1-(6-Nitro-1*H*-indazol-1-yl)ethanone

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In the title molecule, $C_9H_7N_3O_3$, the indazole moiety is essentially planar and the mean plane of the acetyl substituent is twisted by 5.3 (1)° from its plane. In the crystal, weak C—H···O and C—H···N hydrogen bonds form layers parallel to (102), which are associated through π-stacking interactions to form a three-dimensional network. The structure was refined as a two-component twin.

3D view
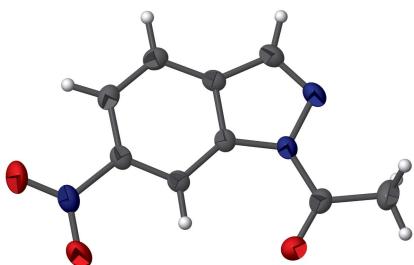
Chemical scheme
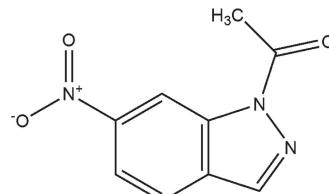
Structure description

The diverse pharmacological properties exhibited by 1*H*-indazoles have sparked the emergence of novel methods toward their synthesis. Indazole is a frequently found motif in drug substances with important biological activities such as antimicrobial (Li *et al.*, 2003), anti-inflammatory (Lin *et al.*, 2008) and anticancer effects (Zhu *et al.*, 2007). The crystal structure study of the title compound constitutes a continuation of our previous work on indazole derivatives (Mohamed Abdelahi *et al.*, 2017; El Brahmi *et al.*, 2012).

The indazole moiety is planar to within 0.0093 (16) Å for (C6) with an r.m.s. deviation from the mean plane of 0.005 Å. The acetyl group is slightly twisted out of the indazole plane, as indicated by the dihedral angle of 5.3 (1)° between it and the N2/C8/C9/O1 plane. This orientation may be due in part to the intramolecular C2—H2···O1 hydrogen bond (Table 1 and Fig. 1).

In the crystal, the molecules form dimers through pairwise C7—H7···N1 hydrogen bonds which are linked into sheets parallel to (102) by C4—H4···O1 hydrogen bonds (Table 1 and Fig. 2). The sheets stack along the *a*-axis direction and are associated through head-to-head π-stacking interactions (Fig. 3) with centroid···centroid distances of 3.892 (1) Å.

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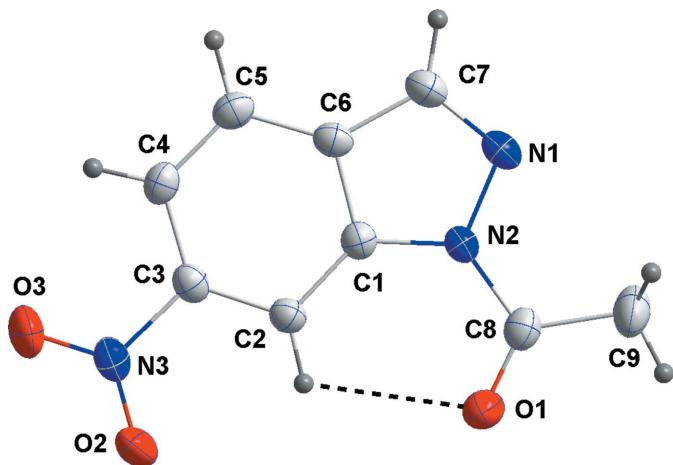
Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids. The intramolecular C—H···O interaction is shown by a dashed line.

Synthesis and crystallization

A mixture of 6-nitro-1H-indazole (0.6 g, 3 mmol), acetic acid (2 ml) and acetic anhydride (10 ml) were heated under reflux for 24 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue obtained was recrystallized from ethanol to afford the title compound as colorless crystals (yield: 70%).

Refinement

Crystal and refinement details are presented in Table 2. The structure was refined as a two-component twin.

Acknowledgements

References

Brandenburg, K. & Putz, H. (2012). *DIAMOND*, Crystal Impact GbR, Bonn, Germany.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1	0.94 (2)	2.46 (2)	2.929 (2)	111.3 (16)
C4—H4···O1^i	0.95 (3)	2.37 (3)	3.213 (2)	148 (2)
C7—H7···N1^{ii}	0.95 (2)	2.65 (2)	3.328 (2)	129.2 (18)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_7N_3O_3$
M_r	205.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	3.8919 (1), 20.4831 (6), 11.2580 (4)
β (°)	92.757 (1)
V (Å^3)	896.43 (5)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.00
Crystal size (mm)	$0.25 \times 0.18 \times 0.07$
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.79, 0.93
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12167, 11998, 9449
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.140, 1.03
No. of reflections	11998
No. of parameters	165
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.29

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS, Inc., Madison, Wisconsin, USA.

El Brahmi, N., Benchidmi, M., Essassi, E. M., Ladeira, S. & El Ammari, L. (2012). *Acta Cryst.* E**68**, o3368.

Figure 2
Packing viewed along the a-axis direction with C—H···O and C—H···N hydrogen bonds shown as dashed lines.
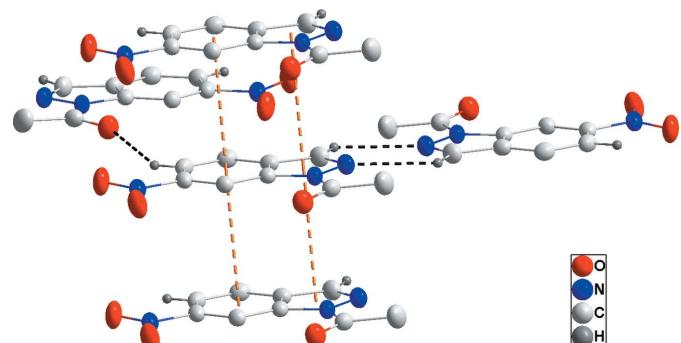

Figure 3
Details of the π-stacking interactions (orange dashed lines) and the intermolecular C—H···O and C—H···N hydrogen bonds (black dashed lines).

Li, X., Chu, S., Feher, V. A., Khalili, M., Nie, Z., Margosiak, S., Nikulin, V., Levin, J., Sprankle, K. G., Tedder, M. E., Almassy, R., Appelt, K. & Yager, K. M. (2003). *J. Med. Chem.* **46**, 5663–5673.

Lin, X., Busch-Petersen, V., Deng, J., Edwards, V., Zhang, V. & Kerns, J. K. (2008). *Synlett*, pp. 3216–3220.

Mohamed Abdelahi, M. M., El Bakri, Y., Benchidmi, M., Essassi, E. M. & Mague, J. T. (2017). *IUCrData*, **2**, x170432.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2009). *TWINABS*, University of Göttingen, Göttingen, Germany.

Sheldrick, G. M. (2015a). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst.* C**71**, 3–8.

Zhu, G. D., Gong, J., Gandhi, V. B., Woods, K., Luo, Y., Liu, X., Guan, R., Klinghofer, V., Johnson, E. F., Stoll, V. S., Mamo, M., Li, Q., Rosenberg, S. H. & Giranda, V. L. (2007). *Bioorg. Med. Chem.* **15**, 2441–2452.

full crystallographic data

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1-(6-Nitro-1*H*-indazol-1-yl)ethanone

Crystal data

$C_9H_7N_3O_3$	$F(000) = 424$
$M_r = 205.18$	$D_x = 1.520$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 3.8919\ (1)$ Å	Cell parameters from 7750 reflections
$b = 20.4831\ (6)$ Å	$\theta = 4.3$–$72.2°$
$c = 11.2580\ (4)$ Å	$\mu = 1.00$ mm^{-1}
$\beta = 92.757\ (1)°$	$T = 150$ K
$V = 896.43\ (5)$ Å^3	Plate, colourless
$Z = 4$	$0.25 \times 0.18 \times 0.07$ mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer	$T_{min} = 0.79$, $T_{max} = 0.93$
Radiation source: INCOATEC IμS micro-focus source	12167 measured reflections
	11998 independent reflections
Mirror monochromator	9449 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.038$
ω scans	$\theta_{max} = 72.2°$, $\theta_{min} = 4.3°$
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)	$h = -4 \rightarrow 4$
	$k = -25 \rightarrow 24$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.140$	All H-atom parameters refined
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.0964P]$
11998 reflections	where $P = (F_o^2 + 2F_c^2)/3$
165 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Experimental. Analysis of 1886 reflections having I/σ(I) > 12 and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008) showed the crystal to belong to the monoclinic system and to be twinned by a 180° rotation about the *b* axis. The raw data were processed using the multi-component version of *SAINT* under control of the two-component orientation file generated by *CELL_NOW*.

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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. Refined as a 2-component twin.

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

	x	y	z	U_{iso}*/U_{eq}
O1	1.0289 (4)	0.63313 (7)	0.16899 (13)	0.0386 (4)
O2	0.8908 (5)	0.85449 (7)	0.26601 (14)	0.0455 (5)
O3	0.6050 (5)	0.89484 (7)	0.40880 (16)	0.0489 (5)
N1	0.6127 (4)	0.55971 (8)	0.40377 (15)	0.0325 (4)
N2	0.7342 (4)	0.60698 (7)	0.32890 (14)	0.0267 (4)
N3	0.7188 (4)	0.84860 (7)	0.35434 (15)	0.0324 (4)
C1	0.6747 (5)	0.66903 (8)	0.37279 (16)	0.0243 (4)
C2	0.7481 (5)	0.73060 (8)	0.32808 (16)	0.0252 (4)
H2	0.861 (6)	0.7372 (11)	0.257 (2)	0.032 (6)*
C3	0.6468 (5)	0.78218 (8)	0.39653 (17)	0.0265 (4)
C4	0.4795 (5)	0.77587 (9)	0.50369 (17)	0.0285 (5)
H4	0.420 (6)	0.8142 (13)	0.545 (2)	0.040 (6)*
C5	0.4104 (5)	0.71433 (9)	0.54587 (17)	0.0295 (4)
H5	0.293 (6)	0.7092 (11)	0.621 (2)	0.034 (6)*
C6	0.5103 (5)	0.66033 (9)	0.47964 (16)	0.0262 (4)
C7	0.4820 (5)	0.59099 (10)	0.49217 (18)	0.0323 (5)
H7	0.378 (6)	0.5673 (11)	0.553 (2)	0.038 (6)*
C8	0.9034 (5)	0.59016 (9)	0.22604 (18)	0.0302 (5)
C9	0.9149 (7)	0.51924 (11)	0.1962 (3)	0.0448 (6)
H9A	1.039 (9)	0.4957 (16)	0.261 (3)	0.069 (9)*
H9B	0.693 (11)	0.5004 (16)	0.191 (3)	0.082 (11)*
H9C	1.034 (8)	0.5145 (14)	0.126 (3)	0.060 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0437 (9)	0.0361 (8)	0.0371 (8)	−0.0018 (6)	0.0129 (6)	−0.0027 (6)
O2	0.0670 (11)	0.0297 (8)	0.0409 (9)	−0.0095 (7)	0.0128 (8)	0.0042 (6)
O3	0.0630 (12)	0.0241 (8)	0.0602 (11)	0.0065 (6)	0.0101 (8)	−0.0024 (7)
N1	0.0365 (10)	0.0245 (8)	0.0366 (9)	−0.0034 (6)	0.0023 (7)	0.0061 (6)
N2	0.0303 (9)	0.0209 (7)	0.0289 (8)	−0.0003 (6)	0.0022 (6)	0.0015 (6)
N3	0.0377 (10)	0.0239 (8)	0.0350 (9)	−0.0012 (6)	−0.0043 (7)	−0.0001 (7)
C1	0.0240 (9)	0.0242 (9)	0.0245 (9)	0.0001 (6)	−0.0024 (7)	−0.0002 (7)
C2	0.0262 (10)	0.0253 (9)	0.0240 (9)	−0.0011 (6)	0.0001 (7)	0.0019 (7)
C3	0.0278 (10)	0.0239 (9)	0.0273 (10)	−0.0012 (6)	−0.0035 (8)	0.0019 (7)
C4	0.0285 (10)	0.0292 (10)	0.0276 (10)	0.0026 (7)	−0.0010 (8)	−0.0053 (7)

C5	0.0288 (10)	0.0359 (10)	0.0238 (9)	0.0006 (7)	0.0010 (8)	−0.0006 (7)
C6	0.0249 (10)	0.0288 (9)	0.0248 (9)	−0.0016 (7)	−0.0004 (7)	0.0038 (7)
C7	0.0352 (11)	0.0295 (10)	0.0322 (10)	−0.0035 (7)	0.0029 (8)	0.0064 (8)
C8	0.0273 (10)	0.0303 (10)	0.0328 (10)	0.0018 (7)	0.0007 (8)	−0.0046 (8)
C9	0.0441 (14)	0.0339 (11)	0.0573 (16)	0.0001 (9)	0.0103 (12)	−0.0146 (10)

Geometric parameters (Å, º)

O1—C8	1.207 (2)	C3—C4	1.404 (3)
O2—N3	1.231 (2)	C4—C5	1.378 (3)
O3—N3	1.223 (2)	C4—H4	0.95 (3)
N1—C7	1.307 (3)	C5—C6	1.399 (3)
N1—N2	1.382 (2)	C5—H5	0.99 (2)
N2—C1	1.387 (2)	C6—C7	1.432 (3)
N2—C8	1.402 (3)	C7—H7	0.95 (2)
N3—C3	1.472 (2)	C8—C9	1.492 (3)
C1—C2	1.393 (2)	C9—H9A	0.98 (3)
C1—C6	1.401 (3)	C9—H9B	0.95 (4)
C2—C3	1.377 (3)	C9—H9C	0.94 (3)
C2—H2	0.94 (2)		
C7—N1—N2	106.15 (15)	C4—C5—C6	118.39 (18)
N1—N2—C1	110.90 (15)	C4—C5—H5	119.9 (13)
N1—N2—C8	121.30 (15)	C6—C5—H5	121.7 (13)
C1—N2—C8	127.76 (16)	C5—C6—C1	120.47 (17)
O3—N3—O2	123.58 (17)	C5—C6—C7	134.97 (18)
O3—N3—C3	118.35 (17)	C1—C6—C7	104.55 (16)
O2—N3—C3	118.07 (16)	N1—C7—C6	112.12 (17)
N2—C1—C2	131.33 (18)	N1—C7—H7	119.9 (14)
N2—C1—C6	106.28 (15)	C6—C7—H7	128.0 (14)
C2—C1—C6	122.39 (17)	O1—C8—N2	118.59 (17)
C3—C2—C1	115.06 (18)	O1—C8—C9	125.0 (2)
C3—C2—H2	121.5 (14)	N2—C8—C9	116.44 (18)
C1—C2—H2	123.4 (14)	C8—C9—H9A	109.4 (19)
C2—C3—C4	124.57 (17)	C8—C9—H9B	112 (2)
C2—C3—N3	117.68 (17)	H9A—C9—H9B	105 (3)
C4—C3—N3	117.76 (16)	C8—C9—H9C	108.1 (18)
C5—C4—C3	119.12 (17)	H9A—C9—H9C	109 (3)
C5—C4—H4	122.0 (15)	H9B—C9—H9C	113 (3)
C3—C4—H4	118.8 (15)		
C7—N1—N2—C1	−0.2 (2)	N3—C3—C4—C5	−179.61 (16)
C7—N1—N2—C8	177.70 (17)	C3—C4—C5—C6	0.0 (3)
N1—N2—C1—C2	−179.35 (18)	C4—C5—C6—C1	−0.4 (3)
C8—N2—C1—C2	2.9 (3)	C4—C5—C6—C7	−179.1 (2)
N1—N2—C1—C6	0.2 (2)	N2—C1—C6—C5	−179.16 (16)
C8—N2—C1—C6	−177.56 (17)	C2—C1—C6—C5	0.4 (3)
N2—C1—C2—C3	179.40 (18)	N2—C1—C6—C7	−0.1 (2)

C6—C1—C2—C3	−0.1 (3)	C2—C1—C6—C7	179.50 (17)
C1—C2—C3—C4	−0.3 (3)	N2—N1—C7—C6	0.2 (2)
C1—C2—C3—N3	179.68 (15)	C5—C6—C7—N1	178.8 (2)
O3—N3—C3—C2	173.97 (17)	C1—C6—C7—N1	0.0 (2)
O2—N3—C3—C2	−6.0 (3)	N1—N2—C8—O1	−174.05 (18)
O3—N3—C3—C4	−6.0 (3)	C1—N2—C8—O1	3.5 (3)
O2—N3—C3—C4	173.97 (17)	N1—N2—C8—C9	5.6 (3)
C2—C3—C4—C5	0.4 (3)	C1—N2—C8—C9	−176.86 (19)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2⋯O1	0.94 (2)	2.46 (2)	2.929 (2)	111.3 (16)
C4—H4⋯O1[i]	0.95 (3)	2.37 (3)	3.213 (2)	148 (2)
C7—H7⋯N1[ii]	0.95 (2)	2.65 (2)	3.328 (2)	129.2 (18)

Symmetry codes: (i) $x-1$, $-y+3/2$, $z+1/2$; (ii) $-x+1$, $-y+1$, $-z+1$.