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(*Z*)-*α*-5-Bromo-*N*-*tert*-butyl-2-methoxyphenylnitrone

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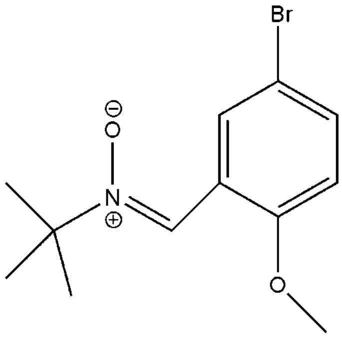
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.028; wR factor = 0.081; data-to-parameter ratio = 14.8.

The title compound, $C_{12}H_{16}BrNO_2$, was synthesized in 95% yield by condensation of 5-bromo-2-methoxybenzaldehyde and *N*-*tert*-butyl-hydroxylamine acetate in the presence of triethylamine as the base and anhydrous magnesium sulfate as the dehydrating agent. The C═N bond leads to a plane containing all atoms of the side chain, excluding the three methyl groups; this plane makes a dihedral angle of 14.44 (3)° with the ring plane.

Related literature

For general background, see: Merino & Padwa (2004); Torsell (1988); Janzen (1971); Usuki *et al.* (2006); Zhang *et al.* (2000); Floyd (2006); Soldaini *et al.* (2007); Yao *et al.* (2007). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{12}H_{16}BrNO_2$
M_r = 286.17
Monoclinic, $P2_1/c$
a = 10.7519 (11) Å
b = 10.0159 (10) Å
c = 11.8287 (12) Å
β = 98.426 (2)°
V = 1260.1 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.25 mm^{-1}
T = 298 (2) K
0.6 × 0.1 × 0.04 mm

Data collection

Siemens SMART PLATFORM CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.600, T_{max} = 0.880
9284 measured reflections
2221 independent reflections
1950 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.081
S = 1.00
2221 reflections
150 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

Thomas DeLegge and Derek Janssen also contributed to this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2299).

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supplementary materials

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(*Z*)-[illegible]-5-Bromo-*N*-*tert*-butyl-2-methoxyphenylnitrone

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Comment

Nitrones are versatile organic compounds widely used as 1,3-dipoles in cycloadditions (Merino & Padwa, 2004; Torsell, 1988), spin trapping agents in free radical chemistry (Janzen, 1971; Usuki *et al.*, 2006) and also in biological studies (Zhang *et al.*, 2000). Recently they have also been employed as therapeutics in age-related diseases (Floyd, 2006). Nitrones undergo many reactions, such as the Behrend Rearrangement, nitrone-oxime *O*-ether rearrangement, and thermolytic alkene elimination (Torsell, 1988). While the most conventional procedures for the preparation of nitrones have been the condensation of *N*-monosubstituted hydroxylamines with carbonyl compounds and the *N*-alkylation of oximes (Torsell, 1988), a newly reported high yielding and chemoselective procedure for the conversion of imines to nitrones using catalytic amounts of methyltrioxorhenium represents a breakthrough in nitrone synthesis (Soldaini *et al.*, 2007). We have recently shown that nitrones derived from aromatic aldehydes can be used as convenient precursors to carbocyclic carbene ligands for the synthesis of novel and catalytically useful Pd compounds (Yao *et al.*, 2007). The formation of nitrone-based Pd complexes involves the selective C—H activation of the aromatic ring *via* orthopalladation directed by the oxygen atom on the nitrone moiety. It can be expected that the stereochemistry around the C=N of the nitrone group would have a pronounced effect in formation of the $C_{carbene}$—Pd bond. For this purpose, we have synthesized the title compound, (I), and reported herein its crystal structure.

In the molecule of the title compound, (I), (Fig. 1) the bond lengths and angles are generally within normal ranges (Allen *et al.*, 1987). The C8=N1 double bond leads to a plane containing C9, O2, N1, C8 and C5 atoms, and the dihedral angle between (C1—C6) ring and the plane of (N1/O2/C5/C8/C) is 14.44 (3)°.

Experimental

An oven-dried Schlenk flask was charged with 5-bromo-2-methoxybenzaldehyde (215 mg, 1.0 mmol), *N*-*tert*-butyl hydroxylamine acetate (298 mg, 2.0 mmol) and anhydrous magnesium sulfate (362 mg, 3.0 mmol) under argon. Triethylamine (350 µl, 253 mg, 2.5 mmol) was then added *via* syringe followed by anhydrous benzene (6 ml, distilled from sodium/benzophenone). After stirring at 363 K in a Schlenk flask for 15 d, the reaction mixture was filtered to remove the magnesium sulfate and the filtrate concentrated to dryness with a rotary evaporator. The crude mixture was purified by flash column chromatography on silica gel (60 230–400 mesh) using a 11:1 (*v*/*v*) dichloromethane/ethyl acetate solution as the eluent to give the title compound (yield; 270 mg, 95%, m.p. 372–373 K), as white solid. Crystals suitable for X-ray analysis were grown by slow solvent diffusion by layering hexane over a solution of the nitrone in dichloromethane. ^{1}H-NMR (500 MHz, in $CDCl_3$ at 25°C): δ 9.54 (1 H, d, $J = 2.5$ Hz), 7.95 (1 H, s), 7.36 (1*H*, dd, $J = 2.5$ and 8.5 Hz), 6.69 (1 H, d, $J = 8.5$ Hz), 3.80 (3*H*, s), 1.56 (9 H, s). 13 C-NMR (125 MHz, $CDCl_3$): δ156.0, 133.3, 130.7, 123.0, 121.9, 113.3, 111.3, 71.4, 55.9, 28.3. Anal. Calcd for $C_{12}H_{16}BrNO_2$: C, 50.37; H, 5.64; N, 4.89. Found: C, 50.34; H, 5.55; N 4.82.

Refinement

H atoms were positioned geometrically with C—H = 0.93 and 0.96 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for aromatic H and $x = 1.5$ for methyl H atoms.

Figures

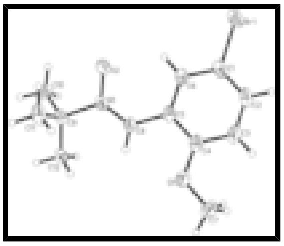

Fig. 1.

(*Z*)-α-5-Bromo-*N*-*tert*-butyl-2-methoxyphenylnitrone

Crystal data

$C_{12}H_{16}BrNO_2$	$F_{000} = 584$
$M_r = 286.17$	$D_x = 1.508$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 372-373 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 10.7519 (11)$ Å	Cell parameters from 637 reflections
$b = 10.0159 (10)$ Å	$\theta = -14$–14°
$c = 11.8287 (12)$ Å	$\mu = 3.25$ mm^{-1}
$\beta = 98.426 (2)$°	$T = 298 (2)$ K
$V = 1260.1 (2)$ Å^3	Plate, colorless
$Z = 4$	0.6 × 0.1 × 0.04 mm

Data collection

Siemens SMART CCD PLATFORM diffractometer	2221 independent reflections
Radiation source: fine-focus sealed tube	1950 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.018$
Detector resolution: 0 pixels mm^{-1}	$\theta_{max} = 25.0$°
$T = 293(2)$ K	$\theta_{min} = 1.9$°
ω scans	$h = -12\rightarrow12$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$k = -11\rightarrow11$
$T_{min} = 0.600$, $T_{max} = 0.880$	$l = -14\rightarrow13$
9284 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.6983P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.54$ e Å^{-3}
2221 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}
150 parameters	Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0048 (9)
Secondary atom site location: difference Fourier map	

Special details

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 $F^2 > 2\text{sigma}(F^2)$ 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.

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Br1	0.63640 (2)	1.08818 (3)	0.11983 (3)	0.06566 (15)
O1	0.27617 (18)	1.07684 (18)	0.46435 (16)	0.0588 (5)
O2	0.20183 (18)	0.8842 (2)	0.08330 (15)	0.0592 (5)
N1	0.16209 (17)	0.87311 (19)	0.18066 (16)	0.0397 (4)
C1	0.5214 (2)	1.0907 (2)	0.2277 (2)	0.0501 (6)
C2	0.5503 (3)	1.1622 (3)	0.3274 (3)	0.0592 (7)
H2	0.6241	1.2118	0.3409	0.071*
C3	0.4689 (3)	1.1596 (3)	0.4070 (3)	0.0597 (7)
H3	0.4877	1.2085	0.4742	0.072*
C4	0.3592 (2)	1.0853 (2)	0.3883 (2)	0.0484 (6)
C5	0.3288 (2)	1.0120 (2)	0.2859 (2)	0.0421 (5)
C6	0.4117 (2)	1.0173 (2)	0.2052 (2)	0.0455 (5)
H6	0.3929	0.9715	0.1364	0.055*
C7	0.3052 (3)	1.1467 (3)	0.5702 (2)	0.0667 (8)
H71	0.3852	1.1173	0.6090	0.100*
H72	0.2414	1.1290	0.6172	0.100*

H73	0.3085	1.2409	0.5557	0.100*
C8	0.2159 (2)	0.9307 (2)	0.2740 (2)	0.0420 (5)
H8	0.1783	0.9185	0.3392	0.050*
C9	0.0438 (2)	0.7883 (2)	0.17651 (19)	0.0413 (5)
C10	0.0712 (3)	0.6562 (3)	0.1223 (2)	0.0539 (6)
H101	0.1031	0.6726	0.0519	0.081*
H102	−0.0048	0.6048	0.1072	0.081*
H103	0.1326	0.6076	0.1734	0.081*
C11	−0.0599 (2)	0.8639 (3)	0.1020 (3)	0.0603 (7)
H111	−0.0713	0.9495	0.1356	0.090*
H112	−0.1368	0.8140	0.0962	0.090*
H113	−0.0371	0.8760	0.0272	0.090*
C12	0.0096 (3)	0.7633 (3)	0.2947 (2)	0.0548 (6)
H121	0.0803	0.7249	0.3427	0.082*
H122	−0.0604	0.7029	0.2891	0.082*
H123	−0.0127	0.8462	0.3271	0.082*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03918 (18)	0.0856 (3)	0.0715 (2)	−0.01188 (13)	0.00567 (13)	0.01389 (14)
O1	0.0474 (11)	0.0666 (12)	0.0622 (11)	−0.0067 (8)	0.0068 (9)	−0.0208 (9)
O2	0.0464 (10)	0.0871 (13)	0.0445 (10)	−0.0183 (9)	0.0076 (8)	0.0022 (9)
N1	0.0325 (10)	0.0430 (10)	0.0430 (10)	−0.0023 (8)	0.0036 (8)	0.0011 (8)
C1	0.0358 (13)	0.0470 (14)	0.0656 (16)	−0.0030 (10)	0.0013 (11)	0.0114 (11)
C2	0.0394 (14)	0.0499 (15)	0.085 (2)	−0.0124 (11)	−0.0010 (13)	−0.0011 (14)
C3	0.0487 (15)	0.0535 (15)	0.0732 (18)	−0.0087 (12)	−0.0039 (13)	−0.0147 (13)
C4	0.0385 (14)	0.0432 (13)	0.0612 (15)	0.0008 (10)	0.0001 (11)	−0.0041 (11)
C5	0.0350 (12)	0.0372 (11)	0.0522 (13)	0.0003 (9)	−0.0001 (10)	0.0014 (10)
C6	0.0374 (12)	0.0436 (12)	0.0531 (13)	−0.0015 (10)	−0.0013 (10)	0.0045 (10)
C7	0.0638 (19)	0.0736 (18)	0.0598 (17)	0.0012 (15)	−0.0007 (14)	−0.0184 (15)
C8	0.0354 (12)	0.0420 (12)	0.0482 (13)	−0.0031 (9)	0.0050 (10)	−0.0026 (10)
C9	0.0336 (11)	0.0404 (12)	0.0492 (12)	−0.0059 (9)	0.0038 (9)	−0.0009 (10)
C10	0.0563 (16)	0.0473 (14)	0.0578 (15)	−0.0035 (12)	0.0067 (12)	−0.0081 (12)
C11	0.0372 (14)	0.0570 (15)	0.0822 (19)	−0.0030 (12)	−0.0064 (13)	0.0019 (14)
C12	0.0503 (15)	0.0586 (15)	0.0585 (15)	−0.0161 (12)	0.0182 (12)	−0.0092 (12)

Geometric parameters (Å, °)

Br1—C1	1.903 (3)	C7—H71	0.9600
O1—C4	1.360 (3)	C7—H72	0.9600
O1—C7	1.429 (3)	C7—H73	0.9600
O2—N1	1.290 (3)	C8—H8	0.9300
N1—C8	1.304 (3)	C9—C12	1.517 (3)
N1—C9	1.525 (3)	C9—C10	1.518 (3)
C1—C2	1.376 (4)	C9—C11	1.518 (3)
C1—C6	1.382 (3)	C10—H101	0.9600
C2—C3	1.377 (4)	C10—H102	0.9600
C2—H2	0.9300	C10—H103	0.9600

C3—C4	1.384 (4)	C11—H111	0.9600
C3—H3	0.9300	C11—H112	0.9600
C4—C5	1.413 (3)	C11—H113	0.9600
C5—C6	1.399 (3)	C12—H121	0.9600
C5—C8	1.452 (3)	C12—H122	0.9600
C6—H6	0.9300	C12—H123	0.9600

C4—O1—C7	118.0 (2)	N1—C8—C5	126.3 (2)
O2—N1—C8	123.66 (19)	N1—C8—H8	116.9
O2—N1—C9	113.76 (17)	C5—C8—H8	116.9
C8—N1—C9	122.57 (19)	C12—C9—C10	109.5 (2)
C2—C1—C6	121.4 (3)	C12—C9—C11	111.1 (2)
C2—C1—Br1	119.61 (19)	C10—C9—C11	111.2 (2)
C6—C1—Br1	118.9 (2)	C12—C9—N1	112.07 (18)
C1—C2—C3	119.3 (2)	C10—C9—N1	106.65 (19)
C1—C2—H2	120.3	C11—C9—N1	106.18 (18)
C3—C2—H2	120.3	C9—C10—H101	109.5
C2—C3—C4	120.9 (3)	C9—C10—H102	109.5
C2—C3—H3	119.6	H101—C10—H102	109.5
C4—C3—H3	119.6	C9—C10—H103	109.5
O1—C4—C3	123.7 (2)	H101—C10—H103	109.5
O1—C4—C5	116.3 (2)	H102—C10—H103	109.5
C3—C4—C5	120.0 (2)	C9—C11—H111	109.5
C6—C5—C4	118.4 (2)	C9—C11—H112	109.5
C6—C5—C8	124.2 (2)	H111—C11—H112	109.5
C4—C5—C8	117.4 (2)	C9—C11—H113	109.5
C1—C6—C5	120.0 (2)	H111—C11—H113	109.5
C1—C6—H6	120.0	H112—C11—H113	109.5
C5—C6—H6	120.0	C9—C12—H121	109.5
O1—C7—H71	109.5	C9—C12—H122	109.5
O1—C7—H72	109.5	H121—C12—H122	109.5
H71—C7—H72	109.5	C9—C12—H123	109.5
O1—C7—H73	109.5	H121—C12—H123	109.5
H71—C7—H73	109.5	H122—C12—H123	109.5
H72—C7—H73	109.5		

Fig. 1