



Crystal structure of 3-chloro-1-methyl-5-nitro-1*H*-indazole

Assoman Kouakou,^{a*} El Mostapha Rakib,^a Mohamed Chigr,^a Mohamed Saadi^b and Lahcen El Ammari^b

^aLaboratoire de Chimie Organique et Analytique, Université Sultan Moulay Slimane, Faculté des Sciences et Techniques, Béni-Mellal, BP 523, Morocco, and ^bLaboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Université Mohammed V, Avenue Ibn Battouta, BP 1014, Rabat, Morocco. *Correspondence e-mail: assoman_k@yahoo.fr

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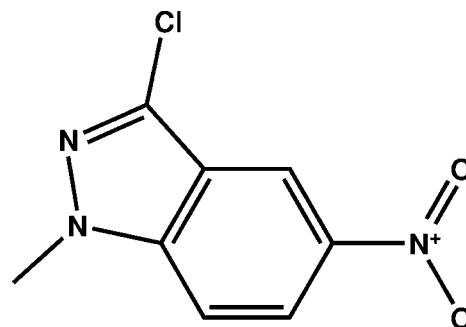
The molecule of the title compound, C₈H₆ClN₃O₂, is built up from fused five- and six-membered rings connected to a chlorine atom and to nitro and methyl groups. The indazole system is essentially planar with the largest deviation from the mean plane being 0.007 (2) Å. No classical hydrogen bonds are observed in the structure. Two molecules form a dimer organised by a symmetry centre *via* a close contact between a nitro-O atom and the chlorine atom [at 3.066 (2) Å this is shorter than the sum of their van der Waals radii].

Keywords: crystal structure; indazole derivative; Cl⋯O short contact.

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1. Related literature

For biological activities such as antimicrobial, anticancer, antiinflammatory, antiplatelet and selective 5-HT₆ antagonists of the title compound and derivatives, see: Schmidt *et al.* (2008); Shafakat Ali *et al.* (2012); Abbassi *et al.* (2014); Plescia *et al.* (2010); Lee *et al.* (2001); Liu *et al.* (2011).



2. Experimental

2.1. Crystal data

C ₈ H ₆ ClN ₃ O ₂	$V = 868.5 (6) \text{ \AA}^3$
$M_r = 211.61$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 3.8273 (2) \text{ \AA}$	$\mu = 0.41 \text{ mm}^{-1}$
$b = 14.678 (6) \text{ \AA}$	$T = 296 \text{ K}$
$c = 15.549 (6) \text{ \AA}$	$0.31 \times 0.27 \times 0.21 \text{ mm}$
$\beta = 96.130 (9)^\circ$	

2.2. Data collection

Bruker X8 APEX Diffractometer	19793 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2009)	2243 independent reflections
$T_{\min} = 0.654$, $T_{\max} = 0.747$	1963 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.028$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	127 parameters
$wR(F^2) = 0.115$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{\max} = 0.36 \text{ e \AA}^{-3}$
2243 reflections	$\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *ORTEP-3* (Burnett & Johnson, 1996; Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: ZP2019).

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supporting information

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Crystal structure of 3-chloro-1-methyl-5-nitro-1*H*-indazole

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S1. Comment

Indazole derivatives are a versatile class of compounds that have found use in biology, catalysis, and medicinal chemistry. They exhibit a variety of biological activities such as anti-microbial, anti-cancer, anti-inflammatory, anti-platelet, and selective 5-HT₆ antagonists (Schmidt *et al.*, 2008, Shafakat Ali *et al.*, 2012, Abbassi *et al.*, 2014, Plescia *et al.*, 2010, Lee *et al.*, 2001, Liu *et al.*, 2011).

The two fused five- and six-membered rings (N2N3 C1 to C7) part of the molecule are almost planar, with a maximum deviation of -0.007 (2) Å at C1 atom (Fig.1). The chlorine atom and the nitro group linked to the indazole ring are nearly coplanar with the largest deviation from the mean plane being -0.070 (2) Å at O1. No classic hydrogen bonds are observed in the structure.

S2. Experimental

To a solution of 3-chloro-5-nitroindazole (6.13 mmol) in acetone (15 ml) was added potassium hydroxide (6.8 mmol). After 15 mn at 298 K, methyl iodide (12.26 mmol) was added dropwise. Upon disappearance of the starting material as indicated by TLC, the resulting mixture was evaporated. The crude material was dissolved with EtOAc (50 ml), washed with water and brine, dried over MgSO₄ and the solvent was evaporated *in vacuo*. The resulting residue was purified by column chromatography (EtOAc/hexane 2/8). The title compound was recrystallized from ethanol at room temperature giving colourless crystals (m.p. 471 K, yield: 70%).

S3. Refinement

H atoms were located in a difference map and treated as riding with C–H = 0.96 Å and C–H = 0.93 Å for methyl and aromatic, respectively. All hydrogen with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ for methyl and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ for aromatic.

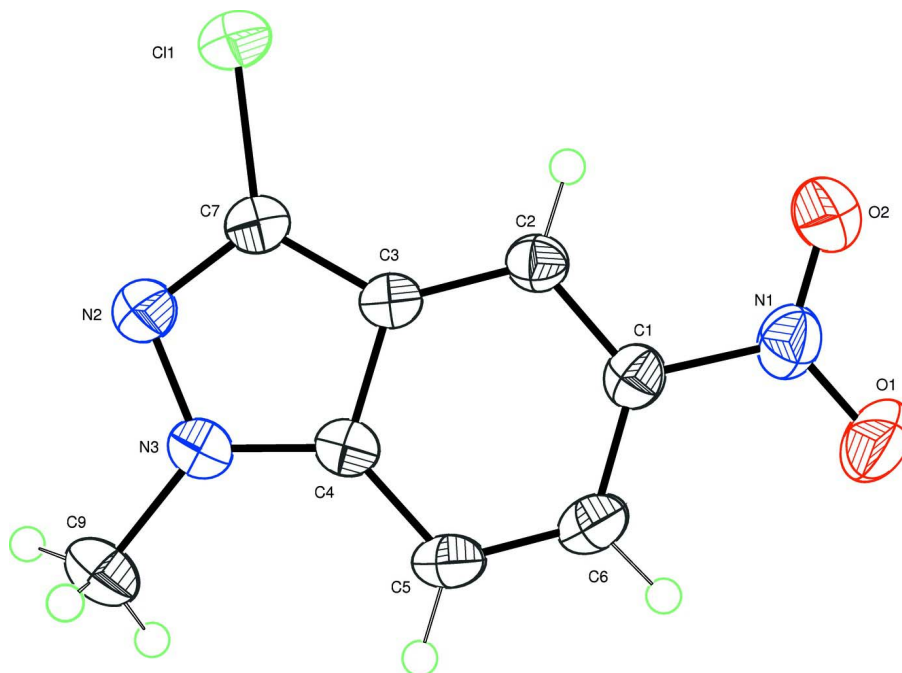


Figure 1

Plot of the molecule of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

3-Chloro-1-methyl-5-nitro-1*H*-indazole

Crystal data

$C_8H_6ClN_3O_2$

$M_r = 211.61$

Monoclinic, $P2_1/n$

$a = 3.8273(2) \text{ \AA}$

$b = 14.678(6) \text{ \AA}$

$c = 15.549(6) \text{ \AA}$

$\beta = 96.130(9)^\circ$

$V = 868.5(6) \text{ \AA}^3$

$Z = 4$

$F(000) = 432$

Data collection

Bruker X8 APEX Diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.654$, $T_{\max} = 0.747$

19793 measured reflections

$D_x = 1.618 \text{ Mg m}^{-3}$

Melting point: 471 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2243 reflections

$\theta = 2.6\text{--}28.7^\circ$

$\mu = 0.41 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colourless

$0.31 \times 0.27 \times 0.21 \text{ mm}$

2243 independent reflections

1963 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 28.7^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -5 \rightarrow 5$

$k = -19 \rightarrow 19$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.115$
 $S = 1.10$
 2243 reflections
 127 parameters
 0 restraints

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.5276P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Special details

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.39641 (14)	0.41233 (3)	0.10469 (3)	0.04683 (17)
N3	0.7340 (4)	0.56202 (10)	0.29223 (9)	0.0345 (3)
N2	0.6938 (4)	0.48003 (10)	0.25083 (10)	0.0358 (3)
N1	0.0460 (5)	0.79442 (11)	0.05310 (10)	0.0416 (4)
O2	-0.0907 (5)	0.75957 (11)	-0.01323 (11)	0.0671 (5)
O1	0.0360 (6)	0.87596 (11)	0.06625 (11)	0.0669 (5)
C3	0.4260 (4)	0.59119 (11)	0.16618 (10)	0.0283 (3)
C4	0.5778 (4)	0.63052 (11)	0.24420 (10)	0.0299 (3)
C2	0.2473 (4)	0.64453 (11)	0.10193 (10)	0.0301 (3)
H2	0.1459	0.6196	0.0502	0.036*
C1	0.2289 (5)	0.73599 (12)	0.11912 (11)	0.0325 (3)
C7	0.5114 (4)	0.49799 (12)	0.17658 (11)	0.0320 (3)
C5	0.5521 (5)	0.72408 (12)	0.26022 (11)	0.0373 (4)
H5	0.6498	0.7497	0.3120	0.045*
C6	0.3773 (5)	0.77622 (12)	0.19662 (12)	0.0381 (4)
H6	0.3564	0.8387	0.2047	0.046*
C9	0.9194 (5)	0.56629 (15)	0.37845 (12)	0.0442 (5)
H9A	1.0018	0.5066	0.3957	0.066*
H9B	1.1160	0.6069	0.3785	0.066*
H9C	0.7634	0.5882	0.4182	0.066*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0591 (3)	0.0334 (2)	0.0457 (3)	0.00152 (19)	-0.0049 (2)	-0.01074 (18)
N3	0.0347 (8)	0.0374 (8)	0.0308 (7)	-0.0012 (6)	0.0006 (6)	-0.0012 (6)
N2	0.0367 (8)	0.0345 (7)	0.0360 (7)	0.0011 (6)	0.0033 (6)	-0.0012 (6)
N1	0.0497 (9)	0.0357 (8)	0.0405 (8)	0.0048 (7)	0.0095 (7)	0.0062 (6)
O2	0.0955 (14)	0.0476 (9)	0.0513 (9)	0.0052 (9)	-0.0246 (9)	0.0045 (7)
O1	0.1054 (15)	0.0352 (8)	0.0589 (10)	0.0147 (9)	0.0037 (9)	0.0054 (7)

C3	0.0266 (8)	0.0304 (8)	0.0285 (7)	-0.0028 (6)	0.0056 (6)	-0.0032 (6)
C4	0.0270 (8)	0.0348 (8)	0.0284 (7)	-0.0043 (6)	0.0051 (6)	-0.0020 (6)
C2	0.0310 (8)	0.0321 (8)	0.0276 (7)	-0.0024 (6)	0.0048 (6)	-0.0014 (6)
C1	0.0342 (9)	0.0315 (8)	0.0328 (8)	-0.0001 (7)	0.0084 (7)	0.0029 (6)
C7	0.0317 (8)	0.0314 (8)	0.0331 (8)	-0.0018 (6)	0.0047 (6)	-0.0039 (6)
C5	0.0430 (10)	0.0359 (9)	0.0330 (8)	-0.0069 (7)	0.0044 (7)	-0.0093 (7)
C6	0.0463 (10)	0.0283 (8)	0.0407 (9)	-0.0028 (7)	0.0100 (8)	-0.0058 (7)
C9	0.0422 (10)	0.0559 (12)	0.0326 (9)	-0.0021 (9)	-0.0055 (8)	-0.0008 (8)

Geometric parameters (Å, °)

C11—C7	1.7086 (18)	C4—C5	1.401 (2)
N3—C4	1.353 (2)	C2—C1	1.372 (2)
N3—N2	1.366 (2)	C2—H2	0.9300
N3—C9	1.450 (2)	C1—C6	1.406 (3)
N2—C7	1.311 (2)	C5—C6	1.367 (3)
N1—O1	1.215 (2)	C5—H5	0.9300
N1—O2	1.218 (2)	C6—H6	0.9300
N1—C1	1.458 (2)	C9—H9A	0.9600
C3—C2	1.390 (2)	C9—H9B	0.9600
C3—C4	1.411 (2)	C9—H9C	0.9600
C3—C7	1.412 (2)		
C4—N3—N2	111.95 (14)	C2—C1—N1	117.97 (16)
C4—N3—C9	128.47 (16)	C6—C1—N1	118.43 (16)
N2—N3—C9	119.56 (16)	N2—C7—C3	113.01 (15)
C7—N2—N3	105.10 (14)	N2—C7—C11	120.27 (14)
O1—N1—O2	122.53 (18)	C3—C7—C11	126.72 (13)
O1—N1—C1	118.81 (17)	C6—C5—C4	117.27 (16)
O2—N1—C1	118.66 (16)	C6—C5—H5	121.4
C2—C3—C4	120.87 (15)	C4—C5—H5	121.4
C2—C3—C7	135.89 (15)	C5—C6—C1	120.43 (16)
C4—C3—C7	103.23 (14)	C5—C6—H6	119.8
N3—C4—C5	131.73 (16)	C1—C6—H6	119.8
N3—C4—C3	106.71 (15)	N3—C9—H9A	109.5
C5—C4—C3	121.56 (16)	N3—C9—H9B	109.5
C1—C2—C3	116.26 (15)	H9A—C9—H9B	109.5
C1—C2—H2	121.9	N3—C9—H9C	109.5
C3—C2—H2	121.9	H9A—C9—H9C	109.5
C2—C1—C6	123.60 (16)	H9B—C9—H9C	109.5