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3-(2-Amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-5-yl)-5-fluoro-3-hydroxy-1-methylindolin-2-one methanol hemisolvate

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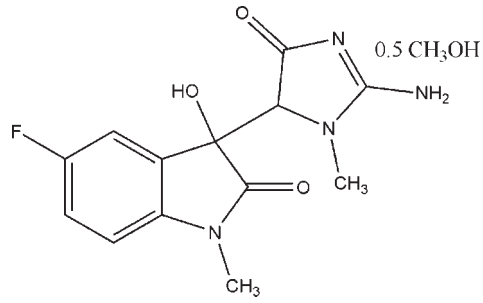
Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.002 Å; disorder in solvent or counterion; R factor = 0.035; wR factor = 0.092; data-to-parameter ratio = 11.6.

In the title compound, $C_{13}H_{13}FN_4O_3\cdot0.5CH_3OH$, molecules are packed in the crystal structure by a series of O—H···N, N—H···O, N—H···F and O—H···O intermolecular hydrogen bonds. The indole and creatinine units make a dihedral angle of 60.80 (4)°.

Related literature

For the biological activity of isatin and its derivatives, see: Pandeya *et al.* (2005); The endogenous oxindoles 5-hydroxyoxindole and isatin are antiproliferative and proapoptotic, see: Cane *et al.* (2000). For the *in vitro* cytotoxicity evaluation of some substituted isatin derivatives, see: Vine *et al.* (2007). For 2-indol-3-yl-methylenequinuclidin-3-ols and NADPH oxidase activity, see: Sekhar *et al.* (2003) and for novel substituted (*Z*)-2-(*N*-benzylindol-3-ylmethylene)quinuclidin-3-one and (*Z*)-(±)-2-(*N*-benzylindol-3-yl methylene)quinuclidin-3-ol derivatives as potent thermal sensitizing agents, see: Sonar *et al.* (2007). For the crystal and molecular structure of isatin, see: Frolova *et al.* (1988), for 3-(2-amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-5-yl)-3-hydroxyindolin-2-one monohydrate, see: Penthala *et al.* (2009) and for 1,1′-diacetyl-3-hydroxy-2,2′,3,3′-tetrahydro-3,3′-bi(1*H*-indole)-2,2′-dione, see: Usman *et al.* (2002). For the aldol condensation enolate mechanism *via* a six-membered transition state, see: Zimmerman & Traxler (1957).



Experimental

Crystal data

$C_{13}H_{13}FN_4O_3\cdot0.5CH_4O$
M_r = 308.30
Monoclinic, $I2/a$
a = 14.3088 (3) Å
b = 10.7900 (2) Å
c = 18.1286 (5) Å
β = 107.676 (1)°
V = 2666.77 (10) Å^3
Z = 8
Cu $K\alpha$ radiation
μ = 1.04 mm^{-1}
T = 90 K
0.15 × 0.03 × 0.02 mm

Data collection

Bruker X8 Proteum diffractometer
Absorption correction: multi-scan (*SADABS* in *APEX2*; Bruker, 2006)
T_{min} = 0.805, T_{max} = 0.979
19606 measured reflections
2448 independent reflections
2196 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 1.04
2448 reflections
211 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N2^{i}	0.84	1.97	2.8074 (16)	171
N3—H3A···O3^{ii}	0.88	2.25	3.1265 (16)	177
N3—H3B···O1^{iii}	0.88	2.12	2.8490 (17)	140
N3—H3B···F1^{iv}	0.88	2.45	2.8743 (14)	110
O1S—H1S4···O3	0.84	2.01	2.846 (3)	171

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and local procedures.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2556).

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supplementary materials

Acta Cryst. (2009). E**65**, o2909-o2910 [**doi:10.1107/S1600536809043797**]

3-(2-Amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-5-yl)-5-fluoro-3-hydroxy-1-methylindolin-2-one methanol hemisolvate

N. R. Penthala, T. R. Y. Reddy, S. Parkin and P. A. Crooks

Comment

Isatin analogs display diverse biological activities, (Pandeya *et al.*, 2005; Cane *et al.*, 2000 and Vine *et al.*, 2007). In continuation of our work on radiosensitizers (Sekhar *et al.*, 2003; Sonar *et al.*, 2007), we focused on the design, synthesis and structural analysis of a series of 3-(2-amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-5-yl)-3 -hydroxyindolin-2-one analogs with different substituents on the indole moiety. The main aim of X-ray analysis of the title compound was to confirm the stereochemistry of the molecule and to obtain detailed information on the structural conformation, which may be useful in structure-activity relationship (SAR) analysis. The title compound was prepared by the aldol condensation of 5-fluoro-*N*-methyl indol-2,3-dione with 2-amino- 1-methyl-1*H*-imidazol-4(5*H*)-one (creatinine) in the presence of sodium acetate in acetic acid under microwave irradiation. The compound was crystallized from methyl alcohol. This aldol condensation reaction proceeds by the formation of the E-enolate, as per the Zimmerman-Traxler model (Zimmerman & Traxler, 1957). The molecular structure and the atom-numbering scheme are shown in Fig.1. The isatin ring is planar with r.m.s. deviation of 0.0232 (11) Å and the creatinine ring has r.m.s. deviation of 0.0307 (8) Å. with bond distances and angles comparable with those previously reported for other isatin derivatives (Frolova *et al.*, 1988; Usman *et al.*, 2002 and Penthala *et al.* (2009). The indole and creatinine moieties make a dihedral angle of 60.80 (4) °. Intermolecular O—H···N, N—H···O, N—H···F and O—H···O hydrogen bonds stabilize the crystal structure and form a supramolecular aggregation.

Experimental

A mixture of 5-fluoro-*N*-methyl isatin (1 mmol), creatinine (1.1 mmol) and sodium acetate (1.2 mmol) in acetic acid (1 ml) was irradiated in a domestic microwave oven for 30 sec with intermittent cooling every 5 sec. The reaction mixture was allowed to cool to room temperature, 10 ml of saturated sodium bicarbonate solution was added, and the mixture was stirred for 10 minutes. The precipitate thus obtained was collected by filtration, washed with cold water and dried, to afford the crude product. Crystallization from methyl alcohol gave a white crystalline product of 3-(2-amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-5-yl)- 5-fluoro-3-hydroxy-1-methylindolin-2-one methanolate, which was suitable for X-ray analysis. ^{1}H NMR (DMSO-d_6): δ 3.05 (*s*, 3H), 3.18 (*s*, 3H), 4.11 (*s*, 1H), 6.58 (*s*, 1H, OH), 6.85–6.89 (*dd*, J=2.7 Hz, J=5.4 Hz, 1H), 6.93–6.97 (*dd*, J=2.7 Hz, J=4.2 Hz, 1H), 7.11–7.18 (*m*, 1H), 7.42 (*bs*, 1H, NH), 7.72 (*bs*, 1H, NH), p.p.m.; ^{13}C NMR (DMSO-d_6): δ 26.08, 32.76, 48.62, 69.87, 76.29, 109.14, 109.25, 111.16, 111.50, 115.42, 115.72, 128.84, 128.95, 140.23, 156.35, 159.49, 171.98, 173.97, 181.85 p.p.m..

Refinement

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained distances of 0.98Å (RCH_3), 1.00 Å (R_3CH), 0.95 Å ($C_{Ar}H$), 0.84 Å (O—H), 0.88 Å (N—H), and with U_{iso}(H) values set to either $1.2U_{eq}$ or $1.5U_{eq}$ (RCH_3, OH) of the attached atom.

The presence of difference map peaks in the vicinity of the 2-fold axis at *ca* (1/4,0.62,0) were consistent with a disordered methanol solvent molecule. This methanol was modelled at half occupancy, such that application of the 2-fold site symmetry generates a full occupancy for the site. There is an O—H···O hydrogen-bonding interaction between this methanol and O3 of the main molecule (see Table 1).

Figures

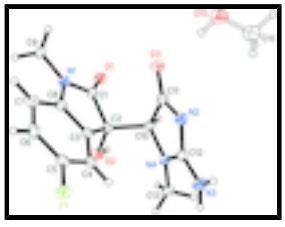


Fig. 1. A view of the molecule with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

3-(2-Amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-5-yl)- 5-fluoro-3-hydroxy-1-methylindolin-2-one methanol hemisolvate

Crystal data

$C_{13}H_{13}FN_4O_3 \cdot 0.5CH_4O$	F_{000} = 1288
M_r = 308.30	D_x = 1.536 Mg m^{-3}
Monoclinic, *I*2/*a*	Cu *K*α radiation, λ = 1.54178 Å
Hall symbol: -I 2ya	Cell parameters from 9961 reflections
a = 14.3088 (3) Å	θ = 4.8–68.5º
b = 10.7900 (2) Å	μ = 1.04 mm^{-1}
c = 18.1286 (5) Å	*T* = 90 K
β = 107.676 (1)º	Rod, colourless
V = 2666.77 (10) Å^3	0.15 × 0.03 × 0.02 mm
Z = 8	

Data collection

Bruker X8 Proteum diffractometer	2448 independent reflections
Radiation source: fine-focus rotating anode	2196 reflections with $I > 2\sigma(I)$
Monochromator: graded multilayer optics	R_{int} = 0.041
Detector resolution: 5.6 pixels mm^{-1}	θ_{max} = 68.5º
T = 90 K	θ_{min} = 4.8º
φ and ω scans	*h* = −17→17
Absorption correction: multi-scan (SADABS in APEX2; Bruker, 2006)	*k* = −13→13
T_{min} = 0.805, T_{max} = 0.979	*l* = −17→21
19606 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.092$

$S = 1.04$

2448 reflections

211 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 3.1985P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.25$ e Å^{-3}

$\Delta\rho_{min} = -0.27$ e Å^{-3}

Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
F1	0.71683 (6)	0.82226 (8)	0.40909 (5)	0.0226 (2)	
O1	0.34944 (7)	0.34900 (10)	0.34227 (6)	0.0220 (2)	
N1	0.40050 (8)	0.53388 (11)	0.40330 (7)	0.0180 (3)	
C1	0.40738 (10)	0.43524 (13)	0.35922 (8)	0.0171 (3)	
O2	0.56972 (7)	0.35213 (9)	0.37870 (6)	0.0182 (2)	
H2	0.5465	0.2822	0.3628	0.027*	
N2	0.48670 (8)	0.61111 (11)	0.17484 (7)	0.0186 (3)	
C2	0.50466 (10)	0.44565 (13)	0.33829 (8)	0.0164 (3)	
O3	0.34268 (7)	0.56370 (9)	0.20215 (6)	0.0207 (2)	
N3	0.64656 (9)	0.58544 (12)	0.16571 (8)	0.0230 (3)	
H3A	0.7006	0.5411	0.1762	0.028*	
H3B	0.6417	0.6549	0.1393	0.028*	
C3	0.54173 (10)	0.57182 (13)	0.37146 (8)	0.0162 (3)	
N4	0.57662 (8)	0.44285 (11)	0.22994 (7)	0.0168 (3)	
C4	0.62309 (10)	0.64045 (13)	0.37024 (8)	0.0168 (3)	
H4	0.6668	0.6122	0.3436	0.020*	
C5	0.63765 (10)	0.75245 (14)	0.40985 (8)	0.0181 (3)	
C6	0.57663 (11)	0.79772 (14)	0.44928 (8)	0.0205 (3)	
H6	0.5904	0.8747	0.4758	0.025*	
C7	0.49419 (11)	0.72920 (14)	0.44984 (8)	0.0206 (3)	
H7	0.4503	0.7582	0.4762	0.025*	
C8	0.47874 (10)	0.61742 (13)	0.41062 (8)	0.0174 (3)	

C9	0.32581 (11)	0.54673 (15)	0.44237 (9)	0.0227 (3)	
H9A	0.2715	0.5971	0.4105	0.034*	
H9B	0.3544	0.5872	0.4926	0.034*	
H9C	0.3013	0.4646	0.4503	0.034*	
C10	0.48606 (10)	0.43188 (13)	0.25013 (8)	0.0158 (3)	
H10	0.4521	0.3519	0.2308	0.019*	
C11	0.42843 (10)	0.54179 (13)	0.20572 (8)	0.0166 (3)	
C12	0.57275 (10)	0.54783 (13)	0.18962 (8)	0.0174 (3)	
C13	0.65283 (10)	0.34938 (13)	0.24071 (9)	0.0200 (3)	
H13A	0.6606	0.3276	0.1904	0.030*	
H13B	0.6344	0.2753	0.2644	0.030*	
H13C	0.7149	0.3822	0.2746	0.030*	
O1S	0.2149 (2)	0.6430 (4)	0.05671 (19)	0.0769 (13)	0.50
H1S4	0.2574	0.6239	0.0984	0.115*	0.50
C1S	0.2489 (9)	0.6226 (3)	−0.0003 (6)	0.0403 (9)	0.5
H1S1	0.3121	0.6649	0.0091	0.060*	0.50
H2S1	0.2026	0.6540	−0.0482	0.060*	0.50
H3S1	0.2580	0.5332	−0.0051	0.060*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0206 (4)	0.0228 (5)	0.0262 (5)	−0.0075 (3)	0.0100 (3)	−0.0027 (3)
O1	0.0189 (5)	0.0224 (5)	0.0266 (6)	−0.0049 (4)	0.0098 (4)	−0.0021 (4)
N1	0.0153 (6)	0.0215 (6)	0.0188 (6)	−0.0016 (5)	0.0076 (5)	−0.0022 (5)
C1	0.0156 (7)	0.0204 (7)	0.0158 (7)	0.0003 (5)	0.0056 (5)	0.0016 (5)
O2	0.0172 (5)	0.0165 (5)	0.0200 (5)	0.0007 (4)	0.0043 (4)	0.0002 (4)
N2	0.0174 (6)	0.0192 (6)	0.0203 (6)	0.0003 (5)	0.0073 (5)	0.0020 (5)
C2	0.0138 (6)	0.0176 (7)	0.0180 (7)	−0.0001 (5)	0.0052 (5)	0.0006 (5)
O3	0.0153 (5)	0.0223 (5)	0.0246 (5)	0.0007 (4)	0.0065 (4)	0.0000 (4)
N3	0.0202 (6)	0.0225 (6)	0.0297 (7)	0.0015 (5)	0.0129 (5)	0.0070 (5)
C3	0.0160 (7)	0.0175 (7)	0.0145 (6)	0.0016 (5)	0.0039 (5)	0.0012 (5)
N4	0.0158 (6)	0.0166 (6)	0.0206 (6)	0.0013 (4)	0.0096 (5)	0.0014 (5)
C4	0.0152 (6)	0.0196 (7)	0.0158 (7)	0.0008 (5)	0.0050 (5)	0.0004 (5)
C5	0.0158 (6)	0.0197 (7)	0.0180 (7)	−0.0029 (5)	0.0037 (5)	0.0029 (5)
C6	0.0231 (7)	0.0192 (7)	0.0184 (7)	−0.0004 (6)	0.0051 (6)	−0.0032 (6)
C7	0.0199 (7)	0.0241 (7)	0.0190 (7)	0.0013 (6)	0.0078 (6)	−0.0028 (6)
C8	0.0147 (6)	0.0211 (7)	0.0160 (7)	0.0000 (5)	0.0039 (5)	0.0012 (5)
C9	0.0184 (7)	0.0321 (8)	0.0206 (7)	−0.0025 (6)	0.0103 (6)	−0.0039 (6)
C10	0.0133 (7)	0.0168 (7)	0.0185 (7)	−0.0015 (5)	0.0069 (5)	−0.0010 (5)
C11	0.0160 (7)	0.0176 (7)	0.0160 (7)	−0.0003 (5)	0.0044 (5)	−0.0027 (5)
C12	0.0181 (7)	0.0184 (7)	0.0160 (7)	−0.0015 (5)	0.0058 (5)	−0.0016 (5)
C13	0.0183 (7)	0.0197 (7)	0.0245 (7)	0.0034 (6)	0.0102 (6)	0.0008 (6)
O1S	0.0548 (19)	0.136 (4)	0.0458 (18)	0.060 (2)	0.0247 (16)	0.038 (2)
C1S	0.0351 (15)	0.0419 (18)	0.0384 (17)	0.012 (4)	0.0029 (13)	−0.033 (4)

Geometric parameters (Å, °)

F1—C5	1.3641 (16)	C4—C5	1.389 (2)

O1—C1	1.2220 (17)	C4—H4	0.9500
N1—C1	1.3525 (19)	C5—C6	1.375 (2)
N1—C8	1.4117 (18)	C6—C7	1.395 (2)
N1—C9	1.4570 (18)	C6—H6	0.9500
C1—C2	1.5539 (19)	C7—C8	1.383 (2)
O2—C2	1.4168 (16)	C7—H7	0.9500
O2—H2	0.8400	C9—H9A	0.9800
N2—C11	1.3606 (18)	C9—H9B	0.9800
N2—C12	1.3615 (18)	C9—H9C	0.9800
C2—C3	1.5175 (19)	C10—C11	1.5270 (19)
C2—C10	1.546 (2)	C10—H10	1.0000
O3—C11	1.2318 (17)	C13—H13A	0.9800
N3—C12	1.3214 (19)	C13—H13B	0.9800
N3—H3A	0.8800	C13—H13C	0.9800
N3—H3B	0.8800	O1S—C1S	1.288 (10)
C3—C4	1.386 (2)	O1S—H1S4	0.8400
C3—C8	1.395 (2)	C1S—H1S1	0.9800
N4—C12	1.3401 (19)	C1S—H2S1	0.9800
N4—C13	1.4543 (18)	C1S—H3S1	0.9800
N4—C10	1.4544 (17)		
C1—N1—C8	111.10 (12)	C7—C8—C3	122.81 (13)
C1—N1—C9	123.91 (12)	C7—C8—N1	127.11 (13)
C8—N1—C9	124.85 (12)	C3—C8—N1	110.08 (12)
O1—C1—N1	125.61 (13)	N1—C9—H9A	109.5
O1—C1—C2	125.69 (13)	N1—C9—H9B	109.5
N1—C1—C2	108.59 (11)	H9A—C9—H9B	109.5
C2—O2—H2	109.5	N1—C9—H9C	109.5
C11—N2—C12	105.90 (12)	H9A—C9—H9C	109.5
O2—C2—C3	109.77 (11)	H9B—C9—H9C	109.5
O2—C2—C10	110.25 (11)	N4—C10—C11	100.60 (11)
C3—C2—C10	115.20 (11)	N4—C10—C2	111.45 (11)
O2—C2—C1	108.60 (11)	C11—C10—C2	111.49 (11)
C3—C2—C1	101.49 (11)	N4—C10—H10	111.0
C10—C2—C1	111.09 (11)	C11—C10—H10	111.0
C12—N3—H3A	120.0	C2—C10—H10	111.0
C12—N3—H3B	120.0	O3—C11—N2	126.72 (13)
H3A—N3—H3B	120.0	O3—C11—C10	123.14 (13)
C4—C3—C8	119.69 (13)	N2—C11—C10	110.09 (11)
C4—C3—C2	131.87 (13)	N3—C12—N4	122.26 (13)
C8—C3—C2	108.42 (12)	N3—C12—N2	123.14 (13)
C12—N4—C13	124.37 (12)	N4—C12—N2	114.60 (12)
C12—N4—C10	108.28 (11)	N4—C13—H13A	109.5
C13—N4—C10	126.78 (11)	N4—C13—H13B	109.5
C3—C4—C5	116.85 (13)	H13A—C13—H13B	109.5
C3—C4—H4	121.6	N4—C13—H13C	109.5
C5—C4—H4	121.6	H13A—C13—H13C	109.5
F1—C5—C6	118.00 (13)	H13B—C13—H13C	109.5
F1—C5—C4	118.03 (12)	C1S—O1S—H1S4	109.5
C6—C5—C4	123.97 (13)	O1S—C1S—H1S1	109.5

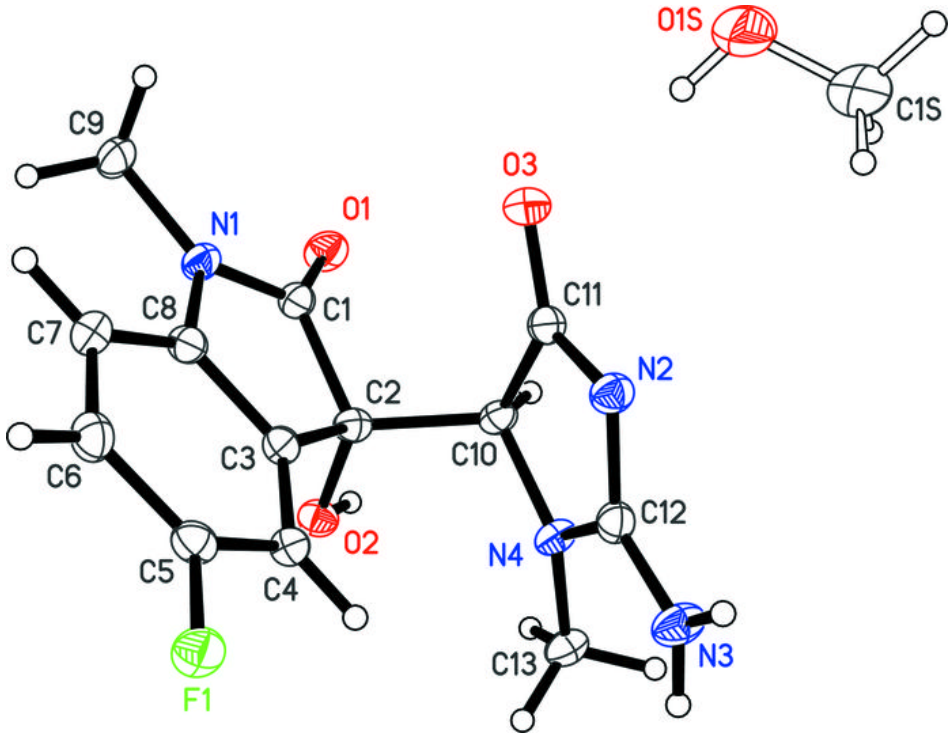
C5—C6—C7	119.17 (13)	O1S—C1S—H2S1	109.5
C5—C6—H6	120.4	H1S1—C1S—H2S1	109.5
C7—C6—H6	120.4	O1S—C1S—H3S1	109.5
C8—C7—C6	117.51 (13)	H1S1—C1S—H3S1	109.5
C8—C7—H7	121.2	H2S1—C1S—H3S1	109.5
C6—C7—H7	121.2		
C8—N1—C1—O1	−179.11 (13)	C2—C3—C8—N1	−2.46 (15)
C9—N1—C1—O1	5.0 (2)	C1—N1—C8—C7	178.43 (14)
C8—N1—C1—C2	4.55 (15)	C9—N1—C8—C7	−5.7 (2)
C9—N1—C1—C2	−171.35 (12)	C1—N1—C8—C3	−1.40 (16)
O1—C1—C2—O2	−66.31 (17)	C9—N1—C8—C3	174.45 (13)
N1—C1—C2—O2	110.02 (12)	C12—N4—C10—C11	6.11 (14)
O1—C1—C2—C3	178.05 (13)	C13—N4—C10—C11	−165.51 (13)
N1—C1—C2—C3	−5.62 (14)	C12—N4—C10—C2	−112.18 (13)
O1—C1—C2—C10	55.09 (18)	C13—N4—C10—C2	76.20 (17)
N1—C1—C2—C10	−128.58 (12)	O2—C2—C10—N4	−60.19 (14)
O2—C2—C3—C4	68.20 (19)	C3—C2—C10—N4	64.70 (15)
C10—C2—C3—C4	−56.9 (2)	C1—C2—C10—N4	179.38 (11)
C1—C2—C3—C4	−177.03 (14)	O2—C2—C10—C11	−171.72 (10)
O2—C2—C3—C8	−110.02 (13)	C3—C2—C10—C11	−46.83 (16)
C10—C2—C3—C8	124.84 (13)	C1—C2—C10—C11	67.85 (14)
C1—C2—C3—C8	4.74 (14)	C12—N2—C11—O3	−176.78 (14)
C8—C3—C4—C5	0.7 (2)	C12—N2—C11—C10	5.73 (15)
C2—C3—C4—C5	−177.33 (13)	N4—C10—C11—O3	175.06 (13)
C3—C4—C5—F1	−179.53 (12)	C2—C10—C11—O3	−66.68 (17)
C3—C4—C5—C6	−0.1 (2)	N4—C10—C11—N2	−7.34 (14)
F1—C5—C6—C7	178.89 (12)	C2—C10—C11—N2	110.92 (13)
C4—C5—C6—C7	−0.6 (2)	C13—N4—C12—N3	−10.8 (2)
C5—C6—C7—C8	0.5 (2)	C10—N4—C12—N3	177.36 (13)
C6—C7—C8—C3	0.1 (2)	C13—N4—C12—N2	168.57 (12)
C6—C7—C8—N1	−179.68 (13)	C10—N4—C12—N2	−3.30 (16)
C4—C3—C8—C7	−0.8 (2)	C11—N2—C12—N3	177.68 (13)
C2—C3—C8—C7	177.70 (13)	C11—N2—C12—N4	−1.65 (16)
C4—C3—C8—N1	179.06 (12)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N2^{i}	0.84	1.97	2.8074 (16)	171
N3—H3A···O3^{ii}	0.88	2.25	3.1265 (16)	177
N3—H3B···O1^{iii}	0.88	2.12	2.8490 (17)	140
N3—H3B···F1^{iv}	0.88	2.45	2.8743 (14)	110
O1S—H1S4···O3	0.84	2.01	2.846 (3)	171

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

Fig. 1


O1S
C1S
C9
O3
N1
O1
C11
C8
C1
C7
N2
C2
C3
C10
C6
C12
O2
N4
C5
C4
C13
N3
F1