# 1-Nitro-4-(1-propyn-1-yl)benzene

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The title compound, $C_9H_7NO_2$, was prepared by alkynylation of 4-iodonitrobenzene with 1,3-dilithiopropyne in the presence of 1 equivalent of CuI and catalytic amounts of $Pd(PPh_3)_2Cl_2$. The complete molecule is generated by crystallographic twofold symmetry with the C—N and C—C≡C—C units lying on the rotation axis. No directional interactions beyond normal van der Waals contacts could be identified in the packing.

3D view
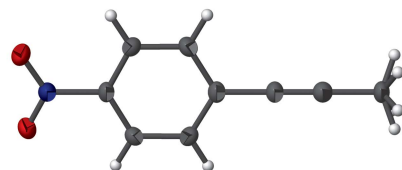


Chemical scheme
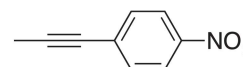
Structure description

One of the most general methods for the synthesis of aromatic alkynes is the alkynylation of halogenated aromatic rings (Negishi & Anastasia, 2003). Today, the Sonogashira reaction is probably the most extensively used protocol for the synthesis of mono and di-substituted acetylenes (Sonogashira *et al.*, 1975). In this reaction an aromatic (or vinyl) halide is treated with the corresponding acetylene, in the presence of catalytic amounts of Pd^0 or Pd^{II} triphenylphosphine complexes, an amine (*i.e.*, Et_2NH) and catalytic amounts of CuI at room temperature.

Specifically 1-propynylarenes, which can be obtained by the above-mentioned alkynylation protocols, using prop-1-yne, are not only very valuable synthetic intermediates, but also these structures are present in a wide number of natural products (Carpita *et al.*, 1985; Christensen & Lam, 1991), many of which have important biological activity (Zhang *et al.*, 2014).

As part of our work in this area, we now report the synthesis and crystal structure of the title compound, **1**. The C7≡C8 distance of 1.195 (4) Å is consistent with previous reported values (Umaña *et al.*, 2018). The complete molecule is generated by a crystallographic twofold axis with atoms C1, C4, C7, C8, C9 and N1 lying on the rotation axis. The nitro group is close to being coplanar with its attached ring as indicated by the O1—
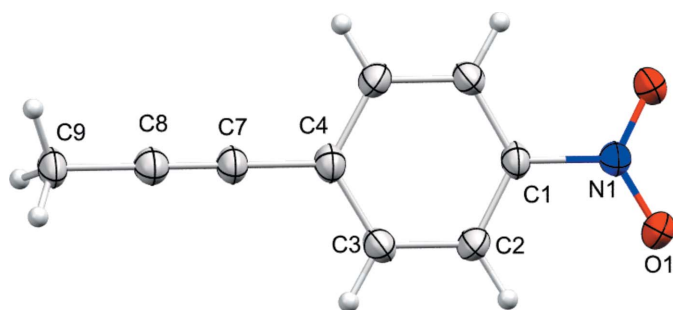
Figure 1
The title molecule, **1**, with 50% probability ellipsoids. Unlabelled atoms are generated by the symmetry operation $\frac{1}{2} - x, y, -z$.

N1—C1—C2^{i} torsion angle of 171.25 (14)° (Fig. 1). The extended structure (Fig. 2) shows neither hydrogen bonding nor aromatic π–π stacking.

Synthesis and crystallization

The title compound, **1**, was synthesized by a variation of the Sonogashira reaction. Thus, 4-iodonitrobenzene, **2**, was treated with the dianion 1,3-dilithiopropyne, **3**, in the presence of one equivalent of CuI (instead of catalytic amounts) and catalytic amounts of Pd(PPh$_3$)$_2$Cl$_2$ (Fig. 3). The 1,3-dilithiopropyne, **3**, was prepared from 2,3-dichloropropene by sequential treatment with magnesium and *n*-BuLi as previously reported (Umaña & Cabezas, 2017; Cabezas *et al.*, 2018). After ether–water partition, the crude reaction was purified by column chromatography (ether:hexane, 30:70), to obtain the title compound, **1**, in 72% yield. The product was recrystallized from ethyl acetate solution at room temperature in the form of pale-yellow blocks.

Refinement

Crystal data, data collection and structure refinement are summarized in Table 1.
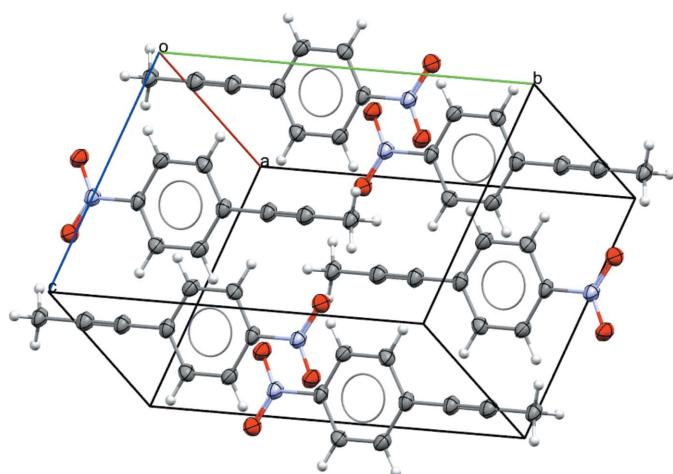
Figure 2
The crystal packing of the title compound.

Table 1
Experimental details.

Crystal data	
Chemical formula	C$_9$H$_7$NO$_2$
M_r	161.16
Crystal system, space group	Monoclinic, $I2/a$
Temperature (K)	100
a, b, c (Å)	7.3633 (13), 12.0641 (16), 8.9185 (19)
β (°)	103.738 (13)
V (Å^3)	769.6 (2)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.83
Crystal size (mm)	0.15 × 0.13 × 0.10
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.509, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7605, 717, 571
R_{int}	0.109
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.179, 1.13
No. of reflections	717
No. of parameters	60
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.26, −0.37

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *shelXle* (Hübschle, 2011) and *publCIF* (Westrip, 2010).

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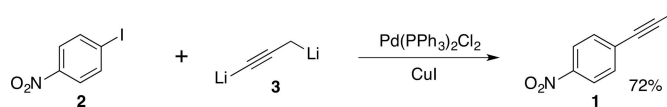
Figure 3
A synthetic scheme for the preparation of title compound **1**.

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full crystallographic data

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Crystal data

$C_9H_7NO_2$	$F(000) = 336$
$M_r = 161.16$	$D_x = 1.391$ Mg m^{-3}
Monoclinic, $I2/a$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 7.3633\,(13)$ Å	Cell parameters from 4037 reflections
$b = 12.0641\,(16)$ Å	$\theta = 6.3$–68.4°
$c = 8.9185\,(19)$ Å	$\mu = 0.83$ mm^{-1}
$\beta = 103.738\,(13)°$	$T = 100$ K
$V = 769.6\,(2)$ Å^3	Block, pale yellow
$Z = 4$	$0.15 \times 0.13 \times 0.10$ mm

Data collection

Bruker D8 Venture diffractometer	717 independent reflections
Radiation source: Incoatec Microsource	571 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.109$
Absorption correction: multi-scan (SADABS; Bruker, 2015)	$\theta_{max} = 69.2°$, $\theta_{min} = 6.3°$
$T_{min} = 0.509$, $T_{max} = 0.753$	$h = -8 \rightarrow 8$
7605 measured reflections	$k = -14 \rightarrow 14$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.1002P)^2 + 0.5352P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.179$	
$S = 1.13$	$(\Delta/\sigma)_{max} < 0.001$
717 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
60 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
0 restraints	Extinction correction: SHELXL2018 (Sheldrick, 2015b),
Primary atom site location: structure-invariant direct methods	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0025 (10)

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. All H atoms were located initially by difference Fourier synthesis and relocated to idealized locations (C—H = 0.95–0.98 Å) and refined as riding atoms.

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

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
O1	0.3309 (2)	0.64648 (13)	0.11827 (18)	0.0376 (6)	
N1	0.250000	0.5986 (2)	0.000000	0.0286 (7)	
C1	0.250000	0.4765 (2)	0.000000	0.0266 (8)	
C2	0.3613 (3)	0.42172 (19)	0.1242 (2)	0.0286 (7)	
H2	0.435644	0.461834	0.208422	0.034*	
C3	0.3623 (3)	0.30639 (19)	0.1232 (3)	0.0299 (7)	
H3	0.439548	0.266962	0.206608	0.036*	
C4	0.250000	0.2484 (2)	0.000000	0.0282 (8)	
C7	0.250000	0.1283 (2)	0.000000	0.0298 (8)	
C8	0.250000	0.0292 (3)	0.000000	0.0317 (8)	
C9	0.250000	−0.0924 (3)	0.000000	0.0337 (9)	
H9A	0.132345	−0.119488	−0.065837	0.040*	0.5
H9B	0.262645	−0.119487	0.105581	0.040*	0.5
H9C	0.355010	−0.119487	−0.039745	0.040*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0414 (10)	0.0234 (10)	0.0409 (11)	−0.0031 (7)	−0.0042 (7)	−0.0041 (7)
N1	0.0262 (13)	0.0213 (14)	0.0351 (15)	0.000	0.0008 (10)	0.000
C1	0.0249 (15)	0.0172 (16)	0.0371 (18)	0.000	0.0058 (13)	0.000
C2	0.0262 (12)	0.0232 (13)	0.0333 (13)	−0.0029 (8)	0.0011 (9)	−0.0031 (9)
C3	0.0280 (12)	0.0238 (14)	0.0350 (14)	0.0020 (8)	0.0018 (9)	0.0051 (9)
C4	0.0273 (16)	0.0203 (17)	0.0373 (18)	0.000	0.0080 (12)	0.000
C7	0.0297 (17)	0.0205 (18)	0.0375 (19)	0.000	0.0048 (13)	0.000
C8	0.0285 (16)	0.026 (2)	0.0387 (19)	0.000	0.0041 (13)	0.000
C9	0.0313 (17)	0.0174 (17)	0.049 (2)	0.000	0.0021 (14)	0.000

Geometric parameters (Å, º)

N1—O1	1.226 (2)	C7—C8	1.195 (4)
N1—C1	1.473 (4)	C8—C9	1.468 (4)
C1—C2^i	1.380 (3)	C9—H9A	0.9800
C1—C2	1.380 (3)	C9—H9B	0.9800
C2—C3	1.391 (3)	C9—H9C	0.9800
C2—H2	0.9500	C9—H9A^i	0.9800
C3—C4	1.396 (3)	C9—H9B^i	0.9800
C3—H3	0.9500	C9—H9C^i	0.9800
C4—C7	1.449 (4)		
O1—N1—O1^i	123.7 (3)	H9A—C9—H9B	109.5
O1—N1—C1	118.13 (13)	C8—C9—H9C	109.5

O1ⁱ—N1—C1	118.13 (13)	H9A—C9—H9C	109.5
C2ⁱ—C1—C2	122.8 (3)	H9B—C9—H9C	109.5
C2ⁱ—C1—N1	118.59 (14)	C8—C9—H9Aⁱ	109.474 (4)
C2—C1—N1	118.59 (14)	H9A—C9—H9Aⁱ	141.1
C1—C2—C3	118.4 (2)	H9B—C9—H9Aⁱ	56.3
C1—C2—H2	120.8	H9C—C9—H9Aⁱ	56.2
C3—C2—H2	120.8	C8—C9—H9Bⁱ	109.469 (5)
C2—C3—C4	120.2 (2)	H9A—C9—H9Bⁱ	56.3
C2—C3—H3	119.9	H9B—C9—H9Bⁱ	141.1
C4—C3—H3	119.9	H9C—C9—H9Bⁱ	56.3
C3—C4—C3ⁱ	119.9 (3)	H9Aⁱ—C9—H9Bⁱ	109.5
C3—C4—C7	120.06 (14)	C8—C9—H9Cⁱ	109.469 (4)
C3ⁱ—C4—C7	120.06 (14)	H9A—C9—H9Cⁱ	56.2
C8—C7—C4	180.0	H9B—C9—H9Cⁱ	56.3
C7—C8—C9	180.0	H9C—C9—H9Cⁱ	141.1
C8—C9—H9A	109.5	H9Aⁱ—C9—H9Cⁱ	109.5
C8—C9—H9B	109.5	H9Bⁱ—C9—H9Cⁱ	109.5
O1—N1—C1—C2ⁱ	171.25 (14)	N1—C1—C2—C3	−179.44 (14)
O1ⁱ—N1—C1—C2ⁱ	−8.75 (14)	C1—C2—C3—C4	−1.1 (3)
O1—N1—C1—C2	−8.75 (14)	C2—C3—C4—C3ⁱ	0.57 (14)
O1ⁱ—N1—C1—C2	171.25 (14)	C2—C3—C4—C7	−179.43 (14)
C2ⁱ—C1—C2—C3	0.56 (14)		

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