Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Received 29 March 2015
Accepted 23 April 2015

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; thiochromene; isoxazole; pyrrole; chromenopyrrole; thiopyran; C—H···π interactions

CCDC references: 1061279; 1061278; 1061277

Supporting information: this article has supporting information at journals.iucr.org/e

Crystal structures of methyl 3-(4-isopropylphenyl)-1-methyl-1,2,3,3a,4,9b-hexahydrothiochromeno-[4,3-*b*]pyrrole-3a-carboxylate, methyl 1-methyl-3-(*o*-tolyl)-1,2,3,3a,4,9b-hexahydrothiochromeno-[4,3-*b*]pyrrole-3a-carboxylate and methyl 1-methyl-3-(*o*-tolyl)-3,3a,4,9b-tetrahydro-1*H*-thiochromeno-[4,3-*c*]isoxazole-3a-carboxylate

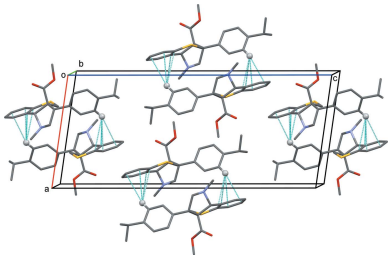
R. Raja,[a] M. Suresh,[b] R. Raghunathan[b] and A. SubbiahPandi[a]*

[a]Department of Physics, Presidency College (Autonomous), Chennai 600 005, India, and [b]Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 602 025, India. *Correspondence e-mail: aspandian59@gmail.com

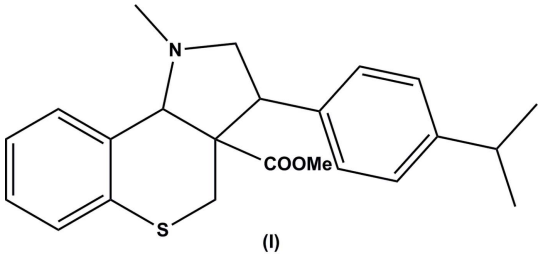
In the title compounds, $C_{23}H_{27}NO_2S$, (I), and $C_{21}H_{23}NO_2S$, (II), the pyrrole rings have envelope conformations with the C atom substituted by the benzene ring as the flap. In the third title compound, $C_{20}H_{21}NO_3S$, (III), the isoxazole ring has a twisted conformation on the C—C bond substituted by the benzene ring and the carboxylate group. In all three compounds, the thiopyran ring has a half-chair conformation. The mean plane of the pyrrole ring is inclined to the mean plane of the thiopyran ring by 57.07 (9), 58.98 (9) and 60.34 (12)° in (I), (II) and (III), respectively. The benzene rings are inclined to one another by 73.26 (10)° in (I), 65.781)° in (II) and 63.37 (13)° in (III). In the crystals of all three compounds, there are no classical hydrogen bonds present. Only in the crystal of compound (I) are molecules linked by a pair of C—H···π interactions, forming inversion dimers. The isopropyl group in compound (I) is disordered over two sets of sites and has a refined occupancy ratio of 0.586 (13):0.414 (13).

1. Chemical context

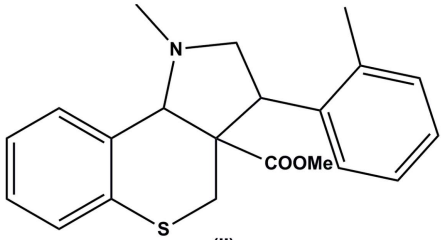
Pyrrole derivatives are of considerable synthetic importance due to their extensive use in drug discovery (Toja *et al.*, 1987) which is linked to their pharmacological activity such as anti-inflammatory (Muchowski *et al.*, 1985), cytotoxicity (Dannhardt *et al.*, 2000) and their use in the treatment of hyperlipidemias (Holub *et al.*, 2004) and as antitumour agents (Krowicki *et al.*, 1988). Other pyrrole-containing heterocyclic compounds have been reported previously for biological studies (Almerico *et al.*, 1998). Pyrrole derivatives have biological activity such as COX-1/COX-2 inhibitors (Dannhardt *et al.*, 2000) as well as cytotoxic activity against a variety of marine and human tumour models (Evans *et al.*, 2003). Isoxazoline derivatives have been shown to be efficient precursors for the preparation of many synthetic intermediates including γ-amino alcohols and β-hydroxy ketones (Kozikowski, 1984). They display interesting biological properties such as herbicidal, plant-growth regulatory and antitumour activities (Howe & Shelton, 1990). Chromenopyrrole compounds are used in the treatment of impulsive disorders (Caine & Koob, 1993). Continuing our interest in such compounds, we have synthesized the title compounds and report herein on their crystal structures.



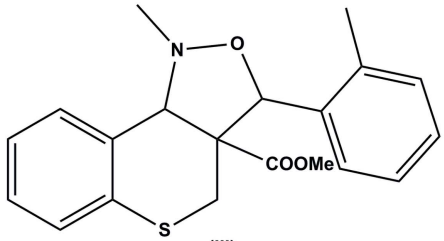
OPEN ACCESS



(I)



(II)



(III)

2. Structural commentary

The title compounds (I) and (II) differ only by the substituent on the benzene ring; 4-isopropylphenyl in (I) and *o*-tolyl in (II). Compounds (II) and (III) differ only in that (II) has a pyrrole ring while (III) has an isoxazole ring.

The molecular structure of compound (I) is shown in Fig. 1. The five-membered methyl-substituted pyrrole ring adopts an envelope conformation with atom C9 as the flap, deviating from the mean plane defined by the plane of the other ring atoms by 0.0167 Å. The puckering parameters of this ring are q_2 = 0.4713 (15) Å and φ_2 = 41.27 (19)°. The thiopyran ring has a half-chair conformation, with the lowest asymmetry parameters ΔC2(S1—C7) = 8.34 (16) Å. The mean plane of the pyrrole ring makes dihedral angles of 57.07 (9) and 63.29 (10)° with the mean plane of the thiopyran ring and the benzene ring, respectively.

The molecular structure of the compound (II) is illustrated in Fig. 2. The bond lengths and bond angles are similar to those in compound (I). The pyrrole ring (N1/C8–C12) adopts an envelope conformation with atom C9 atom as the flap having asymmetry parameters (Nardelli, 1983) ΔCS(C9) = 4.51 Å and with puckering parameters q_2 = 0.4673 (18) Å, φ_2 = 223.5 (2)°. As in (I), the thiopyran ring has a half-chair conformation. The mean plane of the pyrrole ring is inclined to thiopyran ring mean plane and the benzene ring by 58.98 (9) and 67.75 (11)°, respectively. The carboxylate group assumes an extended conformation, as can be seen from the C8—C13—O2—C14 torsion angle of 175.4 (2)°.

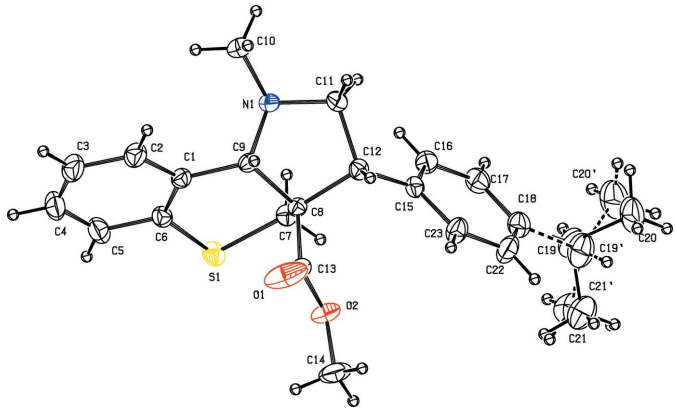


Figure 1
The molecular structure of compound (I), showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

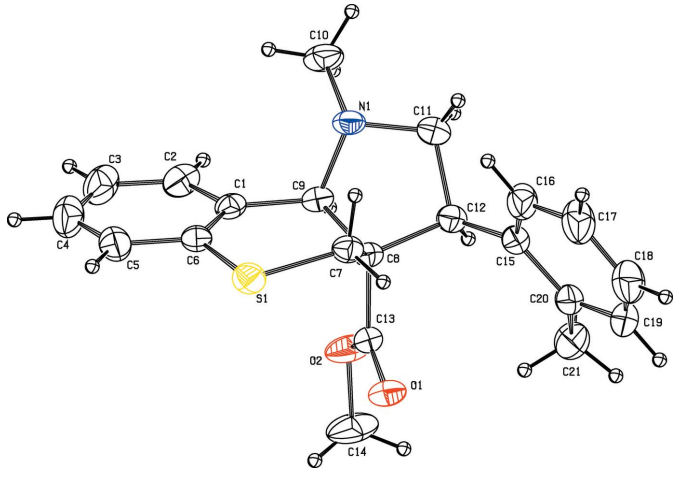


Figure 2
The molecular structure of compound (II), showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

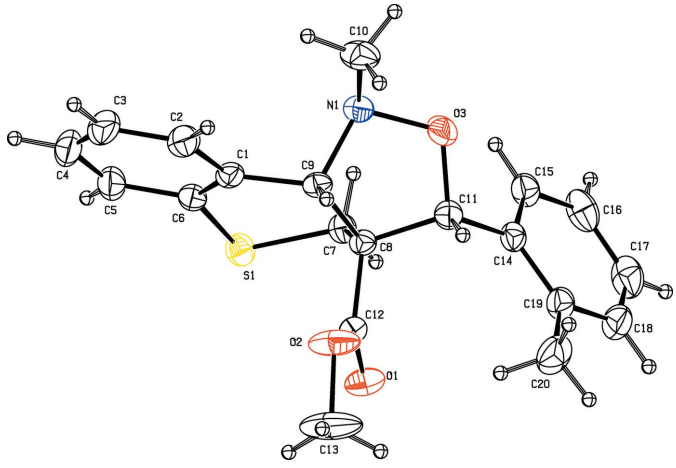


Figure 3
The molecular structure of compound (III), showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

The molecular structure of molecule (III) is shown in Fig. 3. The isoxazole ring (N1/O3/C11/C8/C9) has a twist conformation about bond C9–C8: puckering parameters q_2 =

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

*Cg*3 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17···*Cg*3^{i}	0.93	2.91	3.695 (2)	143

Symmetry code: (i) $-x+1, -y+1, -z$.

0.466 (2) Å, φ_2 = 275.7 (3)°. As in (I) and (II), the thiopyran ring has a half-chair conformation. The dihedral angles between the mean plane of the isoxazole ring and the thiopyran ring mean plane and the benzene ring are 60.34 (12) and 61.30 (14)°, respectively. The geometric parameters of molecule (III) agree well with those reported for (I) and (II), and a closely related structure, 1-methyl-3-(naphthalen-1-yl)-3,3a,4,9b-tetrahydro-1*H*-chromeno[4,3-*c*]isoxazole-3a-carbonitrile (Gangadharan *et al.*, 2011).

3. Supramolecular features

In the crystals of compounds (I), (II) and (III), there are no classical hydrogen bonds present. Only in compound (I) is there a C—H···π interaction present, and molecules are linked by a pair of these interactions forming inversion dimers (Table 1 and Fig. 4).

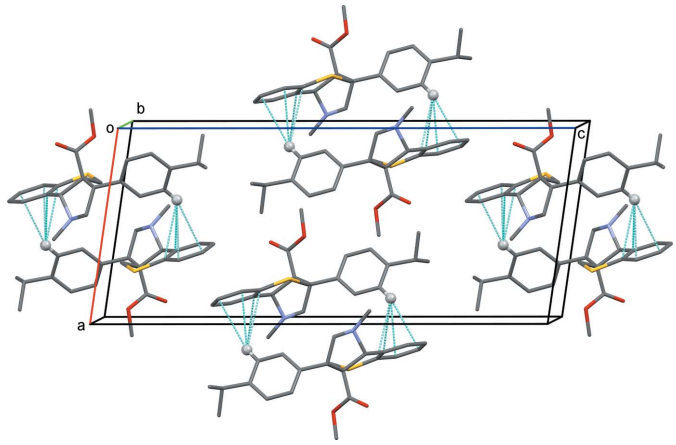


Figure 4
A view along the *b* axis of the crystal packing of compound (I). The dashed cyan lines represent the C—H···centroid distances (see Table 1).

4. Database survey

While a search of the Cambridge Structural Database (CSD, Version 5.36, November 2014; Groom & Allen, 2014) for chromenoisoxazole derivatives revealed over 30 hits, there were no hits for thiochromenopyrroles or thiochromenoisoxazoles.

Table 2
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_{23}H_{27}NO_2S$	$C_{21}H_{21}NO_2S$	$C_{20}H_{21}NO_3S$
M_r	381.52	351.45	355.44
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\overline{1}$	Orthorhombic, *Pbca*
Temperature (K)	293	293	293
a, *b*, *c* (Å)	10.7330 (3), 7.7568 (2), 24.9436 (7)	8.1882 (3), 10.4987 (4), 10.9594 (4)	11.2629 (11), 13.2117 (11), 24.041 (3)
α, β, γ (°)	90, 98.485 (1), 90	104.554 (1), 90.983 (1), 90.134 (1)	90, 90, 90
V (Å^3)	2053.92 (10)	911.74 (6)	3577.3 (6)
Z	4	2	8
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.18	0.19	0.20
Crystal size (mm)	0.35 × 0.30 × 0.25	0.35 × 0.30 × 0.25	0.35 × 0.30 × 0.25
Data collection			
Diffractometer	Bruker *SMART* APEXII CCD	Bruker *SMART* APEXII CCD	Bruker *SMART* APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.941, 0.958	0.935, 0.953	0.932, 0.951
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16824, 3616, 3170	19010, 3210, 2790	37913, 3151, 2536
R_{int}	0.019	0.020	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.595	0.595
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.111, 1.06	0.038, 0.115, 1.07	0.046, 0.111, 1.12
No. of reflections	3616	3210	3151
No. of parameters	272	229	229
No. of restraints	107	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.27	0.26, −0.32	0.22, −0.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3* for Windows (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

5. Synthesis and crystallization

Compound (I): To a solution of methyl (*E*)-2-{[(2-formylphenyl)thio]methyl}-3-phenylacrylate (1 mmol) and sarcosine (1.2 mmol) in acetonitrile (10 ml), was added pyridine (0.2 mmol) and the mixture was refluxed until completion of the reaction (monitored by TLC). The crude product was subjected to column chromatography on silica gel (100–200 mesh) using petroleum ether–ethyl acetate (9:1) as eluent, which successfully provided the pure product as a colourless solid. The product was dissolved in chloroform and heated for 2 min. The resulting solution were allowed to evaporate slowly at room temperature and yielded colourless block-like crystals of compound (I).

Compound (II): Here methyl (*E*)-2-{[(2-formylphenyl)-thio]methyl}-3-(*o*-tolyl) acrylate (1 mmol) and sarcosine (1.2 mmol) in acetonitrile (10 ml) were reacted with pyridine following the same procedure as for compound (I), and colourless crystals of compound (II) were obtained.

Compound (III): Here methyl (*E*)-2-{[(2-formylphenyl)-thio]methyl}-3-(*o*-tolyl) acrylate(1 mmol) and *N*-methyl hydroxylamine hydrochloride (1.1 mmol) in acetonitrile (10 ml) were reacted with pyridine following the same procedure as for compounds (I) and (II), and colourless crystals of compound (III) were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and allowed to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for other H atoms. The isopropyl group in compound (I), atoms C19–C21, is disordered over two sets of sites and has a refined occupancy ratio of 0.586 (13):0.414 (13).

Acknowledgements

The authors thank the Department of Chemistry, IIT, Chennai, India, for the X-ray intensity data collection.

References

Almerico, A. M., Diana, P., Barraja, P., Dattolo, G., Mingoia, F., Loi, A. G., Scintu, F., Milia, C., Puddu, I. & La Colla, P. (1998). *Farmaco*, **53**, 33–40.
Bruker (2008). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Caine, B. & Koob, G. F. (1993). *Science*, **260**, 1814–1816.
Dannhardt, G., Kiefer, W., Krämer, G., Maehrlein, S., Nowe, U. & Fiebich, B. (2000). *Eur. J. Med. Chem.* **35**, 499–510.
Evans, M. A., Smith, D. C., Holub, J. M., Argenti, A., Hoff, M., Dalglish, G. A., Wilson, D. L., Taylor, B. M., Berkowitz, J. D., Burnham, B. S., Krumpe, K., Gupton, J. T., Scarlett, T. C., Durham, R. W. Jr & Hall, I. H. (2003). *Arch. Pharm. Pharm. Med. Chem.* **336**, 181–190.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Gangadharan, R., SethuSankar, K., Murugan, G. & Bakthadoss, M. (2011). *Acta Cryst.* E**67**, o942.
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
Holub, J. M., O'Toole-Colin, K., Getzel, A., Argenti, A., Evans, M. A., Smith, D. C., Dalglish, G. A., Rifat, S., Wilson, D. L., Taylor, B. M., Miott, U., Glersaye, J., Suet Lam, K., McCranor, B. J., Berkowitz, J. D., Miller, R. B., Lukens, J. R., Krumpe, K., Gupton, J. T. & Burnham, B. S. (2004). *Molecules*, **9**, 135–157.
Howe, R. K. & Shelton, B. R. (1990). *J. Org. Chem.* **55**, 4603–4607.
Kozikowski, A. P. (1984). *Acc. Chem. Res.* **17**, 410–416.
Krowicki, K., Balzarini, J., De Clercq, E., Newman, R. A. & Lown, J. W. (1988). *J. Med. Chem.* **31**, 341–345.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Muchowski, J. M., Unger, S. H., Ackrell, J., Cheung, P., Cook, J., Gallegra, P., Halpern, O., Koehler, R. & Kluge, A. F. (1985). *J. Med. Chem.* **28**, 1037–1049.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Toja, E., Depaoli, A., Tuan, G. & Kettenring, J. (1987). *Synthesis*, pp. 272–274.

supporting information

Acta Cryst. (2015). E**71**, 574-577 [doi:10.1107/S2056989015008063]

Crystal structures of methyl 3-(4-isopropylphenyl)-1-methyl-1,2,3,3a,4,9b-hexahydrothiochromeno[4,3-*b*]pyrrole-3a-carboxylate, methyl 1-methyl-3-(*o*-tolyl)-1,2,3,3a,4,9b-hexahydrothiochromeno[4,3-*b*]pyrrole-3a-carboxylate and methyl 1-methyl-3-(*o*-tolyl)-3,3a,4,9b-tetrahydro-1*H*-thiochromeno[4,3-*c*]isoxazole-3a-carboxylate

R. Raja, M. Suresh, R. Raghunathan and A. SubbiahPandi

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008). Molecular graphics: *ORTEP-3* for Windows (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008) for (I); *ORTEP-3* for Windows (Farrugia, 2012) for (II), (III). For all compounds, software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(I) Methyl 3-(4-isopropylphenyl)-1-methyl-1,2,3,3a,4,9b-hexahydrothiochromeno[4,3-*b*]pyrrole-3a-carboxylate

Crystal data

$C_{23}H_{27}NO_2S$
$M_r = 381.52$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 10.7330\ (3)$ Å
$b = 7.7568\ (2)$ Å
$c = 24.9436\ (7)$ Å
$\beta = 98.485\ (1)°$
$V = 2053.92\ (10)$ Å^3
$Z = 4$
$F(000) = 816$
$D_x = 1.234$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3170 reflections
$\theta = 1.7–25.0°$
$\mu = 0.18$ mm^{-1}
$T = 293$ K
Block, colourless
0.35 × 0.30 × 0.25 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.941$, $T_{max} = 0.958$
16824 measured reflections
3616 independent reflections
3170 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.7°$
$h = -12 \rightarrow 12$
$k = -9 \rightarrow 9$
$l = -24 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.111$
$S = 1.06$
3616 reflections
272 parameters
107 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
$w = 1/[\sigma^2(F_o^2) + (0.050P)^2 + 1.0371P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.64364 (15)	0.4800 (2)	0.14949 (7)	0.0333 (4)	
C2	0.60663 (18)	0.4940 (3)	0.20060 (8)	0.0468 (5)	
H2	0.5834	0.6015	0.2124	0.056*	
C3	0.6033 (2)	0.3533 (3)	0.23429 (9)	0.0584 (6)	
H3	0.5765	0.3660	0.2679	0.070*	
C4	0.6398 (2)	0.1946 (3)	0.21793 (9)	0.0606 (6)	
H4	0.6379	0.0994	0.2405	0.073*	
C5	0.67929 (19)	0.1762 (3)	0.16824 (9)	0.0511 (5)	
H5	0.7052	0.0687	0.1576	0.061*	
C6	0.68086 (16)	0.3175 (2)	0.13353 (7)	0.0361 (4)	
C7	0.70294 (16)	0.4766 (2)	0.03604 (7)	0.0327 (4)	
H7A	0.7507	0.4820	0.0060	0.039*	
H7B	0.6142	0.4775	0.0212	0.039*	
C8	0.73260 (14)	0.6355 (2)	0.07149 (6)	0.0279 (4)	
C9	0.64648 (14)	0.6410 (2)	0.11561 (7)	0.0301 (4)	
H9	0.6724	0.7380	0.1399	0.036*	
C10	0.42438 (19)	0.7312 (3)	0.11351 (10)	0.0568 (6)	
H10A	0.4083	0.6368	0.1364	0.085*	
H10B	0.3492	0.7573	0.0889	0.085*	
H10C	0.4495	0.8305	0.1354	0.085*	
C11	0.55213 (17)	0.8256 (2)	0.04721 (8)	0.0399 (4)	
H11A	0.5384	0.9360	0.0636	0.048*	
H11B	0.4980	0.8183	0.0125	0.048*	
C12	0.69127 (16)	0.8060 (2)	0.03967 (7)	0.0324 (4)	
H12	0.7370	0.9003	0.0600	0.039*	

C13	0.87070 (15)	0.6497 (2)	0.09487 (7)	0.0347 (4)	
C14	1.07866 (18)	0.6040 (4)	0.07703 (11)	0.0687 (7)	
H14A	1.1210	0.5552	0.0493	0.103*	
H14B	1.1034	0.5433	0.1105	0.103*	
H14C	1.1010	0.7234	0.0818	0.103*	
C15	0.72199 (16)	0.8169 (2)	−0.01743 (7)	0.0333 (4)	
C16	0.64436 (17)	0.7505 (2)	−0.06219 (7)	0.0420 (4)	
H16	0.5687	0.6984	−0.0575	0.050*	
C17	0.67758 (19)	0.7603 (3)	−0.11355 (8)	0.0486 (5)	
H17	0.6232	0.7158	−0.1428	0.058*	
C18	0.7893 (2)	0.8346 (3)	−0.12255 (8)	0.0515 (5)	
C19	0.8153 (7)	0.8254 (11)	−0.1815 (2)	0.0583 (18)	0.586 (13)
H19	0.7602	0.7432	−0.2035	0.070*	0.586 (13)
C20	0.8006 (10)	1.0118 (12)	−0.2041 (3)	0.102 (3)	0.586 (13)
H20A	0.7144	1.0475	−0.2061	0.153*	0.586 (13)
H20B	0.8248	1.0152	−0.2396	0.153*	0.586 (13)
H20C	0.8536	1.0882	−0.1805	0.153*	0.586 (13)
C21	0.9546 (11)	0.7867 (18)	−0.1814 (5)	0.091 (3)	0.586 (13)
H21A	0.9717	0.7809	−0.2181	0.137*	0.586 (13)
H21B	0.9752	0.6784	−0.1637	0.137*	0.586 (13)
H21C	1.0044	0.8765	−0.1624	0.137*	0.586 (13)
C19′	0.8449 (11)	0.8718 (19)	−0.1752 (3)	0.073 (3)	0.414 (13)
H19′	0.8974	0.9752	−0.1685	0.087*	0.414 (13)
C20′	0.7403 (12)	0.915 (2)	−0.2199 (4)	0.104 (4)	0.414 (13)
H20D	0.6884	1.0039	−0.2079	0.156*	0.414 (13)
H20E	0.6902	0.8143	−0.2295	0.156*	0.414 (13)
H20F	0.7753	0.9552	−0.2509	0.156*	0.414 (13)
C21′	0.9299 (17)	0.728 (2)	−0.1893 (8)	0.088 (4)	0.414 (13)
H21D	0.9944	0.7061	−0.1591	0.132*	0.414 (13)
H21E	0.9681	0.7605	−0.2203	0.132*	0.414 (13)
H21F	0.8810	0.6248	−0.1976	0.132*	0.414 (13)
C22	0.8668 (2)	0.9020 (3)	−0.07806 (9)	0.0568 (6)	
H22	0.9427	0.9532	−0.0829	0.068*	
C23	0.83327 (18)	0.8944 (3)	−0.02667 (8)	0.0462 (5)	
H23	0.8865	0.9422	0.0023	0.055*	
N1	0.52473 (13)	0.68409 (19)	0.08280 (6)	0.0361 (3)	
O1	0.90964 (14)	0.7164 (3)	0.13667 (7)	0.0840 (7)	
O2	0.94460 (11)	0.5889 (2)	0.06139 (6)	0.0505 (4)	
S1	0.73931 (5)	0.27778 (6)	0.07238 (2)	0.04255 (16)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0291 (8)	0.0381 (9)	0.0328 (9)	−0.0026 (7)	0.0045 (7)	0.0019 (7)
C2	0.0467 (11)	0.0570 (12)	0.0382 (10)	−0.0011 (9)	0.0113 (8)	0.0033 (9)
C3	0.0558 (12)	0.0821 (17)	0.0382 (11)	−0.0046 (12)	0.0099 (9)	0.0161 (11)
C4	0.0603 (13)	0.0663 (15)	0.0530 (13)	−0.0048 (11)	0.0011 (10)	0.0293 (12)
C5	0.0538 (12)	0.0402 (11)	0.0565 (13)	−0.0005 (9)	−0.0007 (10)	0.0140 (9)

C6	0.0327 (9)	0.0353 (9)	0.0387 (10)	−0.0027 (7)	0.0000 (7)	0.0054 (8)
C7	0.0379 (9)	0.0283 (8)	0.0321 (9)	−0.0001 (7)	0.0060 (7)	−0.0029 (7)
C8	0.0293 (8)	0.0258 (8)	0.0297 (8)	0.0000 (6)	0.0075 (6)	−0.0021 (7)
C9	0.0293 (8)	0.0287 (8)	0.0336 (9)	−0.0008 (7)	0.0087 (7)	−0.0037 (7)
C10	0.0387 (10)	0.0608 (13)	0.0763 (15)	0.0117 (10)	0.0258 (10)	0.0141 (12)
C11	0.0406 (10)	0.0338 (9)	0.0469 (11)	0.0094 (8)	0.0122 (8)	0.0075 (8)
C12	0.0366 (9)	0.0247 (8)	0.0367 (9)	−0.0019 (7)	0.0079 (7)	−0.0007 (7)
C13	0.0316 (9)	0.0373 (9)	0.0362 (10)	−0.0008 (7)	0.0086 (7)	−0.0024 (8)
C14	0.0303 (10)	0.0772 (17)	0.1015 (19)	0.0028 (11)	0.0199 (11)	−0.0011 (15)
C15	0.0360 (9)	0.0279 (8)	0.0361 (9)	−0.0006 (7)	0.0055 (7)	0.0050 (7)
C16	0.0374 (9)	0.0444 (11)	0.0431 (11)	−0.0042 (8)	0.0022 (8)	0.0043 (8)
C17	0.0507 (11)	0.0549 (12)	0.0377 (11)	0.0014 (10)	−0.0015 (9)	0.0009 (9)
C18	0.0574 (12)	0.0605 (13)	0.0378 (11)	0.0086 (10)	0.0110 (9)	0.0093 (10)
C19	0.056 (3)	0.082 (4)	0.037 (3)	−0.016 (3)	0.010 (2)	−0.003 (2)
C20	0.128 (6)	0.122 (6)	0.063 (4)	0.034 (5)	0.039 (4)	0.048 (4)
C21	0.100 (6)	0.128 (8)	0.057 (5)	0.017 (5)	0.046 (5)	0.013 (5)
C19′	0.090 (6)	0.088 (6)	0.043 (4)	−0.009 (5)	0.018 (4)	0.001 (4)
C20′	0.127 (8)	0.132 (9)	0.053 (5)	0.016 (6)	0.012 (5)	0.031 (5)
C21′	0.085 (7)	0.122 (10)	0.058 (5)	0.015 (7)	0.016 (5)	−0.012 (6)
C22	0.0504 (12)	0.0700 (15)	0.0533 (13)	−0.0146 (11)	0.0186 (10)	0.0108 (11)
C23	0.0446 (10)	0.0521 (12)	0.0418 (11)	−0.0145 (9)	0.0059 (8)	0.0025 (9)
N1	0.0288 (7)	0.0338 (8)	0.0468 (9)	0.0040 (6)	0.0097 (6)	0.0054 (7)
O1	0.0382 (8)	0.1496 (19)	0.0630 (10)	−0.0111 (9)	0.0038 (7)	−0.0553 (12)
O2	0.0319 (6)	0.0652 (9)	0.0575 (8)	0.0022 (6)	0.0169 (6)	−0.0123 (7)
S1	0.0551 (3)	0.0263 (2)	0.0470 (3)	0.00570 (19)	0.0104 (2)	−0.00152 (19)

Geometric parameters (Å, º)

C1—C2	1.394 (2)	C14—H14A	0.9600
C1—C6	1.398 (2)	C14—H14B	0.9600
C1—C9	1.510 (2)	C14—H14C	0.9600
C2—C3	1.382 (3)	C15—C23	1.386 (2)
C2—H2	0.9300	C15—C16	1.390 (2)
C3—C4	1.372 (4)	C16—C17	1.382 (3)
C3—H3	0.9300	C16—H16	0.9300
C4—C5	1.375 (3)	C17—C18	1.378 (3)
C4—H4	0.9300	C17—H17	0.9300
C5—C6	1.398 (3)	C18—C22	1.387 (3)
C5—H5	0.9300	C18—C19	1.539 (5)
C6—S1	1.7599 (19)	C18—C19′	1.546 (7)
C7—C8	1.523 (2)	C19—C21	1.524 (12)
C7—S1	1.8024 (17)	C19—C20	1.551 (11)
C7—H7A	0.9700	C19—H19	0.9800
C7—H7B	0.9700	C20—H20A	0.9600
C8—C13	1.515 (2)	C20—H20B	0.9600
C8—C9	1.539 (2)	C20—H20C	0.9600
C8—C12	1.572 (2)	C21—H21A	0.9600
C9—N1	1.474 (2)	C21—H21B	0.9600

C9—H9	0.9800	C21—H21C	0.9600
C10—N1	1.457 (2)	C19′—C20′	1.500 (14)
C10—H10A	0.9600	C19′—C21′	1.519 (15)
C10—H10B	0.9600	C19′—H19′	0.9800
C10—H10C	0.9600	C20′—H20D	0.9600
C11—N1	1.468 (2)	C20′—H20E	0.9600
C11—C12	1.540 (2)	C20′—H20F	0.9600
C11—H11A	0.9700	C21′—H21D	0.9600
C11—H11B	0.9700	C21′—H21E	0.9600
C12—C15	1.511 (2)	C21′—H21F	0.9600
C12—H12	0.9800	C22—C23	1.383 (3)
C13—O1	1.184 (2)	C22—H22	0.9300
C13—O2	1.321 (2)	C23—H23	0.9300
C14—O2	1.439 (2)		

C2—C1—C6	117.55 (17)	C23—C15—C16	117.15 (16)
C2—C1—C9	118.63 (16)	C23—C15—C12	119.62 (15)
C6—C1—C9	123.77 (15)	C16—C15—C12	123.22 (15)
C3—C2—C1	122.1 (2)	C17—C16—C15	121.20 (17)
C3—C2—H2	119.0	C17—C16—H16	119.4
C1—C2—H2	119.0	C15—C16—H16	119.4
C4—C3—C2	119.6 (2)	C18—C17—C16	121.59 (18)
C4—C3—H3	120.2	C18—C17—H17	119.2
C2—C3—H3	120.2	C16—C17—H17	119.2
C3—C4—C5	120.0 (2)	C17—C18—C22	117.43 (18)
C3—C4—H4	120.0	C17—C18—C19	114.9 (3)
C5—C4—H4	120.0	C22—C18—C19	127.6 (3)
C4—C5—C6	120.7 (2)	C17—C18—C19′	132.0 (5)
C4—C5—H5	119.7	C22—C18—C19′	110.4 (5)
C6—C5—H5	119.7	C19—C18—C19′	18.3 (5)
C1—C6—C5	120.03 (18)	C21—C19—C18	108.9 (7)
C1—C6—S1	123.93 (13)	C21—C19—C20	103.4 (9)
C5—C6—S1	115.96 (15)	C18—C19—C20	106.3 (6)
C8—C7—S1	112.92 (11)	C21—C19—H19	112.6
C8—C7—H7A	109.0	C18—C19—H19	112.6
S1—C7—H7A	109.0	C20—C19—H19	112.6
C8—C7—H7B	109.0	C19—C20—H20A	109.5
S1—C7—H7B	109.0	C19—C20—H20B	109.5
H7A—C7—H7B	107.8	H20A—C20—H20B	109.5
C13—C8—C7	113.01 (13)	C19—C20—H20C	109.5
C13—C8—C9	112.32 (13)	H20A—C20—H20C	109.5
C7—C8—C9	109.95 (13)	H20B—C20—H20C	109.5
C13—C8—C12	108.71 (13)	C19—C21—H21A	109.5
C7—C8—C12	111.61 (13)	C19—C21—H21B	109.5
C9—C8—C12	100.59 (12)	H21A—C21—H21B	109.5
N1—C9—C1	114.12 (13)	C19—C21—H21C	109.5
N1—C9—C8	100.71 (13)	H21A—C21—H21C	109.5
C1—C9—C8	116.20 (13)	H21B—C21—H21C	109.5

N1—C9—H9	108.5	C20′—C19′—C21′	113.7 (14)
C1—C9—H9	108.5	C20′—C19′—C18	109.5 (8)
C8—C9—H9	108.5	C21′—C19′—C18	112.4 (12)
N1—C10—H10A	109.5	C20′—C19′—H19′	107.0
N1—C10—H10B	109.5	C21′—C19′—H19′	107.0
H10A—C10—H10B	109.5	C18—C19′—H19′	107.0
N1—C10—H10C	109.5	C19′—C20′—H20D	109.5
H10A—C10—H10C	109.5	C19′—C20′—H20E	109.5
H10B—C10—H10C	109.5	H20D—C20′—H20E	109.5
N1—C11—C12	106.52 (13)	C19′—C20′—H20F	109.5
N1—C11—H11A	110.4	H20D—C20′—H20F	109.5
C12—C11—H11A	110.4	H20E—C20′—H20F	109.5
N1—C11—H11B	110.4	C19′—C21′—H21D	109.5
C12—C11—H11B	110.4	C19′—C21′—H21E	109.5
H11A—C11—H11B	108.6	H21D—C21′—H21E	109.5
C15—C12—C11	117.38 (14)	C19′—C21′—H21F	109.5
C15—C12—C8	116.04 (13)	H21D—C21′—H21F	109.5
C11—C12—C8	103.18 (13)	H21E—C21′—H21F	109.5
C15—C12—H12	106.5	C23—C22—C18	121.21 (19)
C11—C12—H12	106.5	C23—C22—H22	119.4
C8—C12—H12	106.5	C18—C22—H22	119.4
O1—C13—O2	123.11 (16)	C22—C23—C15	121.41 (18)
O1—C13—C8	124.68 (16)	C22—C23—H23	119.3
O2—C13—C8	112.07 (14)	C15—C23—H23	119.3
O2—C14—H14A	109.5	C10—N1—C11	111.09 (15)
O2—C14—H14B	109.5	C10—N1—C9	115.36 (15)
H14A—C14—H14B	109.5	C11—N1—C9	105.37 (13)
O2—C14—H14C	109.5	C13—O2—C14	117.99 (16)
H14A—C14—H14C	109.5	C6—S1—C7	101.98 (8)
H14B—C14—H14C	109.5		

C6—C1—C2—C3	−1.5 (3)	C8—C12—C15—C23	−93.3 (2)
C9—C1—C2—C3	−179.07 (17)	C11—C12—C15—C16	−36.9 (2)
C1—C2—C3—C4	1.4 (3)	C8—C12—C15—C16	85.7 (2)
C2—C3—C4—C5	−0.1 (3)	C23—C15—C16—C17	0.5 (3)
C3—C4—C5—C6	−1.0 (3)	C12—C15—C16—C17	−178.64 (17)
C2—C1—C6—C5	0.4 (3)	C15—C16—C17—C18	0.7 (3)
C9—C1—C6—C5	177.81 (16)	C16—C17—C18—C22	−1.0 (3)
C2—C1—C6—S1	−176.06 (13)	C16—C17—C18—C19	176.5 (4)
C9—C1—C6—S1	1.3 (2)	C16—C17—C18—C19′	−175.7 (7)
C4—C5—C6—C1	0.8 (3)	C17—C18—C19—C21	−140.0 (8)
C4—C5—C6—S1	177.59 (16)	C22—C18—C19—C21	37.2 (10)
S1—C7—C8—C13	61.01 (16)	C19′—C18—C19—C21	58 (2)
S1—C7—C8—C9	−65.37 (15)	C17—C18—C19—C20	109.2 (7)
S1—C7—C8—C12	−176.10 (11)	C22—C18—C19—C20	−73.6 (8)
C2—C1—C9—N1	−86.08 (19)	C19′—C18—C19—C20	−52 (2)
C6—C1—C9—N1	96.55 (19)	C17—C18—C19′—C20′	33.7 (16)
C2—C1—C9—C8	157.34 (15)	C22—C18—C19′—C20′	−141.3 (12)

C6—C1—C9—C8	−20.0 (2)	C19—C18—C19′—C20′	57 (2)
C13—C8—C9—N1	161.82 (13)	C17—C18—C19′—C21′	−93.5 (12)
C7—C8—C9—N1	−71.42 (15)	C22—C18—C19′—C21′	91.4 (13)
C12—C8—C9—N1	46.38 (14)	C19—C18—C19′—C21′	−71 (2)
C13—C8—C9—C1	−74.36 (18)	C17—C18—C22—C23	0.2 (3)
C7—C8—C9—C1	52.41 (18)	C19—C18—C22—C23	−177.0 (4)
C12—C8—C9—C1	170.21 (13)	C19′—C18—C22—C23	176.0 (6)
N1—C11—C12—C15	132.25 (15)	C18—C22—C23—C15	1.0 (3)
N1—C11—C12—C8	3.27 (17)	C16—C15—C23—C22	−1.3 (3)
C13—C8—C12—C15	81.94 (17)	C12—C15—C23—C22	177.85 (19)
C7—C8—C12—C15	−43.37 (18)	C12—C11—N1—C10	152.28 (16)
C9—C8—C12—C15	−159.95 (14)	C12—C11—N1—C9	26.68 (18)
C13—C8—C12—C11	−148.26 (14)	C1—C9—N1—C10	65.7 (2)
C7—C8—C12—C11	86.43 (16)	C8—C9—N1—C10	−169.06 (15)
C9—C8—C12—C11	−30.15 (15)	C1—C9—N1—C11	−171.39 (14)
C7—C8—C13—O1	−150.6 (2)	C8—C9—N1—C11	−46.15 (16)
C9—C8—C13—O1	−25.5 (3)	O1—C13—O2—C14	0.5 (3)
C12—C8—C13—O1	84.9 (2)	C8—C13—O2—C14	176.23 (17)
C7—C8—C13—O2	33.7 (2)	C1—C6—S1—C7	−11.94 (17)
C9—C8—C13—O2	158.85 (15)	C5—C6—S1—C7	171.45 (14)
C12—C8—C13—O2	−90.74 (17)	C8—C7—S1—C6	43.36 (13)
C11—C12—C15—C23	144.07 (17)		

Hydrogen-bond geometry (Å, º)

Cg3 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17···*Cg*3^{i}	0.93	2.91	3.695 (2)	143

Symmetry code: (i) −*x*+1, −*y*+1, −*z*.

(II) Methyl 1-methyl-3-(*o*-tolyl)-1,2,3,3a,4,9b-hexahydrothiochromeno[4,3-*b*]pyrrole-3a-carboxylate

Crystal data

$C_{21}H_{21}NO_2S$
M_r = 351.45
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.1882 (3) Å
b = 10.4987 (4) Å
c = 10.9594 (4) Å
α = 104.554 (1)°
β = 90.983 (1)°
γ = 90.134 (1)°
V = 911.74 (6) Å^3
Z = 2
F(000) = 372
D_x = 1.280 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2790 reflections
θ = 1.9–25.0°
μ = 0.19 mm^{-1}
T = 293 K
Block, colourless
0.35 × 0.30 × 0.25 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.935, T_{max} = 0.953
19010 measured reflections
3210 independent reflections

2790 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.0°$, $\theta_{min} = 1.9°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.115$
$S = 1.07$
3210 reflections
229 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.2766P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.1321 (2)	0.62046 (16)	0.33099 (15)	0.0424 (4)
C2	0.0560 (3)	0.6916 (2)	0.43961 (18)	0.0589 (5)
H2	−0.0253	0.6509	0.4748	0.071*
C3	0.0976 (3)	0.8203 (2)	0.4965 (2)	0.0759 (7)
H3	0.0434	0.8661	0.5679	0.091*
C4	0.2199 (4)	0.8801 (2)	0.4468 (2)	0.0768 (7)
H4	0.2487	0.9670	0.4845	0.092*
C5	0.2994 (3)	0.81250 (19)	0.3421 (2)	0.0614 (5)
H5	0.3836	0.8534	0.3102	0.074*
C6	0.2560 (2)	0.68236 (17)	0.28217 (16)	0.0444 (4)
C7	0.2650 (2)	0.45327 (17)	0.09015 (16)	0.0435 (4)
H7A	0.1727	0.4687	0.0392	0.052*
H7B	0.3373	0.3921	0.0356	0.052*
C8	0.20327 (18)	0.39039 (15)	0.19172 (15)	0.0389 (4)
C9	0.07923 (18)	0.48030 (16)	0.27409 (15)	0.0397 (4)
H9	0.0487	0.4408	0.3426	0.048*
C10	−0.2119 (2)	0.5208 (2)	0.2449 (2)	0.0627 (5)
H10A	−0.3002	0.4990	0.1844	0.094*
H10B	−0.2028	0.6148	0.2747	0.094*
H10C	−0.2328	0.4835	0.3146	0.094*
C11	−0.0773 (2)	0.3283 (2)	0.1264 (2)	0.0678 (6)
H11A	−0.1131	0.3147	0.0392	0.081*

H11B	−0.1569	0.2884	0.1702	0.081*
C12	0.0921 (2)	0.26691 (17)	0.13364 (18)	0.0475 (4)
H12	0.0856	0.2166	0.1976	0.057*
C15	0.1522 (2)	0.17354 (16)	0.01548 (17)	0.0480 (4)
C16	0.1305 (3)	0.2006 (2)	−0.10163 (19)	0.0648 (6)
H14	0.0742	0.2760	−0.1067	0.078*
C17	0.1898 (3)	0.1190 (2)	−0.2106 (2)	0.0800 (7)
H15	0.1722	0.1387	−0.2878	0.096*
C18	0.2745 (3)	0.0093 (2)	−0.2041 (2)	0.0790 (7)
H16	0.3181	−0.0447	−0.2767	0.095*
C19	0.2953 (3)	−0.02130 (19)	−0.0912 (2)	0.0669 (6)
H17	0.3519	−0.0972	−0.0884	0.080*
C20	0.2343 (2)	0.05785 (17)	0.02048 (19)	0.0520 (4)
C21	0.2546 (3)	0.0131 (2)	0.1378 (2)	0.0727 (6)
H19A	0.3050	−0.0719	0.1187	0.109*
H19B	0.1495	0.0075	0.1738	0.109*
H19C	0.3223	0.0748	0.1969	0.109*
C13	0.3469 (2)	0.34856 (16)	0.26130 (16)	0.0431 (4)
C14	0.4427 (3)	0.3058 (3)	0.4510 (2)	0.0920 (9)
H21A	0.4697	0.2173	0.4077	0.138*
H21B	0.4048	0.3074	0.5338	0.138*
H21C	0.5379	0.3609	0.4579	0.138*
N1	−0.06074 (15)	0.46851 (14)	0.18600 (14)	0.0455 (4)
O1	0.47275 (15)	0.30893 (14)	0.21352 (13)	0.0592 (4)
O2	0.31503 (18)	0.35417 (16)	0.38084 (13)	0.0709 (4)
S1	0.37215 (5)	0.60605 (5)	0.15186 (5)	0.05272 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0429 (9)	0.0469 (9)	0.0392 (9)	0.0106 (7)	−0.0039 (7)	0.0146 (7)
C2	0.0667 (12)	0.0659 (12)	0.0451 (10)	0.0183 (10)	0.0044 (9)	0.0155 (9)
C3	0.1017 (18)	0.0676 (14)	0.0490 (12)	0.0260 (13)	−0.0033 (12)	−0.0027 (11)
C4	0.112 (2)	0.0520 (12)	0.0602 (14)	0.0051 (13)	−0.0200 (13)	0.0042 (10)
C5	0.0735 (13)	0.0514 (11)	0.0618 (12)	−0.0055 (10)	−0.0200 (10)	0.0202 (10)
C6	0.0452 (9)	0.0454 (9)	0.0445 (9)	0.0049 (7)	−0.0109 (7)	0.0158 (7)
C7	0.0355 (8)	0.0514 (10)	0.0436 (9)	0.0035 (7)	0.0040 (7)	0.0118 (7)
C8	0.0316 (8)	0.0413 (8)	0.0440 (9)	0.0044 (6)	−0.0002 (6)	0.0113 (7)
C9	0.0332 (8)	0.0478 (9)	0.0423 (9)	0.0069 (7)	0.0036 (6)	0.0187 (7)
C10	0.0335 (9)	0.0740 (13)	0.0857 (15)	0.0107 (9)	0.0090 (9)	0.0290 (11)
C11	0.0379 (10)	0.0607 (12)	0.0978 (16)	0.0003 (9)	−0.0111 (10)	0.0075 (11)
C12	0.0390 (9)	0.0453 (9)	0.0590 (11)	−0.0005 (7)	−0.0042 (8)	0.0148 (8)
C15	0.0458 (9)	0.0391 (9)	0.0579 (11)	−0.0027 (7)	−0.0109 (8)	0.0109 (8)
C16	0.0859 (15)	0.0476 (11)	0.0579 (12)	0.0018 (10)	−0.0216 (11)	0.0093 (9)
C17	0.114 (2)	0.0635 (14)	0.0567 (13)	−0.0073 (13)	−0.0173 (13)	0.0061 (11)
C18	0.0939 (18)	0.0674 (14)	0.0630 (14)	−0.0041 (12)	−0.0038 (12)	−0.0067 (11)
C19	0.0627 (13)	0.0398 (10)	0.0896 (16)	0.0022 (9)	−0.0081 (11)	0.0011 (10)
C20	0.0483 (10)	0.0390 (9)	0.0684 (12)	−0.0046 (7)	−0.0104 (8)	0.0138 (8)

C21	0.0836 (16)	0.0532 (12)	0.0876 (16)	0.0003 (11)	−0.0119 (12)	0.0305 (11)
C13	0.0373 (9)	0.0401 (9)	0.0509 (10)	0.0046 (7)	−0.0028 (7)	0.0100 (7)
C14	0.0858 (17)	0.131 (2)	0.0647 (14)	0.0513 (16)	−0.0112 (12)	0.0354 (15)
N1	0.0286 (7)	0.0527 (8)	0.0573 (9)	0.0047 (6)	−0.0002 (6)	0.0176 (7)
O1	0.0374 (7)	0.0683 (9)	0.0731 (9)	0.0151 (6)	0.0019 (6)	0.0197 (7)
O2	0.0618 (9)	0.1045 (12)	0.0516 (8)	0.0386 (8)	0.0005 (6)	0.0289 (8)
S1	0.0402 (3)	0.0558 (3)	0.0645 (3)	−0.00397 (19)	0.0072 (2)	0.0190 (2)

Geometric parameters (Å, º)

C1—C6	1.389 (3)	C11—C12	1.540 (2)
C1—C2	1.394 (2)	C11—H11A	0.9700
C1—C9	1.506 (2)	C11—H11B	0.9700
C2—C3	1.377 (3)	C12—C15	1.505 (3)
C2—H2	0.9300	C12—H12	0.9800
C3—C4	1.372 (4)	C15—C16	1.391 (3)
C3—H3	0.9300	C15—C20	1.402 (2)
C4—C5	1.364 (3)	C16—C17	1.380 (3)
C4—H4	0.9300	C16—H14	0.9300
C5—C6	1.401 (3)	C17—C18	1.362 (4)
C5—H5	0.9300	C17—H15	0.9300
C6—S1	1.7495 (18)	C18—C19	1.362 (3)
C7—C8	1.522 (2)	C18—H16	0.9300
C7—S1	1.7967 (17)	C19—C20	1.397 (3)
C7—H7A	0.9700	C19—H17	0.9300
C7—H7B	0.9700	C20—C21	1.483 (3)
C8—C13	1.516 (2)	C21—H19A	0.9600
C8—C9	1.531 (2)	C21—H19B	0.9600
C8—C12	1.573 (2)	C21—H19C	0.9600
C9—N1	1.470 (2)	C13—O1	1.192 (2)
C9—H9	0.9800	C13—O2	1.327 (2)
C10—N1	1.450 (2)	C14—O2	1.453 (2)
C10—H10A	0.9600	C14—H21A	0.9600
C10—H10B	0.9600	C14—H21B	0.9600
C10—H10C	0.9600	C14—H21C	0.9600
C11—N1	1.458 (2)		

C6—C1—C2	117.86 (17)	C12—C11—H11B	110.3
C6—C1—C9	123.26 (15)	H11A—C11—H11B	108.6
C2—C1—C9	118.87 (16)	C15—C12—C11	117.07 (16)
C3—C2—C1	122.0 (2)	C15—C12—C8	116.40 (14)
C3—C2—H2	119.0	C11—C12—C8	102.78 (13)
C1—C2—H2	119.0	C15—C12—H12	106.6
C4—C3—C2	119.3 (2)	C11—C12—H12	106.6
C4—C3—H3	120.3	C8—C12—H12	106.6
C2—C3—H3	120.3	C16—C15—C20	118.02 (18)
C5—C4—C3	120.2 (2)	C16—C15—C12	121.01 (16)
C5—C4—H4	119.9	C20—C15—C12	120.96 (17)

C3—C4—H4	119.9	C17—C16—C15	122.0 (2)
C4—C5—C6	120.9 (2)	C17—C16—H14	119.0
C4—C5—H5	119.5	C15—C16—H14	119.0
C6—C5—H5	119.5	C18—C17—C16	119.5 (2)
C1—C6—C5	119.60 (18)	C18—C17—H15	120.2
C1—C6—S1	124.27 (13)	C16—C17—H15	120.2
C5—C6—S1	116.06 (15)	C19—C18—C17	119.9 (2)
C8—C7—S1	113.57 (12)	C19—C18—H16	120.1
C8—C7—H7A	108.9	C17—C18—H16	120.1
S1—C7—H7A	108.9	C18—C19—C20	122.1 (2)
C8—C7—H7B	108.9	C18—C19—H17	119.0
S1—C7—H7B	108.9	C20—C19—H17	119.0
H7A—C7—H7B	107.7	C19—C20—C15	118.43 (19)
C13—C8—C7	109.75 (13)	C19—C20—C21	118.35 (18)
C13—C8—C9	115.80 (13)	C15—C20—C21	123.19 (19)
C7—C8—C9	110.26 (13)	C20—C21—H19A	109.5
C13—C8—C12	109.12 (13)	C20—C21—H19B	109.5
C7—C8—C12	111.39 (14)	H19A—C21—H19B	109.5
C9—C8—C12	100.21 (12)	C20—C21—H19C	109.5
N1—C9—C1	113.43 (13)	H19A—C21—H19C	109.5
N1—C9—C8	101.16 (13)	H19B—C21—H19C	109.5
C1—C9—C8	116.72 (13)	O1—C13—O2	122.96 (16)
N1—C9—H9	108.4	O1—C13—C8	124.25 (16)
C1—C9—H9	108.4	O2—C13—C8	112.71 (14)
C8—C9—H9	108.4	O2—C14—H21A	109.5
N1—C10—H10A	109.5	O2—C14—H21B	109.5
N1—C10—H10B	109.5	H21A—C14—H21B	109.5
H10A—C10—H10B	109.5	O2—C14—H21C	109.5
N1—C10—H10C	109.5	H21A—C14—H21C	109.5
H10A—C10—H10C	109.5	H21B—C14—H21C	109.5
H10B—C10—H10C	109.5	C10—N1—C11	110.79 (15)
N1—C11—C12	106.89 (14)	C10—N1—C9	114.21 (15)
N1—C11—H11A	110.3	C11—N1—C9	105.48 (13)
C12—C11—H11A	110.3	C13—O2—C14	115.82 (16)
N1—C11—H11B	110.3	C6—S1—C7	102.79 (8)

C6—C1—C2—C3	1.6 (3)	C11—C12—C15—C16	41.8 (3)
C9—C1—C2—C3	−179.75 (17)	C8—C12—C15—C16	−80.2 (2)
C1—C2—C3—C4	−1.4 (3)	C11—C12—C15—C20	−139.27 (18)
C2—C3—C4—C5	−0.1 (3)	C8—C12—C15—C20	98.65 (19)
C3—C4—C5—C6	1.3 (3)	C20—C15—C16—C17	−1.4 (3)
C2—C1—C6—C5	−0.4 (2)	C12—C15—C16—C17	177.5 (2)
C9—C1—C6—C5	−178.98 (15)	C15—C16—C17—C18	−0.9 (4)
C2—C1—C6—S1	176.50 (12)	C16—C17—C18—C19	2.1 (4)
C9—C1—C6—S1	−2.1 (2)	C17—C18—C19—C20	−1.0 (4)
C4—C5—C6—C1	−1.0 (3)	C18—C19—C20—C15	−1.3 (3)
C4—C5—C6—S1	−178.16 (16)	C18—C19—C20—C21	176.6 (2)
S1—C7—C8—C13	−66.15 (15)	C16—C15—C20—C19	2.5 (3)

S1—C7—C8—C9	62.56 (15)	C12—C15—C20—C19	−176.46 (17)
S1—C7—C8—C12	172.89 (10)	C16—C15—C20—C21	−175.41 (19)
C6—C1—C9—N1	−94.84 (18)	C12—C15—C20—C21	5.7 (3)
C2—C1—C9—N1	86.56 (18)	C7—C8—C13—O1	−34.2 (2)
C6—C1—C9—C8	22.2 (2)	C9—C8—C13—O1	−159.81 (16)
C2—C1—C9—C8	−156.42 (15)	C12—C8—C13—O1	88.1 (2)
C13—C8—C9—N1	−163.87 (13)	C7—C8—C13—O2	149.08 (15)
C7—C8—C9—N1	70.79 (15)	C9—C8—C13—O2	23.5 (2)
C12—C8—C9—N1	−46.69 (14)	C12—C8—C13—O2	−88.61 (17)
C13—C8—C9—C1	72.56 (18)	C12—C11—N1—C10	−149.04 (17)
C7—C8—C9—C1	−52.78 (18)	C12—C11—N1—C9	−25.0 (2)
C12—C8—C9—C1	−170.27 (13)	C1—C9—N1—C10	−66.85 (19)
N1—C11—C12—C15	−133.89 (17)	C8—C9—N1—C10	167.34 (14)
N1—C11—C12—C8	−5.0 (2)	C1—C9—N1—C11	171.26 (15)
C13—C8—C12—C15	−77.38 (18)	C8—C9—N1—C11	45.45 (17)
C7—C8—C12—C15	43.94 (19)	O1—C13—O2—C14	−1.3 (3)
C9—C8—C12—C15	160.58 (14)	C8—C13—O2—C14	175.43 (19)
C13—C8—C12—C11	153.30 (16)	C1—C6—S1—C7	10.31 (16)
C7—C8—C12—C11	−85.38 (18)	C5—C6—S1—C7	−172.73 (13)
C9—C8—C12—C11	31.27 (17)	C8—C7—S1—C6	−40.14 (13)

(III) Methyl 1-methyl-3-(*o*-tolyl)-3,3a,4,9b-tetrahydro-1*H*-thiochromeno[4,3-*c*]isoxazole-3a-carboxylate

Crystal data

$C_{20}H_{21}NO_3S$
M_r = 355.44
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 11.2629 (11) Å
b = 13.2117 (11) Å
c = 24.041 (3) Å
V = 3577.3 (6) Å^3
Z = 8

F(000) = 1504
D_x = 1.320 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 2536 reflections
θ = 1.7–25.0°
μ = 0.20 mm^{-1}
T = 293 K
Block, colourless
0.35 × 0.30 × 0.25 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.932, T_{max} = 0.951

37913 measured reflections
3151 independent reflections
2536 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 25.0°, θ_{min} = 1.7°
h = −13→13
k = −15→15
l = −25→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.111
S = 1.12
3151 reflections
229 parameters

0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 3.6376P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ 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}
C6	0.1021 (2)	0.96898 (18)	0.15232 (10)	0.0414 (6)
C5	0.1663 (3)	1.0558 (2)	0.16587 (11)	0.0554 (8)
H2	0.2488	1.0549	0.1644	0.067*
C4	0.1082 (4)	1.1428 (2)	0.18133 (13)	0.0682 (9)
H3	0.1516	1.2001	0.1908	0.082*
C3	−0.0133 (4)	1.1458 (2)	0.18285 (13)	0.0661 (9)
H4	−0.0524	1.2051	0.1928	0.079*
C2	−0.0774 (3)	1.0602 (2)	0.16959 (11)	0.0532 (7)
H5	−0.1599	1.0627	0.1704	0.064*
C1	−0.0216 (2)	0.96998 (17)	0.15496 (9)	0.0387 (6)
C9	−0.0973 (2)	0.87834 (17)	0.14347 (9)	0.0349 (5)
H7	−0.1701	0.8994	0.1244	0.042*
C8	−0.0406 (2)	0.79039 (17)	0.11168 (9)	0.0339 (5)
C7	0.0803 (2)	0.76400 (18)	0.13613 (10)	0.0396 (6)
H9A	0.1108	0.7038	0.1179	0.048*
H9B	0.0713	0.7489	0.1754	0.048*
C12	−0.0283 (2)	0.80429 (18)	0.04923 (10)	0.0402 (6)
C13	−0.1085 (4)	0.8784 (3)	−0.03165 (13)	0.1103 (17)
H11A	−0.0351	0.9079	−0.0439	0.165*
H11B	−0.1734	0.9211	−0.0425	0.165*
H11C	−0.1179	0.8128	−0.0483	0.165*
C11	−0.1353 (2)	0.70812 (18)	0.12471 (10)	0.0405 (6)
H12	−0.2058	0.7209	0.1019	0.049*
C15	−0.0373 (2)	0.5505 (2)	0.15990 (12)	0.0485 (7)
H13	−0.0221	0.5846	0.1930	0.058*
C16	0.0011 (3)	0.4518 (2)	0.15331 (15)	0.0626 (9)
H14	0.0427	0.4197	0.1817	0.075*
C17	−0.0226 (3)	0.4015 (2)	0.10480 (16)	0.0698 (10)
H15	0.0041	0.3355	0.1000	0.084*
C18	−0.0850 (3)	0.4478 (2)	0.06366 (14)	0.0638 (8)
H16	−0.1015	0.4122	0.0312	0.077*
C19	−0.1248 (2)	0.5466 (2)	0.06874 (12)	0.0483 (7)

C20	−0.1961 (3)	0.5916 (3)	0.02205 (13)	0.0751 (10)
H18A	−0.1985	0.5450	−0.0086	0.113*
H18B	−0.1600	0.6538	0.0102	0.113*
H18C	−0.2755	0.6048	0.0347	0.113*
C14	−0.0983 (2)	0.59892 (18)	0.11741 (10)	0.0382 (6)
C10	−0.2337 (3)	0.8711 (2)	0.22232 (12)	0.0608 (8)
H20A	−0.2966	0.8737	0.1954	0.091*
H20B	−0.2167	0.9382	0.2353	0.091*
H20C	−0.2576	0.8295	0.2531	0.091*
N1	−0.12874 (18)	0.82867 (15)	0.19689 (8)	0.0399 (5)
O3	−0.1645 (2)	0.72567 (14)	0.18158 (8)	0.0649 (6)
O1	0.04071 (18)	0.75906 (16)	0.02133 (8)	0.0600 (5)
O2	−0.1069 (2)	0.86808 (17)	0.02891 (7)	0.0757 (7)
S1	0.18494 (6)	0.86516 (5)	0.12793 (3)	0.04623 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C6	0.0534 (15)	0.0403 (14)	0.0303 (13)	−0.0046 (12)	−0.0061 (11)	0.0067 (11)
C5	0.0688 (19)	0.0493 (17)	0.0482 (16)	−0.0181 (15)	−0.0132 (14)	0.0071 (13)
C4	0.105 (3)	0.0420 (18)	0.0574 (19)	−0.0220 (18)	−0.0143 (19)	−0.0011 (14)
C3	0.105 (3)	0.0359 (16)	0.0576 (19)	0.0024 (17)	−0.0008 (18)	−0.0053 (14)
C2	0.0725 (19)	0.0397 (15)	0.0472 (16)	0.0070 (14)	−0.0027 (14)	0.0022 (12)
C1	0.0539 (15)	0.0339 (13)	0.0282 (12)	0.0021 (11)	−0.0056 (11)	0.0023 (10)
C9	0.0377 (12)	0.0378 (13)	0.0293 (12)	0.0064 (10)	−0.0032 (10)	0.0017 (10)
C8	0.0361 (12)	0.0333 (12)	0.0325 (12)	0.0029 (10)	0.0010 (10)	−0.0002 (10)
C7	0.0386 (13)	0.0366 (13)	0.0436 (14)	0.0013 (11)	−0.0005 (11)	0.0016 (11)
C12	0.0456 (14)	0.0384 (14)	0.0364 (13)	−0.0014 (12)	0.0023 (12)	−0.0044 (11)
C13	0.171 (4)	0.129 (3)	0.0311 (17)	0.072 (3)	0.005 (2)	0.0142 (19)
C11	0.0380 (13)	0.0393 (13)	0.0441 (14)	0.0005 (11)	0.0040 (11)	−0.0018 (11)
C15	0.0466 (15)	0.0459 (16)	0.0531 (17)	−0.0084 (13)	−0.0029 (13)	0.0046 (13)
C16	0.0490 (16)	0.0498 (18)	0.089 (2)	0.0048 (14)	0.0027 (16)	0.0217 (17)
C17	0.067 (2)	0.0392 (16)	0.103 (3)	0.0065 (15)	0.025 (2)	−0.0020 (18)
C18	0.072 (2)	0.0492 (17)	0.070 (2)	−0.0109 (16)	0.0155 (17)	−0.0181 (16)
C19	0.0443 (15)	0.0470 (15)	0.0536 (17)	−0.0096 (12)	0.0025 (13)	−0.0044 (13)
C20	0.087 (2)	0.074 (2)	0.064 (2)	−0.0162 (19)	−0.0271 (19)	−0.0084 (17)
C14	0.0329 (12)	0.0365 (13)	0.0451 (14)	−0.0043 (10)	0.0030 (11)	−0.0009 (11)
C10	0.0687 (19)	0.0627 (19)	0.0510 (16)	0.0175 (16)	0.0203 (15)	0.0000 (14)
N1	0.0433 (11)	0.0410 (12)	0.0355 (11)	0.0055 (9)	0.0023 (9)	0.0018 (9)
O3	0.0916 (16)	0.0424 (11)	0.0607 (13)	−0.0102 (10)	0.0396 (12)	−0.0064 (9)
O1	0.0646 (12)	0.0726 (13)	0.0428 (11)	0.0123 (11)	0.0081 (10)	−0.0140 (10)
O2	0.1102 (18)	0.0868 (16)	0.0301 (10)	0.0516 (14)	0.0040 (11)	0.0056 (10)
S1	0.0383 (3)	0.0485 (4)	0.0519 (4)	−0.0047 (3)	−0.0019 (3)	0.0028 (3)

Geometric parameters (Å, º)

C6—C5	1.395 (4)	C13—H11B	0.9600
C6—C1	1.395 (4)	C13—H11C	0.9600

C6—S1	1.759 (3)	C11—O3	1.425 (3)
C5—C4	1.374 (4)	C11—C14	1.512 (3)
C5—H2	0.9300	C11—H12	0.9800
C4—C3	1.369 (5)	C15—C16	1.383 (4)
C4—H3	0.9300	C15—C14	1.387 (4)
C3—C2	1.379 (4)	C15—H13	0.9300
C3—H4	0.9300	C16—C17	1.368 (5)
C2—C1	1.392 (4)	C16—H14	0.9300
C2—H5	0.9300	C17—C18	1.359 (5)
C1—C9	1.506 (3)	C17—H15	0.9300
C9—N1	1.485 (3)	C18—C19	1.385 (4)
C9—C8	1.531 (3)	C18—H16	0.9300
C9—H7	0.9800	C19—C14	1.392 (4)
C8—C12	1.519 (3)	C19—C20	1.503 (4)
C8—C7	1.523 (3)	C20—H18A	0.9600
C8—C11	1.555 (3)	C20—H18B	0.9600
C7—S1	1.793 (2)	C20—H18C	0.9600
C7—H9A	0.9700	C10—N1	1.444 (3)
C7—H9B	0.9700	C10—H20A	0.9600
C12—O1	1.188 (3)	C10—H20B	0.9600
C12—O2	1.317 (3)	C10—H20C	0.9600
C13—O2	1.462 (3)	N1—O3	1.466 (3)
C13—H11A	0.9600		

C5—C6—C1	119.9 (3)	H11B—C13—H11C	109.5
C5—C6—S1	116.4 (2)	O3—C11—C14	109.3 (2)
C1—C6—S1	123.51 (19)	O3—C11—C8	103.74 (19)
C4—C5—C6	120.3 (3)	C14—C11—C8	117.02 (19)
C4—C5—H2	119.9	O3—C11—H12	108.8
C6—C5—H2	119.9	C14—C11—H12	108.8
C3—C4—C5	120.5 (3)	C8—C11—H12	108.8
C3—C4—H3	119.8	C16—C15—C14	120.4 (3)
C5—C4—H3	119.8	C16—C15—H13	119.8
C4—C3—C2	119.5 (3)	C14—C15—H13	119.8
C4—C3—H4	120.2	C17—C16—C15	119.6 (3)
C2—C3—H4	120.2	C17—C16—H14	120.2
C3—C2—C1	121.6 (3)	C15—C16—H14	120.2
C3—C2—H5	119.2	C18—C17—C16	120.2 (3)
C1—C2—H5	119.2	C18—C17—H15	119.9
C2—C1—C6	118.1 (2)	C16—C17—H15	119.9
C2—C1—C9	118.6 (2)	C17—C18—C19	121.8 (3)
C6—C1—C9	123.3 (2)	C17—C18—H16	119.1
N1—C9—C1	109.36 (18)	C19—C18—H16	119.1
N1—C9—C8	101.30 (18)	C18—C19—C14	118.2 (3)
C1—C9—C8	117.7 (2)	C18—C19—C20	118.7 (3)
N1—C9—H7	109.3	C14—C19—C20	123.1 (3)
C1—C9—H7	109.3	C19—C20—H18A	109.5
C8—C9—H7	109.3	C19—C20—H18B	109.5

C12—C8—C7	109.1 (2)	H18A—C20—H18B	109.5
C12—C8—C9	116.09 (19)	C19—C20—H18C	109.5
C7—C8—C9	110.75 (19)	H18A—C20—H18C	109.5
C12—C8—C11	110.23 (19)	H18B—C20—H18C	109.5
C7—C8—C11	112.07 (19)	C15—C14—C19	119.7 (2)
C9—C8—C11	98.24 (18)	C15—C14—C11	119.4 (2)
C8—C7—S1	111.98 (16)	C19—C14—C11	120.8 (2)
C8—C7—H9A	109.2	N1—C10—H20A	109.5
S1—C7—H9A	109.2	N1—C10—H20B	109.5
C8—C7—H9B	109.2	H20A—C10—H20B	109.5
S1—C7—H9B	109.2	N1—C10—H20C	109.5
H9A—C7—H9B	107.9	H20A—C10—H20C	109.5
O1—C12—O2	123.6 (2)	H20B—C10—H20C	109.5
O1—C12—C8	123.8 (2)	C10—N1—O3	104.0 (2)
O2—C12—C8	112.5 (2)	C10—N1—C9	112.9 (2)
O2—C13—H11A	109.5	O3—N1—C9	104.98 (17)
O2—C13—H11B	109.5	C11—O3—N1	109.19 (17)
H11A—C13—H11B	109.5	C12—O2—C13	115.9 (2)
O2—C13—H11C	109.5	C6—S1—C7	101.32 (12)
H11A—C13—H11C	109.5		

C1—C6—C5—C4	−0.6 (4)	C9—C8—C11—O3	−40.3 (2)
S1—C6—C5—C4	175.2 (2)	C12—C8—C11—C14	77.5 (3)
C6—C5—C4—C3	−0.9 (5)	C7—C8—C11—C14	−44.3 (3)
C5—C4—C3—C2	1.0 (5)	C9—C8—C11—C14	−160.7 (2)
C4—C3—C2—C1	0.5 (5)	C14—C15—C16—C17	−0.7 (4)
C3—C2—C1—C6	−2.0 (4)	C15—C16—C17—C18	−1.0 (5)
C3—C2—C1—C9	177.3 (2)	C16—C17—C18—C19	1.1 (5)
C5—C6—C1—C2	2.0 (4)	C17—C18—C19—C14	0.6 (4)
S1—C6—C1—C2	−173.48 (18)	C17—C18—C19—C20	−178.4 (3)
C5—C6—C1—C9	−177.2 (2)	C16—C15—C14—C19	2.3 (4)
S1—C6—C1—C9	7.3 (3)	C16—C15—C14—C11	−177.7 (2)
C2—C1—C9—N1	−82.6 (3)	C18—C19—C14—C15	−2.2 (4)
C6—C1—C9—N1	96.7 (3)	C20—C19—C14—C15	176.6 (3)
C2—C1—C9—C8	162.6 (2)	C18—C19—C14—C11	177.8 (2)
C6—C1—C9—C8	−18.1 (3)	C20—C19—C14—C11	−3.3 (4)
N1—C9—C8—C12	163.35 (19)	O3—C11—C14—C15	−34.3 (3)
C1—C9—C8—C12	−77.5 (3)	C8—C11—C14—C15	83.1 (3)
N1—C9—C8—C7	−71.5 (2)	O3—C11—C14—C19	145.6 (2)
C1—C9—C8—C7	47.7 (3)	C8—C11—C14—C19	−96.9 (3)
N1—C9—C8—C11	46.0 (2)	C1—C9—N1—C10	86.3 (3)
C1—C9—C8—C11	165.10 (19)	C8—C9—N1—C10	−148.7 (2)
C12—C8—C7—S1	64.2 (2)	C1—C9—N1—O3	−161.01 (19)
C9—C8—C7—S1	−64.8 (2)	C8—C9—N1—O3	−36.0 (2)
C11—C8—C7—S1	−173.41 (16)	C14—C11—O3—N1	145.05 (19)
C7—C8—C12—O1	32.1 (3)	C8—C11—O3—N1	19.5 (2)
C9—C8—C12—O1	158.1 (2)	C10—N1—O3—C11	129.1 (2)
C11—C8—C12—O1	−91.4 (3)	C9—N1—O3—C11	10.3 (2)

C7—C8—C12—O2	−151.3 (2)	O1—C12—O2—C13	2.2 (5)
C9—C8—C12—O2	−25.3 (3)	C8—C12—O2—C13	−174.4 (3)
C11—C8—C12—O2	85.2 (3)	C5—C6—S1—C7	163.25 (19)
C12—C8—C11—O3	−162.1 (2)	C1—C6—S1—C7	−21.1 (2)
C7—C8—C11—O3	76.1 (2)	C8—C7—S1—C6	48.96 (19)