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Key indicators

Single-crystal X-ray study
 T = 120 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 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>.

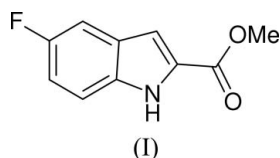
Methyl 5-fluoro-1*H*-indole-2-carboxylate

The geometrical parameters for the title compound, $\text{C}_{10}\text{H}_8\text{FNO}_2$, are normal. In the crystal structure, the molecules form inversion-symmetry-generated dimeric pairs by way of two $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Received 8 August 2006
 Accepted 9 August 2006

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.



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 (\AA) in (I) are $\text{C1}-\text{C2} = 1.396(2)$ [equivalent value in (II) = $1.390(2) \text{ \AA}$], $\text{C2}-\text{C3} = 1.375(2)$ [$1.372(2)$], $\text{C3}-\text{C4} = 1.399(2)$ [$1.404(2)$], $\text{C4}-\text{C5} = 1.356(2)$ [$1.357(2)$], $\text{C5}-\text{C6} = 1.408(2)$ [$1.409(2)$] and $\text{C6}-\text{C1} = 1.416(2)$ [$1.403(2)$]. 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 \AA , max. = $0.0327(11) \text{ \AA}$ 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 $\text{N}-\text{H}\cdots\text{O}$ 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 $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds leads to chains of molecules. There are no $\pi-\pi$ stacking interactions in (I), the shortest intermolecular ring-centroid separation being 4.35 \AA .

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

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

Data collection

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

Refinement

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

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------|------------|-------------|-------------|---------------|
| $N1-H1\cdots O2^i$ | 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The C-bound H atoms were placed in idealized locations ($C-H = 0.95\text{--}0.99 \text{ \AA}$) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. 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*.

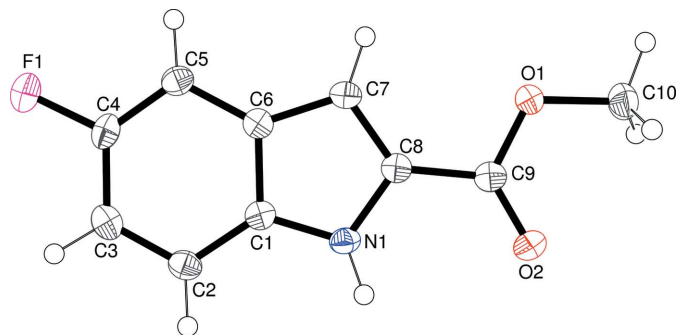


Figure 1

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

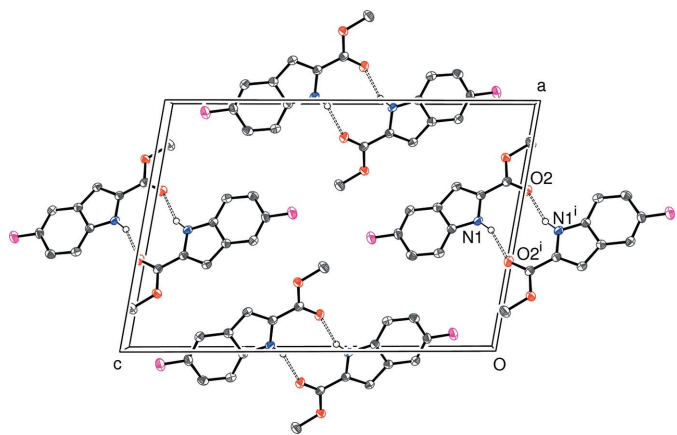


Figure 2

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.

We thank the EPSRC National Crystallography Service (University of Southampton, England) for data collection. ABV thanks Mangalore University for provision of research facilities.

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supporting information

Acta Cryst. (2006). E62, o4050–o4051 [https://doi.org/10.1107/S1600536806031448]

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

$C_{10}H_8FNO_2$

$M_r = 193.17$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 12.4420$ (7) Å

$b = 3.8185$ (1) Å

$c = 18.269$ (1) Å

$\beta = 100.125$ (2)°

$V = 854.43$ (7) Å³

$Z = 4$

$F(000) = 400$

$D_x = 1.502$ 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

$0.41 \times 0.07 \times 0.05$ 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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 27.6$ °, $\theta_{\min} = 4.0$ °

$h = -16 \rightarrow 16$

$k = -4 \rightarrow 4$

$l = -22 \rightarrow 23$

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,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|------------|---------------|----------------------------------|
| 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 (\AA^2)

| | 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, °)

| | | | |
|-------------|--------------|---------------|--------------|
| 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, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1 \cdots O2 ⁱ | 0.883 (18) | 2.019 (18) | 2.8555 (18) | 157.7 (15) |

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