

Weak interactions in the crystal structures of two indole derivatives

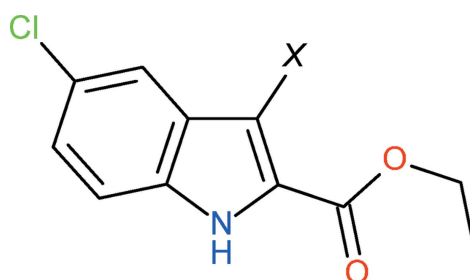
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We describe the syntheses and crystal structures of two indole derivatives, namely a second monoclinic polymorph of ethyl 5-chloro-1*H*-indole-2-carboxylate C₁₁H₁₀ClNO₂, (I), and ethyl 5-chloro-3-iodo-1*H*-indole-2-carboxylate, C₁₁H₉ClINO₂, (II). In their crystal structures, both compounds form inversion dimers linked by pairs of N—H...O hydrogen bonds, which generate *R*₂²(10) loops. The dimers are linked into double chains in (I) and sheets in (II) by a variety of weak interactions, including π – π stacking, C—I... π , C—Cl— π interactions and I...Cl halogen bonds.

1. Chemical context

As part of our ongoing synthetic, biological (Kerr, 2013) and structural studies (Kerr *et al.*, 2016) of variously substituted indole derivatives, we now report the syntheses and crystal structures of ethyl 5-chloro-1*H*-indole-2-carboxylate (I) and ethyl 5-chloro-3-iodo-1*H*-indole-2-carboxylate (II), which differ in the substituent (H or I) at the 3-position of the ring system. Compound (I) is a second monoclinic polymorph of the recently described 5-chloro-1*H*-indole-2-carboxylate (Wu *et al.*, 2013).

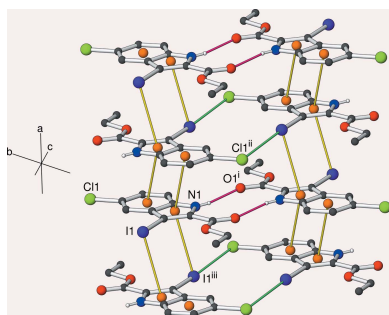


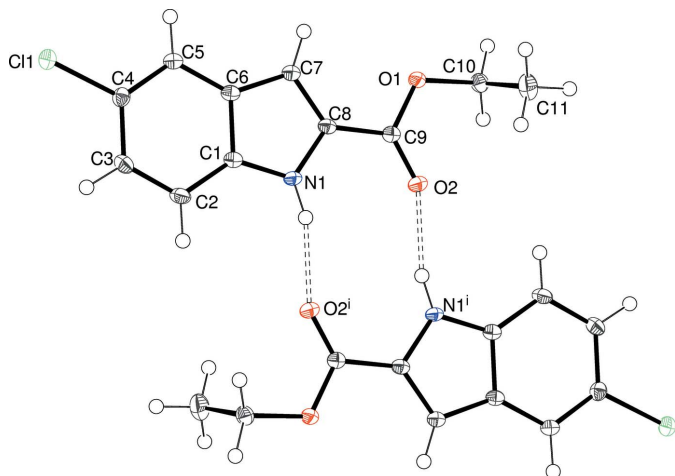
(I) X = H

(II) X = I

2. Structural commentary

Compound (I) crystallizes in space group *P*₂₁/*n* with one molecule in the asymmetric unit (Fig. 1). The dihedral angle between the mean plane of the N1/C1–C8 indole ring system (r.m.s. deviation = 0.010 Å) and the C9/O1/O2 grouping is 2.4 (2)°. The chlorine atom deviates from the indole plane by 0.0625 (14) Å. The C8–C9–O1–C10 torsion angle of

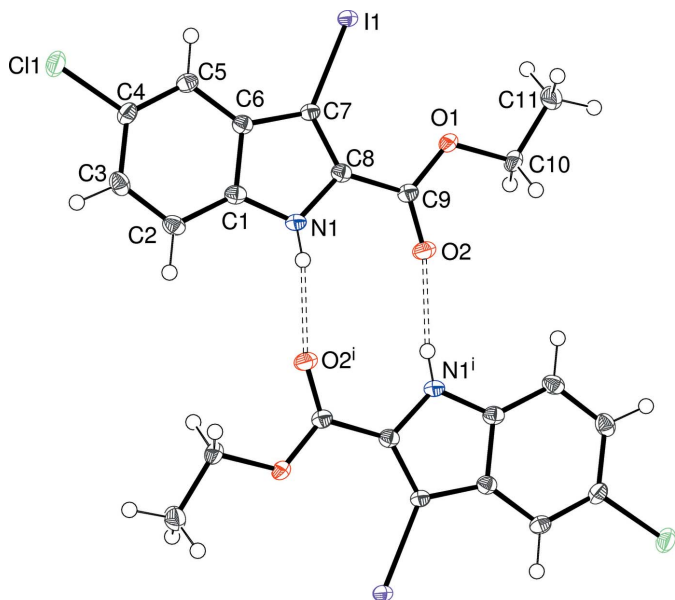



Figure 1

The molecular structure of (I) showing 50% displacement ellipsoids. Also shown with double-dashed lines are the pair of intermolecular N—H \cdots O hydrogen bonds to a nearby molecule related by inversion symmetry, which generate an $R_2^2(10)$ loop. Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

$-178.86(11)^\circ$ indicates an *anti* conformation about the C9—O1 bond, whereas the C9—O1—C10—C11 torsion angle is $-81.73(14)^\circ$ and C11 projects from the mean plane of the other non-hydrogen atoms by $1.298(2) \text{ \AA}$.

In the structure reported by Wu *et al.* (2013), (CCDC refcode VIHMUW), the same molecule also crystallizes in space group $P2_1/n$ [$a = 10.570(3)$, $b = 5.6165(15)$, $c = 18.091(5) \text{ \AA}$, $\beta = 105.681(4)^\circ$, $V = 1034.0(5) \text{ \AA}^3$, $Z = 4$]: the only significant conformational difference compared to (I) is (using our atom-labelling scheme) the C9—O1—C10—C11


Figure 2

The molecular structure of (II) showing 50% displacement ellipsoids. Also shown with double-dashed lines are the pair of intermolecular N—H \cdots O hydrogen bonds to a nearby molecule related by inversion symmetry, which generate an $R_2^2(10)$ loop. Symmetry code: (i) $-x, 2 - y, 1 - z$.

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O2^i$	0.878 (17)	1.977 (17)	2.8288 (15)	163.0 (15)

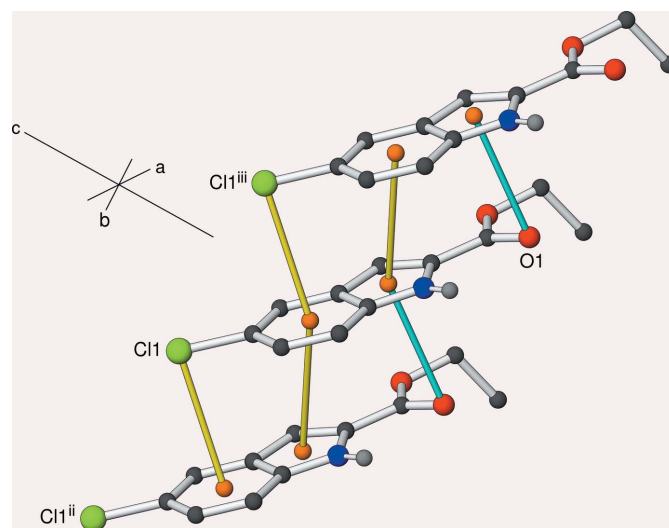
Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

torsion angle of $173.19(12)^\circ$, which indicates that the molecule in the Wu *et al.* polymorph is almost planar (r.m.s. deviation = 0.031 \AA for 15 non-hydrogen atoms). The densities of (I) [$\rho = 1.438 \text{ g cm}^{-3}$] and the Wu polymorph [$\rho = 1.437 \text{ g cm}^{-3}$] are essentially identical.

There is one molecule in the asymmetric unit of (II), which crystallizes in space group $P\bar{1}$, as shown in Fig. 2. The C9/O1/O2 grouping is almost coplanar with the mean-plane of the indole ring system (r.m.s. deviation = 0.009 \AA), as indicated by the dihedral angle of $3.95(7)^\circ$ between C1—C8/N1 and C9/O1/O2. Atoms C11 and I1 deviate from the indole plane by $-0.106(2)$ and $0.081(2) \text{ \AA}$, respectively. The conformation of the C8—C9—O1—C10 bond in (II) [torsion angle = $-177.42(16)^\circ$] is almost the same as the equivalent grouping in (I), but the C9—O1—C10—C11 torsion angle of $-178.33(17)^\circ$ is quite different, and indeed, the complete molecule of (II) is almost planar (r.m.s. deviation = 0.033 \AA for 16 non-hydrogen atoms).

3. Supramolecular features

In the crystal of (I), inversion dimers linked by pairs of N—H \cdots O i [symmetry code: (i) $1 - x, 2 - y, 1 - z$] hydrogen bonds (Table 1, Fig. 1) generate $R_2^2(10)$ loops. The first weak interaction to consider is aromatic π – π stacking between the


Figure 3

Partial packing diagram for (I), showing the formation of [010] chains linked by π – π and C—Cl \cdots π interactions (yellow lines). The long C=O \cdots π contact is indicated by a cyan line. All hydrogen atoms except H1 are omitted for clarity. Symmetry codes (ii) $x, y + 1, z$; (iii) $x, y - 1, z$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O2^i$	0.77 (3)	2.06 (3)	2.821 (2)	168 (3)

Symmetry code: (i) $-x, -y + 2, -z + 1$.

C1–C6 (π_6) ring and the C1/C6/C7/C8/N1 (π_5) five-membered ring displaced by translation in the b -axis direction (Fig. 3). The π_6 – π_5^{ii} [symmetry code: (ii) $x, 1 + y, z$] centroid–centroid separation is 3.7668 (9) Å and the inter-plane angle is 1.30 (7)°. This interaction appears to be reinforced by a weak C–Cl $\cdots\pi_5^{\text{ii}}$ bond (Chifotides & Dunbar, 2013); the chlorine atom lies almost directly above the centre of the six-membered ring displaced in [010] with Cl $\cdots\pi = 3.5363$ (7) Å and C–Cl $\cdots\pi = 86.35$ (5)°. This is very slightly shorter than the contact distance of 3.55 Å for a chlorine atom and a benzene ring, assuming a radius of 1.75 Å for Cl and a half-thickness of 1.8 Å for a benzene ring. Thus, each benzene ring faces a chlorine atom on one face and a five-membered ring on the other (Cl $\cdots\pi_6\cdots\pi_5 = 154.5^\circ$). The carbonyl oxygen atom (O2) of the ester group lies in a reasonable orientation to partake in a C=O $\cdots\pi_5$ bond (Gao *et al.*, 2009) but here the O $\cdots\pi_5^{\text{iii}}$ [symmetry code: (iii) $x, y - 1, z$] separation of 3.4068 (11) Å is significantly greater than the van der Waals' radius sum of 3.32 Å [C=O $\cdots\pi_5 = 88.40$ (8)° and O $\cdots\pi_5\cdots\pi_6 = 153.9^\circ$] and can hardly be considered to be a bond. Taken together, the strong (N–H \cdots O) and weak (π – π , Cl $\cdots\pi$) bonds lead to [010] double chains in the extended structure of (I).

Despite the fact that (I) and the Wu *et al.* (2013) polymorph of the same phase crystallize in the same space group, their

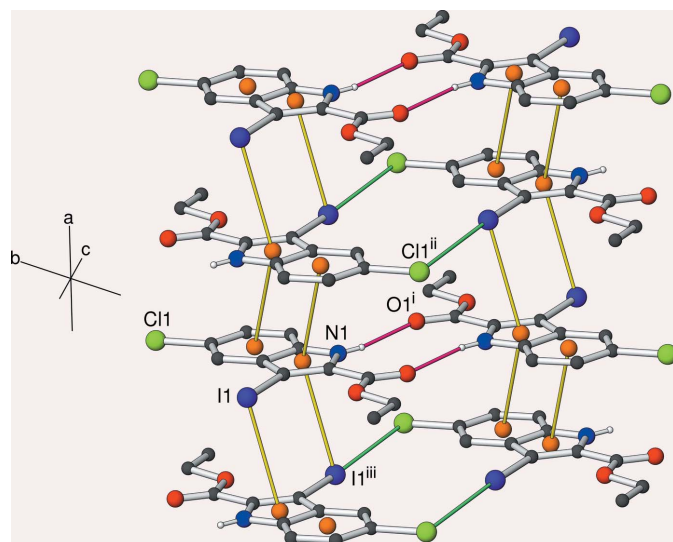


Figure 4
Partial packing diagram for (II), showing part of an (001) sheet. N–H \cdots O hydrogen bonds are indicated by crimson lines, π – π and I $\cdots\pi$ interactions by yellow lines and I \cdots Cl halogen bonds by green lines. All hydrogen atoms except H1 are omitted for clarity. Symmetry codes (i) $-x, 2 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$.

packing motifs are completely different. In the Wu phase, inversion dimers linked by pairs of N–H \cdots O hydrogen bonds also occur but there is no aromatic π – π stacking (the shortest centroid–centroid separation is greater than 4.75 Å) and no C–Cl $\cdots\pi$ contacts. The only significant interaction indicated by a *PLATON* (Spek, 2009) analysis of the structure is a weak C–H $\cdots\pi_5$ bond (H $\cdots\pi = 2.72$ Å). Considered by itself, this interaction links the molecules into [010] chains; taken together, the N–H \cdots O and C–H $\cdots\pi$ interactions generate (110) sheets.

The crystal of (II) also features inversion dimers linked by pairs of N–H \cdots O i [symmetry code: (i) $-x, 2 - y, 1 - z$] hydrogen bonds (Table 2, Fig. 2) involving the equivalent atoms to (I) with the same graph-set motif. Aromatic π – π stacking also occurs in the crystal of (II), but this time the molecules are related by inversion, rather than translation, symmetry: this operation ‘flips’ one of the molecules such that the six-membered ring in each molecule overlaps the five-membered ring in the other (Fig. 6): the π_6 – π_5^{ii} [symmetry code: (ii) $-x, 1 - y, 1 - z$] separation of the centroids of the six- and five-membered rings is 3.6365 (14) Å and the interplanar angle is 0.92 (13)°. The iodine atom of a molecule displaced in the [100] direction lies above the inversion-generated five-membered ring to form a C–I $\cdots\pi_5$ bond with I1 $\cdots\pi_5^{\text{iii}}$ [symmetry code: (iii) $1 - x, 1 - y, 1 - z$] = 3.6543 (11) Å and C7–I1 $\cdots\pi_5^{\text{iii}}$ = 87.00 (7)°. Thus, the five-membered ring faces a six-membered ring on one face and an I atom on the other (I $\cdots\pi_5\cdots\pi_6 = 148.6^\circ$). The I atom also participates in a halogen bond (Desiraju *et al.*, 2013) to the chlorine atom of an inversion-related molecule with I1 \cdots Cl1 $^{\text{iv}}$ [symmetry code: (iv) $1 - x, -y, 1 - z$] = 3.6477 (6) Å (van der Waals contact distance = 3.73 Å), C7–I1 \cdots Cl1 $^{\text{iv}}$ = 173.28 (5)° and C4 $^{\text{iv}}$ –Cl1 $^{\text{iv}}$ \cdots I1 = 104.34 (5)°. These angles clearly define this interaction as a type-II halogen bond (Pedireddi *et al.*, 1994). Taken together, the weak and strong interactions lead to (001) sheets, with the centrosymmetric pairs of I \cdots Cl halogen bonds and pairs of N–H \cdots O hydrogen bonds alternating with respect to the [100] direction (Fig. 4).

4. Database survey

A search of the Cambridge Structural Database (CSD; Groom *et al.*, 2016) revealed 24 indole derivatives with an ester group at the 2-position of the ring system. In terms of halogen substitution, there were 58 5-chloro and just two 3-iodo derivatives. As noted above, VIHMUW (Wu *et al.*, 2013) is a polymorph of (I): crystals of this phase in the form of colourless prisms were obtained by recrystallization from ethanol solution at room temperature, compared to colourless needles obtained from methanol solution at room temperature in the present study.

There has recently been debate on the significance – or otherwise – of weak intermolecular interactions in establishing the packing in molecular crystals (Dunitz, 2015; Thakur *et al.*, 2015). The latter authors mentioned the role of weak interactions in establishing the structures of polymorphs and it is

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₁₁ H ₁₀ ClNO ₂	C ₁₁ H ₉ ClINO ₂
<i>M_r</i>	223.65	349.54
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.7168 (6), 4.5783 (1), 16.5929 (11)	7.7733 (5), 7.8240 (5), 10.4594 (7)
α , β , γ (°)	90, 97.464 (7), 90	86.085 (8), 80.575 (7), 71.308 (6)
<i>V</i> (Å ³)	1033.20 (9)	594.35 (7)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.35	2.90
Crystal size (mm)	0.70 × 0.04 × 0.03	0.17 × 0.10 × 0.02
Data collection		
Diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD
Absorption correction	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2012)	Multi-scan (<i>CrystalClear</i> ; Rigaku, 2012)
<i>T</i> _{min} , <i>T</i> _{max}	0.793, 0.990	0.638, 0.944
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7035, 2340, 2051	7837, 2739, 2640
<i>R</i> _{int}	0.022	0.031
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.649	0.650
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.082, 1.09	0.022, 0.058, 1.04
No. of reflections	2340	2739
No. of parameters	139	149
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.33, -0.23	1.18, -0.44

Computer programs: *CrystalClear* (Rigaku, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *ATOMS* (Dowty, 2006) and *publCIF* (Westrip, 2010).

striking to us how different the packing motifs of (I) and VIHMUW are.

5. Synthesis and crystallization

To prepare (I), a mixture of ethyl 2-(2-[4-chlorophenyl]hydrazono)propanoate (2.29 g, 9.51 mmol), prepared from *p*-chlorophenylhydrazine hydrochloride and ethyl pyruvate according to a published method (Zhang *et al.*, 2011) and PPA (22.54 g) were refluxed in toluene (40 ml) for 3 h. After cooling, the solvent was decanted off and the solid residue was washed with toluene (3 × 50 ml). Evaporation of the combined organic phases under reduced pressure gave a yellow solid, flash chromatography of which (1:6 ethyl acetate, hexanes) afforded ethyl 5-chloro-1*H*-indole-2-carboxylate as a yellow solid (1.34 g, 63%). Colourless needles of (I) were recrystallized from methanol solution at room temperature. δ C(101 MHz; CDCl₃) 162.0 (Cq), 135.2 (Cq), 128.9 (Cq), 128.6 (Cq), 126.7 (Cq), 126.0 (CH), 121.9 (CH), 113.1 (CH), 108.1 (CH), 61.5 (CH₂) and 14.5 (CH₃); δ H(400 MHz; CDCl₃) 8.91 (1 H, *br s*), 7.67 (1 H, *s*), 7.35–7.28 (2 H, *m*), 7.15 (1 H, *s*), 4.41 (2 H, *q*, *J* 7.1) and 1.41 (3 H, *t*, *J* 7.1); *R*_f 0.29 (1:6 EtOAc, hexanes); m.p. 440–441 K; IR (Nujol, cm⁻¹) 3310, 1728, 1697, 1264, 1080 and 877; HRMS (ESI) for C₁₁H₁₁³⁵ClNO₂ [*M* + *H*]⁺ calculated 224.0479, found 224.0466.

To prepare (II), potassium hydroxide (1.804 g, 32.2 mmol) was added to a solution of (I) (1.215 g, 5.43 mmol) in dry DMF

(6.0 ml) at 273 K and stirred for 10 min. Separately, a solution of iodine (1.710 g, 6.74 mmol) in dry DMF (6.75 ml) was prepared. The two liquids were combined and stirred over ice for 90 min. Pouring the reaction mixture into a saturated aqueous solution of ammonium chloride and sodium thio-sulfate (60 ml) precipitated a brown solid. This was collected by filtration and purified by flash chromatography (1:8 ethyl acetate, hexanes) to afford ethyl 5-chloro-3-iodo-1*H*-indole-2-carboxylate as a yellow solid (1.825 g, 80%). Pale-yellow plates of (II) were recrystallized from methanol solution at room temperature. δ C(101 MHz; DMSO-*d*₆) 160.5 (Cq), 135.8 (Cq), 132.1 (Cq), 128.9 (Cq), 126.5 (CH), 126.3 (Cq), 121.8 (CH), 115.4 (CH), 65.2 (Cq), 61.4 (CH₂) and 14.6 (CH₃); δ H(400 MHz; DMSO-*d*₆) 12.42 (1 H, *br s*), 7.47 (1 H, *d*, *J* 8.4), 7.39 (1 H, *d*, *J* 1.6), 7.31 (1 H, *dd*, *J* 2.0, 9.2), 4.36 (2 H, *q*, *J* 7.2) and 1.36 (3 H, *t*, *J* 7.0); *R*_f 0.13 (1:8 ethyl acetate, hexanes); m.p. 412 K, IR (KBr, cm⁻¹) 3291, 2977, 1744, 1683, 1514, 1332, 1115, 1080, 772, 749 and 604; HRMS (ESI) for C₁₁H₁₀³⁵ClINO₂ [*M* + *H*]⁺ calculated 349.9445, found 349.9453.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The N-bound H atoms were located in difference maps and their positions freely refined. The C-bound H atoms were placed geometrically (C–H =

0.93–0.98 Å) and refined as riding atoms. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ or $1.5U_{\text{eq}}(\text{methyl carrier})$ was applied in all cases. The $-\text{CH}_3$ groups were allowed to rotate, but not to tip, to best fit the electron density.

Acknowledgements

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supporting information

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Computing details

For both compounds, data collection: *CrystalClear* (Rigaku, 2012); cell refinement: *CrystalClear* (Rigaku, 2012); data reduction: *CrystalClear* (Rigaku, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *ATOMS* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) Ethyl 5-chloro-1*H*-indole-2-carboxylate*Crystal data*

C₁₁H₁₀ClNO₂

$M_r = 223.65$

Monoclinic, $P2_1/n$

$a = 13.7168$ (6) Å

$b = 4.5783$ (1) Å

$c = 16.5929$ (11) Å

$\beta = 97.464$ (7)°

$V = 1033.20$ (9) Å³

$Z = 4$

$F(000) = 464$

$D_x = 1.438$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6396 reflections

$\theta = 3.0$ – 27.5 °

$\mu = 0.35$ mm⁻¹

$T = 100$ K

Rod, colourless

$0.70 \times 0.04 \times 0.03$ mm

Data collection

Rigaku Mercury CCD
diffractometer

ω scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2012)

$T_{\min} = 0.793$, $T_{\max} = 0.990$

7035 measured reflections

2340 independent reflections

2051 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.0$ °

$h = -17 \rightarrow 17$

$k = -4 \rightarrow 5$

$l = -19 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.082$

$S = 1.09$

2340 reflections

139 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.4177P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.33$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.52594 (9)	0.5040 (3)	0.35005 (8)	0.0142 (3)
C2	0.62255 (10)	0.4033 (3)	0.35004 (8)	0.0176 (3)
H2	0.6742	0.4669	0.3899	0.021*
C3	0.63988 (9)	0.2090 (3)	0.29013 (8)	0.0171 (3)
H3	0.7044	0.1360	0.2883	0.021*
C4	0.56188 (10)	0.1181 (3)	0.23127 (8)	0.0153 (3)
C5	0.46670 (9)	0.2127 (3)	0.23045 (8)	0.0146 (3)
H5	0.4157	0.1459	0.1905	0.017*
C6	0.44761 (9)	0.4121 (3)	0.29091 (8)	0.0134 (3)
C7	0.36151 (9)	0.5605 (3)	0.30827 (8)	0.0136 (3)
H7	0.2972	0.5434	0.2795	0.016*
C8	0.38999 (9)	0.7341 (3)	0.37519 (7)	0.0135 (3)
C9	0.33337 (9)	0.9388 (3)	0.41806 (7)	0.0133 (3)
C10	0.17639 (10)	1.1516 (3)	0.42258 (8)	0.0174 (3)
H10A	0.1186	1.2025	0.3829	0.021*
H10B	0.2134	1.3334	0.4376	0.021*
C11	0.14202 (11)	1.0204 (4)	0.49746 (9)	0.0271 (3)
H11A	0.1002	1.1610	0.5214	0.041*
H11B	0.1044	0.8421	0.4825	0.041*
H11C	0.1991	0.9728	0.5371	0.041*
N1	0.48871 (8)	0.6981 (3)	0.40047 (7)	0.0147 (2)
H1	0.5235 (12)	0.789 (4)	0.4411 (10)	0.018*
O1	0.23886 (6)	0.9493 (2)	0.38517 (5)	0.0152 (2)
O2	0.36753 (7)	1.0841 (2)	0.47654 (6)	0.0184 (2)
Cl1	0.58935 (2)	-0.12275 (8)	0.15557 (2)	0.01929 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0137 (6)	0.0138 (6)	0.0147 (6)	-0.0016 (5)	-0.0002 (5)	0.0003 (5)
C2	0.0128 (6)	0.0196 (7)	0.0193 (6)	-0.0010 (5)	-0.0026 (5)	-0.0010 (5)
C3	0.0123 (6)	0.0175 (7)	0.0213 (7)	0.0013 (5)	0.0012 (5)	0.0009 (6)
C4	0.0175 (6)	0.0126 (6)	0.0164 (6)	-0.0001 (5)	0.0040 (5)	-0.0007 (5)
C5	0.0144 (6)	0.0146 (6)	0.0140 (6)	-0.0017 (5)	-0.0008 (5)	0.0004 (5)
C6	0.0134 (6)	0.0126 (6)	0.0135 (6)	-0.0014 (5)	-0.0007 (5)	0.0020 (5)
C7	0.0130 (6)	0.0140 (6)	0.0134 (6)	-0.0011 (5)	-0.0004 (4)	0.0008 (5)
C8	0.0122 (6)	0.0149 (6)	0.0129 (6)	-0.0012 (5)	-0.0007 (4)	0.0014 (5)
C9	0.0142 (6)	0.0132 (6)	0.0122 (6)	-0.0014 (5)	0.0007 (4)	0.0025 (5)
C10	0.0149 (6)	0.0169 (7)	0.0203 (7)	0.0043 (5)	0.0013 (5)	-0.0010 (5)

C11	0.0248 (7)	0.0318 (9)	0.0265 (8)	0.0035 (7)	0.0106 (6)	0.0017 (7)
N1	0.0125 (5)	0.0175 (6)	0.0130 (5)	-0.0004 (5)	-0.0023 (4)	-0.0027 (4)
O1	0.0126 (4)	0.0171 (5)	0.0154 (4)	0.0015 (4)	-0.0005 (3)	-0.0023 (4)
O2	0.0164 (5)	0.0218 (5)	0.0158 (5)	-0.0001 (4)	-0.0018 (4)	-0.0050 (4)
C11	0.01786 (17)	0.01983 (19)	0.02054 (18)	0.00168 (13)	0.00388 (12)	-0.00493 (13)

Geometric parameters (Å, °)

C1—N1	1.3644 (18)	C7—H7	0.9500
C1—C2	1.4032 (18)	C8—N1	1.3744 (16)
C1—C6	1.4215 (17)	C8—C9	1.4599 (19)
C2—C3	1.3774 (19)	C9—O2	1.2187 (16)
C2—H2	0.9500	C9—O1	1.3405 (15)
C3—C4	1.4145 (19)	C10—O1	1.4543 (16)
C3—H3	0.9500	C10—C11	1.5098 (19)
C4—C5	1.3739 (18)	C10—H10A	0.9900
C4—C11	1.7488 (14)	C10—H10B	0.9900
C5—C6	1.4059 (18)	C11—H11A	0.9800
C5—H5	0.9500	C11—H11B	0.9800
C6—C7	1.4240 (18)	C11—H11C	0.9800
C7—C8	1.3800 (18)	N1—H1	0.878 (17)
N1—C1—C2	130.00 (12)	N1—C8—C9	119.57 (11)
N1—C1—C6	107.86 (11)	C7—C8—C9	130.46 (12)
C2—C1—C6	122.13 (13)	O2—C9—O1	123.78 (12)
C3—C2—C1	117.63 (12)	O2—C9—C8	124.37 (12)
C3—C2—H2	121.2	O1—C9—C8	111.85 (11)
C1—C2—H2	121.2	O1—C10—C11	111.24 (12)
C2—C3—C4	120.17 (12)	O1—C10—H10A	109.4
C2—C3—H3	119.9	C11—C10—H10A	109.4
C4—C3—H3	119.9	O1—C10—H10B	109.4
C5—C4—C3	123.13 (12)	C11—C10—H10B	109.4
C5—C4—C11	119.00 (10)	H10A—C10—H10B	108.0
C3—C4—C11	117.87 (10)	C10—C11—H11A	109.5
C4—C5—C6	117.55 (12)	C10—C11—H11B	109.5
C4—C5—H5	121.2	H11A—C11—H11B	109.5
C6—C5—H5	121.2	C10—C11—H11C	109.5
C5—C6—C1	119.38 (12)	H11A—C11—H11C	109.5
C5—C6—C7	133.66 (12)	H11B—C11—H11C	109.5
C1—C6—C7	106.95 (11)	C1—N1—C8	108.85 (11)
C8—C7—C6	106.38 (11)	C1—N1—H1	124.7 (11)
C8—C7—H7	126.8	C8—N1—H1	126.4 (11)
C6—C7—H7	126.8	C9—O1—C10	116.19 (10)
N1—C8—C7	109.96 (12)		
N1—C1—C2—C3	-178.66 (14)	C1—C6—C7—C8	0.37 (15)
C6—C1—C2—C3	-0.1 (2)	C6—C7—C8—N1	-0.63 (15)
C1—C2—C3—C4	0.2 (2)	C6—C7—C8—C9	178.10 (13)

C2—C3—C4—C5	-0.5 (2)	N1—C8—C9—O2	-0.4 (2)
C2—C3—C4—C11	178.63 (11)	C7—C8—C9—O2	-178.99 (14)
C3—C4—C5—C6	0.8 (2)	N1—C8—C9—O1	179.38 (11)
C11—C4—C5—C6	-178.38 (10)	C7—C8—C9—O1	0.8 (2)
C4—C5—C6—C1	-0.67 (19)	C2—C1—N1—C8	178.35 (14)
C4—C5—C6—C7	178.26 (14)	C6—C1—N1—C8	-0.40 (15)
N1—C1—C6—C5	179.20 (11)	C7—C8—N1—C1	0.65 (15)
C2—C1—C6—C5	0.3 (2)	C9—C8—N1—C1	-178.23 (12)
N1—C1—C6—C7	0.01 (15)	O2—C9—O1—C10	0.89 (18)
C2—C1—C6—C7	-178.85 (12)	C8—C9—O1—C10	-178.86 (11)
C5—C6—C7—C8	-178.65 (14)	C11—C10—O1—C9	-81.73 (14)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O2 ⁱ	0.878 (17)	1.977 (17)	2.8288 (15)	163.0 (15)

Symmetry code: (i) $-x+1, -y+2, -z+1$.**(II) Ethyl 5-chloro-3-iodo-1*H*-indole-2-carboxylate***Crystal data*C₁₁H₉ClINO₂*M_r* = 349.54Triclinic, *P*1̄*a* = 7.7733 (5) Å*b* = 7.8240 (5) Å*c* = 10.4594 (7) Å*α* = 86.085 (8)°*β* = 80.575 (7)°*γ* = 71.308 (6)°*V* = 594.35 (7) Å³*Z* = 2*F*(000) = 336*D_x* = 1.953 Mg m⁻³Mo *Kα* radiation, *λ* = 0.71073 Å

Cell parameters from 7985 reflections

θ = 2.7–27.5°*μ* = 2.90 mm⁻¹*T* = 100 K

Plate, colourless

0.17 × 0.10 × 0.02 mm

*Data collection*Rigaku Mercury CCD
diffractometer*ω* scansAbsorption correction: multi-scan
(CrystalClear; Rigaku, 2012)*T_{min}* = 0.638, *T_{max}* = 0.944

7837 measured reflections

2739 independent reflections

2640 reflections with *I* > 2σ(*I*)*R_{int}* = 0.031*θ_{max}* = 27.5°, *θ_{min}* = 2.8°*h* = -8→10*k* = -10→10*l* = -12→13*Refinement*Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.022*wR*(*F*²) = 0.058*S* = 1.04

2739 reflections

149 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement*w* = 1/[σ²(*F_o*²) + (0.0409*P*)² + 0.1325*P*]where *P* = (*F_o*² + 2*F_c*²)/3(Δ/σ)_{max} = 0.002Δρ_{max} = 1.18 e Å⁻³Δρ_{min} = -0.44 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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0847 (3)	0.5746 (3)	0.6457 (2)	0.0165 (4)
C2	-0.0166 (3)	0.5738 (3)	0.7698 (2)	0.0190 (4)
H2	-0.0956	0.6824	0.8097	0.023*
C3	0.0037 (3)	0.4078 (3)	0.8316 (2)	0.0204 (4)
H3	-0.0631	0.4013	0.9154	0.024*
C4	0.1227 (3)	0.2486 (3)	0.7712 (2)	0.0185 (4)
C5	0.2249 (3)	0.2468 (3)	0.6505 (2)	0.0176 (4)
H5	0.3045	0.1374	0.6122	0.021*
C6	0.2064 (3)	0.4142 (3)	0.5863 (2)	0.0160 (4)
C7	0.2860 (3)	0.4665 (3)	0.46397 (19)	0.0144 (4)
C8	0.2117 (3)	0.6518 (3)	0.45207 (19)	0.0155 (4)
C9	0.2427 (3)	0.7849 (3)	0.3534 (2)	0.0162 (4)
C10	0.4005 (3)	0.8407 (3)	0.1517 (2)	0.0196 (4)
H10A	0.4584	0.9185	0.1879	0.023*
H10B	0.2863	0.9183	0.1211	0.023*
C11	0.5308 (3)	0.7311 (3)	0.0411 (2)	0.0260 (5)
H11A	0.5687	0.8125	-0.0247	0.039*
H11B	0.4686	0.6612	0.0024	0.039*
H11C	0.6392	0.6488	0.0740	0.039*
N1	0.0899 (2)	0.7153 (2)	0.56278 (17)	0.0159 (3)
H1	0.030 (4)	0.814 (4)	0.576 (3)	0.019*
O1	0.3601 (2)	0.71212 (19)	0.24936 (14)	0.0179 (3)
O2	0.1685 (2)	0.9465 (2)	0.36622 (16)	0.0232 (3)
Cl1	0.14126 (8)	0.04416 (8)	0.85625 (5)	0.02534 (12)
I1	0.48122 (2)	0.28666 (2)	0.33716 (2)	0.01543 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0128 (9)	0.0169 (9)	0.0192 (10)	-0.0027 (7)	-0.0041 (7)	-0.0020 (8)
C2	0.0143 (9)	0.0213 (10)	0.0191 (10)	-0.0020 (8)	-0.0017 (7)	-0.0036 (8)
C3	0.0156 (9)	0.0278 (11)	0.0163 (10)	-0.0053 (8)	-0.0015 (7)	0.0002 (8)
C4	0.0171 (9)	0.0168 (9)	0.0207 (10)	-0.0044 (8)	-0.0049 (8)	0.0049 (8)
C5	0.0139 (9)	0.0160 (9)	0.0207 (10)	-0.0013 (8)	-0.0038 (7)	0.0001 (8)
C6	0.0135 (9)	0.0170 (9)	0.0168 (9)	-0.0027 (7)	-0.0038 (7)	-0.0015 (7)
C7	0.0126 (8)	0.0125 (8)	0.0171 (9)	-0.0024 (7)	-0.0021 (7)	-0.0009 (7)
C8	0.0129 (8)	0.0163 (9)	0.0169 (9)	-0.0031 (7)	-0.0033 (7)	-0.0016 (7)
C9	0.0144 (9)	0.0143 (9)	0.0195 (10)	-0.0038 (7)	-0.0025 (7)	-0.0004 (7)
C10	0.0222 (10)	0.0162 (9)	0.0197 (10)	-0.0068 (8)	-0.0013 (8)	0.0043 (8)

C11	0.0347 (12)	0.0227 (11)	0.0205 (11)	-0.0121 (10)	0.0024 (9)	-0.0009 (8)
N1	0.0139 (8)	0.0129 (8)	0.0186 (8)	-0.0010 (6)	-0.0016 (6)	-0.0018 (6)
O1	0.0206 (7)	0.0125 (6)	0.0188 (7)	-0.0044 (6)	-0.0001 (6)	0.0020 (5)
O2	0.0240 (8)	0.0135 (7)	0.0268 (8)	-0.0018 (6)	0.0023 (6)	-0.0001 (6)
C11	0.0254 (3)	0.0228 (3)	0.0242 (3)	-0.0060 (2)	-0.0008 (2)	0.0092 (2)
I1	0.01470 (9)	0.01248 (9)	0.01706 (9)	-0.00172 (6)	-0.00130 (6)	-0.00153 (6)

Geometric parameters (Å, °)

C1—N1	1.361 (3)	C7—I1	2.0660 (19)
C1—C2	1.405 (3)	C8—N1	1.380 (3)
C1—C6	1.417 (3)	C8—C9	1.463 (3)
C2—C3	1.384 (3)	C9—O2	1.216 (3)
C2—H2	0.9500	C9—O1	1.330 (2)
C3—C4	1.409 (3)	C10—O1	1.453 (2)
C3—H3	0.9500	C10—C11	1.515 (3)
C4—C5	1.376 (3)	C10—H10A	0.9900
C4—C11	1.752 (2)	C10—H10B	0.9900
C5—C6	1.406 (3)	C11—H11A	0.9800
C5—H5	0.9500	C11—H11B	0.9800
C6—C7	1.421 (3)	C11—H11C	0.9800
C7—C8	1.383 (3)	N1—H1	0.77 (3)
N1—C1—C2	129.80 (19)	N1—C8—C9	117.43 (17)
N1—C1—C6	108.08 (18)	C7—C8—C9	133.80 (19)
C2—C1—C6	122.11 (19)	O2—C9—O1	123.5 (2)
C3—C2—C1	117.05 (19)	O2—C9—C8	122.96 (19)
C3—C2—H2	121.5	O1—C9—C8	113.50 (17)
C1—C2—H2	121.5	O1—C10—C11	106.61 (17)
C2—C3—C4	120.58 (19)	O1—C10—H10A	110.4
C2—C3—H3	119.7	C11—C10—H10A	110.4
C4—C3—H3	119.7	O1—C10—H10B	110.4
C5—C4—C3	123.23 (19)	C11—C10—H10B	110.4
C5—C4—C11	119.08 (16)	H10A—C10—H10B	108.6
C3—C4—C11	117.69 (16)	C10—C11—H11A	109.5
C4—C5—C6	117.06 (19)	C10—C11—H11B	109.5
C4—C5—H5	121.5	H11A—C11—H11B	109.5
C6—C5—H5	121.5	C10—C11—H11C	109.5
C5—C6—C1	119.95 (19)	H11A—C11—H11C	109.5
C5—C6—C7	133.51 (19)	H11B—C11—H11C	109.5
C1—C6—C7	106.53 (18)	C1—N1—C8	109.37 (17)
C8—C7—C6	107.32 (17)	C1—N1—H1	124 (2)
C8—C7—I1	129.30 (15)	C8—N1—H1	127 (2)
C6—C7—I1	123.36 (14)	C9—O1—C10	115.06 (16)
N1—C8—C7	108.70 (18)		
N1—C1—C2—C3	179.0 (2)	C1—C6—C7—I1	178.14 (13)
C6—C1—C2—C3	-1.6 (3)	C6—C7—C8—N1	0.2 (2)

C1—C2—C3—C4	0.5 (3)	I1—C7—C8—N1	-178.26 (13)
C2—C3—C4—C5	0.4 (3)	C6—C7—C8—C9	176.9 (2)
C2—C3—C4—C11	179.75 (16)	I1—C7—C8—C9	-1.5 (3)
C3—C4—C5—C6	-0.2 (3)	N1—C8—C9—O2	1.2 (3)
C11—C4—C5—C6	-179.59 (15)	C7—C8—C9—O2	-175.3 (2)
C4—C5—C6—C1	-0.8 (3)	N1—C8—C9—O1	-179.20 (16)
C4—C5—C6—C7	-179.7 (2)	C7—C8—C9—O1	4.3 (3)
N1—C1—C6—C5	-178.72 (18)	C2—C1—N1—C8	179.1 (2)
C2—C1—C6—C5	1.7 (3)	C6—C1—N1—C8	-0.4 (2)
N1—C1—C6—C7	0.5 (2)	C7—C8—N1—C1	0.1 (2)
C2—C1—C6—C7	-179.05 (18)	C9—C8—N1—C1	-177.20 (17)
C5—C6—C7—C8	178.7 (2)	O2—C9—O1—C10	2.2 (3)
C1—C6—C7—C8	-0.4 (2)	C8—C9—O1—C10	-177.42 (16)
C5—C6—C7—I1	-2.8 (3)	C11—C10—O1—C9	-178.33 (17)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O2 ⁱ	0.77 (3)	2.06 (3)	2.821 (2)	168 (3)

Symmetry code: (i) $-x, -y+2, -z+1$.