (8)
C11—C17—H17B	109.3	O51—S51—O52	118.56 (16)
H17A—C17—H17B	107.9	O51—S51—N5	107.30 (15)
C12—C11—C16	118.5 (3)	O52—S51—N5	107.20 (13)
C12—C11—C17	120.5 (3)	O51—S51—C51	109.00 (19)
C16—C11—C17	121.0 (3)	O52—S51—C51	107.11 (19)
C11—C12—C13	121.1 (4)	N5—S51—C51	107.16 (16)
C11—C12—H12	119.4	S51—C51—H51A	109.5
C13—C12—H12	119.4	S51—C51—H51B	109.5
C12—C13—C14	119.2 (3)	H51A—C51—H51B	109.5

C12—C13—H13	120.4	S51—C51—H51C	109.5
C14—C13—H13	120.4	H51A—C51—H51C	109.5
C15—C14—C13	120.9 (4)	H51B—C51—H51C	109.5
C7A—N1—N2—C3	0.8 (3)	C12—C11—C16—C15	−0.1 (6)
C17—N1—N2—C3	175.0 (3)	C17—C11—C16—C15	178.4 (3)
N1—N2—C3—C3A	−0.1 (3)	C14—C15—C16—C11	−0.9 (6)
N1—N2—C3—C31	−179.5 (2)	N2—C3—C31—C32	164.3 (3)
N2—C3—C3A—C7A	−0.5 (3)	C3A—C3—C31—C32	−15.0 (5)
C31—C3—C3A—C7A	178.8 (3)	N2—C3—C31—C36	−14.6 (4)
N2—C3—C3A—C4	177.5 (3)	C3A—C3—C31—C36	166.1 (3)
C31—C3—C3A—C4	−3.1 (5)	C36—C31—C32—C33	−1.5 (5)
C7A—C3A—C4—N5	16.3 (4)	C3—C31—C32—C33	179.6 (3)
C3—C3A—C4—N5	−161.6 (3)	C31—C32—C33—C34	0.6 (5)
C3A—C4—N5—C6	−51.5 (3)	C32—C33—C34—C35	1.0 (5)
C3A—C4—N5—S51	165.85 (18)	C32—C33—C34—C37	−178.2 (4)
C4—N5—C6—C7	70.6 (3)	C33—C34—C35—C36	−1.6 (5)
S51—N5—C6—C7	−147.5 (2)	C37—C34—C35—C36	177.7 (4)
N5—C6—C7—C7A	−46.5 (3)	C34—C35—C36—C31	0.6 (5)
N2—N1—C7A—C3A	−1.2 (3)	C32—C31—C36—C35	1.0 (5)
C17—N1—C7A—C3A	−174.8 (3)	C3—C31—C36—C35	179.9 (3)
N2—N1—C7A—C7	−179.3 (3)	C35—C34—C37—F32B	80 (2)
C17—N1—C7A—C7	7.0 (5)	C33—C34—C37—F32B	−100 (2)
C3—C3A—C7A—N1	1.0 (3)	C35—C34—C37—F31A	−84.2 (17)
C4—C3A—C7A—N1	−177.4 (2)	C33—C34—C37—F31A	95.0 (17)
C3—C3A—C7A—C7	179.2 (3)	C35—C34—C37—F32A	42.1 (13)
C4—C3A—C7A—C7	0.8 (4)	C33—C34—C37—F32A	−138.7 (13)
C6—C7—C7A—N1	−167.7 (3)	C35—C34—C37—F33A	156.8 (14)
C6—C7—C7A—C3A	14.5 (4)	C33—C34—C37—F33A	−24.0 (15)
C7A—N1—C17—C11	68.1 (4)	C35—C34—C37—F31B	−41.3 (17)
N2—N1—C17—C11	−105.1 (3)	C33—C34—C37—F31B	137.9 (17)
N1—C17—C11—C12	59.0 (4)	C35—C34—C37—F33B	−153 (2)
N1—C17—C11—C16	−119.4 (4)	C33—C34—C37—F33B	26 (2)
C16—C11—C12—C13	1.2 (5)	C6—N5—S51—O51	38.9 (3)
C17—C11—C12—C13	−177.3 (3)	C4—N5—S51—O51	179.7 (2)
C11—C12—C13—C14	−1.4 (6)	C6—N5—S51—O52	167.3 (2)
C12—C13—C14—C15	0.4 (6)	C4—N5—S51—O52	−51.9 (2)
C12—C13—C14—Cl14	179.8 (3)	C6—N5—S51—C51	−78.0 (3)
C13—C14—C15—C16	0.7 (6)	C4—N5—S51—C51	62.8 (3)
Cl14—C14—C15—C16	−178.7 (3)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15···O52ⁱ	0.93	2.44	3.339 (4)	163
C17—H17A···O51ⁱⁱ	0.97	2.57	3.487 (4)	158

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, *y*−1/2, −*z*+3/2.

(III) 1-(3-<ethylphenyl)-5-methylsulfonyl-3-[4-(trifluoromethyl)phenyl]-4,5,6,7-tetrahydro-1*H*-pyrazolo[4,3-
c]pyridine

Crystal data

$C_{22}H_{22}F_3N_3O_2S$	$F(000) = 936$
$M_r = 449.48$	$D_x = 1.427$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.8408$ (10) Å	Cell parameters from 4392 reflections
$b = 8.7145$ (6) Å	$\theta = 1.7–26.7°$
$c = 18.0898$ (13) Å	$\mu = 0.21$ mm^{-1}
$\beta = 106.470$ (2)°	$T = 296$ K
$V = 2092.4$ (3) Å^3	Block, colourless
$Z = 4$	$0.34 \times 0.24 \times 0.22$ mm

Data collection

Bruker Kappa APEXII diffractometer	4391 independent reflections
Radiation source: fine focus sealed tube	2953 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.045$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$\theta_{max} = 26.7°$, $\theta_{min} = 2.4°$
$T_{min} = 0.946$, $T_{max} = 0.956$	$h = -17 \rightarrow 17$
33310 measured reflections	$k = -10 \rightarrow 10$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 1.101P]$
$wR(F^2) = 0.112$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
4391 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
310 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
0 restraints	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
N1	0.73177 (12)	0.6156 (2)	0.51672 (9)	0.0328 (4)	
N2	0.69346 (12)	0.6065 (2)	0.57743 (9)	0.0331 (4)	
C3	0.59874 (14)	0.6585 (2)	0.55104 (11)	0.0292 (4)	
C3A	0.57717 (14)	0.7005 (2)	0.47255 (11)	0.0301 (4)	
C4	0.48518 (15)	0.7636 (3)	0.41515 (11)	0.0364 (5)	
H4A	0.4267	0.7024	0.4153	0.044*	
H4B	0.4733	0.8682	0.4286	0.044*	
N5	0.50150 (13)	0.7597 (2)	0.33856 (10)	0.0383 (4)	
C6	0.60024 (16)	0.8150 (3)	0.33435 (13)	0.0443 (6)	

H6A	0.6132	0.9164	0.3571	0.053*
H6B	0.6006	0.8220	0.2809	0.053*
C7	0.68157 (16)	0.7042 (3)	0.37754 (12)	0.0406 (5)
H7A	0.6783	0.6100	0.3484	0.049*
H7B	0.7477	0.7495	0.3850	0.049*
C7A	0.66397 (15)	0.6718 (2)	0.45297 (11)	0.0321 (5)
C17	0.83560 (14)	0.5690 (3)	0.52546 (13)	0.0375 (5)
H17A	0.8755	0.5907	0.5778	0.045*
H17B	0.8624	0.6301	0.4910	0.045*
C11	0.84674 (14)	0.4017 (3)	0.50869 (12)	0.0369 (5)
C12	0.81108 (16)	0.2891 (3)	0.54804 (13)	0.0419 (5)
H12	0.7796	0.3181	0.5850	0.050*
C13	0.82091 (18)	0.1344 (3)	0.53402 (15)	0.0527 (7)
C14	0.8700 (2)	0.0946 (4)	0.47966 (18)	0.0693 (9)
H14	0.8783	−0.0086	0.4697	0.083*
C15	0.9063 (2)	0.2042 (4)	0.44039 (19)	0.0704 (9)
H15	0.9393	0.1749	0.4044	0.084*
C16	0.89437 (17)	0.3587 (3)	0.45389 (14)	0.0529 (7)
H16	0.9181	0.4330	0.4265	0.063*
C18	0.7774 (2)	0.0146 (3)	0.57530 (18)	0.0787 (9)
H18A	0.7133	−0.0185	0.5427	0.118*
H18B	0.7687	0.0573	0.6219	0.118*
H18C	0.8223	−0.0716	0.5876	0.118*
C31	0.53696 (14)	0.6687 (2)	0.60515 (11)	0.0294 (4)
C32	0.43873 (16)	0.7240 (3)	0.58234 (13)	0.0447 (6)
H19	0.4102	0.7532	0.5314	0.054*
C33	0.38283 (17)	0.7360 (3)	0.63451 (13)	0.0460 (6)
H33	0.3171	0.7729	0.6185	0.055*
C34	0.42433 (16)	0.6936 (3)	0.70989 (12)	0.0375 (5)
C35	0.52071 (18)	0.6367 (3)	0.73315 (13)	0.0446 (6)
H35	0.5484	0.6059	0.7840	0.054*
C36	0.57651 (16)	0.6253 (3)	0.68124 (12)	0.0401 (5)
H36	0.6420	0.5876	0.6977	0.048*
C37	0.3650 (2)	0.7116 (4)	0.76638 (15)	0.0552 (7)
F31A	0.2712 (4)	0.7447 (19)	0.7364 (3)	0.120 (5)	0.579 (19)
F32A	0.3654 (11)	0.5891 (10)	0.8068 (8)	0.143 (6)	0.579 (19)
F33A	0.3997 (8)	0.8211 (16)	0.8150 (7)	0.142 (6)	0.579 (19)
F31B	0.2894 (10)	0.6221 (17)	0.7546 (8)	0.109 (7)	0.421 (19)
F32B	0.4157 (6)	0.689 (2)	0.8372 (3)	0.102 (6)	0.421 (19)
F33B	0.3293 (14)	0.8486 (10)	0.7660 (10)	0.120 (7)	0.421 (19)
S51	0.40470 (4)	0.79046 (7)	0.26402 (3)	0.04040 (17)
O51	0.43430 (14)	0.7467 (2)	0.19768 (9)	0.0603 (5)
O52	0.32052 (12)	0.71828 (19)	0.27996 (10)	0.0542 (5)
C51	0.38223 (19)	0.9882 (3)	0.25797 (15)	0.0562 (7)
H51A	0.3247	1.0095	0.2150	0.084*
H51B	0.4401	1.0402	0.2509	0.084*
H51C	0.3696	1.0234	0.3046	0.084*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0276 (9)	0.0379 (10)	0.0354 (9)	0.0034 (8)	0.0130 (7)	−0.0004 (8)
N2	0.0299 (9)	0.0393 (10)	0.0330 (9)	0.0046 (8)	0.0137 (7)	0.0014 (8)
C3	0.0292 (10)	0.0278 (10)	0.0318 (11)	0.0004 (8)	0.0107 (8)	−0.0014 (8)
C3A	0.0290 (10)	0.0321 (11)	0.0303 (10)	0.0007 (9)	0.0103 (8)	−0.0014 (9)
C4	0.0335 (11)	0.0458 (13)	0.0314 (11)	0.0052 (10)	0.0115 (9)	0.0029 (9)
N5	0.0335 (10)	0.0495 (12)	0.0315 (10)	0.0003 (8)	0.0085 (8)	0.0067 (8)
C6	0.0425 (13)	0.0543 (15)	0.0402 (13)	−0.0027 (11)	0.0185 (10)	0.0090 (11)
C7	0.0361 (12)	0.0517 (14)	0.0382 (12)	−0.0014 (11)	0.0177 (10)	−0.0002 (11)
C7A	0.0331 (11)	0.0341 (11)	0.0302 (11)	−0.0012 (9)	0.0108 (9)	−0.0030 (9)
C17	0.0253 (10)	0.0477 (13)	0.0420 (12)	0.0030 (10)	0.0135 (9)	−0.0011 (10)
C11	0.0245 (10)	0.0472 (14)	0.0373 (12)	0.0056 (10)	0.0056 (9)	−0.0071 (10)
C12	0.0359 (12)	0.0476 (14)	0.0382 (12)	0.0058 (11)	0.0041 (10)	−0.0038 (11)
C13	0.0444 (14)	0.0435 (15)	0.0582 (16)	0.0070 (12)	−0.0051 (12)	−0.0065 (12)
C14	0.0532 (17)	0.0545 (18)	0.090 (2)	0.0176 (14)	0.0040 (16)	−0.0264 (16)
C15	0.0517 (17)	0.081 (2)	0.083 (2)	0.0128 (16)	0.0265 (15)	−0.0307 (18)
C16	0.0378 (13)	0.0697 (18)	0.0546 (15)	0.0042 (12)	0.0189 (11)	−0.0131 (13)
C18	0.089 (2)	0.0484 (17)	0.085 (2)	−0.0031 (16)	0.0013 (18)	0.0071 (15)
C31	0.0307 (11)	0.0292 (10)	0.0309 (10)	−0.0009 (8)	0.0131 (8)	−0.0023 (8)
C32	0.0328 (12)	0.0695 (17)	0.0319 (12)	0.0070 (11)	0.0095 (9)	0.0032 (11)
C33	0.0315 (12)	0.0662 (17)	0.0444 (14)	0.0044 (11)	0.0174 (10)	−0.0034 (12)
C34	0.0405 (12)	0.0385 (13)	0.0400 (12)	−0.0033 (10)	0.0216 (10)	−0.0022 (10)
C35	0.0543 (15)	0.0486 (14)	0.0352 (12)	0.0073 (12)	0.0195 (11)	0.0085 (10)
C36	0.0394 (12)	0.0445 (13)	0.0381 (12)	0.0104 (10)	0.0137 (10)	0.0072 (10)
C37	0.0575 (17)	0.0675 (19)	0.0504 (16)	0.0015 (16)	0.0314 (13)	−0.0003 (15)
F31A	0.051 (3)	0.249 (15)	0.073 (3)	0.037 (5)	0.040 (2)	0.029 (5)
F32A	0.206 (13)	0.130 (6)	0.153 (11)	0.059 (7)	0.150 (11)	0.079 (6)
F33A	0.136 (8)	0.186 (11)	0.139 (9)	−0.060 (7)	0.099 (7)	−0.115 (8)
F31B	0.099 (9)	0.144 (11)	0.120 (9)	−0.068 (8)	0.087 (8)	−0.048 (7)
F32B	0.079 (4)	0.201 (16)	0.033 (3)	0.028 (7)	0.029 (3)	0.006 (5)
F33B	0.177 (15)	0.071 (5)	0.174 (13)	0.046 (7)	0.152 (12)	0.027 (6)
S51	0.0433 (3)	0.0389 (3)	0.0345 (3)	−0.0008 (3)	0.0037 (2)	0.0037 (2)
O51	0.0725 (12)	0.0735 (13)	0.0317 (9)	0.0111 (10)	0.0095 (8)	−0.0011 (8)
O52	0.0430 (9)	0.0535 (10)	0.0580 (11)	−0.0130 (8)	0.0009 (8)	0.0122 (8)
C51	0.0569 (16)	0.0429 (14)	0.0644 (16)	0.0032 (12)	0.0099 (13)	0.0096 (12)

Geometric parameters (Å, º)

N1—N2	1.351 (2)	C15—C16	1.387 (4)
N1—C7A	1.355 (2)	C15—H15	0.9300
N1—C17	1.458 (2)	C16—H16	0.9300
N2—C3	1.341 (2)	C18—H18A	0.9600
C3—C3A	1.414 (3)	C18—H18B	0.9600
C3—C31	1.474 (3)	C18—H18C	0.9600
C3A—C7A	1.368 (3)	C31—C36	1.382 (3)
C3A—C4	1.501 (3)	C31—C32	1.390 (3)

C4—N5	1.466 (3)	C32—C33	1.384 (3)
C4—H4A	0.9700	C32—H19	0.9300
C4—H4B	0.9700	C33—C34	1.372 (3)
N5—C6	1.471 (3)	C33—H33	0.9300
N5—S51	1.6311 (17)	C34—C35	1.373 (3)
C6—C7	1.520 (3)	C34—C37	1.489 (3)
C6—H6A	0.9700	C35—C36	1.378 (3)
C6—H6B	0.9700	C35—H35	0.9300
C7—C7A	1.480 (3)	C36—H36	0.9300
C7—H7A	0.9700	C37—F31B	1.275 (6)
C7—H7B	0.9700	C37—F32B	1.289 (7)
C17—C11	1.506 (3)	C37—F31A	1.290 (5)
C17—H17A	0.9700	C37—F33B	1.291 (7)
C17—H17B	0.9700	C37—F32A	1.293 (5)
C11—C12	1.382 (3)	C37—F33A	1.294 (6)
C11—C16	1.388 (3)	S51—O52	1.4237 (17)
C12—C13	1.386 (3)	S51—O51	1.4255 (18)
C12—H12	0.9300	S51—C51	1.749 (2)
C13—C14	1.388 (4)	C51—H51A	0.9600
C13—C18	1.506 (4)	C51—H51B	0.9600
C14—C15	1.369 (4)	C51—H51C	0.9600
C14—H14	0.9300		
N2—N1—C7A	112.11 (15)	C14—C15—H15	119.8
N2—N1—C17	119.84 (16)	C16—C15—H15	119.8
C7A—N1—C17	128.05 (17)	C15—C16—C11	119.5 (3)
C3—N2—N1	105.09 (15)	C15—C16—H16	120.3
N2—C3—C3A	110.61 (17)	C11—C16—H16	120.3
N2—C3—C31	118.47 (17)	C13—C18—H18A	109.5
C3A—C3—C31	130.88 (18)	C13—C18—H18B	109.5
C7A—C3A—C3	105.18 (17)	H18A—C18—H18B	109.5
C7A—C3A—C4	121.52 (18)	C13—C18—H18C	109.5
C3—C3A—C4	133.30 (18)	H18A—C18—H18C	109.5
N5—C4—C3A	108.52 (16)	H18B—C18—H18C	109.5
N5—C4—H4A	110.0	C36—C31—C32	117.93 (19)
C3A—C4—H4A	110.0	C36—C31—C3	120.29 (18)
N5—C4—H4B	110.0	C32—C31—C3	121.77 (18)
C3A—C4—H4B	110.0	C33—C32—C31	120.9 (2)
H4A—C4—H4B	108.4	C33—C32—H19	119.6
C4—N5—C6	115.83 (17)	C31—C32—H19	119.6
C4—N5—S51	117.84 (14)	C34—C33—C32	120.0 (2)
C6—N5—S51	117.44 (14)	C34—C33—H33	120.0
N5—C6—C7	109.18 (18)	C32—C33—H33	120.0
N5—C6—H6A	109.8	C33—C34—C35	119.9 (2)
C7—C6—H6A	109.8	C33—C34—C37	119.8 (2)
N5—C6—H6B	109.8	C35—C34—C37	120.3 (2)
C7—C6—H6B	109.8	C34—C35—C36	120.1 (2)
H6A—C6—H6B	108.3	C34—C35—H35	120.0

C7A—C7—C6	107.69 (17)	C36—C35—H35	120.0
C7A—C7—H7A	110.2	C35—C36—C31	121.2 (2)
C6—C7—H7A	110.2	C35—C36—H36	119.4
C7A—C7—H7B	110.2	C31—C36—H36	119.4
C6—C7—H7B	110.2	F31B—C37—F32B	105.2 (6)
H7A—C7—H7B	108.5	F31B—C37—F33B	105.7 (6)
N1—C7A—C3A	107.02 (17)	F32B—C37—F33B	104.2 (6)
N1—C7A—C7	126.75 (18)	F31A—C37—F32A	105.3 (5)
C3A—C7A—C7	126.15 (19)	F31A—C37—F33A	104.8 (5)
N1—C17—C11	113.69 (17)	F32A—C37—F33A	106.4 (5)
N1—C17—H17A	108.8	F31B—C37—C34	114.0 (3)
C11—C17—H17A	108.8	F32B—C37—C34	114.6 (4)
N1—C17—H17B	108.8	F31A—C37—C34	114.9 (3)
C11—C17—H17B	108.8	F33B—C37—C34	112.2 (3)
H17A—C17—H17B	107.7	F32A—C37—C34	112.7 (3)
C12—C11—C16	119.2 (2)	F33A—C37—C34	112.0 (3)
C12—C11—C17	120.74 (19)	O52—S51—O51	119.96 (11)
C16—C11—C17	120.1 (2)	O52—S51—N5	106.72 (9)
C11—C12—C13	121.9 (2)	O51—S51—N5	106.70 (10)
C11—C12—H12	119.1	O52—S51—C51	107.87 (12)
C13—C12—H12	119.1	O51—S51—C51	107.40 (12)
C12—C13—C14	117.8 (3)	N5—S51—C51	107.65 (11)
C12—C13—C18	120.7 (3)	S51—C51—H51A	109.5
C14—C13—C18	121.5 (3)	S51—C51—H51B	109.5
C15—C14—C13	121.2 (3)	H51A—C51—H51B	109.5
C15—C14—H14	119.4	S51—C51—H51C	109.5
C13—C14—H14	119.4	H51A—C51—H51C	109.5
C14—C15—C16	120.4 (3)	H51B—C51—H51C	109.5
C7A—N1—N2—C3	0.0 (2)	C14—C15—C16—C11	1.2 (4)
C17—N1—N2—C3	179.28 (17)	C12—C11—C16—C15	−0.8 (3)
N1—N2—C3—C3A	0.2 (2)	C17—C11—C16—C15	178.4 (2)
N1—N2—C3—C31	−177.72 (17)	N2—C3—C31—C36	0.0 (3)
N2—C3—C3A—C7A	−0.3 (2)	C3A—C3—C31—C36	−177.4 (2)
C31—C3—C3A—C7A	177.3 (2)	N2—C3—C31—C32	178.9 (2)
N2—C3—C3A—C4	179.7 (2)	C3A—C3—C31—C32	1.5 (3)
C31—C3—C3A—C4	−2.7 (4)	C36—C31—C32—C33	0.5 (3)
C7A—C3A—C4—N5	9.7 (3)	C3—C31—C32—C33	−178.4 (2)
C3—C3A—C4—N5	−170.3 (2)	C31—C32—C33—C34	0.2 (4)
C3A—C4—N5—C6	−45.2 (2)	C32—C33—C34—C35	−1.1 (4)
C3A—C4—N5—S51	168.19 (14)	C32—C33—C34—C37	178.0 (2)
C4—N5—C6—C7	67.6 (2)	C33—C34—C35—C36	1.4 (4)
S51—N5—C6—C7	−145.72 (16)	C37—C34—C35—C36	−177.8 (2)
N5—C6—C7—C7A	−47.5 (2)	C34—C35—C36—C31	−0.7 (4)
N2—N1—C7A—C3A	−0.2 (2)	C32—C31—C36—C35	−0.3 (3)
C17—N1—C7A—C3A	−179.38 (19)	C3—C31—C36—C35	178.7 (2)
N2—N1—C7A—C7	176.8 (2)	C33—C34—C37—F31B	68.1 (11)
C17—N1—C7A—C7	−2.4 (3)	C35—C34—C37—F31B	−112.8 (11)

C3—C3A—C7A—N1	0.3 (2)	C33—C34—C37—F32B	−170.6 (10)
C4—C3A—C7A—N1	−179.72 (18)	C35—C34—C37—F32B	8.5 (11)
C3—C3A—C7A—C7	−176.7 (2)	C33—C34—C37—F31A	10.4 (9)
C4—C3A—C7A—C7	3.3 (3)	C35—C34—C37—F31A	−170.4 (9)
C6—C7—C7A—N1	−160.2 (2)	C33—C34—C37—F33B	−52.1 (12)
C6—C7—C7A—C3A	16.2 (3)	C35—C34—C37—F33B	127.1 (11)
N2—N1—C17—C11	89.5 (2)	C33—C34—C37—F32A	131.1 (10)
C7A—N1—C17—C11	−91.3 (3)	C35—C34—C37—F32A	−49.8 (10)
N1—C17—C11—C12	−56.3 (3)	C33—C34—C37—F33A	−108.9 (9)
N1—C17—C11—C16	124.5 (2)	C35—C34—C37—F33A	70.2 (10)
C16—C11—C12—C13	−0.4 (3)	C4—N5—S51—O52	−37.73 (19)
C17—C11—C12—C13	−179.62 (19)	C6—N5—S51—O52	176.24 (17)
C11—C12—C13—C14	1.2 (3)	C4—N5—S51—O51	−167.12 (16)
C11—C12—C13—C18	−177.3 (2)	C6—N5—S51—O51	46.85 (19)
C12—C13—C14—C15	−0.8 (4)	C4—N5—S51—C51	77.85 (19)
C18—C13—C14—C15	177.7 (3)	C6—N5—S51—C51	−68.2 (2)
C13—C14—C15—C16	−0.3 (4)		

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C17—H17A⋯O51[i]	0.97	2.52	3.426 (3)	155
C33—H33⋯Cg1[ii]	0.93	2.70	3.488 (3)	144

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