IUCrData

ISSN 2414-3146

3-Chloro-2-ethyl-6-nitro-2*H*-indazole

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Received 30 April 2017
Accepted 1 May 2017

Edited by J. Simpson, University of Otago, New Zealand

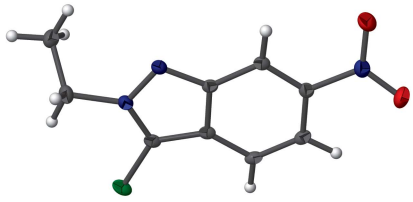
Keywords: crystal structure; indazole; hydrogen bond; π-stacking.

CCDC reference: 1547138

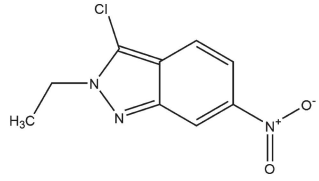
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_9H_8ClN_3O_2$, the orientation of the ethyl substituent is partly determined by an intramolecular C—H···Cl hydrogen bond. The indazole moiety is slightly folded with an angle of 0.70 (8)° between the five- and six-membered rings. In the crystal, molecules pack in layers parallel to [100] through C—H···π(ring) and N···O···π(ring) interactions.

3D view



Chemical scheme



Structure description

The indazole nucleus is important pharmaceutically and is a key subunit in many drugs that display a broad range of pharmacological properties. These include HIV protease inhibition (Patel *et al.*, 1999) and antiarrhythmic, analgesic and antitumor activities (Mosti *et al.*, 2000) together with antihypertensive properties (Bouissane *et al.*, 2006; Abbassi *et al.*, 2012). As a continuation of our studies of indazole derivatives (Mohamed Abdelahi *et al.*, 2017), we report the synthesis and structure of the title compound.

In the title molecule, the indazole portion is very slightly folded, as indicated by the dihedral angle of 0.70 (8)° between the five- and six-membered rings. The orientation of the ethyl substituent is determined, in part, by an intramolecular C8—H8*B*···Cl1 hydrogen bond (Table 1 and Fig. 1). Head-to-tail offset π–π-stacking interactions between indazole ring systems [centroid–centroid distance = 3.5291 (7) Å, dihedral angle = 0.70 (6)°] form dimers that are connected into layers parallel to [100] by a combination of C5—H5···*Cg*2 (Table 1) and N3···O1···*Cg*1 interactions [*Cg*1 is the centroid of the C1/C6/C7/N1/N2 ring; O1···*Cg*1 = 3.421 (1) Å and N3···O1···*Cg*1 = 126.66 (8)°] (Fig. 2). The ethyl substituents protrude from the faces of the layers.

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

*Cg*2 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*B*···Cl1	0.938 (18)	2.689 (17)	3.2158 (15)	116.3 (12)
C5—H5···*Cg*2^{i}	0.961 (16)	2.698 (15)	3.5418 (13)	147 (1)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_8ClN_3O_2$
M_r	225.63
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, *b*, *c* (Å)	11.2363 (7), 7.4063 (5), 12.1247 (8)
β (°)	111.051 (1)
V (Å^3)	941.67 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.39
Crystal size (mm)	0.34 × 0.19 × 0.16
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.85, 0.94
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17539, 2543, 2183
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.686
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.103, 1.13
No. of reflections	2543
No. of parameters	168
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.68, −0.20

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Synthesis and crystallization

To a solution of 6-nitro-1*H*-indazole (0.8 g, 5 mmol) in tetrahydrofuran (30 ml) was added bromoethane (0.8 g, 5 mmol), potassium carbonate (1.24 g, 9 mmol) and a catalytic quantity of tetra-*n*-butylammonium iodide. The mixture was stirred at room temperature for 48 h. The solution was filtered and the solvent removed under reduced pressure. The residue was recrystallized from ethanol solution to afford the title compound as colourless crystals (yield: 66%).

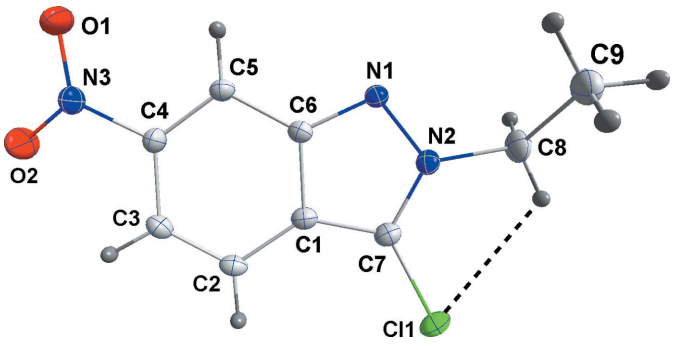


Figure 1
The structure of the title molecule, showing the atom-labelling scheme, with ellipsoids drawn at the 50% probability level. The intramolecular C—H···Cl hydrogen bond is shown as a dashed line.

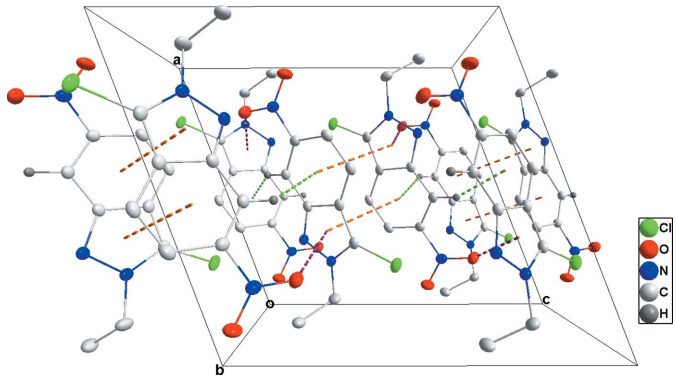


Figure 2
Packing projected onto [010] giving a side view of one sheet of molecules. The π–π stacking, C—H···π(ring) and N···O···π(ring) interactions are shown, respectively, as orange, green and purple dashed lines.

Refinement

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

Acknowledgements

JTM thanks Tulane University for support of the Tulane Crystallography Laboratory.

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full crystallographic data

IUCrData (2017). **2**, x170652 [https://doi.org/10.1107/S2414314617006526]

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Crystal data

$C_9H_8ClN_3O_2$
M_r = 225.63
Monoclinic, $P2_1/c$
a = 11.2363 (7) Å
b = 7.4063 (5) Å
c = 12.1247 (8) Å
β = 111.051 (1)°
V = 941.67 (11) Å^3
Z = 4
$F(000)$ = 464
D_x = 1.592 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8820 reflections
θ = 3.3–29.1°
μ = 0.39 mm^{-1}
T = 100 K
Column, colourless
0.34 × 0.19 × 0.16 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.85, T_{max} = 0.94
17539 measured reflections
2543 independent reflections
2183 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 29.2°, θ_{min} = 1.9°
h = −15→15
k = −10→10
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.103
S = 1.13
2543 reflections
168 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.0386P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, collected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = –30.00 and 210.00°. The scan time was 15 sec/frame.

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. 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 $F^2 > 2\text{sigma}(F^2)$ 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}
Cl1	0.74446 (3)	0.21393 (4)	0.48713 (3)	0.02049 (12)
O1	0.24410 (9)	0.46570 (14)	0.76126 (8)	0.0248 (2)
O2	0.13166 (8)	0.34576 (15)	0.59292 (8)	0.0278 (2)
N1	0.68668 (9)	0.49160 (14)	0.73487 (9)	0.0163 (2)
N2	0.75445 (9)	0.42256 (14)	0.67233 (9)	0.0164 (2)
N3	0.23394 (9)	0.39466 (14)	0.66663 (9)	0.0183 (2)
C1	0.56070 (11)	0.31391 (15)	0.58095 (10)	0.0139 (2)
C2	0.44490 (11)	0.23172 (16)	0.50971 (10)	0.0156 (2)
H2	0.4420 (13)	0.161 (2)	0.4443 (13)	0.016 (3)*
C3	0.33951 (11)	0.26044 (16)	0.53900 (11)	0.0162 (2)
H3	0.2548 (13)	0.211 (2)	0.4925 (12)	0.017 (4)*
C4	0.34978 (10)	0.36817 (16)	0.63905 (10)	0.0148 (2)
C5	0.45943 (11)	0.45167 (16)	0.70990 (10)	0.0144 (2)
H5	0.4606 (15)	0.530 (2)	0.7734 (14)	0.024 (4)*
C6	0.56820 (11)	0.42364 (15)	0.67937 (10)	0.0138 (2)
C7	0.68450 (11)	0.31794 (16)	0.58110 (10)	0.0155 (2)
C8	0.89008 (11)	0.4693 (2)	0.70924 (12)	0.0224 (3)
H8A	0.8929 (17)	0.595 (3)	0.7003 (16)	0.040 (5)*
H8B	0.9192 (16)	0.408 (2)	0.6562 (15)	0.032 (4)*
C9	0.96158 (12)	0.4151 (2)	0.83598 (12)	0.0252 (3)
H9A	1.0501 (16)	0.443 (2)	0.8538 (14)	0.028 (4)*
H9B	0.9544 (18)	0.279 (3)	0.8467 (18)	0.042 (5)*
H9C	0.9260 (16)	0.479 (2)	0.8872 (15)	0.030 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02732 (18)	0.01884 (19)	0.02015 (18)	0.00613 (10)	0.01440 (13)	0.00185 (11)
O1	0.0233 (5)	0.0309 (5)	0.0238 (5)	−0.0004 (4)	0.0127 (4)	−0.0047 (4)
O2	0.0150 (4)	0.0373 (6)	0.0277 (5)	−0.0025 (4)	0.0037 (4)	−0.0031 (4)
N1	0.0164 (4)	0.0199 (5)	0.0135 (5)	−0.0013 (4)	0.0064 (4)	−0.0008 (4)
N2	0.0157 (5)	0.0203 (5)	0.0141 (5)	0.0002 (4)	0.0064 (4)	0.0018 (4)
N3	0.0165 (5)	0.0183 (5)	0.0204 (5)	0.0007 (4)	0.0069 (4)	0.0025 (4)
C1	0.0185 (5)	0.0115 (5)	0.0118 (5)	0.0020 (4)	0.0054 (4)	0.0024 (4)
C2	0.0206 (5)	0.0129 (6)	0.0113 (5)	0.0010 (4)	0.0033 (4)	0.0001 (4)
C3	0.0178 (5)	0.0140 (5)	0.0137 (5)	−0.0014 (4)	0.0020 (4)	0.0010 (4)
C4	0.0151 (5)	0.0146 (6)	0.0149 (5)	0.0009 (4)	0.0056 (4)	0.0025 (4)

C5	0.0172 (5)	0.0139 (6)	0.0123 (5)	0.0007 (4)	0.0055 (4)	0.0011 (4)
C6	0.0166 (5)	0.0127 (5)	0.0114 (5)	−0.0005 (4)	0.0043 (4)	0.0015 (4)
C7	0.0195 (5)	0.0151 (6)	0.0126 (5)	0.0027 (4)	0.0067 (4)	0.0028 (4)
C8	0.0159 (5)	0.0301 (8)	0.0228 (6)	−0.0025 (5)	0.0086 (5)	0.0032 (5)
C9	0.0160 (6)	0.0361 (8)	0.0221 (7)	0.0018 (5)	0.0052 (5)	−0.0014 (6)

Geometric parameters (Å, º)

Cl1—C7	1.7021 (12)	C2—H2	0.942 (15)
O1—N3	1.2297 (13)	C3—C4	1.4216 (17)
O2—N3	1.2299 (13)	C3—H3	0.986 (14)
N1—N2	1.3532 (14)	C4—C5	1.3704 (16)
N1—C6	1.3545 (14)	C5—C6	1.4138 (16)
N2—C7	1.3480 (15)	C5—H5	0.961 (16)
N2—C8	1.4672 (15)	C8—C9	1.5102 (19)
N3—C4	1.4687 (15)	C8—H8A	0.94 (2)
C1—C7	1.3907 (16)	C8—H8B	0.938 (18)
C1—C2	1.4151 (16)	C9—H9A	0.961 (17)
C1—C6	1.4210 (15)	C9—H9B	1.03 (2)
C2—C3	1.3696 (17)	C9—H9C	0.972 (17)
N2—N1—C6	103.39 (9)	C4—C5—H5	121.7 (10)
C7—N2—N1	113.42 (9)	C6—C5—H5	122.3 (10)
C7—N2—C8	128.42 (10)	N1—C6—C5	127.09 (11)
N1—N2—C8	118.16 (10)	N1—C6—C1	112.40 (10)
O1—N3—O2	123.60 (10)	C5—C6—C1	120.51 (10)
O1—N3—C4	118.47 (10)	N2—C7—C1	107.55 (10)
O2—N3—C4	117.93 (10)	N2—C7—Cl1	123.72 (9)
C7—C1—C2	135.24 (11)	C1—C7—Cl1	128.73 (10)
C7—C1—C6	103.24 (10)	N2—C8—C9	111.24 (10)
C2—C1—C6	121.52 (10)	N2—C8—H8A	105.9 (11)
C3—C2—C1	117.78 (11)	C9—C8—H8A	110.6 (11)
C3—C2—H2	122.2 (9)	N2—C8—H8B	104.9 (10)
C1—C2—H2	120.0 (9)	C9—C8—H8B	112.3 (10)
C2—C3—C4	119.72 (11)	H8A—C8—H8B	111.6 (16)
C2—C3—H3	122.7 (8)	C8—C9—H9A	107.5 (10)
C4—C3—H3	117.5 (8)	C8—C9—H9B	110.7 (11)
C5—C4—C3	124.56 (11)	H9A—C9—H9B	107.7 (14)
C5—C4—N3	117.89 (10)	C8—C9—H9C	109.4 (10)
C3—C4—N3	117.54 (10)	H9A—C9—H9C	112.6 (14)
C4—C5—C6	115.90 (11)	H9B—C9—H9C	109.0 (15)
C6—N1—N2—C7	0.66 (13)	C4—C5—C6—C1	−0.31 (16)
C6—N1—N2—C8	−179.85 (10)	C7—C1—C6—N1	0.68 (13)
C7—C1—C2—C3	179.92 (13)	C2—C1—C6—N1	−179.12 (10)
C6—C1—C2—C3	−0.35 (17)	C7—C1—C6—C5	−179.29 (10)
C1—C2—C3—C4	−0.73 (17)	C2—C1—C6—C5	0.91 (17)
C2—C3—C4—C5	1.40 (19)	N1—N2—C7—C1	−0.26 (14)

C2—C3—C4—N3	−179.97 (10)	C8—N2—C7—C1	−179.68 (12)
O1—N3—C4—C5	−11.20 (16)	N1—N2—C7—Cl1	179.83 (8)
O2—N3—C4—C5	168.15 (11)	C8—N2—C7—Cl1	0.40 (18)
O1—N3—C4—C3	170.07 (11)	C2—C1—C7—N2	179.52 (13)
O2—N3—C4—C3	−10.58 (16)	C6—C1—C7—N2	−0.25 (12)
C3—C4—C5—C6	−0.82 (18)	C2—C1—C7—Cl1	−0.6 (2)
N3—C4—C5—C6	−179.46 (10)	C6—C1—C7—Cl1	179.66 (9)
N2—N1—C6—C5	179.15 (11)	C7—N2—C8—C9	−122.97 (13)
N2—N1—C6—C1	−0.82 (13)	N1—N2—C8—C9	57.62 (16)
C4—C5—C6—N1	179.72 (11)		

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*B*···Cl1	0.938 (18)	2.689 (17)	3.2158 (15)	116.3 (12)
C5—H5···*Cg*2^{i}	0.961 (16)	2.698 (15)	3.5418 (13)	147 (1)

Symmetry code: (i) −*x*+1, *y*+1/2, −*z*+3/2.