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2-[4-(2-Fluorophenyl)piperazin-1-ylmethyl]-4,6-dimethylisothiazolo[5,4-*b*]pyridin-3(2*H*)-one

Zbigniew Karczmarzyk[a]* and Wiesław Malinka[b]

[a]Department of Chemistry, University of Podlasie, ul. 3 Maja 54, 08-110 Siedlce, Poland, and [b]Department of Chemistry of Drugs, Wrocław Medical University, ul. Tamka 1, 50-137 Wrocław, Poland
Correspondence e-mail: kar@ap.siedlce.pl

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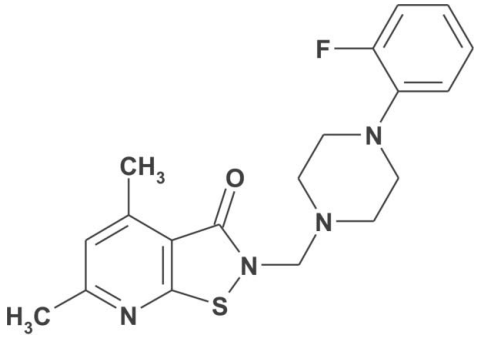
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.058; wR factor = 0.208; data-to-parameter ratio = 17.1.

In the title molecule, $C_{19}H_{21}FN_4OS$, the piperazine ring adopts a chair conformation. A conjugation effect of the lone pair of the tertiary N atom with the π-electron system of the fluorophenyl ring is diminished by the steric effect of the 2-F substituent. The crystal structure contains short intermolecular C—H$\cdots X$ (X = N, O) contacts and π–π interactions [with a ring centroid-to-centroid separation of 3.5908 (18) Å].

Related literature

For background information, see Malinka *et al.* (2005). For structure interpretation tools, see: Allen *et al.* (1987); Cremer & Pople (1975); Nardelli (1983); Spek (2003). For related structures, see: Karczmarzyk & Malinka (1998, 2004, 2005).



Experimental

Crystal data

$C_{19}H_{21}FN_4OS$
M_r = 372.46
Monoclinic, $P2_1/n$
a = 8.118 (1) Å
b = 10.551 (2) Å
c = 22.054 (2) Å
β = 92.13 (1)°
V = 1887.7 (5) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.74 mm^{-1}
T = 293 (2) K
0.35 × 0.20 × 0.10 mm

Data collection

Kuma KM-4 four-circle diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.582, T_{max} = 0.842
4806 measured reflections
4034 independent reflections
2273 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
2 standard reflections
every 100 reflections
intensity decay: 0.3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.208
S = 0.98
4034 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C33—H331$\cdots$N7^{i}	0.93	2.60	3.486 (5)	160
C36—H361$\cdots$O3^{ii}	0.93	2.34	3.240 (4)	161

Symmetry codes: (i) $-x+\frac{5}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *KM4B8* (Gałdecki *et al.*, 1996); cell refinement: *KM4B8*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1995); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2454).

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supplementary materials

Acta Cryst. (2007). E**63**, o3514 [**doi:10.1107/S1600536807033971**]

2-[4-(2-Fluorophenyl)piperazin-1-ylmethyl]-4,6-dimethylisothiazolo[5,4-*b*]pyridin-3(2*H*)-one

Z. Karczmarzyk and W. Malinka

Comment

Recently we described synthesis, structure, conformation and analgesic action of a series of derivatives of 2-(4-arylpiperazin-1-ylmethyl)isothiazolo[5,4-*b*]pyridin-3(2*H*)-one (Malinka *et al.*, 2005). In our SAR studies we found that the potency of the analgesic effect is highly influenced by the nature of the substituent present at aromatic ring of the 4-arylpiperazine substructure. The best analgesic results were obtained for phenylpiperazine derivatives of isothiazolopyridine with electron-withdrawing substituents (*o*-Cl, *o*-F, *p*-NO_2, *m*-CF_3), while the derivatives with *o*-electron-donating groups (*o*-OCH_3, *o*-CH_3) and compound with unsubstituted phenyl ring were inactive in the analgesic tests. As a continuation of our investigations, in this paper we report the results of the X-ray structure determination of title compound which proved to be the most active as an analgesic agent in the analyzed series of arylpiperazine derivatives of isothiazolopyridine.

The bond lengths and angles do not differ significantly from those reported for other related structures (*e.g.* Karczmarzyk & Malinka, 2005). The pyridine and isothiazole rings are planar to within 0.005 (3) and 0.029 (3) Å, respectively, and they are inclined at an angle of 0.96 (7)°.

The 4-(2-fluorophenyl)piperazin-1-ylmethyl substituent has a *cis-gauche-trans* conformation with the torsion angles S1—N2—C12—N21 of 25.7 (4)°, N2—C12—N21—C22 of 86.5 (4)° and N2—C12—N21—C26 of −146.9 (3)°. These torsion angles indicates a similar spatial orientation of the substituent in relation to the fused bicyclic system in the title compound and unsubstituted-phenylpiperazine derivative of isothiazolopyridine [the torsion angles are 24.5 (2), 77.9 (2) and −159.3 (2)°, respectively; Karczmarzyk & Malinka, 1998]. The piperazine ring adopts a chair conformation with puckering parameters of Q = 0.582 (4) Å and θ = 180.0 (4)° (Cremer & Pople, 1975). The N24—C31 bond length of 1.406 (4) Å, shorter than an average non-conjugated C_{ar}—N (Nsp^3, pyramidal) single bond of 1.426 (11) Å (Allen *et al.*, 1987), and the sum of the bond angles around N24 of 342.00° are typical for conjugation of the lone pair at N24 with the π system of the benzene ring. This conjugation is characteristic for *meta* and *para* electron-attracting substitution (Karczmarzyk & Malinka, 2005) and in the unsubstituted-phenylpiperazine system it is diminished by the steric effect of the 2-F group of the benzene ring. It is confirmed by the change of the dihedral angle between the mean planes of the aromatic and piperazine rings from 6.15 (6)° for the unsubstituted benzene ring in the phenylpiperazine derivative of isothiazolopyridine to 37.72 (13)° in the title compound. It is worthy to mention that this dihedral angle is close to 60° for other 2-substituted phenylpiperazine derivatives (Karczmarzyk & Malinka, 2004). In conclusion, the observed similarity of the structural features at crystals of the title compound and its unsubstituted analogue may suggest that within series of analgesic isothiazolopyridines fluorine does not resemble other halogens but mimics a hydrogen atom.

In the crystal structure, molecules are linked into chains parallel to [010] direction *via* short intermolecular C—H···*X* (*X* = N, O) contacts (Table 1; Spek, 2003; Nardelli, 1983). Additionally, pairs of pyridine rings belonging to inversion-related molecules overlap, with a centroid-to-centroid separation of 3.5908 (18) Å. The shortest intermolecular contact [$N7\cdots C4^{i}$ = 3.586 (4) Å; symmetry code: (i) = 1 − *x*, −*y*, −*z*] is characteristic of π···π interactions.

Experimental

The title compound was prepared from 2-hydroxymethyl-4,6-dimethylisothiazolo[5,4-*b*]pyridin-3(2*H*)-one and commercially available *N*-(2-fluorophenyl)piperazine, according to the method of Malinka *et al.* (2005). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a hexane solution of the title compound.

Refinement

All H atoms were located in a difference Fourier map and subsequently treated as riding with C—H distances of 0.93 (aromatic), 0.97 (CH_2) and 0.96 Å (CH_3) and $U_{iso} = 1.5U_{eq}$(C).

Figures

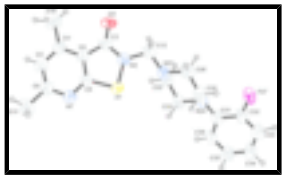

Fig. 1. A view of the title molecule showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

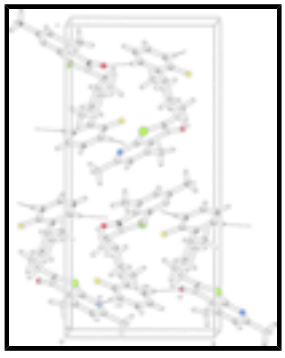

Fig. 2. The molecular packing of the title compound. Dashed lines indicate intermolecular hydrogen bonds.

2-[4-(2-Fluorophenyl)piperazin-1-ylmethyl]-4,6- dimethylisothiazolo[5,4-*b*]pyridin-3(2*H*)-one

Crystal data

$C_{19}H_{21}FN_4OS$	$F_{000} = 784$
$M_r = 372.46$	$D_x = 1.311$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation $\lambda = 1.54178$ Å
Hall symbol: -P 2yn	Cell parameters from 25 reflections
$a = 8.118$ (1) Å	$\theta = 20.6$–$39.7°$
$b = 10.551$ (2) Å	$\mu = 1.74$ mm^{-1}
$c = 22.054$ (2) Å	$T = 293$ (2) K
$\beta = 92.13$ (1)°	Prism, colourless
$V = 1887.7$ (5) Å^3	0.35 × 0.20 × 0.10 mm
$Z = 4$	

Data collection

Kuma KM-4 four-circle diffractometer	R_{int} = 0.038
Radiation source: fine-focus sealed tube	θ_{max} = 80.2º
Monochromator: graphite	θ_{min} = 4.0º
T = 293(2) K	h = −10→10
ω–2θ scans	k = −13→1
Absorption correction: ψ scan (North *et al.*, 1968)	l = −28→1
T_{min} = 0.582, T_{max} = 0.842	2 standard reflections
4806 measured reflections	every 100 reflections
4034 independent reflections	intensity decay: 0.3%
2273 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.058	$w = 1/[\sigma^2(F_o^2) + (0.1364P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.208	$(\Delta/\sigma)_{max} < 0.001$
S = 0.98	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
4034 reflections	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
236 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0028 (7)
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.

Weighted least-squares planes through the starred atoms (Nardelli, Musatti, Domiano & Andreetti Ric·Sci.(1965),15(II—A),807). Equation of the plane: m1*X+m2*Y+m3*Z=d

Plane 1 m1 = 0.39138(0.00077) m2 = −0.44517(0.00107) m3 = −0.80539(0.00071) D = −0.19003(0.00587) Atom d s d/s (d/s)**2 S1 * 0.0019 0.0008 2.259 5.103 N2 * −0.0253 0.0026 − 9.692 93.931 C3 * 0.0286 0.0031 9.244 85.443 C9 * −0.0035 0.0028 − 1.250 1.564 C8 * −0.0110 0.0027 − 4.097 16.782 C12 0.2009 0.0042 48.095 2313.111 O3 0.1087 0.0026 42.553 1810.724 ========== Sum((d/s)**2) for starred atoms 202.821 Chi-squared at 95% for 2 degrees of freedom: 5.99 The group of atoms deviates significantly from planarity

Plane 2 m1 = 0.40648(0.00105) m2 = −0.44475(0.00112) m3 = −0.79811(0.00082) D = −0.11803(0.00486) Atom d s d/s (d/s)**2 C4 * 0.0047 0.0031 1.512 2.285 C5 * −0.0029 0.0032 − 0.891 0.795 C6 * 0.0015 0.0030 0.495 0.245 N7 * −0.0017 0.0025 − 0.712

0.507 C8 * 0.0039 0.0027 1.443 2.081 C9 * −0.0049 0.0028 − 1.737 3.017 C10 0.0178 0.0041 4.334 18.785 C11 − 0.0208 0.0038 − 5.476 29.989 ========== Sum((d/s)**2) for starred atoms 8.931 Chi-squared at 95% for 3 degrees of freedom: 7.81 The group of atoms deviates significantly from planarity

Plane 3 m1 = 0.39562(0.00050) m2 = −0.44354(0.00065) m3 = −0.80421(0.00028) D = −0.16267(0.00293) Atom d s d/s (d/s)**2 S1 * 0.0040 0.0008 4.776 22.809 N2 * −0.0286 0.0026 − 10.988 120.734 C3 * 0.0190 0.0031 6.160 37.941 C4 * 0.0135 0.0031 4.303 18.512 C5 * 0.0110 0.0032 3.402 11.573 C6 * 0.0041 0.0030 1.346 1.813 N7 * −0.0157 0.0024 − 6.395 40.891 C8 * −0.0149 0.0027 − 5.543 30.723 C9 * −0.0134 0.0028 − 4.733 22.399 C10 0.0388 0.0041 9.426 88.842 C11 − 0.0125 0.0038 − 3.284 10.784 C12 0.1995 0.0042 47.777 2282.667 O3 0.0948 0.0026 37.134 1378.943 N21 − 0.1758 0.0027 − 66.314 4397.555 N24 − 1.1240 0.0025 − 452.430 204693.344 F37 − 0.0215 0.0022 − 9.734 94.749 ========== Sum((d/s)**2) for starred atoms 307.394 Chi-squared at 95% for 6 degrees of freedom: 12.60 The group of atoms deviates significantly from planarity

Plane 4 m1 = −0.01782(0.00194) m2 = 0.68699(0.00140) m3 = −0.72645(0.00130) D = −5.64159(0.01863) Atom d s d/s (d/s)**2 C22 * 0.0050 0.0035 1.415 2.003 C23 * −0.0045 0.0033 − 1.342 1.800 C25 * 0.0052 0.0036 1.445 2.087 C26 * −0.0064 0.0040 − 1.607 2.584 N21 0.6619 0.0026 250.471 62735.781 N24 − 0.6719 0.0025 − 265.708 70600.602 ========== Sum((d/s)**2) for starred atoms 8.474 Chi-squared at 95% for 1 degrees of freedom: 3.84 The group of atoms deviates significantly from planarity

Plane 5 m1 = 0.51053(0.00123) m2 = 0.32124(0.00143) m3 = −0.79760(0.00090) D = −1.41382(0.01995) Atom d s d/s (d/s)**2 C31 * 0.0049 0.0030 1.662 2.762 C32 * −0.0091 0.0033 − 2.733 7.467 C33 * 0.0057 0.0038 1.469 2.159 C34 * 0.0048 0.0040 1.202 1.445 C35 * −0.0083 0.0040 − 2.076 4.312 C36 * 0.0012 0.0035 0.334 0.111 F37 − 0.0514 0.0022 − 23.295 542.672 ========== Sum((d/s)**2) for starred atoms 18.256 Chi-squared at 95% for 3 degrees of freedom: 7.81 The group of atoms deviates significantly from planarity

Dihedral angles formed by LSQ-planes Plane - plane angle (s.u.) angle (s.u.) 1 2 0.96 (0.07) 179.04 (0.07) 1 3 0.27 (0.06) 179.73 (0.06) 1 4 74.20 (0.10) 105.80 (0.10) 1 5 45.64 (0.10) 134.36 (0.10) 2 3 0.72 (0.07) 179.28 (0.07) 2 4 74.51 (0.11) 105.49 (0.11) 2 5 45.48 (0.10) 134.52 (0.10) 3 4 74.19 (0.10) 105.81 (0.10) 3 5 45.50 (0.09) 134.50 (0.09) 4 5 37.72 (0.13) 142.28 (0.13)

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 $F^2 > 2\text{sigma}(F^2)$ 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}
S1	0.75858 (9)	0.00660 (7)	0.14207 (4)	0.0852 (3)
F37	1.3924 (3)	−0.3219 (2)	0.34144 (10)	0.1181 (8)
O3	0.4193 (3)	−0.2394 (2)	0.14045 (12)	0.1003 (7)
N7	0.5886 (3)	0.1699 (2)	0.07058 (11)	0.0799 (6)
N2	0.6544 (3)	−0.1274 (2)	0.16009 (12)	0.0843 (7)
N21	0.8861 (3)	−0.1781 (2)	0.22261 (12)	0.0897 (7)
N24	1.1390 (3)	−0.1550 (3)	0.31417 (11)	0.0820 (7)
C3	0.5003 (4)	−0.1421 (3)	0.13382 (14)	0.0801 (7)
C4	0.3158 (3)	0.0006 (3)	0.06429 (14)	0.0832 (8)
C5	0.3164 (4)	0.1154 (3)	0.03479 (14)	0.0880 (8)
H51	0.2234	0.1396	0.0118	0.132*
C6	0.4515 (4)	0.1965 (3)	0.03820 (13)	0.0833 (8)
C8	0.5869 (3)	0.0578 (3)	0.09931 (12)	0.0725 (6)
C9	0.4580 (3)	−0.0282 (3)	0.09857 (13)	0.0730 (7)
C10	0.1704 (4)	−0.0873 (4)	0.05983 (19)	0.1168 (13)

H101	0.1227	−0.0850	0.0194	0.175*
H102	0.0897	−0.0612	0.0880	0.175*
H103	0.2058	−0.1721	0.0693	0.175*
C11	0.4497 (5)	0.3222 (3)	0.00618 (17)	0.1058 (11)
H111	0.4093	0.3111	−0.0350	0.159*
H112	0.5594	0.3560	0.0064	0.159*
H113	0.3790	0.3798	0.0267	0.159*
C12	0.7451 (5)	−0.2303 (3)	0.1903 (2)	0.1081 (11)
H121	0.6747	−0.2735	0.2182	0.162*
H122	0.7803	−0.2912	0.1605	0.162*
C22	0.8501 (4)	−0.1351 (3)	0.28346 (16)	0.0929 (9)
H221	0.8205	−0.2073	0.3080	0.139*
H222	0.7571	−0.0775	0.2813	0.139*
C23	0.9964 (4)	−0.0693 (3)	0.31254 (15)	0.0869 (9)
H231	1.0217	0.0063	0.2897	0.130*
H232	0.9717	−0.0440	0.3535	0.130*
C25	1.1750 (4)	−0.1964 (4)	0.25276 (15)	0.0974 (10)
H251	1.2689	−0.2533	0.2542	0.146*
H252	1.2025	−0.1235	0.2283	0.146*
C26	1.0277 (5)	−0.2630 (4)	0.22462 (18)	0.1053 (11)
H261	1.0516	−0.2900	0.1838	0.158*
H262	1.0029	−0.3377	0.2482	0.158*
C31	1.2764 (4)	−0.1165 (3)	0.35029 (13)	0.0808 (8)
C32	1.4039 (4)	−0.2024 (3)	0.36426 (15)	0.0899 (9)
C33	1.5384 (5)	−0.1744 (4)	0.39968 (17)	0.1053 (11)
H331	1.6207	−0.2344	0.4067	0.158*
C34	1.5514 (5)	−0.0558 (5)	0.42506 (17)	0.1141 (12)
H341	1.6429	−0.0347	0.4496	0.171*
C35	1.4283 (5)	0.0317 (4)	0.41392 (17)	0.1094 (11)
H351	1.4364	0.1115	0.4317	0.164*
C36	1.2938 (5)	0.0027 (3)	0.37695 (15)	0.0916 (9)
H361	1.2128	0.0637	0.3696	0.137*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0741 (4)	0.0758 (5)	0.1050 (6)	−0.0140 (3)	−0.0071 (3)	0.0038 (4)
F37	0.1243 (16)	0.1012 (15)	0.1289 (16)	0.0506 (13)	0.0062 (13)	−0.0048 (12)
O3	0.1020 (16)	0.0845 (14)	0.1152 (17)	−0.0338 (12)	0.0147 (13)	0.0025 (12)
N7	0.0837 (14)	0.0740 (14)	0.0821 (14)	−0.0071 (12)	0.0060 (11)	−0.0042 (12)
N2	0.0807 (14)	0.0686 (14)	0.1033 (17)	−0.0096 (11)	−0.0016 (13)	0.0046 (13)
N21	0.0961 (17)	0.0767 (15)	0.0960 (18)	0.0080 (13)	−0.0023 (14)	0.0006 (13)
N24	0.0857 (14)	0.0824 (16)	0.0787 (14)	0.0255 (13)	0.0125 (11)	0.0030 (12)
C3	0.0801 (17)	0.0766 (18)	0.0845 (17)	−0.0113 (14)	0.0153 (13)	−0.0085 (15)
C4	0.0680 (14)	0.102 (2)	0.0800 (17)	−0.0075 (15)	0.0084 (12)	−0.0106 (16)
C5	0.0776 (17)	0.106 (2)	0.0805 (18)	0.0051 (16)	0.0025 (14)	−0.0052 (17)
C6	0.096 (2)	0.084 (2)	0.0699 (15)	0.0073 (16)	0.0070 (14)	−0.0067 (14)
C8	0.0725 (14)	0.0696 (15)	0.0756 (15)	−0.0086 (13)	0.0070 (11)	−0.0073 (13)

C9	0.0691 (14)	0.0775 (17)	0.0728 (15)	−0.0066 (12)	0.0101 (11)	−0.0107 (13)
C10	0.0724 (18)	0.147 (4)	0.130 (3)	−0.029 (2)	−0.0076 (18)	0.004 (3)
C11	0.128 (3)	0.091 (2)	0.098 (2)	0.006 (2)	0.001 (2)	0.0080 (19)
C12	0.113 (3)	0.075 (2)	0.135 (3)	0.0018 (18)	−0.013 (2)	0.005 (2)
C22	0.0853 (19)	0.087 (2)	0.107 (2)	0.0202 (16)	0.0153 (17)	0.0086 (18)
C23	0.0853 (18)	0.088 (2)	0.0878 (19)	0.0295 (16)	0.0047 (14)	−0.0015 (16)
C25	0.094 (2)	0.112 (3)	0.0863 (19)	0.028 (2)	0.0123 (16)	−0.0109 (19)
C26	0.110 (3)	0.101 (3)	0.105 (2)	0.027 (2)	0.004 (2)	−0.015 (2)
C31	0.0869 (18)	0.085 (2)	0.0710 (16)	0.0260 (15)	0.0123 (14)	0.0117 (14)
C32	0.092 (2)	0.096 (2)	0.0824 (18)	0.0322 (17)	0.0139 (15)	0.0046 (16)
C33	0.099 (2)	0.125 (3)	0.091 (2)	0.034 (2)	0.0041 (18)	0.011 (2)
C34	0.101 (2)	0.148 (4)	0.092 (2)	0.015 (3)	−0.0056 (19)	0.013 (3)
C35	0.125 (3)	0.117 (3)	0.086 (2)	0.005 (2)	−0.006 (2)	0.005 (2)
C36	0.104 (2)	0.084 (2)	0.0873 (19)	0.0227 (17)	0.0080 (16)	0.0102 (16)

Geometric parameters (Å, °)

S1—N2	1.702 (3)	C11—H111	0.9600
S1—C8	1.739 (3)	C11—H112	0.9600
F37—C32	1.360 (4)	C11—H113	0.9600
O3—C3	1.231 (3)	C12—H121	0.9700
N7—C8	1.342 (4)	C12—H122	0.9700
N7—C6	1.330 (4)	C22—C23	1.499 (5)
N2—C3	1.368 (4)	C22—H221	0.9700
N2—C12	1.458 (4)	C22—H222	0.9700
N21—C12	1.436 (4)	C23—H231	0.9700
N21—C26	1.457 (4)	C23—H232	0.9700
N21—C22	1.456 (4)	C25—C26	1.501 (5)
N24—C31	1.406 (4)	C25—H251	0.9700
N24—C25	1.463 (4)	C25—H252	0.9700
N24—C23	1.468 (3)	C26—H261	0.9700
C3—C9	1.465 (4)	C26—H262	0.9700
C4—C5	1.375 (5)	C31—C36	1.393 (5)
C4—C9	1.390 (4)	C31—C32	1.401 (4)
C4—C10	1.502 (4)	C32—C33	1.351 (5)
C5—C6	1.391 (4)	C33—C34	1.373 (6)
C5—H51	0.9300	C33—H331	0.9300
C6—C11	1.503 (5)	C34—C35	1.376 (5)
C8—C9	1.384 (4)	C34—H341	0.9300
C10—H101	0.9600	C35—C36	1.373 (5)
C10—H102	0.9600	C35—H351	0.9300
C10—H103	0.9600	C36—H361	0.9300
N2—S1—C8	89.40 (13)	N2—C12—H122	109.9
C8—N7—C6	114.6 (3)	H121—C12—H122	108.3
C3—N2—C12	123.2 (3)	N21—C22—C23	110.8 (3)
C3—N2—S1	116.7 (2)	N21—C22—H221	109.5
C12—N2—S1	118.6 (2)	C23—C22—H221	109.5
C12—N21—C26	113.1 (3)	N21—C22—H222	109.5
C12—N21—C22	113.2 (3)	C23—C22—H222	109.5

C26—N21—C22	110.4 (3)	H221—C22—H222	108.1
C31—N24—C25	115.4 (2)	N24—C23—C22	109.7 (3)
C31—N24—C23	116.4 (3)	N24—C23—H231	109.7
C25—N24—C23	110.2 (2)	C22—C23—H231	109.7
O3—C3—N2	121.9 (3)	N24—C23—H232	109.7
O3—C3—C9	129.2 (3)	C22—C23—H232	109.7
N2—C3—C9	108.9 (2)	H231—C23—H232	108.2
C5—C4—C9	115.6 (3)	N24—C25—C26	109.8 (3)
C5—C4—C10	122.0 (3)	N24—C25—H251	109.7
C9—C4—C10	122.4 (3)	C26—C25—H251	109.7
C4—C5—C6	122.2 (3)	N24—C25—H252	109.7
C4—C5—H51	118.9	C26—C25—H252	109.7
C6—C5—H51	118.9	H251—C25—H252	108.2
N7—C6—C5	122.8 (3)	N21—C26—C25	109.9 (3)
N7—C6—C11	115.6 (3)	N21—C26—H261	109.7
C5—C6—C11	121.6 (3)	C25—C26—H261	109.7
N7—C8—C9	126.3 (3)	N21—C26—H262	109.7
N7—C8—S1	120.5 (2)	C25—C26—H262	109.7
C9—C8—S1	113.1 (2)	H261—C26—H262	108.2
C8—C9—C4	118.4 (3)	C36—C31—C32	115.4 (3)
C8—C9—C3	111.7 (3)	C36—C31—N24	124.5 (3)
C4—C9—C3	129.9 (3)	C32—C31—N24	120.1 (3)
C4—C10—H101	109.5	F37—C32—C33	117.4 (3)
C4—C10—H102	109.5	F37—C32—C31	118.6 (3)
H101—C10—H102	109.5	C33—C32—C31	124.1 (4)
C4—C10—H103	109.5	C32—C33—C34	118.9 (3)
H101—C10—H103	109.5	C32—C33—H331	120.6
H102—C10—H103	109.5	C34—C33—H331	120.6
C6—C11—H111	109.5	C35—C34—C33	119.6 (4)
C6—C11—H112	109.5	C35—C34—H341	120.2
H111—C11—H112	109.5	C33—C34—H341	120.2
C6—C11—H113	109.5	C34—C35—C36	120.9 (4)
H111—C11—H113	109.5	C34—C35—H351	119.6
H112—C11—H113	109.5	C36—C35—H351	119.6
N21—C12—N2	108.7 (3)	C35—C36—C31	121.2 (3)
N21—C12—H121	109.9	C35—C36—H361	119.4
N2—C12—H121	109.9	C31—C36—H361	119.4
N21—C12—H122	109.9		

C8—S1—N2—C3	3.4 (2)	C22—N21—C12—N2	86.5 (4)
C8—S1—N2—C12	169.7 (3)	C3—N2—C12—N21	−168.9 (3)
C12—N2—C3—O3	9.2 (5)	S1—N2—C12—N21	25.7 (4)
S1—N2—C3—O3	174.9 (2)	C12—N21—C22—C23	−174.0 (3)
C12—N2—C3—C9	−169.9 (3)	C26—N21—C22—C23	58.1 (4)
S1—N2—C3—C9	−4.3 (3)	C31—N24—C23—C22	−168.1 (3)
C9—C4—C5—C6	1.0 (4)	C25—N24—C23—C22	58.0 (4)
C10—C4—C5—C6	−179.2 (3)	N21—C22—C23—N24	−57.4 (3)
C8—N7—C6—C5	0.6 (4)	C31—N24—C25—C26	166.6 (3)
C8—N7—C6—C11	179.3 (3)	C23—N24—C25—C26	−59.0 (4)
C4—C5—C6—N7	−0.8 (5)	C12—N21—C26—C25	173.6 (3)

C4—C5—C6—C11	−179.4 (3)	C22—N21—C26—C25	−58.5 (4)
C6—N7—C8—C9	−0.9 (4)	N24—C25—C26—N21	59.0 (4)
C6—N7—C8—S1	178.3 (2)	C25—N24—C31—C36	122.2 (3)
N2—S1—C8—N7	179.2 (2)	C23—N24—C31—C36	−9.3 (4)
N2—S1—C8—C9	−1.4 (2)	C25—N24—C31—C32	−61.2 (4)
N7—C8—C9—C4	1.2 (4)	C23—N24—C31—C32	167.3 (3)
S1—C8—C9—C4	−178.1 (2)	C36—C31—C32—F37	177.8 (3)
N7—C8—C9—C3	178.7 (3)	N24—C31—C32—F37	1.0 (4)
S1—C8—C9—C3	−0.6 (3)	C36—C31—C32—C33	−1.6 (5)
C5—C4—C9—C8	−1.2 (4)	N24—C31—C32—C33	−178.5 (3)
C10—C4—C9—C8	179.0 (3)	F37—C32—C33—C34	−177.9 (3)
C5—C4—C9—C3	−178.1 (3)	C31—C32—C33—C34	1.5 (6)
C10—C4—C9—C3	2.1 (5)	C32—C33—C34—C35	−0.1 (6)
O3—C3—C9—C8	−176.1 (3)	C33—C34—C35—C36	−1.1 (6)
N2—C3—C9—C8	3.0 (3)	C34—C35—C36—C31	0.9 (6)
O3—C3—C9—C4	1.0 (5)	C32—C31—C36—C35	0.3 (5)
N2—C3—C9—C4	−180.0 (3)	N24—C31—C36—C35	177.1 (3)
C26—N21—C12—N2	−146.9 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C33—H331···N7^{i}	0.93	2.60	3.486 (5)	160
C36—H361···O3^{ii}	0.93	2.34	3.240 (4)	161

Symmetry codes: (i) −*x*+5/2, *y*−1/2, −*z*+1/2; (ii) −*x*+3/2, *y*+1/2, −*z*+1/2.

Fig. 1

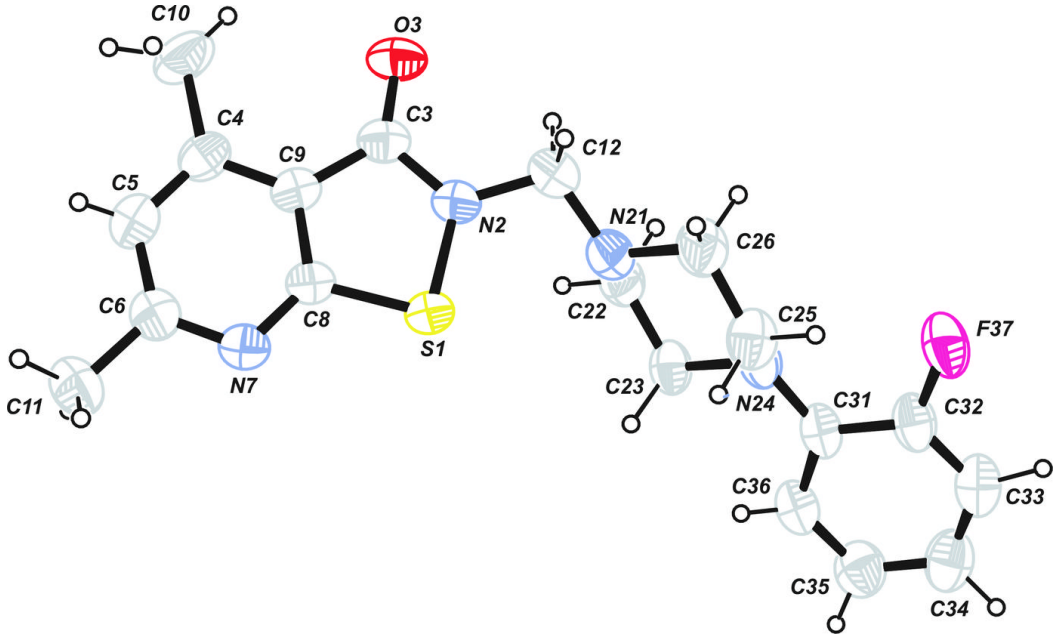
C10
O3
C4
C3
C9
C12
C5
N2
N21
C26
C6
C8
C22
C25
F37
S1
C23
N24
C31
C32
N7
C11
C36
C33
C35
C34

Fig. 2