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(*Z*)-*N*-*tert*-Butyl-*C*-(2,3,4-trimethoxyphenyl)nitrone

Hao Guo,* Mark Zabawa, Joyce Woo, Chong Zheng and Qingwei Yao

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA
Correspondence e-mail: hguo@niu.edu

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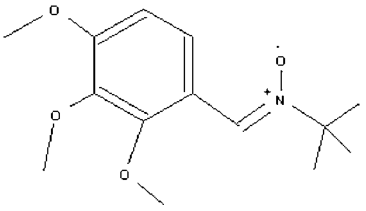
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.042; wR factor = 0.124; data-to-parameter ratio = 14.3.

The title compound, $C_{14}H_{21}NO_4$, was synthesized in 91% yield by condensation of 2,3,4-trimethoxybenzaldehyde and *N*-*tert*-butylhydroxylamine acetate in the presence of triethylamine as the base and anhydrous magnesium sulfate as the dehydrating agent. The structure features a benzene ring and side chains. The C═N double bond leads to a planar C═N(—O)—C group; this group is not coplanar with the benzene ring. The N═C—C$_{ar}$—C$_{ar}$ torsion angle is 10.2 (2)°.

Related literature

For related literature, see: Floyd (2006); Jasen (1971); Merino & Padwa (2004); Soldaini *et al.* (2007); Torsell (1988); Usuki *et al.* (2006); Yao *et al.* (2007); Zhang *et al.* (2000).



Experimental

Crystal data

$C_{14}H_{21}NO_4$
M_r = 267.32
Triclinic, $P\overline{1}$
a = 8.7424 (15) Å
b = 9.5039 (17) Å
c = 9.8424 (17) Å
α = 74.055 (3)°
β = 68.612 (3)°
γ = 82.108 (3)°
V = 731.5 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 (2) K
0.50 × 0.40 × 0.40 mm

Data collection

Siemens SMART CCD PLATFORM diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000) T_{min} = 0.857, T_{max} = 0.965
5580 measured reflections
2563 independent reflections
2189 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.124
S = 1.07
2563 reflections
179 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 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: HJ3042).

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supplementary materials

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(*Z*)-*N*-*tert*-Butyl-*C*-(2,3,4-trimethoxyphenyl)nitrone

H. Guo, M. Zabawa, J. Woo, C. Zheng and **Q. Yao**

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 (Jasen, 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 as we believe that the oxygen initially ligates the palladium species and directs the subsequent *ortho*-palladation. For this purpose, we have prepared the title compound and its structure analyzed by X-ray crystallography. The C7=N1 double bond leads to a plane containing C8, O1, N1, C7 and C6 which is not coplanar with the phenyl ring; the torsion angle N1 - C7 - C6 - C1 is −10.2 (3) °.

Experimental

An oven-dried Schlenk flask was charged with 2,3,4-Trimethoxybenzaldehyde (196 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 µ*L*, 253 mg, 2.5 mmol) was then added *via* syringe followed by anhydrous benzene (6 ml, distilled from sodium/benzophenone). After stirring at 90°C in a Schlenk flask for 8 days, 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 neat ethyl acetate as the eluent to give the title compound (244 mg, 91%) as white solid, m.p. 122–123°C. ^{1}H-NMR (500 MHz, in $CDCl_3$ at 25°C): δ 9.09 (1 H, d, $J = 9.1$ Hz), 7.82 (1 H, s), 6.66 (1 H, d, $J = 9.1$ Hz), 3.87 (3 H, s), 3.84 (3 H, s), 3.80 (3 H, s), 1.55 (9 H, s). ^{13}C-NMR (125 MHz, $CDCl_3$): δ155.2, 152.2, 141.4, 124.2, 124.0, 118.1, 106.8, 70.4, 61.5, 60.8, 55.9, 28.3. Anal. Calcd for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24. Found: C, 63.04; H, 7.90; N 5.15. Crystals suitable for X-ray analysis were grown by slow solvent diffusion by layering hexane over a solution of the nitrone in dichloromethane.

Refinement

H atoms atoms are treated by constrained refinement. The bond lengths of the hydrogen atoms to their parent atoms in six methyl groups are all equal to 0.96 Å while the others are equal to 0.93 Å.

Figures

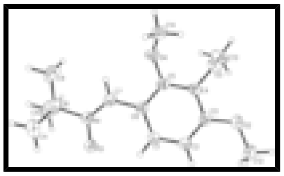
Fig. 1.

(*Z*)-*N*-*tert*-Butyl-*C*-(2,3,4-trimethoxyphenyl)nitrone

Crystal data

$C_{14}H_{21}NO_4$

$M_r = 267.32$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 8.7424$ (15) Å

$b = 9.5039$ (17) Å

$c = 9.8424$ (17) Å

$\alpha = 74.055$ (3)°

$\beta = 68.612$ (3)°

$\gamma = 82.108$ (3)°

$V = 731.5$ (2) Å^3

$Z = 2$

$F_{000} = 288$

$D_x = 1.214$ Mg m^{-3}

Melting point: 395-396 K

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

Cell parameters from 427 reflections

$\theta = -14$–14°

$\mu = 0.09$ mm^{-1}

$T = 293$ (2) K

Plate, colorless

0.50 × 0.40 × 0.40 mm

Data collection

Siemens SMART CCD PLATFORM diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 0 pixels mm^{-1}

$T = 293(2)$ K

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2000)

$T_{min} = 0.857$, $T_{max} = 0.965$

5580 measured reflections

2563 independent reflections

2189 reflections with $I > 2\sigma(I)$

$R_{int} = 0.017$

$\theta_{max} = 25.0$°

$\theta_{min} = 2.2$°

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 0.113P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.124$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
2563 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
179 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.024 (6)
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}
O1	0.75304 (15)	1.17217 (13)	0.34565 (15)	0.0717 (4)
O2	1.29356 (14)	0.62646 (12)	0.30972 (13)	0.0647 (3)
O3	1.09014 (13)	0.54726 (11)	0.20004 (11)	0.0584 (3)
O4	0.82513 (12)	0.72922 (12)	0.16273 (12)	0.0610 (3)
N1	0.70119 (15)	1.11834 (13)	0.26398 (14)	0.0523 (3)
C1	1.00430 (18)	0.94615 (16)	0.31636 (17)	0.0518 (4)
H1	0.9838	1.0337	0.3462	0.062*
C2	1.13649 (18)	0.85577 (16)	0.33577 (17)	0.0532 (4)
H2	1.2046	0.8837	0.3767	0.064*
C3	1.16811 (17)	0.72379 (16)	0.29453 (16)	0.0496 (4)
C4	1.06241 (17)	0.68092 (15)	0.23628 (15)	0.0481 (3)
C5	0.93260 (17)	0.77314 (16)	0.21437 (15)	0.0481 (3)
C6	0.90073 (17)	0.90925 (16)	0.25308 (16)	0.0484 (3)
C7	0.76466 (18)	0.99913 (17)	0.22132 (17)	0.0526 (4)
H7	0.7175	0.9683	0.1642	0.063*
C8	0.55423 (19)	1.20292 (18)	0.22727 (18)	0.0600 (4)

C9	0.5125 (3)	1.1466 (3)	0.1152 (3)	0.0883 (6)
H93	0.4750	1.0486	0.1604	0.132*
H92	0.6087	1.1466	0.0275	0.132*
H91	0.4275	1.2089	0.0867	0.132*
C10	0.4129 (2)	1.1846 (3)	0.3765 (2)	0.0886 (6)
H103	0.3178	1.2403	0.3611	0.133*
H102	0.4435	1.2190	0.4457	0.133*
H101	0.3880	1.0830	0.4170	0.133*
C11	0.6005 (3)	1.3618 (2)	0.1600 (2)	0.0835 (6)
H113	0.5067	1.4208	0.1458	0.125*
H112	0.6879	1.3701	0.0647	0.125*
H111	0.6363	1.3949	0.2268	0.125*
C12	1.4108 (2)	0.6695 (2)	0.3579 (3)	0.0795 (6)
H123	1.4613	0.7567	0.2879	0.119*
H122	1.4935	0.5924	0.3627	0.119*
H121	1.3569	0.6883	0.4557	0.119*
C13	1.0042 (3)	0.43237 (19)	0.3183 (2)	0.0809 (6)
H133	1.0439	0.4156	0.4007	0.121*
H132	1.0216	0.3447	0.2832	0.121*
H131	0.8889	0.4588	0.3514	0.121*
C14	0.8909 (2)	0.7105 (2)	0.0131 (2)	0.0747 (5)
H143	0.9072	0.8047	−0.0570	0.112*
H142	0.8155	0.6581	−0.0035	0.112*
H141	0.9942	0.6561	−0.0011	0.112*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0737 (8)	0.0711 (7)	0.0942 (9)	0.0155 (6)	−0.0461 (7)	−0.0434 (7)
O2	0.0582 (6)	0.0675 (7)	0.0777 (7)	0.0129 (5)	−0.0316 (6)	−0.0285 (6)
O3	0.0680 (7)	0.0514 (6)	0.0548 (6)	−0.0026 (5)	−0.0134 (5)	−0.0216 (5)
O4	0.0507 (6)	0.0757 (7)	0.0690 (7)	−0.0063 (5)	−0.0217 (5)	−0.0342 (6)
N1	0.0497 (7)	0.0544 (7)	0.0547 (7)	−0.0009 (5)	−0.0195 (5)	−0.0147 (6)
C1	0.0526 (8)	0.0492 (8)	0.0589 (9)	−0.0023 (6)	−0.0211 (7)	−0.0187 (6)
C2	0.0500 (8)	0.0579 (9)	0.0590 (9)	−0.0043 (6)	−0.0231 (7)	−0.0189 (7)
C3	0.0447 (7)	0.0540 (8)	0.0479 (8)	−0.0008 (6)	−0.0134 (6)	−0.0130 (6)
C4	0.0487 (8)	0.0488 (8)	0.0439 (7)	−0.0049 (6)	−0.0092 (6)	−0.0148 (6)
C5	0.0438 (7)	0.0551 (8)	0.0465 (7)	−0.0091 (6)	−0.0117 (6)	−0.0161 (6)
C6	0.0454 (7)	0.0512 (8)	0.0488 (8)	−0.0042 (6)	−0.0147 (6)	−0.0138 (6)
C7	0.0502 (8)	0.0571 (8)	0.0563 (8)	−0.0015 (6)	−0.0213 (7)	−0.0189 (7)
C8	0.0497 (8)	0.0659 (10)	0.0597 (9)	0.0058 (7)	−0.0200 (7)	−0.0102 (7)
C9	0.0826 (13)	0.1032 (15)	0.0964 (15)	0.0171 (11)	−0.0562 (12)	−0.0270 (12)
C10	0.0535 (10)	0.1182 (17)	0.0748 (12)	0.0084 (10)	−0.0133 (9)	−0.0105 (11)
C11	0.0779 (12)	0.0673 (11)	0.0897 (13)	0.0123 (9)	−0.0241 (10)	−0.0081 (10)
C12	0.0618 (10)	0.0927 (13)	0.1025 (14)	0.0184 (9)	−0.0449 (10)	−0.0404 (11)
C13	0.1072 (15)	0.0552 (9)	0.0737 (12)	−0.0161 (10)	−0.0179 (10)	−0.0171 (8)
C14	0.0801 (12)	0.0939 (13)	0.0658 (11)	−0.0018 (10)	−0.0364 (9)	−0.0298 (10)

Geometric parameters (Å, °)

O1—N1	1.2918 (16)	C8—C9	1.520 (3)
O2—C3	1.3586 (18)	C8—C10	1.520 (2)
O2—C12	1.421 (2)	C9—H93	0.9600
O3—C4	1.3788 (17)	C9—H92	0.9600
O3—C13	1.414 (2)	C9—H91	0.9600
O4—C5	1.3739 (16)	C10—H103	0.9600
O4—C14	1.425 (2)	C10—H102	0.9600
N1—C7	1.299 (2)	C10—H101	0.9600
N1—C8	1.5240 (19)	C11—H113	0.9600
C1—C2	1.381 (2)	C11—H112	0.9600
C1—C6	1.396 (2)	C11—H111	0.9600
C1—H1	0.9300	C12—H123	0.9600
C2—C3	1.385 (2)	C12—H122	0.9600
C2—H2	0.9300	C12—H121	0.9600
C3—C4	1.402 (2)	C13—H133	0.9600
C4—C5	1.380 (2)	C13—H132	0.9600
C5—C6	1.411 (2)	C13—H131	0.9600
C6—C7	1.445 (2)	C14—H143	0.9600
C7—H7	0.9300	C14—H142	0.9600
C8—C11	1.518 (3)	C14—H141	0.9600

C3—O2—C12	117.46 (13)	H93—C9—H92	109.5
C4—O3—C13	113.76 (12)	C8—C9—H91	109.5
C5—O4—C14	116.22 (12)	H93—C9—H91	109.5
O1—N1—C7	122.97 (12)	H92—C9—H91	109.5
O1—N1—C8	114.34 (12)	C8—C10—H103	109.5
C7—N1—C8	122.64 (13)	C8—C10—H102	109.5
C2—C1—C6	121.58 (13)	H103—C10—H102	109.5
C2—C1—H1	119.2	C8—C10—H101	109.5
C6—C1—H1	119.2	H103—C10—H101	109.5
C1—C2—C3	120.34 (13)	H102—C10—H101	109.5
C1—C2—H2	119.8	C8—C11—H113	109.5
C3—C2—H2	119.8	C8—C11—H112	109.5
O2—C3—C2	125.16 (13)	H113—C11—H112	109.5
O2—C3—C4	115.39 (13)	C8—C11—H111	109.5
C2—C3—C4	119.42 (13)	H113—C11—H111	109.5
O3—C4—C5	120.53 (13)	H112—C11—H111	109.5
O3—C4—C3	119.60 (13)	O2—C12—H123	109.5
C5—C4—C3	119.87 (13)	O2—C12—H122	109.5
O4—C5—C4	120.03 (12)	H123—C12—H122	109.5
O4—C5—C6	118.53 (13)	O2—C12—H121	109.5
C4—C5—C6	121.32 (13)	H123—C12—H121	109.5
C1—C6—C5	117.41 (13)	H122—C12—H121	109.5
C1—C6—C7	125.82 (13)	O3—C13—H133	109.5
C5—C6—C7	116.77 (13)	O3—C13—H132	109.5
N1—C7—C6	126.98 (14)	H133—C13—H132	109.5
N1—C7—H7	116.5	O3—C13—H131	109.5

C6—C7—H7	116.5
C11—C8—C9	109.38 (16)
C11—C8—C10	111.50 (16)
C9—C8—C10	111.30 (17)
C11—C8—N1	106.89 (14)
C9—C8—N1	111.94 (14)
C10—C8—N1	105.73 (13)
C8—C9—H93	109.5
C8—C9—H92	109.5
H133—C13—H131	109.5
H132—C13—H131	109.5
O4—C14—H143	109.5
O4—C14—H142	109.5
H143—C14—H142	109.5
O4—C14—H141	109.5
H143—C14—H141	109.5
H142—C14—H141	109.5

Fig. 1