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5-Nitro-1-(prop-2-yn-1-yl)-1*H*-indazole

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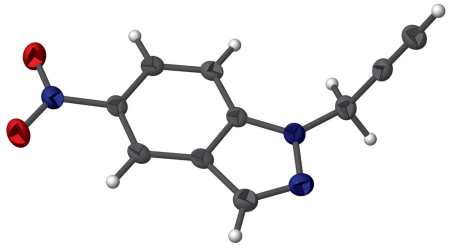
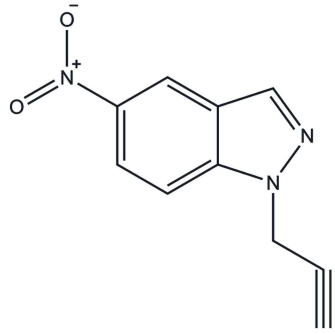
Structural data: full structural data are available from iucrdata.iucr.org

The packing of the title molecule, $C_{10}H_7N_3O_2$, features the formation of weak dimers *via* pairwise C—H···O interactions across centers of symmetry. The prop-2-yn-1-yl moiety is twisted out of the plane of the indazole unit by 78.53 (17)°.

3D view



Chemical scheme



Structure description

Recently there has been considerable interest in the chemistry of indazoles. This is undoubtedly due to a broad variety of biological functions of indazole derivatives such as anti-inflammatory (Schmidt *et al.*, 2008), antibacterial (Shafakat Ali *et al.*, 2012) and antitumor activities (Abbassi *et al.*, 2014). The present work is a continuation of our work on indazole derivatives (El Brahmi *et al.*, 2011). In contrast to 1-(5-nitro-1*H*-indazol-1-yl)ethanone, the nitro group here is within a degree of planarity with the indazole moiety (Fig. 1). However, the prop-2-yn-1-yl moiety is twisted out of the plane of the indazole unit by 78.53 (17)°. In the crystal, molecules are linked by pairs of C3—H3···O2 interactions, forming inversion dimers (Fig. 2 and Table 1).

Synthesis and crystallization

To a solution of 5-nitro-1*H*-indazole (1 g, 6.13 mmol) in acetone (30 ml) was added potassium hydroxide (0.38 g, 6.8 mmol). After 15 min of stirring at room temperature, propargyl bromide (1.09 ml, 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

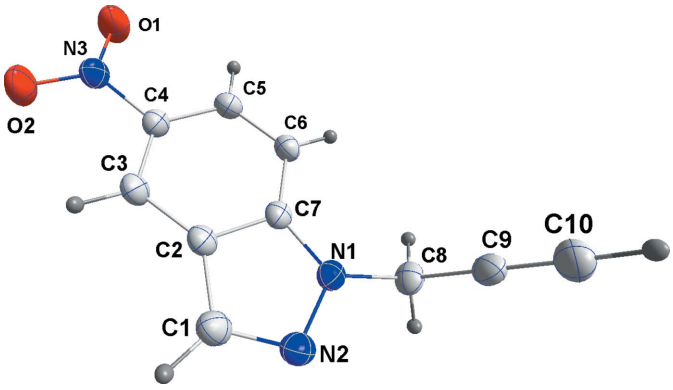


Figure 1
The title molecule with the atom-labeling scheme and 50% probability ellipsoids.

by column chromatography (EtOAc/hexane 1/9). The title compound was recrystallized from ethanol at room temperature giving colorless crystals (yield: 57%; m.p. 355–357 K).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Trial refinements with both the single component reflection file extracted from the full data set by *TWINABS* and with the full twinned data set indicated that the former refinement gave better results, as judged by lower values for R_1, wR_2, su's and residual features in the final difference map.

Acknowledgements

The support of NSF-MRI Grant No. 1228232 for the purchase of the diffractometer and Tulane University for support of the Tulane Crystallography Laboratory are gratefully acknowledged.

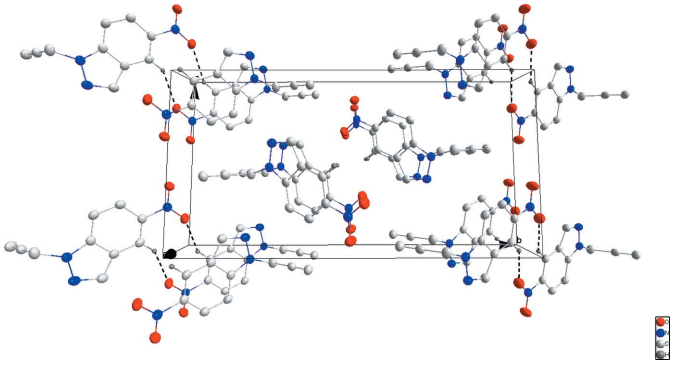


Figure 2
Packing viewed down the *a* axis with C—H···O interactions shown as dotted lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O2^{i}	0.95	2.47	3.298 (2)	146

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_7N_3O_2$
M_r	201.19
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	4.0105 (1), 21.0705 (7), 10.7451 (4)
β (°)	96.323 (2)
V (Å^3)	902.47 (5)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.90
Crystal size (mm)	0.22 × 0.17 × 0.14
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.58, 0.88
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11748, 1747, 1561
R_{int}	0.045
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.124, 1.04
No. of reflections	1747
No. of parameters	141
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.21

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

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full crystallographic data

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Crystal data

$C_{10}H_7N_3O_2$
M_r = 201.19
Monoclinic, $P2_1/n$
a = 4.0105 (1) Å
b = 21.0705 (7) Å
c = 10.7451 (4) Å
β = 96.323 (2)°
V = 902.47 (5) Å^3
Z = 4
$F(000)$ = 416
D_x = 1.481 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 6907 reflections
θ = 4.2–72.4°
μ = 0.90 mm^{-1}
T = 150 K
Block, colourless
0.22 × 0.17 × 0.14 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro–focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min} = 0.58, T_{max} = 0.88
11748 measured reflections
1747 independent reflections
1561 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 72.4°, θ_{min} = 4.2°
h = −4→4
k = −26→26
l = −12→−2

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.124
S = 1.04
1747 reflections
141 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2 + 0.2542P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0086 (15)

Special details

Experimental. Analysis of 644 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 *a* 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 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. H-atoms attached to aromatic and carbon atoms were placed in calculated positions (C—H = 0.95 − 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 times those of the attached atoms. Trial refinements with both the single component reflection file extracted from the full data set by *TWINABS* and with the full twinned data set indicated that the former refinement gave better results as judged by lower values for R1, wR2, su's and residual features in the final difference map.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.6905 (4)	0.49477 (6)	0.13174 (12)	0.0456 (4)
O2	0.9003 (3)	0.52591 (5)	0.31507 (11)	0.0416 (4)
N1	0.2066 (3)	0.28236 (6)	0.47196 (12)	0.0268 (3)
N2	0.3207 (4)	0.29212 (6)	0.59556 (12)	0.0315 (3)
N3	0.7330 (3)	0.48851 (6)	0.24594 (13)	0.0299 (3)
C1	0.4940 (4)	0.34546 (7)	0.59953 (15)	0.0318 (4)
H1	0.6022	0.3638	0.6740	0.038*
C2	0.4980 (4)	0.37187 (7)	0.47786 (14)	0.0255 (3)
C3	0.6386 (4)	0.42590 (7)	0.42929 (14)	0.0261 (4)
H3	0.7658	0.4556	0.4815	0.031*
C4	0.5824 (4)	0.43369 (6)	0.30145 (14)	0.0251 (4)
C5	0.3948 (4)	0.39102 (7)	0.22039 (14)	0.0272 (4)
H5	0.3651	0.3990	0.1329	0.033*
C6	0.2552 (4)	0.33801 (7)	0.26761 (14)	0.0262 (4)
H6	0.1280	0.3087	0.2146	0.031*
C7	0.3087 (4)	0.32901 (6)	0.39784 (15)	0.0241 (3)
C8	−0.0010 (4)	0.22729 (7)	0.43653 (16)	0.0305 (4)
H8A	−0.1252	0.2349	0.3530	0.037*
H8B	−0.1677	0.2221	0.4972	0.037*
C9	0.1934 (4)	0.16838 (7)	0.43243 (14)	0.0276 (4)
C10	0.3423 (4)	0.12015 (7)	0.42753 (16)	0.0327 (4)
H10	0.462 (5)	0.0839 (10)	0.4232 (18)	0.043 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0688 (10)	0.0379 (7)	0.0298 (6)	−0.0131 (6)	0.0035 (6)	0.0046 (5)
O2	0.0524 (8)	0.0313 (6)	0.0400 (7)	−0.0131 (5)	0.0002 (6)	−0.0025 (5)

N1	0.0272 (7)	0.0240 (6)	0.0296 (7)	0.0018 (5)	0.0058 (5)	−0.0004 (5)
N2	0.0380 (8)	0.0301 (7)	0.0269 (7)	0.0044 (5)	0.0055 (6)	0.0007 (5)
N3	0.0340 (7)	0.0247 (7)	0.0312 (7)	0.0007 (5)	0.0046 (5)	−0.0007 (5)
C1	0.0400 (9)	0.0278 (8)	0.0276 (8)	0.0028 (6)	0.0039 (7)	−0.0011 (6)
C2	0.0273 (7)	0.0225 (7)	0.0268 (8)	0.0043 (5)	0.0040 (6)	−0.0036 (6)
C3	0.0284 (8)	0.0221 (7)	0.0274 (8)	0.0030 (5)	0.0017 (6)	−0.0048 (6)
C4	0.0252 (8)	0.0209 (7)	0.0296 (8)	0.0029 (5)	0.0052 (6)	−0.0011 (6)
C5	0.0287 (8)	0.0282 (8)	0.0251 (7)	0.0028 (5)	0.0042 (6)	−0.0026 (6)
C6	0.0246 (8)	0.0267 (7)	0.0274 (8)	0.0007 (5)	0.0033 (6)	−0.0055 (6)
C7	0.0233 (7)	0.0208 (7)	0.0291 (8)	0.0043 (5)	0.0066 (6)	−0.0018 (5)
C8	0.0258 (8)	0.0265 (7)	0.0402 (9)	−0.0016 (6)	0.0082 (6)	−0.0001 (6)
C9	0.0299 (8)	0.0266 (8)	0.0268 (8)	−0.0042 (6)	0.0058 (6)	0.0014 (6)
C10	0.0374 (9)	0.0265 (8)	0.0342 (9)	0.0022 (6)	0.0031 (7)	−0.0020 (6)

Geometric parameters (Å, º)

O1—N3	1.2272 (18)	C3—H3	0.9500
O2—N3	1.2302 (18)	C4—C5	1.410 (2)
N1—C7	1.3564 (19)	C5—C6	1.372 (2)
N1—N2	1.3718 (18)	C5—H5	0.9500
N1—C8	1.4542 (19)	C6—C7	1.405 (2)
N2—C1	1.320 (2)	C6—H6	0.9500
N3—C4	1.4608 (19)	C8—C9	1.469 (2)
C1—C2	1.423 (2)	C8—H8A	0.9900
C1—H1	0.9500	C8—H8B	0.9900
C2—C3	1.397 (2)	C9—C10	1.183 (2)
C2—C7	1.410 (2)	C10—H10	0.91 (2)
C3—C4	1.377 (2)		
C7—N1—N2	111.70 (12)	C5—C4—N3	117.93 (13)
C7—N1—C8	128.73 (14)	C6—C5—C4	120.17 (14)
N2—N1—C8	119.56 (13)	C6—C5—H5	119.9
C1—N2—N1	106.10 (13)	C4—C5—H5	119.9
O1—N3—O2	122.77 (13)	C5—C6—C7	117.03 (14)
O1—N3—C4	118.37 (13)	C5—C6—H6	121.5
O2—N3—C4	118.85 (13)	C7—C6—H6	121.5
N2—C1—C2	111.26 (14)	N1—C7—C6	131.27 (14)
N2—C1—H1	124.4	N1—C7—C2	106.46 (14)
C2—C1—H1	124.4	C6—C7—C2	122.28 (14)
C3—C2—C7	120.44 (14)	N1—C8—C9	113.07 (13)
C3—C2—C1	135.07 (14)	N1—C8—H8A	109.0
C7—C2—C1	104.48 (14)	C9—C8—H8A	109.0
C4—C3—C2	116.19 (14)	N1—C8—H8B	109.0
C4—C3—H3	121.9	C9—C8—H8B	109.0
C2—C3—H3	121.9	H8A—C8—H8B	107.8
C3—C4—C5	123.89 (14)	C10—C9—C8	178.21 (17)
C3—C4—N3	118.16 (13)	C9—C10—H10	178.1 (14)

C7—N1—N2—C1	0.38 (17)	N3—C4—C5—C6	178.43 (13)
C8—N1—N2—C1	−178.83 (13)	C4—C5—C6—C7	0.0 (2)
N1—N2—C1—C2	−0.14 (18)	N2—N1—C7—C6	179.25 (14)
N2—C1—C2—C3	179.98 (16)	C8—N1—C7—C6	−1.6 (3)
N2—C1—C2—C7	−0.13 (18)	N2—N1—C7—C2	−0.47 (16)
C7—C2—C3—C4	−0.4 (2)	C8—N1—C7—C2	178.66 (13)
C1—C2—C3—C4	179.45 (16)	C5—C6—C7—N1	−179.96 (14)
C2—C3—C4—C5	0.2 (2)	C5—C6—C7—C2	−0.3 (2)
C2—C3—C4—N3	−178.21 (12)	C3—C2—C7—N1	−179.74 (13)
O1—N3—C4—C3	178.20 (14)	C1—C2—C7—N1	0.35 (16)
O2—N3—C4—C3	−0.8 (2)	C3—C2—C7—C6	0.5 (2)
O1—N3—C4—C5	−0.3 (2)	C1—C2—C7—C6	−179.39 (14)
O2—N3—C4—C5	−179.27 (14)	C7—N1—C8—C9	102.40 (18)
C3—C4—C5—C6	0.1 (2)	N2—N1—C8—C9	−78.53 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O2^{i}	0.95	2.47	3.298 (2)	146

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