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Methyl 5-fluoro-1*H*-indole-2-carboxylate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.110
Data-to-parameter ratio = 14.7

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

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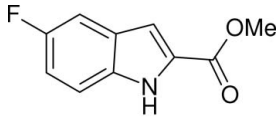
The geometrical parameters for the title compound, $C_{10}H_8FNO_2$, are normal. In the crystal structure, the molecules form inversion-symmetry-generated dimeric pairs by way of two N—H···O hydrogen bonds.

Comment

Several indolecarboxylic acid derivatives show biological activity: methyl indole-3-carboxylate, extracted from a marine microorganism (Hu *et al.*, 2005), is cytotoxic against the K562 human leukaemia strain. Methyl indole-2-carboxylic acid may serve as a glycine site antagonist and hence aid in the treatment of human brain injuries (Morzyk-Ociepa *et al.*, 2004). 5-Fluoroindole-3-acetic acid (Antolic *et al.*, 1996) has plant-growth regulating activity. The crystal structure of methyl indole-2-carboxylate has been deposited [Parsons, S., McNab, H. & Wood, P. (2004). refcode OCAQEP] with the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002). As part of our ongoing research in this area, the structure of the related title compound, (I) (Fig. 1), prepared by the Fischer indole synthesis reaction (Narayana *et al.*, 2005), is now presented.



(I)

The geometrical parameters for (I) are consistent with those of the compounds noted above. In particular, methyl indole-2-carboxylic acid, (II) (Morzyk-Ociepa *et al.*, 2004), has almost identical geometry to (I). For example, the benzene-ring bond lengths (Å) in (I) are C1—C2 = 1.396 (2) [equivalent value in (II) = 1.390 (2) Å], C2—C3 = 1.375 (2) [1.372 (2)], C3—C4 = 1.399 (2) [1.404 (2)], C4—C5 = 1.356 (2) [1.357 (2)], C5—C6 = 1.408 (2) [1.409 (2)] and C6—C1 = 1.416 (2) [1.403 (2)]. Apart from the methyl H atoms, the molecule in (I) is essentially planar [r.m.s. deviation of the non-H atoms from the mean plane = 0.031 Å, max. = 0.0327 (11) Å for N1]. The bond angle sum about N1 is 359.7°. The crystal packing in (I) exhibits inversion-symmetry-generated dimeric pairs of molecules linked by two N—H···O hydrogen bonds (Table 1 and Fig. 2). A similar pairing arrangement was seen in the structure of methyl indole-2-carboxylate (CSD refcode OCAQEP) although the overall structure is different to (I). Conversely, in methyl indole-2-carboxylic acid (Morzyk-Ociepa *et al.*, 2004) a completely different arrangement of N—H···O and O—H···O hydrogen bonds leads to chains of molecules. There are no π–π stacking interactions in (I), the shortest intermolecular ring-centroid separation being 4.35 Å.

Experimental

Methyl pyruvate-4-fluorophenylhydrazone (2 g, 0.0095 mol) was added to 10 g polyphosphoric acid and continuously stirred for proper mixing. The reaction mass was slowly heated to 353–363 K and maintained for 4 h. The progress of the reaction was monitored by TLC. The reaction mass was cooled and water (100 ml) was added to break up the lumps until it became a slurry. The separated solid was filtered off and washed with water. The dried crude product was charcoalized in ethyl acetate, filtered over hyflo/silica gel, slowly cooled to room temperature and kept overnight with stirring. After recrystallization from ethyl acetate, colourless crystals of (I) were obtained in 60% yield (m.p. 474 K). Analysis found (calculated) for $C_{10}H_8FNO_2$: C 62.11 (62.18), H 4.09 (4.17), N 7.13 (7.25)%.

Crystal data

$C_{10}H_8FNO_2$
M_r = 193.17
Monoclinic, $P2_1/n$
a = 12.4420 (7) Å
b = 3.8185 (1) Å
c = 18.269 (1) Å
β = 100.125 (2)°
V = 854.43 (7) Å^3
Z = 4
D_x = 1.502 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 120 (2) K
Needle, colourless
0.41 × 0.07 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.952, T_{max} = 0.994
10458 measured reflections
1937 independent reflections
1311 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 27.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.110
S = 1.03
1937 reflections
132 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.014 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.883 (18)	2.019 (18)	2.8555 (18)	157.7 (15)

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

The N-bound H atom was located in a difference map and its position was freely refined with U_{iso}(H) = 1.2U_{eq}(N). The C-bound H atoms were placed in idealized locations (C—H = 0.95–0.99 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The methyl group was rotated about its C—N bond to best fit the electron density.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*, *DENZO* (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*.

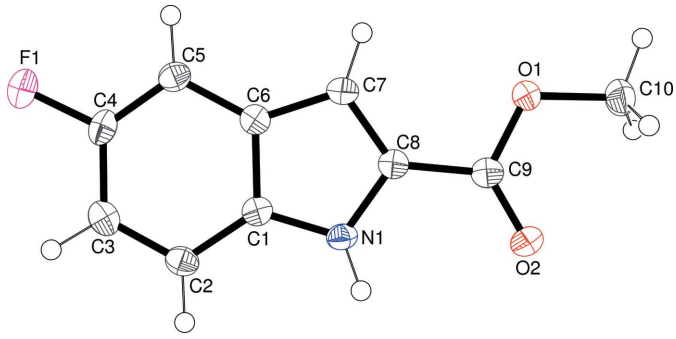


Figure 1
View of (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms.

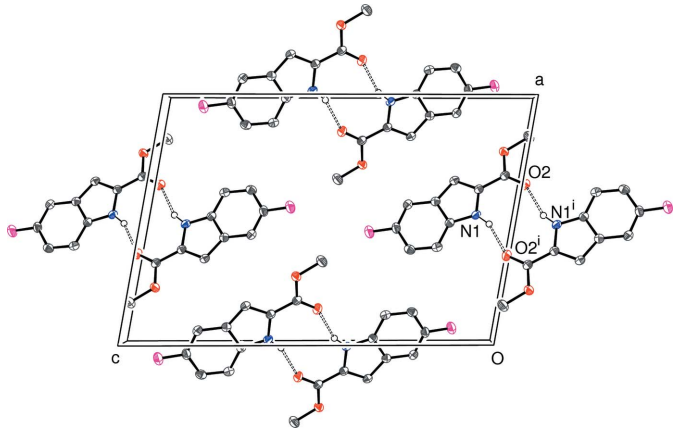


Figure 2
Unit cell packing in (I) with all H atoms except H1 omitted for clarity and hydrogen bonds indicated by dashed lines. See Table 1 for symmetry code.

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supporting information

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Crystal data

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Hall symbol: -P 2yn
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$c = 18.269$ (1) Å
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$V = 854.43$ (7) Å^3
$Z = 4$
$F(000) = 400$
$D_x = 1.502$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2189 reflections
$\theta = 1.0$–$27.5°$
$\mu = 0.12$ mm^{-1}
$T = 120$ K
Needle, colourless
0.41 × 0.07 × 0.05 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)
$T_{min} = 0.952$, $T_{max} = 0.994$
10458 measured reflections
1937 independent reflections
1311 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.6°$, $\theta_{min} = 4.0°$
$h = -16\rightarrow16$
$k = -4\rightarrow4$
$l = -22\rightarrow23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.110$
$S = 1.03$
1937 reflections
132 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difmap and geom
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.014 (3)

Special details

Experimental. 1H NMR (CDCl3, 300?MHz): δ 3.92 (s, 3H, –CH3), 7.01 (dt, 1H, Ar—H), 7.10 (s, 1H, Ar—H), 7.25 (dd, J =2.4 and 9.3 Hz, 1H, Ar—H), 7.44 (dd, J = 4.2 and 8.7 Hz, 1H, Ar—H), 11.38 (br s, 1H, –NH–, exchangeable with D2O).

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	0.48721 (12)	0.2695 (4)	0.17446 (9)	0.0207 (4)
C2	0.39008 (13)	0.1753 (4)	0.19763 (9)	0.0241 (4)
H2	0.3330	0.0610	0.1649	0.029*
C3	0.38010 (13)	0.2540 (4)	0.26959 (9)	0.0255 (4)
H3	0.3156	0.1922	0.2877	0.031*
C4	0.46546 (14)	0.4259 (4)	0.31588 (9)	0.0252 (4)
C5	0.56073 (13)	0.5227 (4)	0.29536 (9)	0.0232 (4)
H5	0.6165	0.6391	0.3288	0.028*
C6	0.57298 (13)	0.4421 (4)	0.22209 (9)	0.0204 (4)
C7	0.65781 (12)	0.4953 (4)	0.18042 (9)	0.0210 (4)
H7	0.7259	0.6068	0.1972	0.025*
C8	0.62237 (12)	0.3543 (4)	0.11111 (9)	0.0200 (4)
C9	0.67713 (12)	0.3284 (4)	0.04739 (9)	0.0216 (4)
C10	0.83499 (14)	0.4799 (5)	−0.00077 (10)	0.0318 (4)
H10A	0.9051	0.5999	0.0142	0.048*
H10B	0.7929	0.5979	−0.0442	0.048*
H10C	0.8481	0.2360	−0.0134	0.048*
N1	0.51896 (10)	0.2191 (3)	0.10736 (8)	0.0213 (3)
H1	0.4827 (14)	0.101 (4)	0.0694 (10)	0.026*
O1	0.77453 (9)	0.4888 (3)	0.05982 (6)	0.0247 (3)
O2	0.64084 (9)	0.1788 (3)	−0.01054 (6)	0.0286 (3)
F1	0.44961 (8)	0.5000 (3)	0.38680 (5)	0.0356 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0213 (8)	0.0185 (8)	0.0214 (9)	0.0024 (6)	0.0017 (7)	0.0013 (6)
C2	0.0209 (8)	0.0225 (9)	0.0277 (10)	−0.0002 (7)	0.0013 (7)	0.0015 (7)
C3	0.0231 (9)	0.0231 (9)	0.0313 (10)	0.0032 (7)	0.0076 (7)	0.0044 (7)
C4	0.0299 (9)	0.0267 (9)	0.0199 (9)	0.0059 (7)	0.0071 (7)	0.0002 (7)
C5	0.0240 (9)	0.0229 (9)	0.0216 (9)	0.0012 (6)	0.0007 (7)	0.0004 (7)
C6	0.0212 (8)	0.0168 (8)	0.0229 (9)	0.0027 (6)	0.0030 (6)	0.0023 (6)
C7	0.0200 (8)	0.0189 (8)	0.0230 (9)	−0.0008 (6)	0.0002 (7)	0.0007 (7)
C8	0.0207 (8)	0.0176 (8)	0.0210 (9)	0.0025 (6)	0.0015 (6)	0.0031 (6)
C9	0.0223 (8)	0.0196 (8)	0.0216 (9)	0.0029 (7)	0.0001 (7)	0.0037 (7)
C10	0.0327 (10)	0.0346 (10)	0.0310 (11)	−0.0048 (8)	0.0137 (8)	−0.0018 (8)
N1	0.0191 (7)	0.0225 (7)	0.0208 (8)	0.0001 (5)	−0.0004 (5)	−0.0027 (6)

O1	0.0231 (6)	0.0287 (7)	0.0231 (7)	−0.0044 (5)	0.0064 (5)	−0.0024 (5)
O2	0.0289 (7)	0.0352 (7)	0.0210 (7)	−0.0044 (5)	0.0022 (5)	−0.0051 (5)
F1	0.0394 (6)	0.0447 (7)	0.0254 (6)	−0.0011 (5)	0.0127 (5)	−0.0044 (5)

Geometric parameters (Å, º)

C1—N1	1.366 (2)	C7—C8	1.375 (2)
C1—C2	1.396 (2)	C7—H7	0.9500
C1—C6	1.416 (2)	C8—N1	1.377 (2)
C2—C3	1.375 (2)	C8—C9	1.452 (2)
C2—H2	0.9500	C9—O2	1.2173 (18)
C3—C4	1.399 (2)	C9—O1	1.3412 (19)
C3—H3	0.9500	C10—O1	1.444 (2)
C4—C5	1.356 (2)	C10—H10A	0.9800
C4—F1	1.3739 (19)	C10—H10B	0.9800
C5—C6	1.408 (2)	C10—H10C	0.9800
C5—H5	0.9500	N1—H1	0.883 (18)
C6—C7	1.420 (2)		
N1—C1—C2	129.66 (14)	C8—C7—H7	126.6
N1—C1—C6	108.14 (14)	C6—C7—H7	126.6
C2—C1—C6	122.19 (15)	C7—C8—N1	109.76 (14)
C3—C2—C1	117.52 (15)	C7—C8—C9	130.19 (15)
C3—C2—H2	121.2	N1—C8—C9	120.04 (14)
C1—C2—H2	121.2	O2—C9—O1	123.19 (15)
C2—C3—C4	119.59 (15)	O2—C9—C8	125.07 (15)
C2—C3—H3	120.2	O1—C9—C8	111.74 (13)
C4—C3—H3	120.2	O1—C10—H10A	109.5
C5—C4—F1	118.81 (14)	O1—C10—H10B	109.5
C5—C4—C3	124.63 (16)	H10A—C10—H10B	109.5
F1—C4—C3	116.56 (14)	O1—C10—H10C	109.5
C4—C5—C6	116.71 (15)	H10A—C10—H10C	109.5
C4—C5—H5	121.6	H10B—C10—H10C	109.5
C6—C5—H5	121.6	C1—N1—C8	108.52 (13)
C5—C6—C1	119.36 (15)	C1—N1—H1	126.1 (11)
C5—C6—C7	133.90 (15)	C8—N1—H1	125.1 (11)
C1—C6—C7	106.74 (14)	C9—O1—C10	115.88 (12)
C8—C7—C6	106.83 (14)		
N1—C1—C2—C3	178.99 (15)	C1—C6—C7—C8	−0.57 (16)
C6—C1—C2—C3	−0.5 (2)	C6—C7—C8—N1	0.64 (17)
C1—C2—C3—C4	0.7 (2)	C6—C7—C8—C9	−178.29 (15)
C2—C3—C4—C5	−0.5 (3)	C7—C8—C9—O2	175.35 (15)
C2—C3—C4—F1	179.30 (13)	N1—C8—C9—O2	−3.5 (2)
F1—C4—C5—C6	−179.78 (12)	C7—C8—C9—O1	−4.2 (2)
C3—C4—C5—C6	0.0 (2)	N1—C8—C9—O1	176.93 (12)
C4—C5—C6—C1	0.2 (2)	C2—C1—N1—C8	−179.43 (15)
C4—C5—C6—C7	−179.57 (16)	C6—C1—N1—C8	0.09 (17)

N1—C1—C6—C5	−179.56 (13)	C7—C8—N1—C1	−0.46 (17)
C2—C1—C6—C5	0.0 (2)	C9—C8—N1—C1	178.59 (13)
N1—C1—C6—C7	0.30 (16)	O2—C9—O1—C10	1.0 (2)
C2—C1—C6—C7	179.86 (14)	C8—C9—O1—C10	−179.46 (13)
C5—C6—C7—C8	179.26 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.883 (18)	2.019 (18)	2.8555 (18)	157.7 (15)

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