Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl 4-[5-(4-fluorophenyl)-4-(pyridin-4-yl)-1*H*-imidazol-2-ylsulfanyl]butanoate

Pierre Koch,[a] Christiane Bäuerlein,[a] Dieter Schollmeyer[b] and Stefan Laufer[a]*

[a]Institute of Pharmacy, Department of Pharmaceutical and Medicinal Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany, and [b]Department of Organic Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55099 Mainz, Germany
Correspondence e-mail: stefan.laufer@uni-tuebingen.de

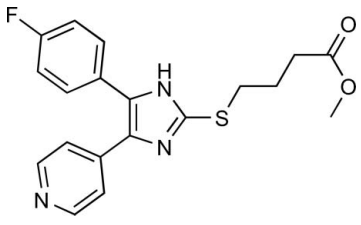
Received 17 April 2008; accepted 27 May 2008

Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.006 Å; R factor = 0.076; wR factor = 0.189; data-to-parameter ratio = 13.1.

The title compound, $C_{19}H_{18}FN_3O_2S$, was synthesized in the course of studies on 2-alkylsufanylimidazoles as p38 mitogen-activated protein kinase inhibitors. The synthesis was achieved by nucleophilic substitution of 4-(4-fluorophenyl)-5-(pyridin-4-yl)-1,3-dihydroimidazole-2-thione with methyl 4-bromobutanoate. The five-membered heterocycle makes dihedral angles of 32.4 (2) and 18.3 (2)° with the fluorophenyl and pyridinyl rings, respectively, indicating a low degree of conjugation between these rings. Intramolecular C—H···N and intermolecular N—H···N hydrogen bonds as well as C—H···π interactions seem to be effective in stabilization of the crystal structure.

Related literature

Substituted imidazoles as small-molecule inhibitors of p38 MAP kinase have been reviewed by Peifer *et al.* (2006) and Wagner & Laufer (2006). For the preparation of 4-(4-fluorophenyl)-5-(pyridin-4-yl)-1,3-dihydroimidazole-2-thione, see: Lantos *et al.* (1988). For related literature, see: Laufer, Striegel & Wagner (2002); Laufer, Wagner & Kotschenreuther (2002); Laufer & Koch (2008); Wang *et al.* (1998); Peifer *et al.* (2007).



Experimental

Crystal data

$C_{19}H_{18}FN_3O_2S$
M_r = 371.42
Orthorhombic, $Pca2_1$
a = 18.494 (4) Å
b = 12.4367 (10) Å
c = 7.5255 (5) Å
V = 1730.9 (4) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.92 mm^{-1}
T = 193 (2) K
0.55 × 0.12 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: Gaussian (*PLATON*; Spek, 2003)
T_{min} = 0.61, T_{max} = 0.85
3363 measured reflections
3086 independent reflections
2869 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.188
S = 1.14
3086 reflections
236 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 e Å^{-3}
Absolute structure: Flack (1983), 1307 Friedel pairs
Flack parameter: −0.02 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5···N17^{i}	0.90	1.95	2.849 (4)	174

Symmetry code: (i) $x+\frac{1}{2}, -y+1, z$.

Table 2
Nonconventional C—H···X contacts (Å, °).

C–H···A	C–H	H···A	C–H···A	C···A
C13–H13B···$Cg1^{ii}$	0.98	2.65	156	3.566 (6)
C7–H7A···N2	0.99	2.57	100	2.910 (5)

Symmetry code: (ii) $x, y-1, z$. $Cg1$ is the centroid of the C20–C25 ring.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the EU, part of the EU-Craft Programme, Framework Project 6 'MACROCEPT'.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2140).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Dräger, M. & Gattow, G. (1971). *Acta Chem. Scand.* **25**, 761–762.
Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Lantos, I., Gombatz, K., McGuire, M., Pridgen, L., Remich, J. & Shilcrat, S. (1988). *J. Org. Chem.* **53**, 4223–4227.
Laufer, S. & Koch, P. (2008). *Org. Biomol. Chem.* **6**, 437–439.
Laufer, S. A., Striegel, H.-G. & Wagner, G. K. (2002). *J. Med. Chem.* **45**, 4695–4705.
Laufer, S., Wagner, G. & Kotschenreuther, D. (2002). *Angew. Chem. Int. Ed.* **41**, 2290–2293.
Peifer, C., Kinkel, K., Abadleh, M., Schollmeyer, D. & Laufer, S. (2007). *J. Med. Chem.* **50**, 1213–1221.
Peifer, C., Wagner, G. & Laufer, S. (2006). *Curr. Top. Med. Chem.* **6**, 113–149.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Wagner, G. & Laufer, S. (2006). *Med. Res. Rev.* **26**, 1–62.
Wang, Z., Canagarajah, B. J., Boehm, J. C., Kassisa, S., Cobb, M. H., Young, P. R., Abdel-Meguid, S., Adams, J. L. & Goldsmith, E. J. (1998). *Structure*, **6**, 1117–1128.

supplementary materials

Acta Cryst. (2008). E**64**, o1183-o1184 [**doi:10.1107/S1600536808016000**]

Methyl 4-[5-(4-fluorophenyl)-4-(pyridin-4-yl)-1*H*-imidazol-2-ylsulfanyl]butanoate

P. Koch, C. Bäuerlein, D. Schollmeyer and S. Laufer

Comment

The title compound was prepared in the course of our studies on 2-alkylsulfanyl-4-(4-fluorophenyl)-5-pyridinyl imidazoles as p38 mitogen-activated protein (MAP) kinase inhibitors. The p38 MAP kinase plays a central role for the biosynthesis and release of pro-inflammatory cytokines like TNF-α and IL-1β. Inhibition of p38 MAP kinase is therefore a promising therapeutic strategy for the treatment of inflammatory disorders like psoriasis, inflammatory bowel disease and rheumatoid arthritis. The fundamental SAR for the class of pyridinyl imidazole derivative as p38 MAP kinase inhibitors can be exemplified by the way SB203580 binds to the protein (Wang *et al.*, 1998). There is a crucial hydrogen bond between the pyridin-4-yl moiety and Met109 of the enzyme. The 4-fluorophenyl ring binds to the hydrophobic region I, mainly gaining selectivity. Another possible ligand-protein interaction is a hydrogen bond between Lys53 and N3 of the imidazole core (Peifer *et al.,* 2007).

The analysis of the crystal structure of methyl 4-(5-(4-fluorophenyl)-4-(pyridin-4-yl)-1*H*-imidazol-2-ylthio)butanoate (**I**) is shown in Figure 1. The crystal packing (Figure 2) shows that N5—H5 of the imidazole ring forms an intermolecular N–H···N hydrogen bond to pyridine (N17). The length of the hydrogen bond is 1.95Å (Table 1). Non-conventional C—H···*X* H-bonds are also present in addition to intermolecular N—H···N hydrogen interactions (Table 2).

Experimental

To a stirred solution of 4-(4-fluorophenyl)-5-(pyridin-4-yl)-1,3-dihydroimidazole-2-thione (0.74 mmol) and potassium *tert*-butoxide (0.77 mmol) in dry methanol (15 ml) was added under argon atmosphere after 15 min metyl 4-bromobutanoate (0.77 mmol). The solution was heated for 1 h to reflux temperature. After extraction with water and ethyl acetate the organic layer was washed twice with water, dried over sodium sulfate and evaporated under reduced pressure. The crude product was purified by flash chromatography (silica gel, dichloromethane - ethyl acetate 1:1 to 2:3) to yield methyl 4-(5-(4-fluorophenyl)-4-(pyridin-4-yl)-1*H*-imidazol-2-ylthio)butanoate (**I**) (49%) as a colorless solid. Compound **I** was crystallized from methanol.

Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95Å (aromatic) or 0.98–0.99 Å (sp^3 C-atom). H-atom bonded to N5 was located from a difference Fourier map (N—H = 0.9 Å). All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the U_{eq} of the parent atom).

Figures

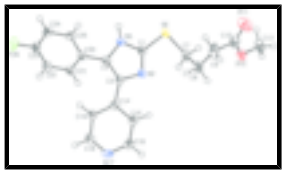


Fig. 1. View of compound **I**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are depicted as circles of arbitrary size.

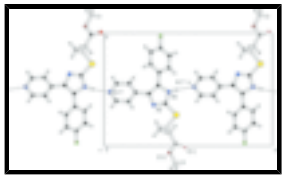


Fig. 2. Part of the crystal packing of compound **I**. The hydrogen bond is shown with dashed lines. View along *c* axis. N17_b:*x* + 1/2, 1 - *y*, *z*

Methyl 4-[5-(4-fluorophenyl)-4-(pyridin-4-yl)-1*H*-imidazol-2-ylsulfanyl]butanoate

Crystal data

$C_{19}H_{18}FN_3O_2S$	F_{000} = 776
M_r = 371.42	D_x = 1.425 Mg m^{-3}
Orthorhombic, *Pca*2$_1$	Cu *K*α radiation λ = 1.54178 Å
Hall symbol: P 2c -2ac	Cell parameters from 25 reflections
a = 18.494 (4) Å	θ = 31–44º
b = 12.4367 (10) Å	μ = 1.92 mm^{-1}
c = 7.5255 (5) Å	*T* = 193 (2) K
V = 1730.9 (4) Å^3	Needle, colourless
Z = 4	0.55 × 0.12 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.051
Monochromator: graphite	θ_{max} = 70.0º
T = 193(2) K	θ_{min} = 3.6º
ω/2θ scans	*h* = −22→22
Absorption correction: gaussian (PLATON; Spek, 2003)	*k* = −15→15
T_{min} = 0.61, T_{max} = 0.85	*l* = −7→9
3363 measured reflections	3 standard reflections
3086 independent reflections	every 60 min
2869 reflections with $I > 2\sigma(I)$	intensity decay: 5%

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.076	$w = 1/[\sigma^2(F_o^2) + (0.1374P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.188$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.14$	$\Delta\rho_{max} = 1.14$ e Å^{-3}
3086 reflections	$\Delta\rho_{min} = -0.60$ e Å^{-3}
236 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 1307 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.02 (3)
Secondary atom site location: difference Fourier map	

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}
C1	0.3643 (2)	0.3750 (3)	0.3172 (5)	0.0204 (8)
N2	0.29502 (16)	0.3630 (3)	0.3227 (4)	0.0203 (7)
C3	0.26668 (19)	0.4629 (3)	0.2819 (5)	0.0179 (7)
C4	0.32215 (19)	0.5351 (3)	0.2524 (5)	0.0183 (8)
N5	0.38455 (15)	0.4764 (2)	0.2738 (4)	0.0173 (6)
H5	0.4314	0.4967	0.2711	0.021*
S6	0.42920 (5)	0.27420 (8)	0.35250 (18)	0.0298 (3)
C7	0.3694 (2)	0.1589 (3)	0.3710 (7)	0.0300 (9)
H7A	0.3312	0.1650	0.2796	0.036*
H7B	0.3975	0.0929	0.3456	0.036*
C8	0.3338 (2)	0.1474 (4)	0.5527 (8)	0.0371 (12)
H8A	0.2967	0.0901	0.5463	0.044*
H8B	0.3089	0.2155	0.5825	0.044*
C9	0.3870 (3)	0.1202 (4)	0.7011 (8)	0.0451 (13)
H9A	0.4239	0.1778	0.7061	0.054*
H9B	0.3604	0.1214	0.8153	0.054*
C10	0.4252 (2)	0.0150 (4)	0.6867 (7)	0.0360 (11)
O11	0.4808 (2)	−0.0057 (4)	0.7602 (7)	0.0621 (12)
O12	0.38975 (17)	−0.0571 (2)	0.5875 (5)	0.0368 (8)
C13	0.4252 (3)	−0.1576 (4)	0.5589 (7)	0.0413 (12)
H13A	0.4738	−0.1447	0.5115	0.062*
H13B	0.3973	−0.2004	0.4737	0.062*
H13C	0.4288	−0.1965	0.6717	0.062*

C14	0.1875 (2)	0.4721 (3)	0.2746 (5)	0.0189 (7)
C15	0.14573 (19)	0.3934 (3)	0.3609 (6)	0.0225 (7)
H15	0.1684	0.3374	0.4260	0.027*
C16	0.07186 (19)	0.3987 (3)	0.3501 (7)	0.0267 (8)
H16	0.0447	0.3439	0.4076	0.032*
N17	0.03515 (16)	0.4759 (3)	0.2637 (6)	0.0270 (8)
C18	0.0753 (2)	0.5502 (3)	0.1816 (6)	0.0244 (9)
H18	0.0509	0.6056	0.1186	0.029*
C19	0.14979 (19)	0.5514 (3)	0.1825 (5)	0.0201 (7)
H19	0.1753	0.6061	0.1207	0.024*
C20	0.32620 (18)	0.6506 (3)	0.2109 (5)	0.0185 (8)
C21	0.2750 (2)	0.7236 (3)	0.2741 (6)	0.0217 (8)
H21	0.2373	0.6988	0.3493	0.026*
C22	0.2782 (2)	0.8313 (3)	0.2294 (6)	0.0261 (9)
H22	0.2423	0.8801	0.2704	0.031*
C23	0.3342 (2)	0.8664 (3)	0.1244 (6)	0.0274 (9)
C24	0.3875 (2)	0.7984 (4)	0.0657 (6)	0.0267 (9)
H24	0.4265	0.8252	−0.0032	0.032*
C25	0.38349 (19)	0.6910 (3)	0.1081 (6)	0.0220 (8)
H25	0.4201	0.6434	0.0672	0.026*
F26	0.33578 (16)	0.9714 (2)	0.0773 (4)	0.0405 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0269 (17)	0.0264 (18)	0.008 (2)	0.0036 (14)	−0.0006 (13)	0.0032 (14)
N2	0.0239 (14)	0.0260 (15)	0.0110 (19)	0.0029 (11)	0.0001 (12)	−0.0007 (12)
C3	0.0263 (18)	0.0242 (17)	0.0031 (17)	0.0023 (13)	0.0009 (14)	−0.0015 (14)
C4	0.0211 (16)	0.032 (2)	0.0019 (18)	0.0020 (14)	0.0004 (13)	−0.0021 (14)
N5	0.0177 (13)	0.0271 (16)	0.0072 (15)	0.0012 (11)	−0.0002 (12)	−0.0022 (12)
S6	0.0229 (5)	0.0303 (5)	0.0362 (7)	0.0068 (3)	0.0024 (4)	0.0086 (4)
C7	0.037 (2)	0.0238 (18)	0.029 (3)	0.0044 (15)	−0.005 (2)	0.0005 (17)
C8	0.039 (2)	0.033 (2)	0.039 (3)	0.0064 (18)	0.011 (2)	0.013 (2)
C9	0.078 (4)	0.033 (2)	0.024 (3)	0.004 (2)	0.005 (3)	0.002 (2)
C10	0.045 (3)	0.037 (2)	0.026 (3)	−0.0026 (18)	0.002 (2)	0.004 (2)
O11	0.059 (2)	0.061 (2)	0.067 (3)	0.009 (2)	−0.027 (2)	−0.019 (2)
O12	0.0440 (17)	0.0313 (16)	0.035 (2)	0.0030 (12)	−0.0122 (15)	0.0029 (15)
C13	0.060 (3)	0.035 (2)	0.029 (3)	0.008 (2)	−0.014 (2)	0.002 (2)
C14	0.0255 (17)	0.0277 (17)	0.0036 (17)	−0.0002 (14)	0.0021 (14)	−0.0047 (14)
C15	0.0294 (17)	0.0239 (16)	0.014 (2)	0.0004 (14)	0.0036 (18)	−0.0007 (15)
C16	0.0281 (18)	0.0265 (18)	0.025 (2)	−0.0021 (14)	0.0060 (18)	−0.0044 (19)
N17	0.0193 (14)	0.0349 (18)	0.027 (2)	−0.0003 (13)	−0.0008 (13)	−0.0080 (15)
C18	0.033 (2)	0.031 (2)	0.010 (2)	0.0058 (15)	−0.0052 (16)	−0.0029 (17)
C19	0.0266 (18)	0.0275 (17)	0.006 (2)	−0.0008 (14)	0.0003 (14)	−0.0004 (15)
C20	0.0224 (17)	0.0276 (18)	0.0055 (18)	−0.0017 (13)	−0.0034 (13)	−0.0007 (14)
C21	0.0266 (18)	0.031 (2)	0.0076 (18)	0.0008 (14)	−0.0018 (15)	0.0005 (15)
C22	0.034 (2)	0.0285 (19)	0.016 (2)	0.0043 (16)	−0.0011 (16)	−0.0031 (16)
C23	0.037 (2)	0.0259 (19)	0.020 (2)	−0.0043 (15)	−0.0059 (17)	0.0033 (16)

C24	0.031 (2)	0.036 (2)	0.013 (2)	−0.0078 (16)	−0.0001 (15)	0.0056 (17)
C25	0.0221 (17)	0.0320 (19)	0.012 (2)	−0.0004 (14)	0.0006 (15)	−0.0026 (16)
F26	0.0596 (17)	0.0272 (12)	0.0346 (18)	−0.0027 (11)	0.0013 (13)	0.0072 (11)

Geometric parameters (Å, °)

C1—N2	1.290 (5)	C13—H13B	0.9800
C1—N5	1.356 (5)	C13—H13C	0.9800
C1—S6	1.756 (4)	C14—C19	1.392 (5)
N2—C3	1.384 (5)	C14—C15	1.405 (5)
C3—C4	1.381 (5)	C15—C16	1.370 (5)
C3—C14	1.470 (5)	C15—H15	0.9500
C4—N5	1.375 (5)	C16—N17	1.344 (6)
C4—C20	1.471 (5)	C16—H16	0.9500
N5—H5	0.9032	N17—C18	1.336 (6)
S6—C7	1.816 (4)	C18—C19	1.378 (5)
C7—C8	1.525 (7)	C18—H18	0.9500
C7—H7A	0.9900	C19—H19	0.9500
C7—H7B	0.9900	C20—C21	1.395 (5)
C8—C9	1.527 (8)	C20—C25	1.405 (5)
C8—H8A	0.9900	C21—C22	1.383 (5)
C8—H8B	0.9900	C21—H21	0.9500
C9—C10	1.491 (6)	C22—C23	1.374 (6)
C9—H9A	0.9900	C22—H22	0.9500
C9—H9B	0.9900	C23—F26	1.354 (5)
C10—O11	1.196 (6)	C23—C24	1.371 (6)
C10—O12	1.339 (6)	C24—C25	1.375 (6)
O12—C13	1.427 (6)	C24—H24	0.9500
C13—H13A	0.9800	C25—H25	0.9500
N2—C1—N5	113.0 (3)	H13A—C13—H13B	109.5
N2—C1—S6	126.2 (3)	O12—C13—H13C	109.5
N5—C1—S6	120.7 (3)	H13A—C13—H13C	109.5
C1—N2—C3	105.3 (3)	H13B—C13—H13C	109.5
C4—C3—N2	109.8 (3)	C19—C14—C15	116.6 (3)
C4—C3—C14	133.1 (3)	C19—C14—C3	124.9 (3)
N2—C3—C14	117.1 (3)	C15—C14—C3	118.4 (3)
N5—C4—C3	105.0 (3)	C16—C15—C14	119.2 (4)
N5—C4—C20	120.0 (3)	C16—C15—H15	120.4
C3—C4—C20	134.9 (3)	C14—C15—H15	120.4
C1—N5—C4	106.9 (3)	N17—C16—C15	124.5 (4)
C1—N5—H5	122.1	N17—C16—H16	117.8
C4—N5—H5	130.9	C15—C16—H16	117.8
C1—S6—C7	99.14 (18)	C18—N17—C16	115.9 (3)
C8—C7—S6	114.0 (3)	N17—C18—C19	124.1 (4)
C8—C7—H7A	108.8	N17—C18—H18	117.9
S6—C7—H7A	108.8	C19—C18—H18	117.9
C8—C7—H7B	108.8	C18—C19—C14	119.7 (4)
S6—C7—H7B	108.8	C18—C19—H19	120.2
H7A—C7—H7B	107.7	C14—C19—H19	120.2

C7—C8—C9	113.4 (4)	C21—C20—C25	117.8 (4)
C7—C8—H8A	108.9	C21—C20—C4	121.9 (3)
C9—C8—H8A	108.9	C25—C20—C4	120.3 (3)
C7—C8—H8B	108.9	C22—C21—C20	121.3 (4)
C9—C8—H8B	108.9	C22—C21—H21	119.4
H8A—C8—H8B	107.7	C20—C21—H21	119.4
C10—C9—C8	116.6 (4)	C23—C22—C21	118.7 (4)
C10—C9—H9A	108.2	C23—C22—H22	120.7
C8—C9—H9A	108.2	C21—C22—H22	120.7
C10—C9—H9B	108.2	F26—C23—C24	119.7 (4)
C8—C9—H9B	108.2	F26—C23—C22	118.3 (4)
H9A—C9—H9B	107.3	C24—C23—C22	122.1 (4)
O11—C10—O12	122.4 (5)	C23—C24—C25	119.1 (4)
O11—C10—C9	124.3 (5)	C23—C24—H24	120.5
O12—C10—C9	113.3 (4)	C25—C24—H24	120.5
C10—O12—C13	116.5 (4)	C24—C25—C20	121.0 (4)
O12—C13—H13A	109.5	C24—C25—H25	119.5
O12—C13—H13B	109.5	C20—C25—H25	119.5
N5—C1—N2—C3	−0.5 (4)	N2—C3—C14—C15	19.8 (5)
S6—C1—N2—C3	−178.3 (3)	C19—C14—C15—C16	0.1 (6)
C1—N2—C3—C4	−0.2 (4)	C3—C14—C15—C16	−177.7 (4)
C1—N2—C3—C14	178.7 (3)	C14—C15—C16—N17	−1.2 (7)
N2—C3—C4—N5	0.8 (4)	C15—C16—N17—C18	1.3 (7)
C14—C3—C4—N5	−177.8 (4)	C16—N17—C18—C19	−0.4 (6)
N2—C3—C4—C20	−177.7 (4)	N17—C18—C19—C14	−0.5 (6)
C14—C3—C4—C20	3.6 (7)	C15—C14—C19—C18	0.7 (6)
N2—C1—N5—C4	1.0 (4)	C3—C14—C19—C18	178.3 (3)
S6—C1—N5—C4	179.0 (3)	N5—C4—C20—C21	−146.2 (4)
C3—C4—N5—C1	−1.1 (4)	C3—C4—C20—C21	32.2 (7)
C20—C4—N5—C1	177.7 (4)	N5—C4—C20—C25	32.5 (5)
N2—C1—S6—C7	5.7 (4)	C3—C4—C20—C25	−149.2 (4)
N5—C1—S6—C7	−172.0 (3)	C25—C20—C21—C22	3.4 (6)
C1—S6—C7—C8	−80.0 (3)	C4—C20—C21—C22	−177.9 (4)
S6—C7—C8—C9	−67.3 (4)	C20—C21—C22—C23	−1.7 (6)
C7—C8—C9—C10	−63.6 (6)	C21—C22—C23—F26	178.2 (4)
C8—C9—C10—O11	158.8 (6)	C21—C22—C23—C24	−1.2 (7)
C8—C9—C10—O12	−23.6 (6)	F26—C23—C24—C25	−177.2 (4)
O11—C10—O12—C13	−6.0 (8)	C22—C23—C24—C25	2.2 (7)
C9—C10—O12—C13	176.3 (4)	C23—C24—C25—C20	−0.4 (6)
C4—C3—C14—C19	20.7 (7)	C21—C20—C25—C24	−2.4 (6)
N2—C3—C14—C19	−157.8 (4)	C4—C20—C25—C24	178.9 (4)
C4—C3—C14—C15	−161.6 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5···N17^{i}	0.90	1.95	2.849 (4)	174

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

Table 2
Nonconventional C–H···X contacts (Å, °).

C–H···A	C–H	H···A	C–H···A	C···A
C13–H13B···Cg1^{ii}	0.98	2.65	156	3.566 (6)
C7–H7A···N2	0.99	2.57	100	2.910 (5)

Symmetry code: (ii) x, y-1, z. Cg1 is the centroid of the C20–C25 ring.

Fig. 1

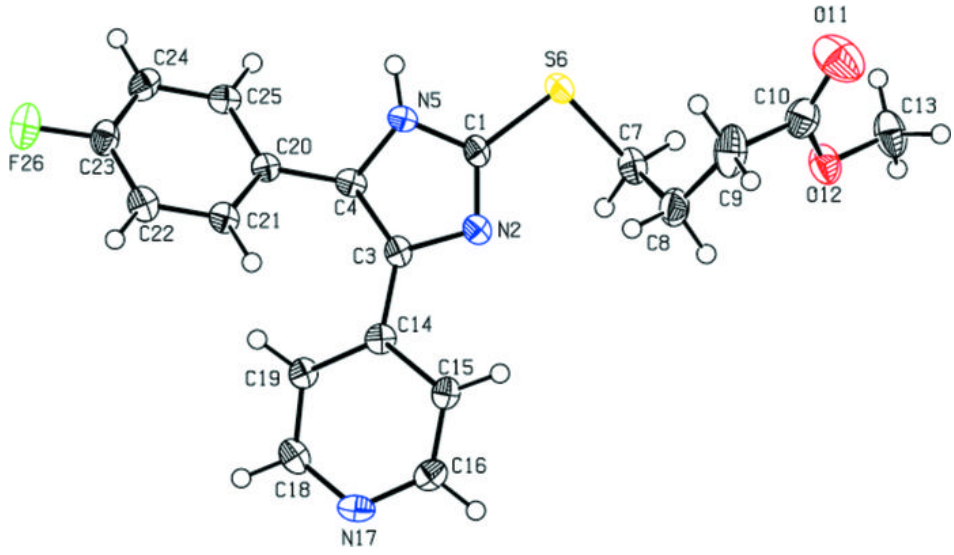

O11
C24
S6
C25
N5
C10
C13
C1
C7
F26
C23
C20
C4
C9
O12
C21
N2
C22
C3
C8
C14
C19
C15
C16
C18
N17

Fig. 2