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2-*tert*-Butoxy-1-phenyl-1-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethane

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Key indicators

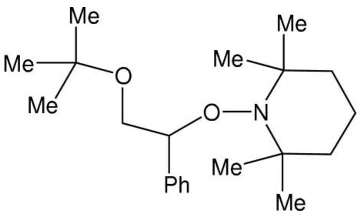
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.001 Å
R factor = 0.039
wR factor = 0.114
Data-to-parameter ratio = 28.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{21}H_{35}NO_2$, contains a piperidine ring in a chair conformation, with a pyramidal N atom and a single (exocyclic) N—O bond in an equatorial orientation.

Comment

Nitroxide-mediated polymerization (NMP) has emerged in recent years as a successful controlled or 'living' radical polymerization technique which can be used to prepare polymers of target molecular weight, narrow polydispersity and complex architecture (block and graft copolymers, star polymers, *etc.*) (Matyjaszewski, 2003). Successful NMP requires the use of a monomolecular initiator, identified as an alkoxyamine, which is derived from a nitroxide. This alkoxyamine should be prepared separately and then added in a known concentration to the monomer to be polymerized. Synthetic routes to alkoxyamines include the trapping of alkyl radicals by free nitroxides at moderate temperatures (Braslau *et al.*, 1997; Miura *et al.*, 1998) and a catalytic route involving Mn–salen complexes [H_2salen is bis(salicylidene)ethylenediamine; Dao *et al.*, 1998]. The title compound, (I), has been synthesized in the course of these studies (Cameron *et al.*, 2000).



(I)

The molecular structure of (I) (Fig. 1) is similar in its main features to the other *N*-oxy-2,2,6,6-tetramethylpiperidinyl derivatives reported by Ermert & Vasella (1993), Jahn *et al.* (2001, 2002) and Leitich *et al.* (2002). The piperidine ring adopts a chair conformation with the N—O1 bond in an equatorial orientation. The N—O1 distance is typical for a single bond (Allen *et al.*, 1987), while the N atom has pyramidal geometry, corresponding to sp^3 hybridization.

Experimental

A solution of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO; 0.187 g, 1.20 mmol) and di-*tert*-butylperoxalate (0.148 g, 0.63 mmol) in styrene (5 ml) was prepared. The mixture was degassed by three freeze/pump/thaw cycles and backflushed with argon after the final cycle. The resulting solution was sealed, then heated overnight at 313 K. After cooling, the solution was dried *in vacuo* to constant mass. The crude solid product obtained was then purified by flash chromatography on silica gel, eluting with a mixture of 40–60 petroleum ether/ethyl acetate (90:10 *v*/*v*). After removal of the solvent, a white crystalline solid was obtained in 79% yield. The characterization data of the isolated product were in agreement with those given in the literature (Bon *et al.*, 1999). ^{1}H NMR (300 MHz): δ 1.04 (*s*, 9H, $CH_3 \times 3$), 0.58, 1.02, 1.19, 1.37 (*br s*, 3H, CH_3), 0.9–1.7 (*br m*, 6H, $CH_2 \times 3$), 3.41 (*m*, 1H, H1), 3.89 (*m*, 1H, H171), 4.74 (*m*, 1H, H172), 7.18–7.35 (*m*, 5H, Ph) p.p.m. (for the H-atom numbering, see Fig. 1).

Crystal data

$C_{21}H_{35}NO_2$
$M_r = 333.50$
Orthorhombic, *Pbca*
$a = 15.532$ (4) Å
$b = 11.119$ (3) Å
$c = 23.247$ (5) Å
$V = 4014.8$ (17) Å^3
$Z = 8$
$D_x = 1.104$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 902 reflections
$\theta = 12.1$–$24.3°$
$\mu = 0.07$ mm^{-1}
$T = 100$ (2) K
Block, colourless
$1.00 \times 0.66 \times 0.14$ mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.579$, $T_{max} = 1.000$
60196 measured reflections

7229 independent reflections
6298 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 32.5°$
$h = -23 \rightarrow 23$
$k = -16 \rightarrow 16$
$l = -34 \rightarrow 35$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.114$
$S = 1.06$
7229 reflections
251 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.7171P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.4422 (8)	C2—C3	1.5399 (11)
O1—N	1.4595 (7)	C3—C4	1.5198 (14)
O2—C17	1.4158 (8)	C4—C5	1.5153 (13)
O2—C18	1.4446 (8)	C5—C6	1.5312 (10)
N—C6	1.4987 (9)	C6—C10	1.5280 (10)
N—C2	1.5033 (9)	C6—C9	1.5353 (11)
C1—C11	1.5168 (9)	C18—C20	1.5187 (10)
C1—C17	1.5228 (9)	C18—C21	1.5200 (11)
C2—C8	1.5354 (11)	C18—C19	1.5238 (11)
C2—C7	1.5377 (12)		
C1—O1—N	112.33 (5)	C5—C4—C3	108.36 (7)
C17—O2—C18	116.92 (5)	C4—C5—C6	112.78 (6)
O1—N—C6	106.17 (5)	C10—C6—C5	107.62 (6)
O1—N—C2	107.19 (5)	O2—C17—C1	108.48 (5)
C6—N—C2	117.35 (5)	O2—C18—C20	103.38 (6)
O1—C1—C11	114.45 (5)	O2—C18—C21	111.07 (6)
O1—C1—C17	105.37 (5)	C20—C18—C21	110.35 (6)
C11—C1—C17	110.04 (5)	O2—C18—C19	111.02 (6)
N—C2—C3	107.44 (6)	C20—C18—C19	110.12 (7)
C4—C3—C2	114.33 (7)	C21—C18—C19	110.68 (7)

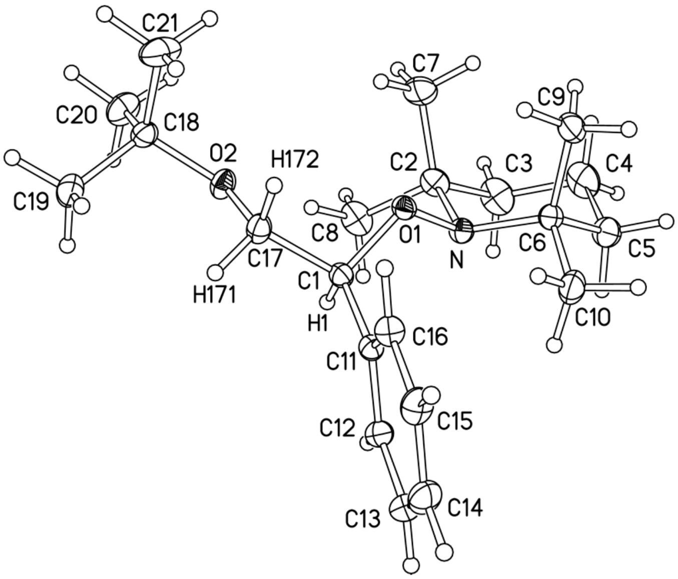


Figure 1
The molecular structure of (I), showing atomic displacement ellipsoids at the 50% probability level.

Methyl groups were treated as threefold symmetrical bodies rotating around C—C bonds, with a refined common U_{iso} for the three H atoms. Other H atoms were treated as riding on the corresponding C atoms, with refined U_{iso} values. C—H distances are 0.95–1.00 Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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