Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

5-Fluoro-1*H*-indole-2-carbohydrazide

William T. A. Harrison,[a]* H. S. Yathirajan,[b] B. V. Ashalatha,[c] K. K. Vijaya Raj[c] and B. Narayana[c]

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, [b]Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India, and [c]Department of Chemistry, Mangalore University, Mangalagangotri 574 199, India

Correspondence e-mail: w.harrison@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.089
Data-to-parameter ratio = 12.4

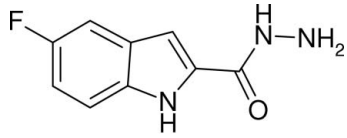
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 4 October 2006
Accepted 4 October 2006

The geometric parameters for the essentially planar molecule of the title compound, $C_9H_8FN_3O$, are normal. A network of N—H···O and N—H···N hydrogen bonds helps to establish the crystal packing.

Comment

As part of our ongoing research into indole carboxylic acid derivatives (Harrison *et al.*, 2006), the synthesis and crystal structure of the title compound, (I) (Fig. 1), are now presented.



(I)

The geometric paramaters for (I) fall within their expected ranges (Allen *et al.*, 1987). The indole ring system is essentially flat (r.m.s. deviation from the mean plane = 0.005 Å). The mean plane of atoms C9, O1, N2 and N3 of the carbohydrazide side chain is slightly twisted away from the indole mean plane [dihedral angle = 5.27 (9)°]. The bond angle sum about N2 is 359°, suggesting sp^2-hybridization for this atom. Conversely, the average bond angle for N3 of 108° suggests sp^3-hybridization.

The crystal packing in (I) is influenced by N—H···O and N—H···N hydrogen bonds (Table 1). Inversion-generated dimeric pairs of molecules are linked by a pair of N3—H3···O1^{iii} hydrogen bonds (Fig. 2). Adjacent molecules are then linked into ribbons by a combination of the N2—H2···O1^{ii} and N1···H1—N3^{i} bonds. In terms of graph theory (Bernstein *et al.*, 1995) these two hydrogen-bonding motifs result in $R_2^2(10)$ and $R_2^2(8)$ loops, respectively. Combining the two results in (001) sheets of molecules. Atom H4, attached to N3, does not participate in hydrogen bonds. A *PLATON* (Spek, 2003) analysis of (I) indicated a short C—H···F contact that may also help to consolidate the crystal packing. In the packing of (I), a zigzag stacking of molecules with respect to the *c* direction is seen (Fig. 3). Any π–π stacking interactions in (I) must be very weak, the shortest intermolecular ring-centroid separation being 4.08 Å.

Experimental

Methyl-5-fluoroindole-2-carboxylate (2.34 g, 0.01 mol) (Harrison *et al.*, 2006) in 25 ml of absolute ethanol was refluxed with 1.0 ml of hydrazine hydrate for 2 h, with the reaction progress monitored by

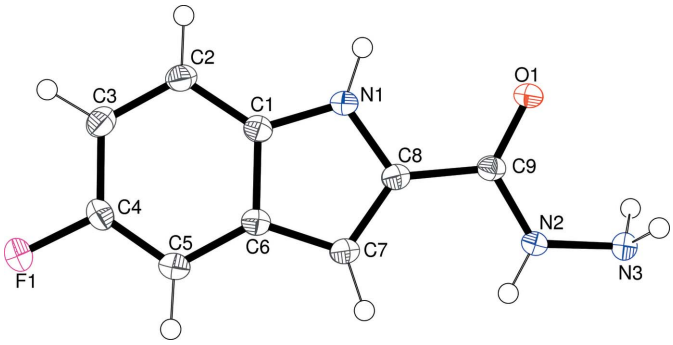


Figure 1
View of the molecular structure of (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms.

thin-layer chromatography. Upon completion, the mixture was cooled to room temperature. The separated solid was filtered off and washed with cold ethanol; cubes of (I) were recrystallized from ethanol (m.p. 505–507 K). Analysis found (calculated) for $C_9H_8FN_3O$: C 55.70 (55.96), H 4.12 (4.17), N 21.65 (21.75)%.

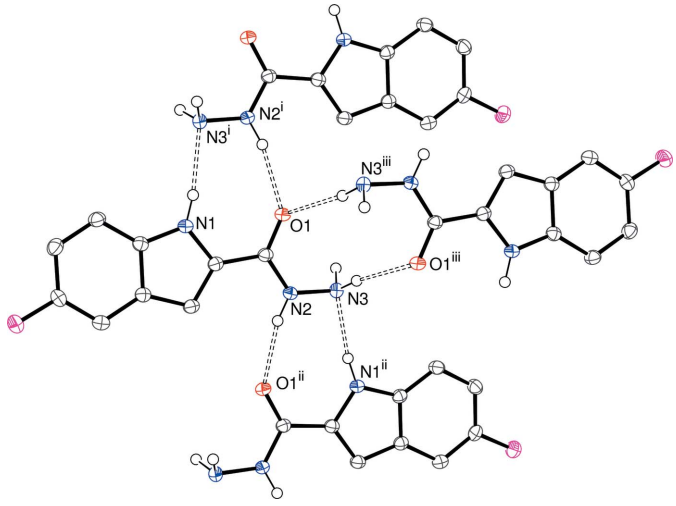


Figure 2
Fragment of the crystal structure of (I), showing the hydrogen-bonding (dashed lines) scheme, with C-bound H atoms omitted for clarity. Symmetry codes as in Table 1.

Crystal data

$C_9H_8FN_3O$	$Z = 8$
$M_r = 193.18$	$D_x = 1.452$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation
$a = 10.0451$ (3) Å	$\mu = 0.11$ mm^{-1}
$b = 9.4978$ (2) Å	$T = 120$ (2) K
$c = 18.5293$ (6) Å	Cube, colourless
$V = 1767.81$ (9) Å^3	0.20 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer	11208 measured reflections
φ and ω scans	1733 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	1497 reflections with $I > 2\sigma(I)$
$T_{min} = 0.978$, $T_{max} = 0.978$	$R_{int} = 0.029$
	$\theta_{max} = 26.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.7328P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.089$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.19$ e Å^{-3}
1733 reflections	Extinction correction: *SHELXL97*
140 parameters	Extinction coefficient: 0.015 (2)
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N3^{i}	0.898 (16)	2.096 (16)	2.9864 (15)	171.3 (13)
N2—H2···O1^{ii}	0.870 (16)	2.073 (16)	2.9193 (14)	163.9 (14)
N3—H3···O1^{iii}	0.920 (16)	2.124 (16)	3.0241 (15)	165.8 (13)
C3—H3A···F1^{iv}	0.95	2.55	3.2082 (15)	127

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

The N-bound H atoms were located in difference maps and their positions were freely refined with U_{iso}(H) set equal to $1.2U_{eq}$(N). The C-bound H atoms were placed in idealized locations (C—H = 0.95 Å) and refined as riding with U_{iso}(H) = $1.2U_{eq}$(C).

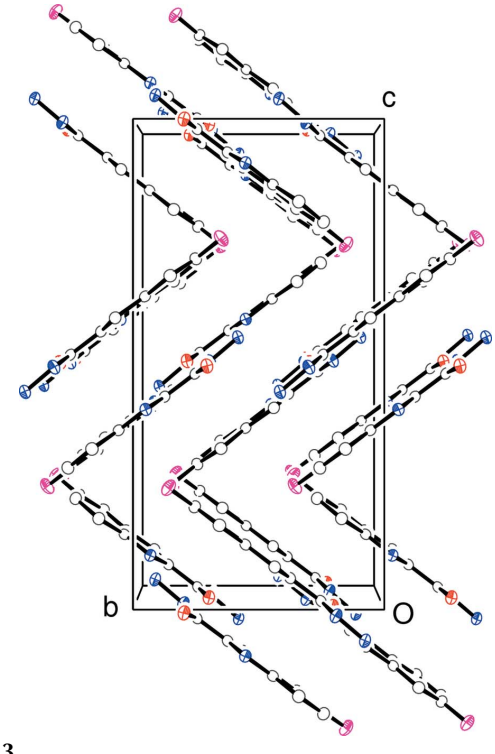


Figure 3
The packing for (I), with all H atoms omitted for clarity.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank the EPSRC National Crystallographic Service (University of Southampton) for data collection. ABV thanks Mangalore University for provision of research facilities.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harrison, W. T. A., Yathirajan, H. S., Ashalatha, B. V., Vijaya Raj, K. K. & Narayana, B. (2006). *Acta Cryst.* E**62**, o4050–o4051.
Nonius (1998). *COLLECT*. Nonius, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Acta Cryst. (2006). E**62**, o4986–o4988 [https://doi.org/10.1107/S1600536806040943]

5-Fluoro-1*H*-indole-2-carbohydrazide

William T. A. Harrison, H. S. Yathirajan, B. V. Ashalatha, K. K. Vijaya Raj and B. Narayana

5-Fluoro-1*H*-indole-2-carbohydrazide

Crystal data

$C_9H_8FN_3O$
$M_r = 193.18$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 10.0451$ (3) Å
$b = 9.4978$ (2) Å
$c = 18.5293$ (6) Å
$V = 1767.81$ (9) Å^3
$Z = 8$
$F(000) = 800$
$D_x = 1.452$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1996 reflections
$\theta = 1.0$–$26.0°$
$\mu = 0.11$ mm^{-1}
$T = 120$ K
Cube, colourless
0.20 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
$T_{min} = 0.978$, $T_{max} = 0.978$
11208 measured reflections
1733 independent reflections
1497 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 26.1°$, $\theta_{min} = 3.7°$
$h = -12 \rightarrow 12$
$k = -11 \rightarrow 10$
$l = -22 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.06$
1733 reflections
140 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difmap (N-H) and geom (others)
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.7328P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.015 (2)

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	0.48589 (12)	0.44387 (13)	0.63425 (6)	0.0181 (3)
C2	0.41098 (13)	0.34193 (14)	0.67046 (7)	0.0217 (3)
H2A	0.3166	0.3410	0.6676	0.026*
C3	0.47908 (13)	0.24262 (14)	0.71057 (7)	0.0228 (3)
H3A	0.4319	0.1713	0.7358	0.027*
C4	0.61805 (13)	0.24800 (13)	0.71369 (7)	0.0216 (3)
C5	0.69439 (13)	0.34626 (13)	0.67917 (7)	0.0211 (3)
H5	0.7887	0.3462	0.6829	0.025*
C6	0.62640 (12)	0.44730 (13)	0.63784 (6)	0.0179 (3)
C7	0.66864 (12)	0.56243 (13)	0.59462 (7)	0.0192 (3)
H7	0.7578	0.5914	0.5863	0.023*
C8	0.55545 (12)	0.62391 (13)	0.56713 (7)	0.0179 (3)
C9	0.54006 (11)	0.74680 (14)	0.51939 (7)	0.0175 (3)
N1	0.44498 (10)	0.55295 (11)	0.59124 (6)	0.0186 (3)
H1	0.3600 (16)	0.5719 (15)	0.5798 (8)	0.022*
N2	0.65387 (10)	0.80349 (11)	0.49559 (6)	0.0208 (3)
H2	0.7311 (16)	0.7653 (16)	0.5037 (8)	0.025*
N3	0.65712 (11)	0.91675 (12)	0.44592 (6)	0.0209 (3)
H3	0.6249 (15)	0.9963 (17)	0.4682 (8)	0.025*
H4	0.6008 (16)	0.8927 (16)	0.4082 (9)	0.025*
O1	0.42915 (8)	0.79502 (10)	0.50288 (5)	0.0217 (2)
F1	0.67988 (8)	0.14679 (8)	0.75401 (4)	0.0297 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0176 (6)	0.0185 (6)	0.0182 (6)	0.0013 (5)	0.0000 (5)	−0.0022 (5)
C2	0.0170 (6)	0.0236 (7)	0.0244 (7)	−0.0007 (5)	0.0022 (5)	−0.0002 (5)
C3	0.0228 (7)	0.0216 (7)	0.0240 (7)	−0.0022 (5)	0.0043 (5)	0.0014 (5)
C4	0.0234 (7)	0.0199 (6)	0.0216 (6)	0.0042 (5)	−0.0017 (5)	0.0022 (5)
C5	0.0168 (6)	0.0237 (7)	0.0229 (6)	0.0013 (5)	−0.0006 (5)	−0.0007 (5)
C6	0.0172 (6)	0.0182 (6)	0.0185 (6)	0.0007 (5)	0.0000 (5)	−0.0029 (5)
C7	0.0154 (6)	0.0205 (6)	0.0216 (6)	−0.0009 (5)	0.0004 (5)	−0.0014 (5)
C8	0.0161 (6)	0.0181 (6)	0.0196 (6)	−0.0007 (5)	0.0008 (5)	−0.0024 (5)
C9	0.0154 (6)	0.0171 (6)	0.0200 (6)	0.0000 (5)	−0.0007 (5)	−0.0035 (5)
N1	0.0139 (5)	0.0197 (6)	0.0223 (6)	0.0003 (4)	0.0001 (4)	0.0013 (4)
N2	0.0139 (5)	0.0206 (6)	0.0280 (6)	0.0011 (4)	−0.0002 (4)	0.0060 (5)
N3	0.0191 (6)	0.0178 (6)	0.0258 (6)	−0.0006 (4)	−0.0007 (4)	0.0039 (5)
O1	0.0140 (4)	0.0213 (5)	0.0297 (5)	0.0008 (3)	−0.0009 (4)	0.0023 (4)
F1	0.0259 (4)	0.0281 (5)	0.0352 (5)	0.0030 (3)	−0.0019 (3)	0.0124 (4)

Geometric parameters (Å, º)

C1—N1	1.3702 (17)	C7—C8	1.3759 (17)
C1—C2	1.3978 (18)	C7—H7	0.9500
C1—C6	1.4133 (18)	C8—N1	1.3730 (16)
C2—C3	1.3820 (19)	C8—C9	1.4727 (18)
C2—H2A	0.9500	C9—O1	1.2428 (14)
C3—C4	1.3981 (19)	C9—N2	1.3384 (16)
C3—H3A	0.9500	N1—H1	0.898 (16)
C4—F1	1.3667 (14)	N2—N3	1.4161 (15)
C4—C5	1.3667 (18)	N2—H2	0.870 (16)
C5—C6	1.4050 (17)	N3—H3	0.920 (16)
C5—H5	0.9500	N3—H4	0.927 (17)
C6—C7	1.4203 (17)		
N1—C1—C2	129.90 (12)	C8—C7—C6	106.77 (11)
N1—C1—C6	108.02 (11)	C8—C7—H7	126.6
C2—C1—C6	122.08 (11)	C6—C7—H7	126.6
C3—C2—C1	117.67 (12)	N1—C8—C7	109.83 (11)
C3—C2—H2A	121.2	N1—C8—C9	119.98 (11)
C1—C2—H2A	121.2	C7—C8—C9	130.19 (11)
C2—C3—C4	119.44 (12)	O1—C9—N2	122.44 (12)
C2—C3—H3A	120.3	O1—C9—C8	122.27 (11)
C4—C3—H3A	120.3	N2—C9—C8	115.28 (10)
F1—C4—C5	118.76 (11)	C1—N1—C8	108.54 (10)
F1—C4—C3	116.78 (11)	C1—N1—H1	125.0 (9)
C5—C4—C3	124.46 (12)	C8—N1—H1	126.4 (9)
C4—C5—C6	116.66 (12)	C9—N2—N3	122.64 (10)
C4—C5—H5	121.7	C9—N2—H2	122.5 (10)
C6—C5—H5	121.7	N3—N2—H2	114.1 (10)
C5—C6—C1	119.69 (11)	N2—N3—H3	108.9 (9)
C5—C6—C7	133.47 (12)	N2—N3—H4	106.8 (10)
C1—C6—C7	106.84 (11)	H3—N3—H4	109.0 (14)
N1—C1—C2—C3	179.90 (12)	C1—C6—C7—C8	0.22 (13)
C6—C1—C2—C3	−0.06 (18)	C6—C7—C8—N1	0.14 (14)
C1—C2—C3—C4	0.29 (19)	C6—C7—C8—C9	179.73 (12)
C2—C3—C4—F1	−179.81 (11)	N1—C8—C9—O1	4.26 (19)
C2—C3—C4—C5	−0.1 (2)	C7—C8—C9—O1	−175.31 (13)
F1—C4—C5—C6	179.40 (11)	N1—C8—C9—N2	−176.29 (11)
C3—C4—C5—C6	−0.27 (19)	C7—C8—C9—N2	4.1 (2)
C4—C5—C6—C1	0.49 (17)	C2—C1—N1—C8	−179.38 (12)
C4—C5—C6—C7	−179.26 (13)	C6—C1—N1—C8	0.58 (14)
N1—C1—C6—C5	179.69 (11)	C7—C8—N1—C1	−0.45 (15)
C2—C1—C6—C5	−0.35 (18)	C9—C8—N1—C1	179.90 (11)
N1—C1—C6—C7	−0.49 (13)	O1—C9—N2—N3	−4.4 (2)
C2—C1—C6—C7	179.47 (11)	C8—C9—N2—N3	176.16 (11)
C5—C6—C7—C8	180.00 (13)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N3^{i}	0.898 (16)	2.096 (16)	2.9864 (15)	171.3 (13)
N2—H2···O1^{ii}	0.870 (16)	2.073 (16)	2.9193 (14)	163.9 (14)
N3—H3···O1^{iii}	0.920 (16)	2.124 (16)	3.0241 (15)	165.8 (13)
C3—H3*A*···F1^{iv}	0.95	2.55	3.2082 (15)	127

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