

2-(3-Bromo-4-methoxyphenyl)-3-nitropyridine

Daniel Limbach, Heiner Detert* and Dieter Schollmeyer

University of Mainz, Institut for Organic Chemistry, Duesbergweg 10-14, 55099 Mainz, Germany. *Correspondence e-mail: detert@uni-mainz.de

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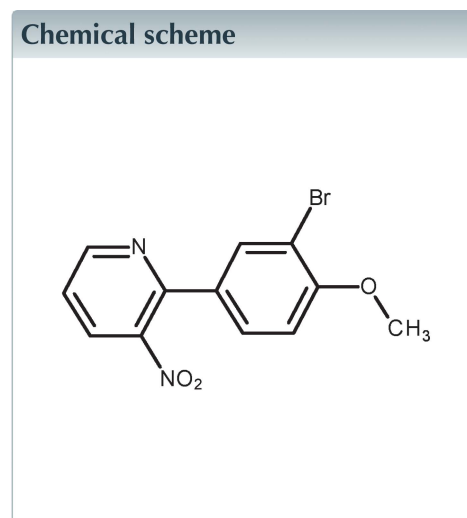
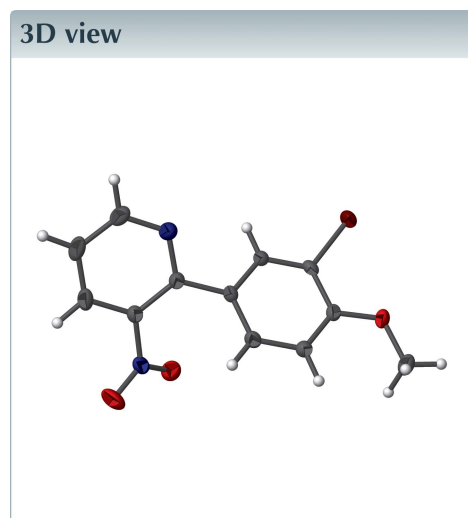
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Keywords: crystal structure; nitro; heterocycle; biaryl.

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

The title compound, $C_{12}H_9BrN_2O_3$, was prepared in two steps from 2-chloro-3-nitropyridine. The nitrobiaryl unit is twisted, with dihedral angles of $35.4(5)^\circ$ between the nitro substituent and the pyridine ring to which it is bound, and $51.0(5)^\circ$ between the nitro group and the benzene ring. In the crystal, the molecules are connected *via* $C-H \cdots O$ hydrogen bonds, forming strands along the *b*-axis direction.



Structure description

2-Nitrobiaryl compounds are central intermediates for the synthesis of carbazoles and carbolines *via* the Cadogan (1962) reaction or from iodonium salts (Letessier *et al.*, 2013).

The title molecule (Fig. 1) is twisted since steric congestion due to the β -nitro group neighbouring the biaryl bond provokes torsion in both units. The dihedral angle between the nitro group and the pyridine ring is $35.4(5)^\circ$, while that between the pyridine and the benzene rings is $39.9(2)^\circ$ while the angle between the planes of the nitro group and the phenyl ring is $51.0(5)^\circ$. The methoxy group lies in the plane of the benzene ring [torsion angle $C14-C13-O16-C17$: $178.9(4)^\circ$] with the methyl group orientated *anti* to the bromo substituent.

The bond lengths in the benzene ring are similar to those in benzene itself except for $C14-C15$, $1.377(5) \text{ \AA}$, and $C11-C12$, $1.385(6) \text{ \AA}$ that are shorter. These may be effected by the bromo substituent Br1. In the pyridine ring, $C1-C6$ [$1.411(5) \text{ \AA}$] is longer than $C3-C4$ [$1.386(7) \text{ \AA}$] as a result of the vicinal nitro and phenyl substituents. The biaryl bridge bond $C1-C10$ [$1.480(5) \text{ \AA}$] is comparable to the equivalent bond in 2-phenylpyridine with an average of 1.478 \AA (Sekine *et al.*, 1994).

There are four molecules in the monoclinic unit cell. Molecules form strands along the *b* axis, connected *via* $C-H \cdots O$ hydrogen bonds (Table 1, Fig. 2).

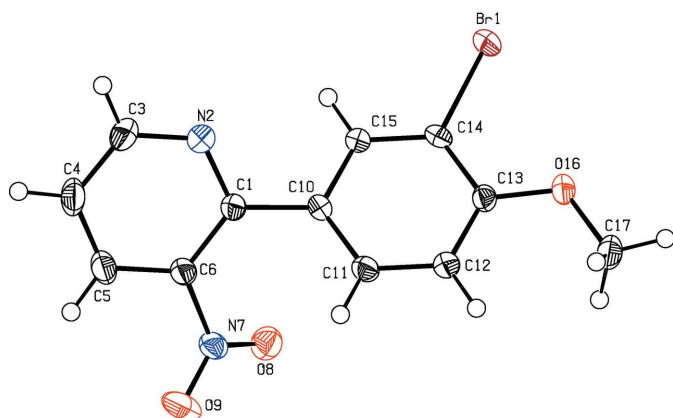


Figure 1
View of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Synthesis and crystallization

2-(3-Bromo-4-methoxyphenyl)-3-nitropyridine was prepared in two steps from 2-chloro-3-nitropyridine. A mixture of the latter (409 mg, 2.58 mmol), *p*-tolylboronic acid (481 mg, 3.54 mmol), and 656 mg sodium bicarbonate in 25 ml of aqueous dimethoxyethane (1/1) was deaerated by passing a nitrogen stream through the mixture before tetrakis-triphenylphosphine palladium (152.4 mg) was added. This mixture was heated in a microwave oven with 300 W for 15 min to 400 K. Thereafter, the mixture was filtered and the residue was washed with ethyl acetate (80 ml). The pooled organic solution was washed with water and brine, dried (MgSO_4), concentrated and the residue was purified by

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C11-H11\cdots O8^i$	0.95	2.50	3.293 (5)	141

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

chromatography on silica gel ($\text{SiO}_2/\text{toluene}$) to yield 220 mg (40%) of a yellow solid with m.p. = 336 K. NBS (126 mg, 0.709 mmol) was added to a solution of anisyl nitropyridine (164 mg, 0.713 mmol) in acetonitrile (15 ml) and the mixture stirred for 30 min at 323 K. After 3 h, additional NBS (59 mg) was added. When the reaction was complete (NMR), the solvent was evaporated, the residue was dissolved in dichloromethane, filtered and dichloromethane exchanged by cyclohexane. Yield: 133 mg (60%) of a yellow solid with m.p. = 415 K. ^1H NMR: (300 MHz, CDCl_3): δ = 8.33 (*dd*, J = 4.7 Hz, J = 1.6 Hz, 1 H); 8.13 (*dd*, J = 8.3 Hz, J = 1.5 Hz, 1 H), 7.87 (*d*, J = 2.3 Hz, 1 H); 7.45 (*dd*, J = 8.6 Hz, J = 2.3 Hz, 1 H); 7.42 (*dd*, J = 4.7 Hz, J = 1.2 Hz, 1 H); 6.96, (*d*, J = 8.6, 1 H), 3.95 (*s*, 3 H); ^{13}C NMR: (75 MHz, CDCl_3): δ = 157.33, 152.26, 151.06, 146.06, 133.46, 132.47, 129.83, 128.62, 122.44, 112.29, 111.77, 56.52; IR (ATR) ν = 3067, 2973, 2913, 2842, 1587, 1556, 1517, 1441, 1352, 1293, 1267, 1183, 1161, 1058, 1014, 879, 863, 819, 806, 677 cm^{-1} ; HR-ESI-MS: 308.9885 ($M+H^+$). Single crystals were grown by recrystallization from chloroform solution.

Table 2
Experimental details.

Crystal data	$\text{C}_{12}\text{H}_9\text{BrN}_2\text{O}_3$
Chemical formula	309.12
M_r	Monoclinic, <i>Ia</i>
Crystal system, space group	193
Temperature (K)	14.7780 (9), 3.9561 (2), 21.1186 (13)
a, b, c (\AA)	β ($^\circ$)
	109.812 (5)
	V (\AA^3)
	1161.58 (12)
	Z
	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.54
Crystal size (mm)	0.40 \times 0.30 \times 0.15
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration (<i>X-RED32</i> ; Stoe & Cie, 2006)
T_{\min} , T_{\max}	0.274, 0.587
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4117, 2669, 2621
R_{int}	0.018
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.665
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.062, 1.07
No. of reflections	2669
No. of parameters	164
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.51, -0.24
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower
Absolute structure parameter	-0.012 (11)

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2006), *SHELXT2014* (Sheldrick, 2015a) and *SHELXL2014* (Sheldrick, 2015b).

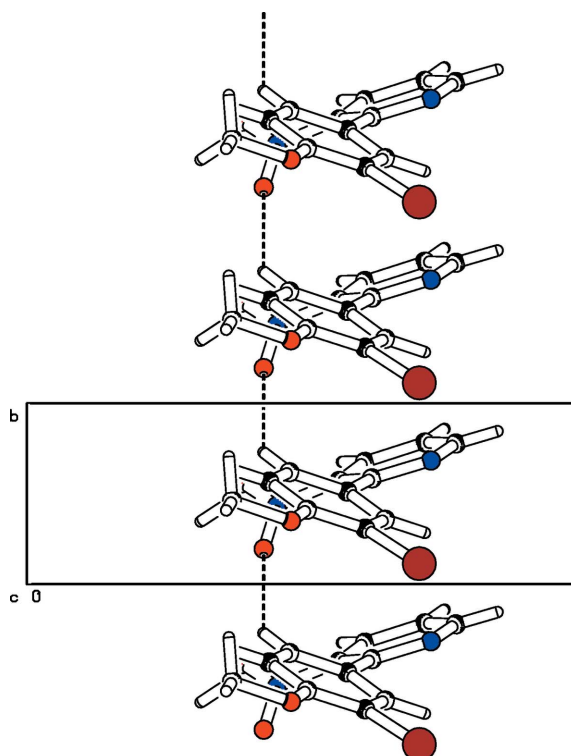


Figure 2
Partial packing diagram, viewed along the *c*-axis direction. Hydrogen bonds are shown as dashed lines.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2017). 2, x171394 [https://doi.org/10.1107/S2414314617013943]

2-(3-Bromo-4-methoxyphenyl)-3-nitropyridine

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2-(3-Bromo-4-methoxyphenyl)-3-nitropyridine

Crystal data

$C_{12}H_9BrN_2O_3$

$M_r = 309.12$

Monoclinic, *Ia*

$a = 14.7780$ (9) Å

$b = 3.9561$ (2) Å

$c = 21.1186$ (13) Å

$\beta = 109.812$ (5)°

$V = 1161.58$ (12) Å³

$Z = 4$

$F(000) = 616$

$D_x = 1.768$ Mg m⁻³

Melting point: 415 K

Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 7578 reflections

$\theta = 2.9$ – 28.4 °

$\mu = 3.54$ mm⁻¹

$T = 193$ K

Block, brown

$0.40 \times 0.30 \times 0.15$ mm

Data collection

Stoe IPDS 2T
diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4
mm long-fine focus

Detector resolution: 6.67 pixels mm⁻¹
rotation method scans

Absorption correction: integration
(X-RED32; Stoe & Cie, 2006)

$T_{\min} = 0.274$, $T_{\max} = 0.587$

4117 measured reflections

2669 independent reflections

2621 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 28.2$ °, $\theta_{\min} = 2.9$ °

$h = -19 \rightarrow 19$

$k = -5 \rightarrow 5$

$l = -28 \rightarrow 27$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.062$

$S = 1.07$

2669 reflections

164 parameters

2 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 1.9908P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.51$ e Å⁻³

$\Delta\rho_{\min} = -0.24$ e Å⁻³

Absolute structure: Classical Flack method
preferred over Parsons because s.u. lower.

Absolute structure parameter: -0.012 (11)

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. Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å (sp^3 C-atom). All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the U_{eq} of the parent atom).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Br1	0.61778 (2)	0.11315 (8)	0.69658 (2)	0.02671 (10)
C1	0.5433 (3)	0.5849 (10)	0.4501 (2)	0.0219 (8)
N2	0.6359 (2)	0.6836 (10)	0.47068 (18)	0.0294 (7)
C3	0.6753 (3)	0.7778 (13)	0.4253 (2)	0.0316 (9)
H3	0.7409	0.8453	0.4411	0.038*
C4	0.6267 (3)	0.7836 (13)	0.3565 (2)	0.0352 (9)
H4	0.6574	0.8587	0.3262	0.042*
C5	0.5323 (3)	0.6768 (12)	0.3335 (2)	0.0314 (8)
H5	0.4961	0.6760	0.2868	0.038*
C6	0.4920 (3)	0.5708 (10)	0.38038 (18)	0.0238 (7)
N7	0.3940 (2)	0.4327 (9)	0.35391 (16)	0.0258 (6)
O8	0.3729 (2)	0.1949 (8)	0.38338 (16)	0.0330 (6)
O9	0.3390 (3)	0.5580 (10)	0.30220 (17)	0.0440 (8)
C10	0.5041 (3)	0.5122 (10)	0.50459 (17)	0.0209 (6)
C11	0.4134 (3)	0.6188 (9)	0.50232 (18)	0.0233 (7)
H11	0.3725	0.7290	0.4631	0.028*
C12	0.3815 (3)	0.5673 (10)	0.55616 (19)	0.0242 (7)
H12	0.3189	0.6388	0.5532	0.029*
C13	0.4411 (3)	0.4110 (9)	0.61472 (18)	0.0210 (7)
C14	0.5325 (3)	0.3077 (9)	0.61701 (17)	0.0208 (6)
C15	0.5640 (3)	0.3563 (9)	0.56332 (18)	0.0213 (7)
H15	0.6265	0.2839	0.5662	0.026*
O16	0.4158 (2)	0.3489 (7)	0.66973 (14)	0.0280 (6)
C17	0.3231 (3)	0.4609 (12)	0.6674 (2)	0.0320 (9)
H17A	0.3180	0.7057	0.6600	0.048*
H17B	0.3139	0.4075	0.7101	0.048*
H17C	0.2736	0.3465	0.6305	0.048*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02555 (15)	0.03387 (17)	0.01840 (14)	0.00404 (19)	0.00444 (10)	0.00558 (18)
C1	0.0211 (18)	0.0256 (19)	0.0198 (18)	0.0020 (13)	0.0082 (14)	−0.0001 (13)
N2	0.0229 (16)	0.0401 (18)	0.0253 (14)	−0.0017 (14)	0.0084 (12)	0.0019 (13)
C3	0.026 (2)	0.037 (2)	0.036 (2)	−0.0036 (18)	0.0158 (18)	0.003 (2)
C4	0.040 (2)	0.043 (2)	0.032 (2)	0.0030 (19)	0.0230 (18)	0.0088 (18)
C5	0.036 (2)	0.040 (2)	0.0216 (17)	0.0053 (17)	0.0139 (16)	0.0047 (15)
C6	0.0230 (17)	0.0292 (18)	0.0195 (16)	0.0040 (13)	0.0075 (13)	0.0007 (13)
N7	0.0248 (15)	0.0320 (17)	0.0190 (14)	0.0032 (13)	0.0054 (12)	−0.0041 (12)
O8	0.0319 (15)	0.0351 (15)	0.0337 (15)	−0.0038 (13)	0.0134 (13)	−0.0005 (13)
O9	0.0379 (18)	0.058 (2)	0.0250 (15)	0.0015 (15)	−0.0042 (13)	0.0055 (14)

C10	0.0216 (15)	0.0251 (16)	0.0159 (14)	0.0001 (13)	0.0061 (13)	0.0014 (13)
C11	0.0222 (17)	0.0272 (17)	0.0193 (16)	0.0047 (13)	0.0053 (14)	0.0022 (13)
C12	0.0208 (16)	0.0308 (19)	0.0209 (17)	0.0022 (14)	0.0070 (13)	0.0005 (14)
C13	0.0221 (16)	0.0242 (16)	0.0178 (15)	-0.0036 (13)	0.0081 (13)	-0.0023 (12)
C14	0.0201 (15)	0.0239 (15)	0.0147 (14)	0.0002 (13)	0.0010 (12)	0.0005 (12)
C15	0.0181 (15)	0.0275 (17)	0.0180 (15)	0.0007 (13)	0.0055 (12)	0.0015 (13)
O16	0.0275 (14)	0.0387 (15)	0.0212 (13)	0.0039 (11)	0.0129 (11)	0.0043 (11)
C17	0.032 (2)	0.040 (2)	0.0302 (19)	0.0052 (17)	0.0185 (17)	0.0067 (17)

Geometric parameters (Å, °)

Br1—C14	1.889 (3)	C10—C11	1.391 (5)
C1—N2	1.346 (5)	C10—C15	1.399 (5)
C1—C6	1.411 (5)	C11—C12	1.385 (6)
C1—C10	1.480 (5)	C11—H11	0.9500
N2—C3	1.332 (6)	C12—C13	1.396 (5)
C3—C4	1.386 (7)	C12—H12	0.9500
C3—H3	0.9500	C13—O16	1.358 (4)
C4—C5	1.378 (7)	C13—C14	1.396 (5)
C4—H4	0.9500	C14—C15	1.377 (5)
C5—C6	1.383 (6)	C15—H15	0.9500
C5—H5	0.9500	O16—C17	1.425 (5)
C6—N7	1.469 (5)	C17—H17A	0.9800
N7—O9	1.223 (5)	C17—H17B	0.9800
N7—O8	1.225 (5)	C17—H17C	0.9800
N2—C1—C6	118.4 (4)	C12—C11—C10	121.3 (3)
N2—C1—C10	115.4 (4)	C12—C11—H11	119.4
C6—C1—C10	126.2 (4)	C10—C11—H11	119.4
C3—N2—C1	119.6 (4)	C11—C12—C13	120.3 (4)
N2—C3—C4	124.2 (4)	C11—C12—H12	119.9
N2—C3—H3	117.9	C13—C12—H12	119.9
C4—C3—H3	117.9	O16—C13—C12	124.3 (3)
C5—C4—C3	117.9 (4)	O16—C13—C14	117.4 (3)
C5—C4—H4	121.1	C12—C13—C14	118.2 (3)
C3—C4—H4	121.1	C15—C14—C13	121.5 (3)
C4—C5—C6	118.1 (4)	C15—C14—Br1	118.7 (3)
C4—C5—H5	120.9	C13—C14—Br1	119.7 (3)
C6—C5—H5	120.9	C14—C15—C10	120.2 (3)
C5—C6—C1	121.7 (4)	C14—C15—H15	119.9
C5—C6—N7	116.7 (3)	C10—C15—H15	119.9
C1—C6—N7	121.6 (4)	C13—O16—C17	117.0 (3)
O9—N7—O8	124.0 (4)	O16—C17—H17A	109.5
O9—N7—C6	117.3 (4)	O16—C17—H17B	109.5
O8—N7—C6	118.7 (3)	H17A—C17—H17B	109.5
C11—C10—C15	118.5 (3)	O16—C17—H17C	109.5
C11—C10—C1	122.7 (3)	H17A—C17—H17C	109.5
C15—C10—C1	118.6 (3)	H17B—C17—H17C	109.5

C6—C1—N2—C3	2.7 (6)	N2—C1—C10—C15	-37.3 (5)
C10—C1—N2—C3	-175.2 (4)	C6—C1—C10—C15	145.0 (4)
C1—N2—C3—C4	0.3 (7)	C15—C10—C11—C12	-1.2 (6)
N2—C3—C4—C5	-1.7 (8)	C1—C10—C11—C12	-175.4 (4)
C3—C4—C5—C6	0.0 (7)	C10—C11—C12—C13	1.1 (6)
C4—C5—C6—C1	3.0 (6)	C11—C12—C13—O16	-179.7 (4)
C4—C5—C6—N7	-175.2 (4)	C11—C12—C13—C14	-0.4 (5)
N2—C1—C6—C5	-4.4 (6)	O16—C13—C14—C15	179.2 (3)
C10—C1—C6—C5	173.3 (4)	C12—C13—C14—C15	-0.1 (5)
N2—C1—C6—N7	173.6 (3)	O16—C13—C14—Br1	-3.5 (4)
C10—C1—C6—N7	-8.7 (6)	C12—C13—C14—Br1	177.2 (3)
C5—C6—N7—O9	-34.8 (5)	C13—C14—C15—C10	-0.1 (6)
C1—C6—N7—O9	147.0 (4)	Br1—C14—C15—C10	-177.4 (3)
C5—C6—N7—O8	143.1 (4)	C11—C10—C15—C14	0.7 (5)
C1—C6—N7—O8	-35.1 (5)	C1—C10—C15—C14	175.1 (3)
N2—C1—C10—C11	136.9 (4)	C12—C13—O16—C17	-1.8 (5)
C6—C1—C10—C11	-40.9 (6)	C14—C13—O16—C17	178.9 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C11—H11 \cdots O8 ⁱ	0.95	2.50	3.293 (5)	141

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