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Methyl 1-methyl-1*H*-indole-3-carboxylate

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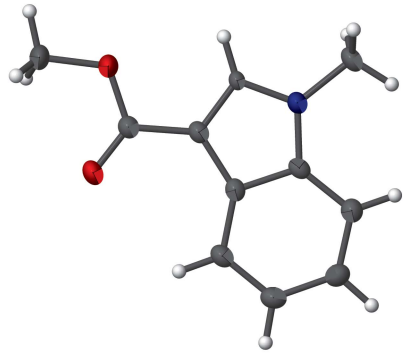
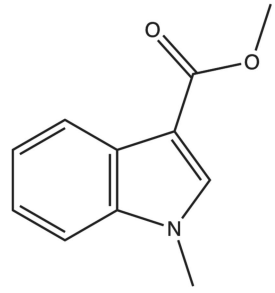
Structural data: full structural data are available from iucrdata.iucr.org

The title indole derivative, $C_{11}H_{11}NO_2$, was synthesized from 1-methyl-1*H*-indole-3-carboxylic acid and methanol. The molecule is planar as it is situated on a mirror plane present in the space group *Pbcm*. In the crystal, molecules form three kinds of intermolecular C—H···O hydrogen bonds, resulting in a sheet structure in the *ab* plane. Parallel sheets interact by C—H···π stacking, stabilizing the crystal packing.

3D view



Chemical scheme



Structure description

The indole moiety is found in a large array of natural products and pharmaceuticals and widely used for its anti-allergic (Shigenaga *et al.*, 1993), central-nervous-system depressant (Sen Gupta *et al.*, 1982) and muscle relaxant (Butera *et al.*, 1978) properties. Indolecarboxylic acid derivatives show biological activity (Morzyk-Ociepa *et al.*, 2004). 5-Fluoroindole-3-acetic acid has plant-growth regulating activity (Antolic *et al.*, 1996). A comprehensive review on the biological importance of the indole nucleus in recent years was published by Sharma *et al.* (2010) and the biomedical importance of indoles was reported on by Kaushik *et al.* (2013). Reviews on indoles as anticancer agents (El Sayed *et al.*, 2015) and on recent developments of indole-containing antiviral agents (Zhang *et al.*, 2015) have been published.

The crystal structures of similar compounds *viz.* indole-3-carboxylic acid (Smith *et al.*, 2003), indole-2-carboxylic acid (Morzyk-Ociepa *et al.*, 2004), methyl 5-fluoro-1*H*-indole-2-carboxylate (Harrison *et al.*, 2006), 5-fluoro-1*H*-indole-2-carbohydrazide (Harrison *et al.*, 2006*a*), methyl 5-chloro-1*H*-indole-2-carboxylate (Butcher *et al.*, 2006), methyl 5-bromo-1*H*-indole-2-carboxylate (Butcher *et al.*, 2007), (4-bromophenyl)(1*H*-indol-7-yl)methanone (Dutkiewicz *et al.*, 2009), 6-fluoro-1*H*-indole-3-carboxylic acid (Lou &

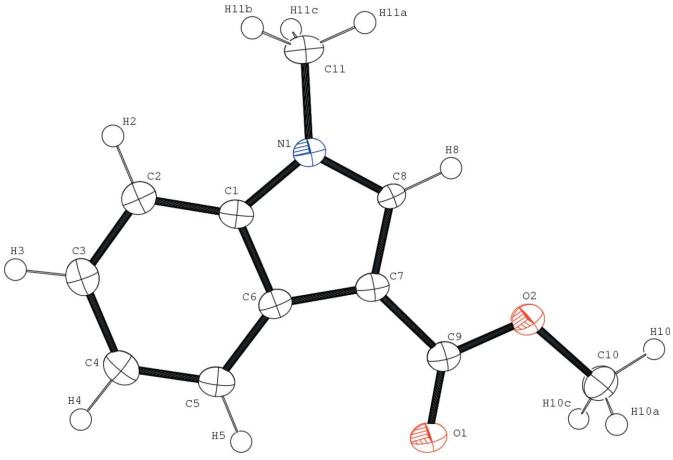


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

Luo, 2012), 5-fluoro-1*H*-indole-3-carboxylic acid (Lu *et al.*, 2012) and 6-bromo-1*H*-indole-3-carboxylic acid (Zhao & Wang, 2012) have been reported.

The molecular structure of the title compound consists of an indole substituted by one methyl and one carboxymethyl group (Fig. 1). The molecule is planar as it is situated on a mirror plane belonging to the space group *Pbcm* (except for hydrogen atoms H10*B*, H10*C*, H11*B* and H11*C*). The N1—C11 bond length of the methyl substituent is 1.453 (3) Å, the C7—C9 bond length of the carboxymethyl substituent is 1.467 (3) Å and the O2—C10 bond of the carboxymethyl substituent is 1.445 (3) Å.

In the crystal, molecules are connected along the *a*- and *b*-axis directions by C—H···O hydrogen bonds, forming two-dimensional sheets (Table 1 and Fig. 2). In addition, a weak C—H···π interaction C11—H11*B*···*Cg*1 (2.69 Å) is observed between neighboring sheets (Table 1 and Fig. 3; *Cg*1 is the centroid of the C1–C6 ring). In the packing of the similar structure methyl indole-3-carboxylate (Hu *et al.*, 2005), the molecules are linked by intermolecular hydrogen bonds and form chains along the *b*-axis direction.

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	A···H	D—H···A
C4—H4···O2^{i}	0.95	2.39	3.318 (3)	167
C11—H11*A*···O1^{ii}	0.98	2.53	3.505 (4)	176
C2—H2···O1^{ii}	0.95	2.46	3.400 (3)	172
C11—H11*B*···*Cg*1^{iii}	0.98	2.69	3.412	131

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

Synthesis and crystallization

1-Methyl-1*H*-indole-3-carboxylic acid (Sigma–Aldrich) (2 g) was taken in a 100 ml round-bottomed flask. 20 ml of methanol and a catalytic amount of conc. H_2SO_4 (2 drops) was added and the reaction mixture was refluxed overnight. The completion of the reaction was confirmed by TLC and the reaction mixture was quenched with water; the precipitate formed was collected by filtration and dried. The product was recrystallized from methanol solution (m.p. 410 K). IR (KBr, cm^{-1}): 1704 (C═O). The UV–vis spectrum was measured in MeOH solution (concentration $\simeq 1.0\times10^{-2}$ m*M*): λ_{max} = 297 nm.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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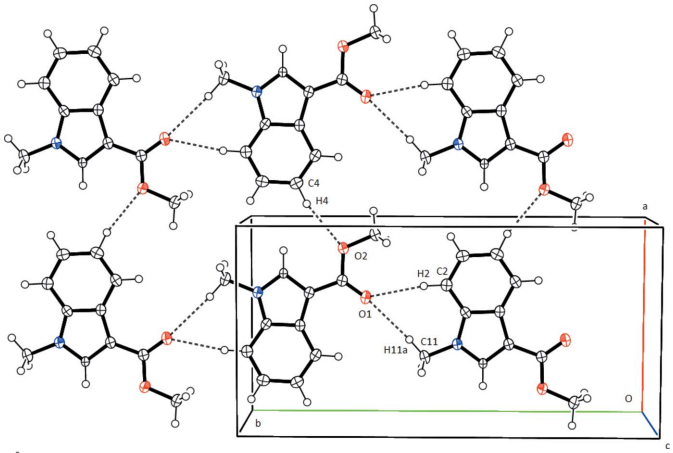

Figure 2
A view of the C—H···O hydrogen bonds (dashed lines) present in the crystal structure of the title compound.

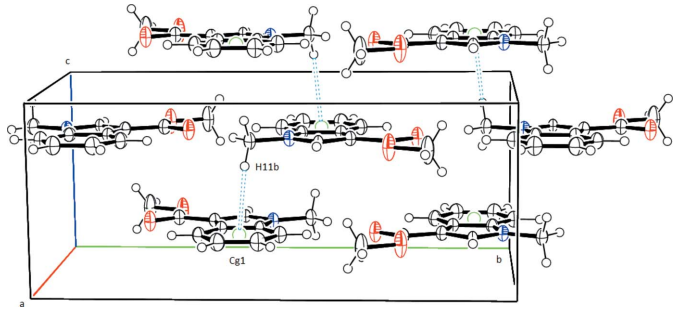

Figure 3
Part of the crystal packing showing the C—H···π stacking interactions. *Cg*1 is the centroid of the C1–C6 ring.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{11}NO_2$
M_r	189.21
Crystal system, space group	Orthorhombic, *Pbcm*
Temperature (K)	173
a, b, c (Å)	8.3019 (17), 16.628 (3), 6.7622 (14)
V (Å^3)	933.5 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.50 × 0.24 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.88, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4700, 1142, 1053
R_{int}	0.018
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.208, 1.12
No. of reflections	1142
No. of parameters	85
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.72, −0.98

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *SHELXTL* (Sheldrick, 2008).

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full crystallographic data

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Methyl 1-methyl-1*H*-indole-3-carboxylate

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Methyl 1-methyl-1*H*-indole-3-carboxylate

Crystal data

$C_{11}H_{11}NO_2$
M_r = 189.21
Orthorhombic, *Pbcm*
a = 8.3019 (17) Å
b = 16.628 (3) Å
c = 6.7622 (14) Å
V = 933.5 (3) Å^3
Z = 4
F(000) = 400
D_x = 1.346 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 3337 reflections
θ = 2.5–27.5°
μ = 0.09 mm^{-1}
T = 173 K
Prism, colorless
0.50 × 0.24 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.88, T_{max} = 0.98
4700 measured reflections
1142 independent reflections
1053 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 27.5°, θ_{min} = 2.5°
h = −10→10
k = −20→21
l = −8→6

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.208
S = 1.12
1142 reflections
85 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1286P)^2 + 0.595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All H atoms were located in difference Fourier maps. C-bound H atoms were constrained using a riding model [C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for indole H atoms, and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms].

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.6055 (2)	0.79479 (11)	0.75	0.0350 (6)	
N1	0.6285 (3)	0.52415 (12)	0.75	0.0240 (5)	
O2	0.8514 (2)	0.73850 (12)	0.75	0.0445 (7)	
C8	0.7251 (3)	0.58886 (12)	0.75	0.0179 (5)	
H8	0.8395	0.589	0.75	0.021*	
C7	0.6279 (3)	0.65316 (14)	0.75	0.0233 (6)	
C6	0.4631 (3)	0.62971 (13)	0.75	0.0225 (6)	
C1	0.4691 (3)	0.54488 (14)	0.75	0.0228 (6)	
C11	0.6944 (3)	0.44316 (16)	0.75	0.0290 (6)	
H11A	0.606	0.4041	0.75	0.044*	
H11B	0.7607	0.4354	0.6317	0.044*	0.5
H11C	0.7607	0.4354	0.8683	0.044*	0.5
C9	0.6900 (3)	0.73575 (15)	0.75	0.0254 (6)	
C2	0.3304 (3)	0.49675 (16)	0.75	0.0284 (6)	
H2	0.3362	0.4397	0.75	0.034*	
C5	0.3130 (3)	0.66896 (16)	0.75	0.0277 (6)	
H5	0.3062	0.726	0.75	0.033*	
C4	0.1759 (3)	0.62199 (17)	0.75	0.0315 (7)	
H4	0.0733	0.6473	0.75	0.038*	
C3	0.1847 (3)	0.53694 (18)	0.75	0.0325 (7)	
H3	0.0877	0.5066	0.75	0.039*	
C10	0.9213 (4)	0.81809 (17)	0.75	0.0488 (10)	
H10A	1.0391	0.8138	0.75	0.073*	
H10B	0.8862	0.8472	0.6317	0.073*	0.5
H10C	0.8862	0.8472	0.8683	0.073*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0301 (10)	0.0179 (9)	0.0569 (13)	0.0022 (7)	0	0
N1	0.0231 (11)	0.0175 (10)	0.0315 (11)	0.0010 (8)	0	0
O2	0.0240 (10)	0.0187 (10)	0.0908 (19)	−0.0017 (7)	0	0
C8	0.0178 (11)	0.0123 (10)	0.0235 (11)	0.0001 (7)	0	0
C7	0.0244 (12)	0.0181 (12)	0.0273 (12)	0.0022 (9)	0	0
C6	0.0251 (13)	0.0181 (11)	0.0244 (11)	−0.0001 (9)	0	0
C1	0.0232 (13)	0.0198 (11)	0.0253 (12)	0.0047 (9)	0	0
C11	0.0314 (13)	0.0181 (12)	0.0375 (14)	0.0056 (9)	0	0
C9	0.0244 (12)	0.0202 (13)	0.0315 (12)	0.0008 (8)	0	0
C2	0.0268 (13)	0.0223 (12)	0.0360 (13)	−0.0003 (10)	0	0
C5	0.0268 (13)	0.0219 (12)	0.0343 (13)	0.0049 (9)	0	0
C4	0.0236 (13)	0.0302 (14)	0.0407 (15)	0.0043 (10)	0	0

C3	0.0226 (12)	0.0300 (14)	0.0450 (16)	−0.0015 (10)	0	0
C10	0.0281 (14)	0.0199 (13)	0.098 (3)	−0.0039 (10)	0	0

Geometric parameters (Å, º)

O1—C9	1.206 (3)	C11—H11A	0.98
N1—C8	1.342 (3)	C11—H11B	0.98
N1—C1	1.368 (3)	C11—H11C	0.98
N1—C11	1.453 (3)	C2—C3	1.382 (4)
O2—C9	1.341 (3)	C2—H2	0.95
O2—C10	1.445 (3)	C5—C4	1.380 (4)
C8—C7	1.340 (3)	C5—H5	0.95
C8—H8	0.95	C4—C3	1.416 (4)
C7—C6	1.423 (3)	C4—H4	0.95
C7—C9	1.467 (3)	C3—H3	0.95
C6—C5	1.407 (3)	C10—H10A	0.98
C6—C1	1.412 (3)	C10—H10B	0.98
C1—C2	1.402 (4)	C10—H10C	0.98
C8—N1—C1	112.1 (2)	O1—C9—O2	123.6 (2)
C8—N1—C11	121.2 (2)	O1—C9—C7	123.9 (2)
C1—N1—C11	126.7 (2)	O2—C9—C7	112.5 (2)
C9—O2—C10	115.6 (2)	C3—C2—C1	116.3 (2)
C7—C8—N1	106.3 (2)	C3—C2—H2	121.9
C7—C8—H8	126.9	C1—C2—H2	121.9
N1—C8—H8	126.9	C4—C5—C6	117.9 (2)
C8—C7—C6	111.1 (2)	C4—C5—H5	121.1
C8—C7—C9	122.4 (2)	C6—C5—H5	121.1
C6—C7—C9	126.5 (2)	C5—C4—C3	121.5 (2)
C5—C6—C1	119.7 (2)	C5—C4—H4	119.3
C5—C6—C7	136.5 (2)	C3—C4—H4	119.3
C1—C6—C7	103.9 (2)	C2—C3—C4	121.9 (2)
N1—C1—C2	130.6 (2)	C2—C3—H3	119.0
N1—C1—C6	106.6 (2)	C4—C3—H3	119.0
C2—C1—C6	122.8 (2)	O2—C10—H10A	109.5
N1—C11—H11A	109.5	O2—C10—H10B	109.5
N1—C11—H11B	109.5	H10A—C10—H10B	109.5
H11A—C11—H11B	109.5	O2—C10—H10C	109.5
N1—C11—H11C	109.5	H10A—C10—H10C	109.5
H11A—C11—H11C	109.5	H10B—C10—H10C	109.5
H11B—C11—H11C	109.5		
C1—N1—C8—C7	0	C7—C6—C1—C2	180.0
C11—N1—C8—C7	180.0	C10—O2—C9—O1	0
N1—C8—C7—C6	0	C10—O2—C9—C7	180.0
N1—C8—C7—C9	180.0	C8—C7—C9—O1	180.0
C8—C7—C6—C5	180.0	C6—C7—C9—O1	0
C9—C7—C6—C5	0	C8—C7—C9—O2	0

C8—C7—C6—C1	0	C6—C7—C9—O2	180.0
C9—C7—C6—C1	180.0	N1—C1—C2—C3	180.0
C8—N1—C1—C2	180.0	C6—C1—C2—C3	0
C11—N1—C1—C2	0	C1—C6—C5—C4	0
C8—N1—C1—C6	0	C7—C6—C5—C4	180.0
C11—N1—C1—C6	180.0	C6—C5—C4—C3	0
C5—C6—C1—N1	180.0	C1—C2—C3—C4	0
C7—C6—C1—N1	0	C5—C4—C3—C2	0
C5—C6—C1—C2	0		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O2^{i}	0.95	2.39	3.318 (3)	167
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