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Ethyl 2-[(*Z*)-2-(2-nitrophenyl)hydrazinylidene]-propanoate

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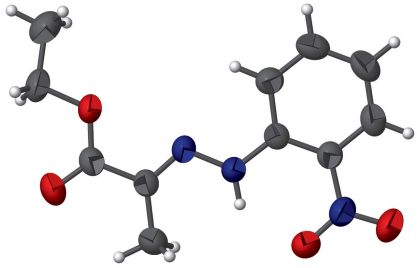
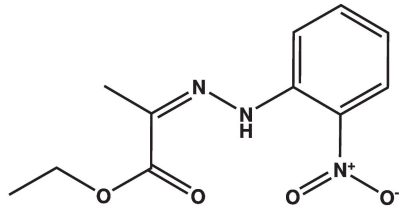
In the molecule of the title compound, $C_{11}H_{13}N_3O_4$, all non-H atoms are nearly coplanar with the largest deviation from the mean plane being 0.152 (2) Å. A strong intramolecular N—H···O hydrogen bond closes a six-membered ring. In the crystal, molecules are linked by π–π interactions [intercentroid distance = 3.724 (2) Å], forming stacks parallel to the *c* axis.

3D view



Chemical scheme



Structure description

The indole ring is an important pharmocophore in modern drug discovery (Kuethe *et al.*, 2005). Phenylhydrazones represent the principal starting material in the synthesis of indole derivatives. Some works have reported the synthesis of indole derivatives from the mixture of the two tautomers of phenylhydrazone without separation (Parmerter *et al.*, 1958; Murakami *et al.*, 1999; Narayana *et al.*, 2005; El Kihel *et al.*, 2013). Among these, Murakami *et al.* (1999) reported the separation of the mixture of indole normal and indole abnormal. However, the synthesis of phenylhydrazone by the condensation of phenylhydrazine with carbonyl compounds or by condensation of *o*-nitroaniline diazonium with ethyl α-methylacetoacetate in basic medium (Japp–Klingemann reaction) lead to two tautomeric products (Murakami *et al.*, 1993; Wagaw *et al.*, 1999; Lipinska *et al.*, 1999). Based on our indole synthesis program (El Kihel *et al.*, 2013, 2007; El Ouar *et al.*, 1995), we report in this work the isolation of the majority product of the mixture of the two tautomers.

The title compound is built up from a 2-nitrophenyl ring linked to an ethyl hydrazono propanoate group, as shown in Fig. 1. Apart from the methyl H atoms, all atoms of the

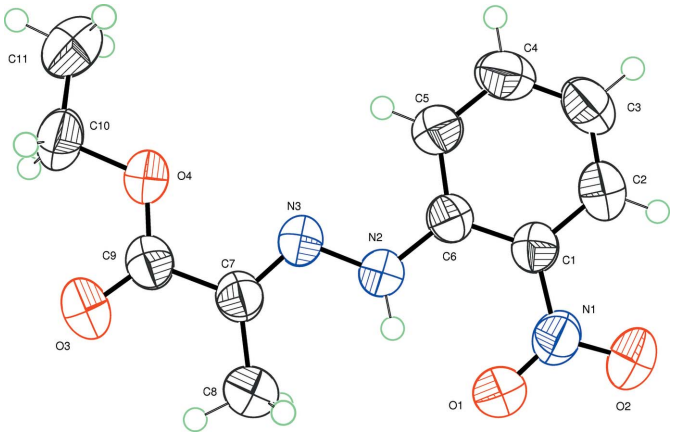


Figure 1
The molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

molecule are almost coplanar with a maximum deviation of 0.152 (2) Å for C11. The conformation of the molecule is stabilized by a strong intramolecular N—H···O hydrogen bond (Table 1).

In the crystal, molecules are linked by π–π interactions [inter-centroid distance = 3.724 (2) Å], forming stacks parallel to the *c* axis (Fig. 2).

Synthesis and crystallization

The title compound was synthesized by mixing 2-nitrophenyhydrazine and ethyl pyruvate in stoichiometric quantity, in ethanol and heated over a steam bath. The crude product was filtered and crystallized from ethanol. Yellow single crystals appeared after two weeks. The crystals were washed with cold ethanol and dried in air at room temperature.

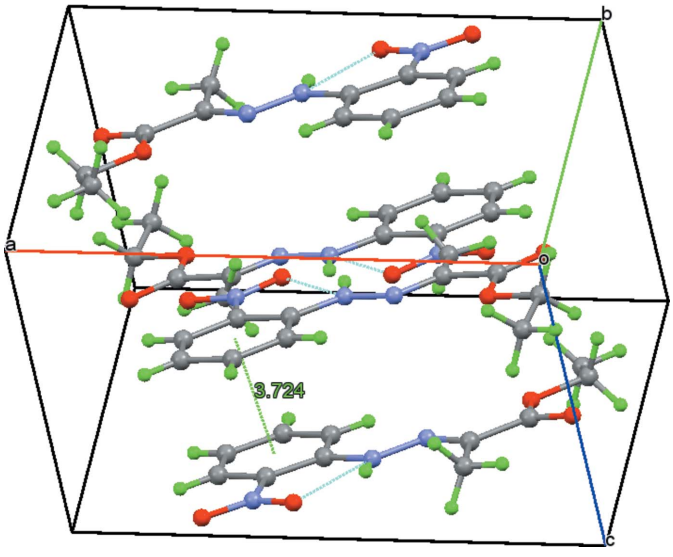


Figure 2
Molecules linked by π–π interactions, forming a three-dimensional network.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···O1	0.88	1.94	2.6085 (17)	132

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{13}N_3O_4$
M_r	251.24
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, *b*, *c* (Å)	11.8614 (4), 15.8834 (6), 6.7495 (2)
β (°)	102.411 (2)
V (Å^3)	1241.89 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.42 × 0.33 × 0.19
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2015)
T_{min}, T_{max}	0.452, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37344, 3487, 1892
R_{int}	0.058
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.049, 0.146, 1.02
No. of reflections	3487
No. of parameters	164
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.22

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The reflection (100) affected by the beam-stop was removed during refinement.

Acknowledgements

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full crystallographic data

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Ethyl 2-[(*Z*)-2-(2-nitrophenyl)hydrazinylidene]propanoate

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Crystal data

$C_{11}H_{13}N_3O_4$
M_r = 251.24
Monoclinic, $P2_1/c$
a = 11.8614 (4) Å
b = 15.8834 (6) Å
c = 6.7495 (2) Å
β = 102.411 (2)°
V = 1241.89 (7) Å^3
Z = 4
$F(000)$ = 528
D_x = 1.344 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3487 reflections
θ = 2.2–29.6°
μ = 0.10 mm^{-1}
T = 296 K
Plate, yellow
0.42 × 0.33 × 0.19 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2015)
T_{min} = 0.452, T_{max} = 0.746
37344 measured reflections
3487 independent reflections
1892 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 29.6°, θ_{min} = 2.2°
h = −16→16
k = −22→22
l = −9→6

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.146
S = 1.02
3487 reflections
164 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.2115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0117 (17)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.65861 (13)	0.28676 (10)	0.4729 (2)	0.0471 (4)
C2	0.75897 (14)	0.23883 (12)	0.5128 (3)	0.0589 (4)
H2	0.8304	0.2655	0.5410	0.071*
C3	0.75360 (16)	0.15360 (12)	0.5110 (3)	0.0653 (5)
H3	0.8209	0.1217	0.5383	0.078*
C4	0.64643 (16)	0.11452 (11)	0.4679 (3)	0.0637 (5)
H4	0.6425	0.0560	0.4661	0.076*
C5	0.54619 (14)	0.16054 (10)	0.4280 (3)	0.0534 (4)
H5	0.4755	0.1328	0.3993	0.064*
C6	0.54875 (12)	0.24845 (9)	0.4298 (2)	0.0438 (3)
C7	0.25524 (13)	0.30082 (10)	0.3148 (2)	0.0480 (4)
C8	0.25598 (16)	0.39424 (11)	0.3224 (4)	0.0789 (6)
H8A	0.1780	0.4147	0.2918	0.118*
H8B	0.2938	0.4126	0.4557	0.118*
H8C	0.2966	0.4158	0.2246	0.118*
C9	0.14199 (13)	0.25757 (11)	0.2633 (2)	0.0516 (4)
C10	0.04194 (14)	0.12833 (12)	0.2233 (3)	0.0683 (5)
H10A	0.0062	0.1356	0.0809	0.082*
H10B	−0.0109	0.1488	0.3039	0.082*
C11	0.06936 (18)	0.03794 (13)	0.2684 (4)	0.0847 (6)
H11A	−0.0005	0.0054	0.2371	0.127*
H11B	0.1216	0.0185	0.1876	0.127*
H11C	0.1046	0.0316	0.4095	0.127*
N1	0.67284 (12)	0.37725 (9)	0.4780 (2)	0.0566 (4)
N2	0.44815 (10)	0.29405 (8)	0.3914 (2)	0.0483 (3)
H2N	0.4542	0.3492	0.3880	0.058*
N3	0.34528 (10)	0.25358 (8)	0.34835 (19)	0.0453 (3)
O1	0.58726 (11)	0.42318 (7)	0.4422 (2)	0.0711 (4)
O2	0.77058 (11)	0.40635 (9)	0.5191 (2)	0.0821 (4)
O3	0.05164 (10)	0.29500 (8)	0.2177 (2)	0.0730 (4)
O4	0.15006 (9)	0.17423 (7)	0.27317 (19)	0.0618 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0443 (8)	0.0505 (9)	0.0472 (9)	−0.0012 (7)	0.0111 (7)	−0.0009 (7)
C2	0.0433 (8)	0.0718 (12)	0.0616 (11)	0.0028 (8)	0.0112 (7)	0.0023 (9)
C3	0.0551 (10)	0.0688 (12)	0.0737 (12)	0.0187 (9)	0.0177 (9)	0.0083 (9)
C4	0.0738 (12)	0.0490 (9)	0.0716 (12)	0.0105 (9)	0.0229 (9)	0.0052 (9)
C5	0.0533 (9)	0.0480 (9)	0.0602 (10)	−0.0013 (7)	0.0153 (8)	−0.0002 (8)
C6	0.0433 (8)	0.0473 (8)	0.0415 (8)	0.0013 (6)	0.0106 (6)	0.0004 (6)
C7	0.0435 (8)	0.0507 (9)	0.0489 (9)	0.0016 (6)	0.0081 (7)	−0.0014 (7)
C8	0.0584 (11)	0.0524 (10)	0.1209 (18)	0.0058 (9)	0.0080 (11)	−0.0006 (11)
C9	0.0435 (8)	0.0579 (10)	0.0530 (10)	0.0030 (7)	0.0095 (7)	−0.0016 (8)
C10	0.0437 (9)	0.0739 (12)	0.0857 (14)	−0.0127 (8)	0.0106 (9)	−0.0092 (10)

C11	0.0770 (13)	0.0692 (13)	0.1053 (18)	−0.0216 (11)	0.0139 (12)	−0.0040 (12)
N1	0.0490 (8)	0.0564 (8)	0.0653 (9)	−0.0086 (6)	0.0142 (7)	−0.0056 (7)
N2	0.0406 (7)	0.0434 (7)	0.0601 (8)	−0.0015 (5)	0.0089 (6)	−0.0003 (6)
N3	0.0397 (6)	0.0499 (7)	0.0461 (7)	−0.0037 (5)	0.0089 (5)	−0.0017 (6)
O1	0.0567 (7)	0.0492 (7)	0.1059 (10)	−0.0022 (6)	0.0143 (7)	−0.0023 (7)
O2	0.0521 (7)	0.0716 (9)	0.1210 (12)	−0.0189 (6)	0.0154 (7)	−0.0065 (8)
O3	0.0443 (7)	0.0746 (9)	0.0952 (10)	0.0100 (6)	0.0041 (6)	0.0009 (7)
O4	0.0386 (6)	0.0560 (7)	0.0885 (9)	−0.0046 (5)	0.0084 (5)	−0.0047 (6)

Geometric parameters (Å, º)

C1—C2	1.390 (2)	C8—H8B	0.9600
C1—C6	1.411 (2)	C8—H8C	0.9600
C1—N1	1.447 (2)	C9—O3	1.2062 (18)
C2—C3	1.355 (3)	C9—O4	1.328 (2)
C2—H2	0.9300	C10—O4	1.4505 (19)
C3—C4	1.388 (3)	C10—C11	1.489 (3)
C3—H3	0.9300	C10—H10A	0.9700
C4—C5	1.372 (2)	C10—H10B	0.9700
C4—H4	0.9300	C11—H11A	0.9600
C5—C6	1.397 (2)	C11—H11B	0.9600
C5—H5	0.9300	C11—H11C	0.9600
C6—N2	1.3722 (18)	N1—O2	1.2233 (17)
C7—N3	1.2849 (18)	N1—O1	1.2311 (17)
C7—C9	1.482 (2)	N2—N3	1.3542 (16)
C7—C8	1.485 (2)	N2—H2N	0.8796
C8—H8A	0.9600		
C2—C1—C6	121.23 (15)	H8A—C8—H8C	109.5
C2—C1—N1	116.67 (14)	H8B—C8—H8C	109.5
C6—C1—N1	122.10 (13)	O3—C9—O4	123.69 (15)
C3—C2—C1	120.59 (16)	O3—C9—C7	122.84 (16)
C3—C2—H2	119.7	O4—C9—C7	113.48 (13)
C1—C2—H2	119.7	O4—C10—C11	107.09 (15)
C2—C3—C4	119.19 (16)	O4—C10—H10A	110.3
C2—C3—H3	120.4	C11—C10—H10A	110.3
C4—C3—H3	120.4	O4—C10—H10B	110.3
C5—C4—C3	121.25 (16)	C11—C10—H10B	110.3
C5—C4—H4	119.4	H10A—C10—H10B	108.6
C3—C4—H4	119.4	C10—C11—H11A	109.5
C4—C5—C6	120.96 (16)	C10—C11—H11B	109.5
C4—C5—H5	119.5	H11A—C11—H11B	109.5
C6—C5—H5	119.5	C10—C11—H11C	109.5
N2—C6—C5	120.64 (14)	H11A—C11—H11C	109.5
N2—C6—C1	122.58 (14)	H11B—C11—H11C	109.5
C5—C6—C1	116.78 (14)	O2—N1—O1	121.46 (15)
N3—C7—C9	116.60 (14)	O2—N1—C1	118.74 (14)
N3—C7—C8	125.38 (15)	O1—N1—C1	119.80 (13)

C9—C7—C8	118.01 (14)	N3—N2—C6	119.79 (13)
C7—C8—H8A	109.5	N3—N2—H2N	122.8
C7—C8—H8B	109.5	C6—N2—H2N	117.2
H8A—C8—H8B	109.5	C7—N3—N2	115.92 (13)
C7—C8—H8C	109.5	C9—O4—C10	116.03 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···O1	0.88	1.94	2.6085 (17)	132