IUCrData

ISSN 2414-3146

# 1-Ethyl-5-nitro-1*H*-indazole

**Mohammed Boulhaoua,[a]* Mohamed El Hafi,[a] Mohammed Benchidmi,[a] El Mokhtar Essassi[a] and Joel T. Mague[b]**

[a]Laboratoire de Chimie Organique Hétérocyclique, URAC 21, Pôle de Compétence Pharmacochimie, Av. Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco, and [b]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. *Correspondence e-mail: mboulhaoua@gmail.com

Received 15 March 2016
Accepted 5 April 2016

Edited by E. R. T. Tiekink, Sunway University, Malaysia

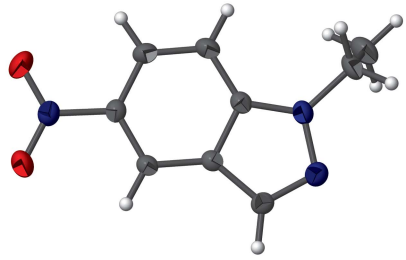
**Keywords:** crystal structure; indazole derivatives; C—H···O hydrogen bonds.

**CCDC reference**: 1472479

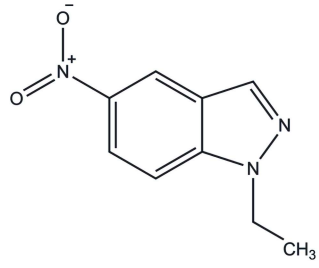
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title molecule, $C_9H_9N_3O_2$, the nitro substituent is twisted by 4.0 (2)° out of the plane of the indazolyl moiety; the ethyl group is perpendicular to the indazolyl plane, with the N—N—C—C torsion angle being 101.4 (2)°. In the molecular packing, C—H···O hydrogen bonds lead to supramolecular chains along [001]. Globally, molecules assemble into layers in the *bc* plane. $\pi$–$\pi$ interactions between five- and six-membered rings consolidate the three-dimensional packing [inter-centroid distance = 3.591 (1) Å]. The sample was refined as an inversion twin.

**3D view**



**Chemical scheme**




## Structure description

As a continuation of our research work devoted to the development of *N*-substituted indazoles (El Brahmi *et al.*, 2012; Boulhaoua *et al.*, 2015), we have studied the action of bromoethane towards 5-nitro-1*H*-indazole under phase-transfer catalysis conditions using tetra-*n*-butylammonium iodide (TBAI) as catalyst and potassium carbonate as base. This readily leads to the title compound (Fig. 1) in good yield. The nitro substituent is twisted 4.0 (2)° out of the plane of the indazolyl moiety while the ethyl group is twisted well out of that plane and away from N2 as indicated by the N2—N1—C8—C9 torsion angle of 101.4 (2)°. The molecules pack in layers in the *bc* plane being partially assembled through C3—H3···O1($-x+\frac{3}{2}$, $-y+2$, $z+\frac{1}{2}$) hydrogen bonds (Table 1 and Fig. 2). The layers interact *via* offset $\pi$–$\pi$-stacking between the C2–C7 ring in one layer and the (C1,C2,N1,N2,C7) ring (related by the symmetry operation $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$) in the next. The distance between the ring centroids is 3.591 (1) Å, the dihedral angle between the planes is 6.82 (9)° and the 'slippage' is 1.08 Å.

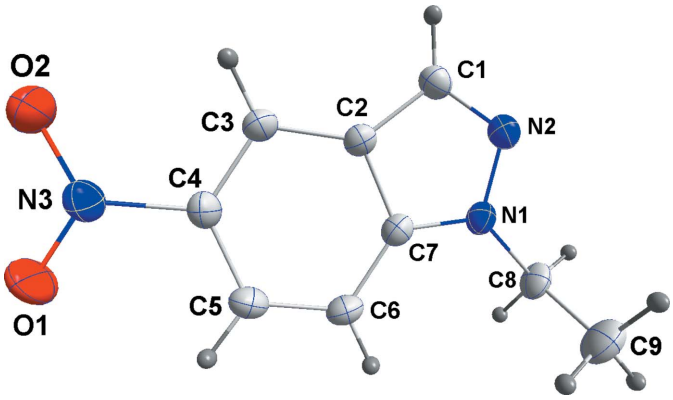



**Figure 1**
The title molecule with labelling scheme and 50% probability ellipsoids.

## Synthesis and crystallization

To a solution of 5-nitro-1*H*-indazole (0.5 g, 3 mmol) in DMF (15 ml) was added bromoethane (0.22 ml, 3 mmol), potassium carbonate (0.83 g, 6 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 solid product was purified by recrystallization from ethanol to afford the title compound as pale-pink crystals (yield: 70%; m.p. = 392–394 K).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The sample was refined as an inversion twin.

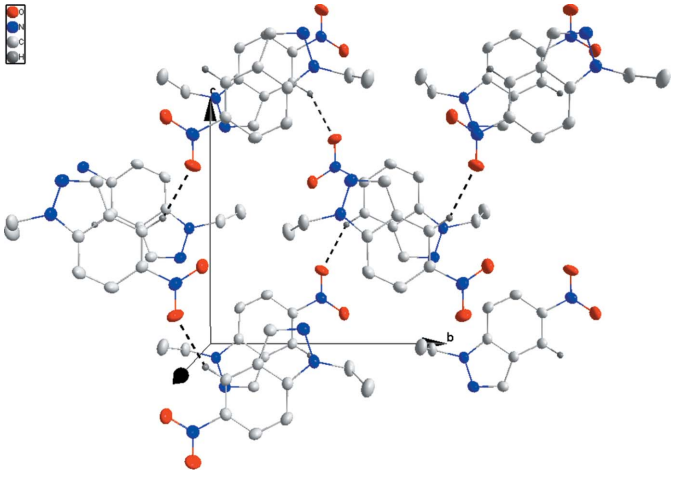



**Figure 2**
Packing viewed along the *a* axis with intermolecular C—H···O hydrogen bonds shown as dashed lines.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C3—H3···O1$^{i}$ | 0.95 | 2.38 | 3.237 (2) | 150 |

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

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_9H_9N_3O_2$ |
| $M_r$ | 191.19 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 150 |
| $a, b, c$ (Å) | 6.7563 (1), 11.2307 (2), 11.7323 (3) |
| $V$ (Å$^3$) | 890.22 (3) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.87 |
| Crystal size (mm) | 0.17 × 0.13 × 0.06 |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE PHOTON 100 CMOS |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2016) |
| $T_{min}$, $T_{max}$ | 0.87, 0.95 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 6805, 1751, 1689 |
| $R_{int}$ | 0.029 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.618 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.032, 0.083, 1.14 |
| No. of reflections | 1751 |
| No. of parameters | 129 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.17, −0.21 |
| Absolute structure | Refined as an inversion twin |
| Absolute structure parameter | 0.3 (3) |

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

## 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.

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# full crystallographic data

*IUCrData* (2016). **1**, x160567 [doi:10.1107/S2414314616005678]

## 1-Ethyl-5-nitro-1*H*-indazole

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### 1-Ethyl-5-nitro-1*H*-indazole

*Crystal data*

$C_9H_9N_3O_2$
$M_r$ = 191.19
Orthorhombic, $P2_12_12_1$
$a$ = 6.7563 (1) Å
$b$ = 11.2307 (2) Å
$c$ = 11.7323 (3) Å
$V$ = 890.22 (3) Å$^3$
$Z$ = 4
$F(000)$ = 400
$D_x$ = 1.427 Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda$ = 1.54178 Å
Cell parameters from 5857 reflections
$\theta$ = 5.5–72.3°
$\mu$ = 0.87 mm$^{-1}$
$T$ = 150 K
Thick plate, pale-pink
0.17 × 0.13 × 0.06 mm

*Data collection*

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC I$\mu$S micro–focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
$T_{min}$ = 0.87, $T_{max}$ = 0.95
6805 measured reflections
1751 independent reflections
1689 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.029
$\theta_{max}$ = 72.2°, $\theta_{min}$ = 5.5°
$h$ = −7→8
$k$ = −13→13
$l$ = −14→13

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.083
$S$ = 1.14
1751 reflections
129 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.0784P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.3 (3)

*Special details*

**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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. Refined as a 2-component inversion twin.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.7819 (3) | 0.97368 (13) | 0.19153 (11) | 0.0424 (4) |
| O2 | 0.7456 (2) | 1.06296 (11) | 0.35322 (11) | 0.0365 (3) |
| N1 | 0.7976 (2) | 0.54673 (13) | 0.52816 (12) | 0.0262 (3) |
| N2 | 0.7894 (2) | 0.58370 (14) | 0.63935 (12) | 0.0283 (3) |
| N3 | 0.7670 (2) | 0.97218 (13) | 0.29620 (13) | 0.0280 (3) |
| C1 | 0.7770 (3) | 0.70071 (15) | 0.63659 (14) | 0.0259 (4) |
| H1 | 0.7690 | 0.7500 | 0.7023 | 0.031* |
| C2 | 0.7771 (2) | 0.74371 (15) | 0.52275 (14) | 0.0215 (3) |
| C3 | 0.7705 (2) | 0.85588 (15) | 0.47110 (13) | 0.0218 (3) |
| H3 | 0.7633 | 0.9271 | 0.5145 | 0.026* |
| C4 | 0.7749 (2) | 0.85723 (15) | 0.35380 (14) | 0.0233 (3) |
| C5 | 0.7852 (3) | 0.75368 (16) | 0.28580 (14) | 0.0273 (4) |
| H5 | 0.7870 | 0.7606 | 0.2051 | 0.033* |
| C6 | 0.7925 (3) | 0.64353 (17) | 0.33526 (14) | 0.0271 (4) |
| H6 | 0.7995 | 0.5729 | 0.2909 | 0.033* |
| C7 | 0.7891 (2) | 0.63988 (15) | 0.45514 (14) | 0.0231 (3) |
| C8 | 0.8223 (3) | 0.42079 (16) | 0.50072 (17) | 0.0309 (4) |
| H8A | 0.8775 | 0.3792 | 0.5680 | 0.037* |
| H8B | 0.9191 | 0.4131 | 0.4378 | 0.037* |
| C9 | 0.6321 (3) | 0.3606 (2) | 0.4662 (2) | 0.0404 (5) |
| H9A | 0.5367 | 0.3657 | 0.5289 | 0.061* |
| H9B | 0.6584 | 0.2768 | 0.4486 | 0.061* |
| H9C | 0.5777 | 0.4002 | 0.3987 | 0.061* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0605 (10) | 0.0423 (8) | 0.0245 (6) | −0.0015 (8) | 0.0002 (7) | 0.0091 (5) |
| O2 | 0.0481 (8) | 0.0226 (6) | 0.0386 (7) | 0.0004 (6) | −0.0015 (7) | 0.0010 (5) |
| N1 | 0.0279 (7) | 0.0210 (7) | 0.0298 (7) | 0.0007 (6) | 0.0013 (6) | 0.0016 (6) |
| N2 | 0.0283 (8) | 0.0293 (7) | 0.0274 (7) | 0.0004 (6) | 0.0016 (6) | 0.0026 (6) |
| N3 | 0.0282 (7) | 0.0276 (8) | 0.0282 (7) | −0.0023 (7) | −0.0014 (6) | 0.0037 (6) |
| C1 | 0.0261 (8) | 0.0278 (8) | 0.0238 (8) | 0.0010 (7) | 0.0020 (7) | 0.0002 (6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0188 (7) | 0.0218 (8) | 0.0239 (7) | −0.0004 (6) | −0.0005 (6) | −0.0019 (6) |
| C3 | 0.0206 (7) | 0.0212 (7) | 0.0238 (7) | −0.0001 (7) | −0.0002 (6) | −0.0024 (6) |
| C4 | 0.0219 (7) | 0.0231 (8) | 0.0249 (7) | −0.0004 (7) | −0.0004 (6) | 0.0026 (6) |
| C5 | 0.0291 (9) | 0.0316 (9) | 0.0213 (7) | −0.0008 (8) | −0.0003 (7) | −0.0032 (6) |
| C6 | 0.0289 (9) | 0.0251 (8) | 0.0274 (8) | −0.0003 (8) | −0.0002 (6) | −0.0066 (7) |
| C7 | 0.0204 (7) | 0.0214 (8) | 0.0275 (8) | 0.0004 (7) | 0.0005 (6) | −0.0011 (6) |
| C8 | 0.0311 (9) | 0.0189 (9) | 0.0427 (10) | 0.0025 (7) | 0.0049 (7) | −0.0002 (7) |
| C9 | 0.0389 (10) | 0.0277 (10) | 0.0545 (12) | −0.0042 (9) | −0.0001 (9) | −0.0083 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—N3 | 1.2322 (19) | C3—H3 | 0.9500 |
| O2—N3 | 1.228 (2) | C4—C5 | 1.412 (2) |
| N1—C7 | 1.353 (2) | C5—C6 | 1.367 (3) |
| N1—N2 | 1.370 (2) | C5—H5 | 0.9500 |
| N1—C8 | 1.460 (2) | C6—C7 | 1.407 (2) |
| N2—C1 | 1.317 (2) | C6—H6 | 0.9500 |
| N3—C4 | 1.458 (2) | C8—C9 | 1.507 (3) |
| C1—C2 | 1.420 (2) | C8—H8A | 0.9900 |
| C1—H1 | 0.9500 | C8—H8B | 0.9900 |
| C2—C3 | 1.399 (2) | C9—H9A | 0.9800 |
| C2—C7 | 1.413 (2) | C9—H9B | 0.9800 |
| C3—C4 | 1.377 (2) | C9—H9C | 0.9800 |
| | | | |
| C7—N1—N2 | 111.52 (14) | C6—C5—H5 | 119.8 |
| C7—N1—C8 | 127.88 (15) | C4—C5—H5 | 119.8 |
| N2—N1—C8 | 120.54 (14) | C5—C6—C7 | 116.74 (16) |
| C1—N2—N1 | 106.35 (14) | C5—C6—H6 | 121.6 |
| O2—N3—O1 | 122.76 (15) | C7—C6—H6 | 121.6 |
| O2—N3—C4 | 119.14 (14) | N1—C7—C6 | 130.88 (17) |
| O1—N3—C4 | 118.10 (14) | N1—C7—C2 | 106.56 (14) |
| N2—C1—C2 | 111.25 (15) | C6—C7—C2 | 122.55 (17) |
| N2—C1—H1 | 124.4 | N1—C8—C9 | 113.35 (16) |
| C2—C1—H1 | 124.4 | N1—C8—H8A | 108.9 |
| C3—C2—C7 | 120.14 (14) | C9—C8—H8A | 108.9 |
| C3—C2—C1 | 135.54 (15) | N1—C8—H8B | 108.9 |
| C7—C2—C1 | 104.32 (14) | C9—C8—H8B | 108.9 |
| C4—C3—C2 | 116.25 (15) | H8A—C8—H8B | 107.7 |
| C4—C3—H3 | 121.9 | C8—C9—H9A | 109.5 |
| C2—C3—H3 | 121.9 | C8—C9—H9B | 109.5 |
| C3—C4—C5 | 123.84 (16) | H9A—C9—H9B | 109.5 |
| C3—C4—N3 | 118.18 (15) | C8—C9—H9C | 109.5 |
| C5—C4—N3 | 117.98 (14) | H9A—C9—H9C | 109.5 |
| C6—C5—C4 | 120.48 (15) | H9B—C9—H9C | 109.5 |
| | | | |
| C7—N1—N2—C1 | −0.37 (19) | N3—C4—C5—C6 | −179.87 (16) |
| C8—N1—N2—C1 | 176.88 (17) | C4—C5—C6—C7 | 0.0 (2) |
| N1—N2—C1—C2 | −0.1 (2) | N2—N1—C7—C6 | −179.89 (17) |

| | | | |
|---|---|---|---|
| N2—C1—C2—C3 | −178.72 (18) | C8—N1—C7—C6 | 3.1 (3) |
| N2—C1—C2—C7 | 0.54 (19) | N2—N1—C7—C2 | 0.70 (18) |
| C7—C2—C3—C4 | 0.4 (2) | C8—N1—C7—C2 | −176.29 (17) |
| C1—C2—C3—C4 | 179.61 (17) | C5—C6—C7—N1 | −178.80 (17) |
| C2—C3—C4—C5 | 0.1 (2) | C5—C6—C7—C2 | 0.5 (2) |
| C2—C3—C4—N3 | 179.61 (14) | C3—C2—C7—N1 | 178.67 (15) |
| O2—N3—C4—C3 | −4.0 (2) | C1—C2—C7—N1 | −0.73 (17) |
| O1—N3—C4—C3 | 176.12 (16) | C3—C2—C7—C6 | −0.8 (2) |
| O2—N3—C4—C5 | 175.51 (17) | C1—C2—C7—C6 | 179.81 (15) |
| O1—N3—C4—C5 | −4.4 (2) | C7—N1—C8—C9 | −81.9 (2) |
| C3—C4—C5—C6 | −0.4 (3) | N2—N1—C8—C9 | 101.4 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C3—H3···O1$^{i}$ | 0.95 | 2.38 | 3.237 (2) | 150 |

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