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1,3-Dimethyl-1*H*-indazol-6-amine

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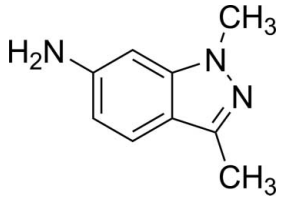
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.055; wR factor = 0.149; data-to-parameter ratio = 17.0.

The molecular skeleton of the title compound, $C_9H_{11}N_3$, is almost planar, with a maximum deviation of 0.0325 (19) Å for the amino N atom. In the crystal, N—H···N hydrogen bonds establish the packing.

Related literature

For the synthesis of the title compound, see: Sorbera *et al.* (2006); Zhao *et al.* (2011). For related structures, see: Qi *et al.*(2010); Long *et al.* (2011). For the application of indazole derivatives in the synthesis of drugs, see: Collot *et al.* (1999).



Experimental

Crystal data

$C_9H_{11}N_3$
M_r = 161.21
Orthorhombic, $Pca2_1$
a = 18.3004 (10) Å
b = 8.3399 (7) Å
c = 5.6563 (1) Å
V = 863.28 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 K
0.22 × 0.18 × 0.12 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.983, T_{max} = 0.991
7967 measured reflections
2002 independent reflections
1588 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.149
S = 1.02
2002 reflections
118 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N1^{i}	0.89 (1)	2.32 (1)	3.203 (2)	169 (2)
N3—H3B···N3^{ii}	0.91 (1)	2.48 (1)	3.384 (2)	175 (2)

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank Mr Hai-Bin Song of Nankai University for the X-ray crystallographic determination and helpful suggestions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2401).

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supplementary materials

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1,3-Dimethyl-1*H*-indazol-6-amine

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Comment

Some derivatives of indazole are important intermediates in the synthesis of drugs (Collot *et al.*1999). Here we report the crystal structure of the title compound(I).

In (I) the bond lengths and angles are normal and comparable with those reported for related compounds (Long *et al.*,2011; Qi *et al.*, 2010). The rings C3/C4/C5/C6/C7/C8 and C3/C2/N1/N2/C8 are almost coplaner forming a dihedral angle 0.82 (14)° (Fig. 1). The indazole ring system is almost planar with the maximal deviation of 0.0325 (19) Å for the atom N3. In the crystal structure intermolecular N–H···N hydrogen bonds (Fig. 2, Table 1) establish the packing.

Experimental

Step 1: Dimethyl carbonate(7.5 g, 3 eq) was added to a solution of 3-methyl-6-nitro-1*H*-indazole(5 g, 1eq) and triethylene diamine(3.1 g, 1eq) in 15 mL DMF. After stirring of 10 h at 353 K, the mixture was poured into 150 mL cold water, after filtering and drying a mixture of 1,3-dimethyl-6-nitro-1*H*-indazole and 2,3-dimethyl -6-nitro-2*H*-indazole were obtained.1,3-Dimethyl-6-nitro-1*H*- indazole (2 g) was obtained by silicagel column chromatography.

Step 2: Pd/C(0.2 g) was added to a solution of 1,3-dimethyl-6-nitro-1*H*-indazole (2 g) in 10 mL ethanol. After the reaction system was kept in vacuum, the mixture was treated with continuous hydrogen stream. After stirring of 8 h, the reaction system was filtered to get yellow solution. The solution was left at room temperature, and colourless crystals were grown slowly.

Refinement

C-bound H atoms were geometrically positioned (C—H 0.93–0.96 Å),and refined as riding with U_{iso}=1.2–1.5U_{eq}(C).

Computing details

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear* (Rigaku/MSC, 2005); data reduction: *CrystalClear* (Rigaku/MSC, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

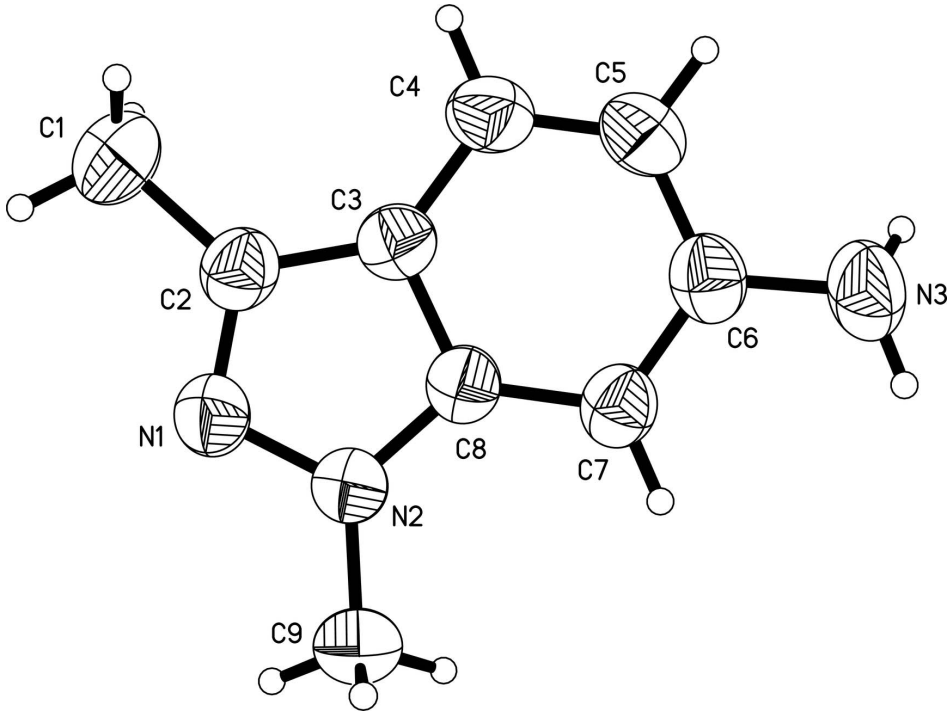

Figure 1

The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

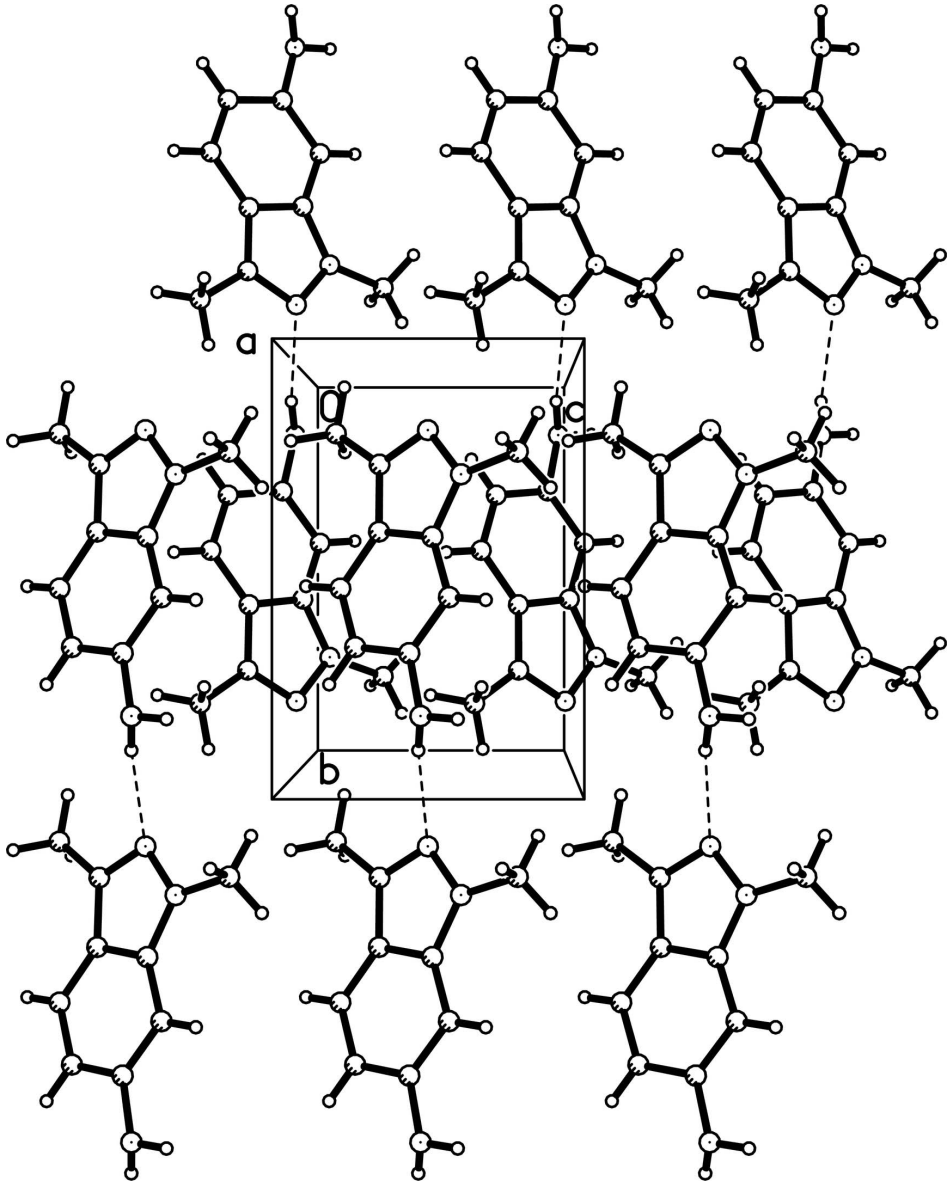

Figure 2

Packing diagram for (I) with hydrogen bonds (dashed lines).

1,3-Dimethyl-1*H*-indazol-6-amine

Crystal data

$C_9H_{11}N_3$
$M_r = 161.21$
Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
$a = 18.3004\ (10)$ Å
$b = 8.3399\ (7)$ Å
$c = 5.6563\ (1)$ Å
$V = 863.28\ (9)$ Å^3
$Z = 4$
$F(000) = 344$
$D_x = 1.240$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2241 reflections
$\theta = 3.3–27.9°$
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Prism, yellow
0.22 × 0.18 × 0.12 mm

Data collection

Rigaku Saturn diffractometer
Radiation source: rotating anode
Confocal monochromator
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.983, T_{max} = 0.991
7967 measured reflections
2002 independent reflections
1588 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 27.8°, θ_{min} = 2.7°
h = −23→24
k = −9→10
l = −7→7

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.149
S = 1.02
2002 reflections
118 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.12 (2)

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.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.10351 (9)	0.83358 (18)	0.4784 (4)	0.0568 (5)
N2	0.14711 (8)	0.72497 (19)	0.5968 (4)	0.0538 (5)
N3	0.19922 (10)	0.1548 (2)	0.4581 (5)	0.0699 (6)
H3A	0.1689 (11)	0.071 (2)	0.449 (5)	0.084*
H3B	0.2287 (12)	0.150 (3)	0.587 (3)	0.084*
C1	0.01866 (14)	0.8321 (3)	0.1420 (6)	0.0785 (8)
H1A	−0.0293	0.7890	0.1680	0.118*
H1B	0.0330	0.8131	−0.0188	0.118*
H1C	0.0182	0.9454	0.1721	0.118*
C2	0.07147 (10)	0.7530 (3)	0.3043 (5)	0.0549 (5)
C3	0.09469 (10)	0.5900 (2)	0.3044 (4)	0.0493 (5)
C4	0.08096 (11)	0.4531 (3)	0.1658 (5)	0.0596 (6)
H4	0.0489	0.4579	0.0384	0.072*
C5	0.11558 (12)	0.3130 (3)	0.2223 (5)	0.0615 (6)
H5	0.1072	0.2228	0.1295	0.074*

C6	0.16353 (10)	0.3008 (2)	0.4163 (5)	0.0559 (6)
C7	0.17824 (11)	0.4336 (2)	0.5559 (4)	0.0529 (5)
H7	0.2102	0.4277	0.6836	0.063*
C8	0.14298 (9)	0.5768 (2)	0.4964 (4)	0.0472 (5)
C9	0.19061 (12)	0.7763 (3)	0.7940 (5)	0.0624 (6)
H9A	0.1936	0.6913	0.9081	0.094*
H9B	0.1685	0.8688	0.8655	0.094*
H9C	0.2388	0.8032	0.7402	0.094*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0555 (9)	0.0501 (9)	0.0648 (12)	0.0046 (6)	−0.0046 (8)	−0.0011 (9)
N2	0.0544 (8)	0.0497 (9)	0.0573 (10)	0.0024 (7)	−0.0077 (8)	−0.0037 (8)
N3	0.0716 (13)	0.0426 (9)	0.0956 (17)	−0.0012 (7)	−0.0004 (12)	0.0028 (11)
C1	0.0711 (14)	0.0782 (15)	0.0862 (19)	0.0149 (11)	−0.0214 (14)	0.0054 (14)
C2	0.0474 (9)	0.0563 (11)	0.0610 (12)	0.0026 (8)	−0.0019 (9)	0.0031 (10)
C3	0.0462 (9)	0.0521 (11)	0.0496 (11)	−0.0036 (7)	−0.0001 (8)	0.0017 (9)
C4	0.0581 (11)	0.0599 (12)	0.0608 (13)	−0.0082 (9)	−0.0086 (10)	−0.0051 (11)
C5	0.0655 (12)	0.0509 (11)	0.0682 (15)	−0.0097 (9)	−0.0008 (11)	−0.0082 (10)
C6	0.0517 (10)	0.0463 (10)	0.0696 (15)	−0.0031 (8)	0.0064 (10)	0.0027 (10)
C7	0.0509 (9)	0.0495 (11)	0.0581 (12)	−0.0016 (7)	0.0008 (9)	0.0074 (9)
C8	0.0429 (8)	0.0461 (10)	0.0526 (11)	−0.0025 (6)	0.0018 (8)	0.0037 (9)
C9	0.0663 (13)	0.0651 (13)	0.0556 (13)	−0.0020 (10)	−0.0097 (10)	−0.0054 (11)

Geometric parameters (Å, º)

N1—C2	1.329 (3)	C3—C8	1.404 (3)
N1—N2	1.380 (2)	C3—C4	1.407 (3)
N2—C8	1.362 (2)	C4—C5	1.367 (3)
N2—C9	1.436 (3)	C4—H4	0.9300
N3—C6	1.401 (3)	C5—C6	1.409 (3)
N3—H3A	0.893 (9)	C5—H5	0.9300
N3—H3B	0.909 (10)	C6—C7	1.387 (3)
C1—C2	1.487 (3)	C7—C8	1.399 (3)
C1—H1A	0.9600	C7—H7	0.9300
C1—H1B	0.9600	C9—H9A	0.9600
C1—H1C	0.9600	C9—H9B	0.9600
C2—C3	1.424 (3)	C9—H9C	0.9600
C2—N1—N2	106.43 (17)	C5—C4—H4	120.6
C8—N2—N1	111.14 (17)	C3—C4—H4	120.6
C8—N2—C9	128.72 (17)	C4—C5—C6	122.2 (2)
N1—N2—C9	120.11 (17)	C4—C5—H5	118.9
C6—N3—H3A	112.3 (15)	C6—C5—H5	118.9
C6—N3—H3B	116.7 (15)	C7—C6—N3	120.5 (2)
H3A—N3—H3B	112.6 (15)	C7—C6—C5	120.41 (19)
C2—C1—H1A	109.5	N3—C6—C5	119.0 (2)
C2—C1—H1B	109.5	C6—C7—C8	117.1 (2)
H1A—C1—H1B	109.5	C6—C7—H7	121.4

C2—C1—H1C	109.5	C8—C7—H7	121.4
H1A—C1—H1C	109.5	N2—C8—C7	130.43 (19)
H1B—C1—H1C	109.5	N2—C8—C3	106.65 (16)
N1—C2—C3	110.53 (19)	C7—C8—C3	122.91 (18)
N1—C2—C1	121.3 (2)	N2—C9—H9A	109.5
C3—C2—C1	128.1 (2)	N2—C9—H9B	109.5
C8—C3—C4	118.65 (18)	H9A—C9—H9B	109.5
C8—C3—C2	105.24 (18)	N2—C9—H9C	109.5
C4—C3—C2	136.1 (2)	H9A—C9—H9C	109.5
C5—C4—C3	118.7 (2)	H9B—C9—H9C	109.5

C2—N1—N2—C8	0.5 (2)	N3—C6—C7—C8	177.1 (2)
C2—N1—N2—C9	178.8 (2)	C5—C6—C7—C8	0.7 (3)
N2—N1—C2—C3	−0.9 (2)	N1—N2—C8—C7	179.1 (2)
N2—N1—C2—C1	178.5 (2)	C9—N2—C8—C7	1.0 (3)
N1—C2—C3—C8	0.9 (2)	N1—N2—C8—C3	0.1 (2)
C1—C2—C3—C8	−178.4 (2)	C9—N2—C8—C3	−178.0 (2)
N1—C2—C3—C4	−178.9 (2)	C6—C7—C8—N2	−179.1 (2)
C1—C2—C3—C4	1.8 (4)	C6—C7—C8—C3	−0.2 (3)
C8—C3—C4—C5	−0.5 (3)	C4—C3—C8—N2	179.25 (18)
C2—C3—C4—C5	179.2 (2)	C2—C3—C8—N2	−0.6 (2)
C3—C4—C5—C6	1.0 (4)	C4—C3—C8—C7	0.2 (3)
C4—C5—C6—C7	−1.1 (3)	C2—C3—C8—C7	−179.67 (19)
C4—C5—C6—N3	−177.6 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N1^{i}	0.89 (1)	2.32 (1)	3.203 (2)	169 (2)
N3—H3*B*···N3^{ii}	0.91 (1)	2.48 (1)	3.384 (2)	175 (2)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1/2, *y*, *z*+1/2.