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Eclipsed Ground-State Conformations of the *tert*-Butyl–X Bond in *N*-*tert*-Butoxy- and *N*-Neopentyl-2,2,6,6-tetramethylpiperidine. X-ray Crystal Structure Determinations and Molecular Mechanics Calculations

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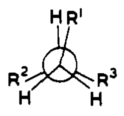
Abstract: X-ray crystallographic studies of derivatives of *N*-methoxy- and *N*-*tert*-butoxy-2,2,6,6-tetramethylpiperidine show that as expected the N–O bond is staggered with respect to the C–H bonds of the methoxy group in the former case, yet it *eclipses* a C–methyl bond of the *tert*-butyl group in the latter case. Molecular mechanics calculations confirm this and show that likewise the preferred conformation of *N*-neopentyl-2,2,6,6-tetramethylpiperidine has the CH_2 to *tert*-butyl group bond *eclipsed*, whereas in the corresponding *N*-ethyl compound the CH_2 to methyl bond is staggered. Calculations of tetramethylcyclohexyl analogues and of axial conformations of all of these molecules are reported.

Introduction

There have been several recent reports of preferred eclipsed conformations of single bonds joining saturated atoms. Such conformations about the central bond in a fragment $R^1X\text{-}YR^2R^3$ (**1**: X = CH_2, NH, O, etc.; Y = CH, N, etc.) are observed[1–4] when the R groups have a high steric demand, since rotation to put R^1 as far as possible from R^2 and R^3 leads to these three groups more or less eclipsing lone pairs or hydrogen atoms along the central bond as in **2**. In other examples, eclipsing of the carbon-to-sulfur bond in compounds of type **3** was recently described,[5–7] and the 1,2-disubstituted ethane **4** adopts an eclipsed conformation due to the overwhelming demands of the long-range interactions of *tert*-butyl moieties in the two substituent 2,4,6-tri-*tert*-butylphenyl groups[8] (the two hydrogens in closest contact represent a 1–14 interaction!). Here there are two minima separated by about 120° of rotation as a substituted phenyl group may eclipse one or other hydrogen along the central bond.



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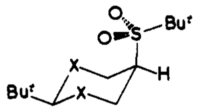

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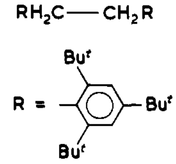

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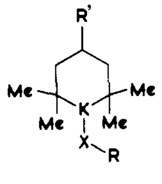
We now report examples which are a *complete* inversion of the normal conformational picture[9] in that a saturated bond has a threefold rotational potential with three successive *eclipsed* double minima and three sucessive *staggered* transition states in the 360° bond rotation cycle. In **5–8**, *N*-alkoxy and *N*-alkyl derivatives of 2,2,6,6-tetramethylpiperidine (TMP), the *tert*-butyl groups of **5** and **7** prefer to be eclipsed while in the analogous methyl compounds **6** and **8** the methyl groups are conventionally staggered.



TMP derivatives		TMC derivatives
K = —N—		K = —CH—
	—X—R	
R' = OCOPh		R' = H
5	$-O-Bu^t$	**9**
6	$-O-Me$	**10**
R' = H		R' = H
7	$-CH_2-Bu^t$	**11**
8	$-CH_2-Me$	**12**

The exocyclic α-bond is not the object of this investigation although such α-bonds are eclipsed. Nitrogen–oxygen bonds however are known to prefer far-from-staggered conformations,[10,11] while the eclipsed N–CH_2 bond in **7** and **8** fits the well-demonstrated[1–4] stereotype **1**. Attention is directed rather to the next, β, bond in the side chain.

Compounds **5** and **6** have been synthesized, with ester groups in the 4-position to obtain crystalline products, and their crystal structures have been determined by X-ray diffraction. Molecular mechanics calculations have been carried out on these molecules

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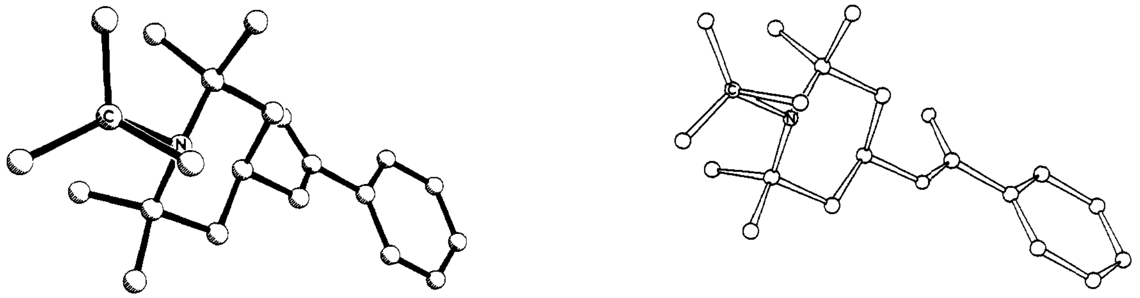

Figure 1. View of the X-ray crystal structure (left) and the MMX calculated structure (right) for **5**. The carbon atom C indicated obscures the oxygen atom and one C–methyl bond of the *tert*-butyl group almost eclipses the N–O bond. Hydrogen atoms are not shown.

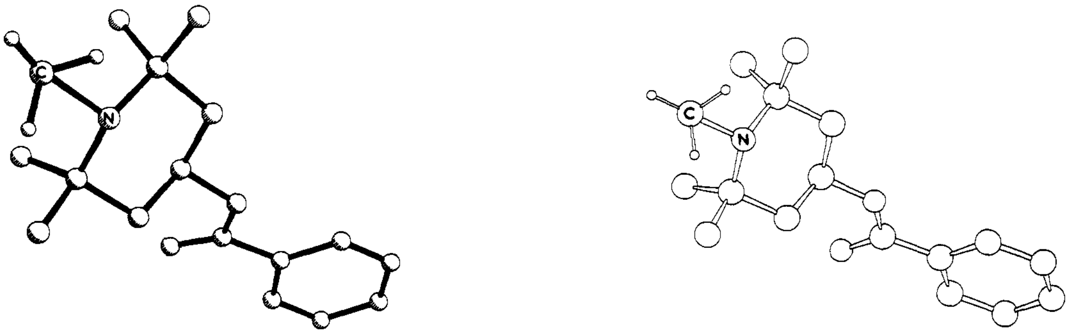

Figure 2. View of the X-ray crystal structure (left) and the MMX calculated structure (right) for **6**. The carbon atom C indicated obscures the oxygen atom and the N–O bond is staggered with respect to the C–H bonds of that *O*-methyl group. Only *O*-methyl group hydrogens are shown.

using MMX,[12] which is parametrized for the N–O bond. Allinger's MM3 program[13] has been used for **7** and **8** and for the analogous compounds **9–12** with a tetramethylcyclohexyl (TMC) ring. The set of all these compounds but with the *N*-alkyl or *N*-alkoxy side chain in the axial position has also been calculated.

Results and Discussion

Both **5** and **6** have been described in the patent literature,[14,15] but significant details of their synthesis were omitted. The *tert*-butoxy compound **5** was prepared by treatment of the nitroxyl of 4-benzoyloxy-TMP with *tert*-butyl iodide and tributyltin hydride.[14] Consideration of the likely reaction mechanism suggests that the reported *tert*-butoxy compound **5** and the corresponding *N*-hydroxy compound should be produced in equal amounts, and this was confirmed experimentally. The methoxy compound **6** had been synthesized by heating the same nitroxyl with di-*tert*-butyl peroxide under pressure,[15] but for the present work it was more conveniently prepared as for **5**, using methyl iodide instead of *tert*-butyl iodide.

Full details of the crystal structure determination of **5** and **6** are given in the Experimental Section and in the supplementary material. Relevant aspects are illustrated in Figures 1 and 2, which show that in both compounds the α-bond is eclipsed, while the β-bond is eclipsed for the *tert*-butyl compound **5** but staggered for the methyl compound **6**. Table I reports some significant structural parameters, entries E_1 and E_2 for compound **5** being for two conformationally similar but non-identical molecules in the unit cell.

Figure 3 shows a Newman projection view along the N–O and O–C bonds of **5** and **6** as determined experimentally. A and B show that in both compounds the α N–O bond is eclipsed while C and D show that the β O–C bond is eclipsed in the *tert*-butyl compound **5** but staggered in the methyl compound **6**. MMX molecular mechanics calculations[12] of the preferred gas-phase conformation of **5** and **6** lead to the structures shown in Figures 1 and 2, and significant experimental and calculated parameters are given in Table I. Calculations agree reasonably well with the experimental solid-state observations and confirm in particular the staggered and eclipsed β-bonds in **5** and **6**, respectively. Such agreement lends credibility to the calculations for **7–12** and for the axial conformations of these compounds discussed below.

Table I. Experimental (X-ray Crystallography) and Calculated Structural Parameters for Compounds **5–8**

	5			**6**		**7**	**8**
	exptl[a]						
	E_1	E_2	calcd	exptl	calcd	calcd	calcd
Torsion Angles (deg)							
β bond							
N1–X–C–R	1.9	5.3	14.0	52.6	60.5	9.9	60.3
	123.6	128.3	135.4	–66.4	–60.4	131.0	–60.3
	–121.6	–108.6	–116.7	165.0	–179.9	–112.1	180.0
H–X–C–R						–6.9	–56.7
						–13.0	56.7
α bond							
C2,6–N–X–R	119.2	116.1	113.6	115.4	113.6	–12.3	106.3
	–116.0	–119.8	–115.8	–117.4	–113.7	17.1	–106.3
Bond Angles of N (deg)[b]							
	116.7	116.1	115.8	118.5	117.5	117.8	120.7
	106.1	106.7	111.5	106.2	111.1	114.7	115.2
	106.2	105.6	111.0	106.9	111.0	115.1	115.2
Bond Length (pm)							
N–X	145.6	146.9	149.0	145.4	148.0	149.1	147.8
X–C	146.1	147.9	144.0	141.8	142.0	156.0	153.2
Bond Angles at X (deg)							
	118.9	118.4	122.3	110.3	113.6	117.8	112.9

[a] There are two independent molecules in the unit cell, see text. [b] The largest value is for the endocyclic C–N–C bond angle.

Significant results of MM3 molecular mechanics calculations[13] for *N*-alkyl-TMP derivatives **7** and **8** are shown in Table I, and Figure 4 shows Newman projection views. In both **7** and **8** the preferred conformation of the α-bond is eclipsed. For the β-bonds, the conformation along the *tert*-butyl–CH_2 bond in **7** is eclipsed,

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[12] MMX forcefield as in PCMODEL, Serena Software, Bloomington, Indiana. See: Gajewski, J. J.; Gilbert, K. K.; McKelvey, J. *Advances in Molecular Modelling*; JAI Press: Greenwich, 1992; Vol.2.

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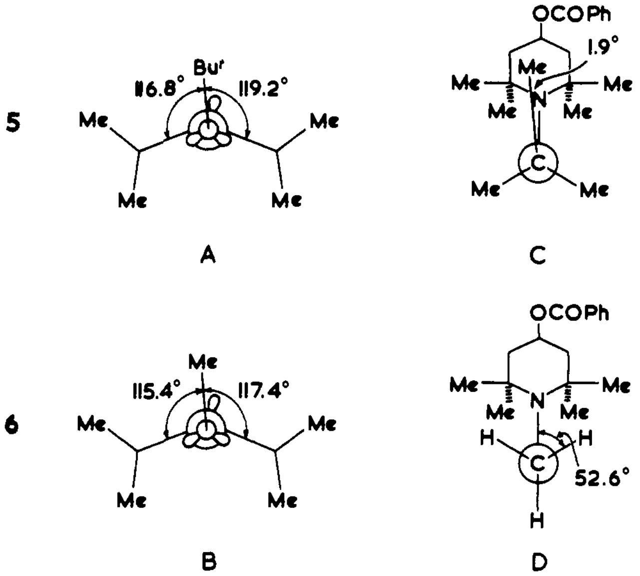

Figure 3. Newman projection along the α- and β-bonds of **5** and **6** as determined crystallographically and some significant torsion angles.

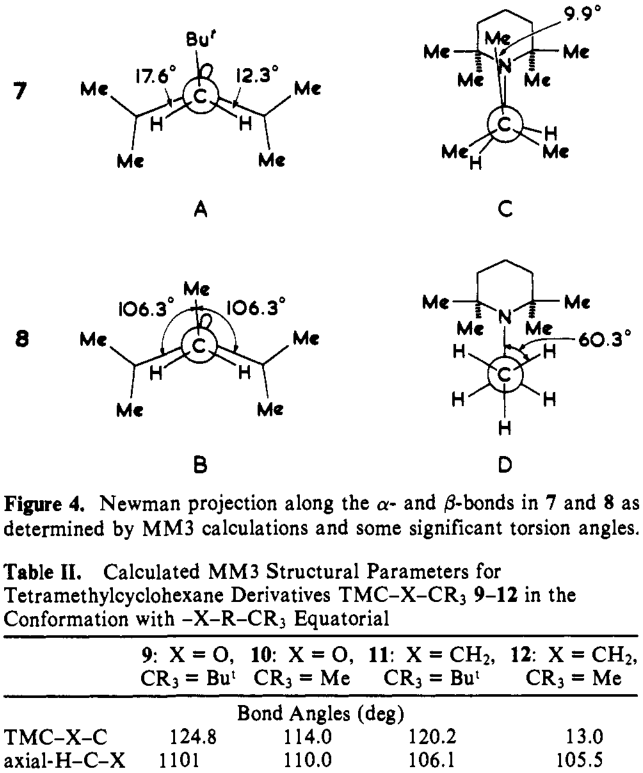

Figure 4. Newman projection along the α- and β-bonds in **7** and **8** as determined by MM3 calculations and some significant torsion angles.

Table II. Calculated MM3 Structural Parameters for Tetramethylcyclohexane Derivatives TMC-X-CR_3 **9–12** in the Conformation with -X-R-CR_3 Equatorial

	9: X = O, CR_3 = Bu^t	**10**: X = O, CR_3 = Me	**11**: X = CH_2, CR_3 = Bu^t	**12**: X = CH_2, CR_3 = Me
	Bond Angles (deg)			
TMC-X-C	124.8	114.0	120.2	13.0
axial-H-C-X	1101	110.0	106.1	105.5
	Bond Length (pm)			
TMC-X	143.5	143.1	157.5	156.6
X-C	143.4	142.0	155.9	153.7
	Torsion Angles (deg)			
β bond	62.2	60.8	-60.8	60.2
	-62.1	-60.9	56.1	-56.8
	180.0	180.0	-55.1	56.7
α bond	0.0	0.0	0.2	0.4
	117.7	116.3	-8.3	113.8
	-117.8	-116.3	8.9	-112.9

while the CH_3–CH_2 bond in **8** is staggered. For comparison, results from MM3 calculations for analogous alkyl- and alkoxy-TMC derivatives **9–12** are shown in Table II. While the α-bond is calculated to be eclipsed in all cases, the β-bonds are staggered for both R = methyl and *tert*-butyl. Thus the β-bond is measured to be eclipsed in **5** and is calculated to be so for both **5** and **7**, with average dihedral angles less than 11°. Torsional angles are not precisely 0° and 120°, so from the symmetry of the *tert*-butyl group there are equivalent minima on either side of perfect eclipsing *and* a second and third set of double minima after +120° and −120° of rotation. The calculated rotational profile for the *tert*-butyl to CH_2 bond in **7** is shown in Figure 5, a threefold potential with double minima almost precisely 60° out of phase with the classical potential for a saturated carbon–carbon bond such as that shown for 2,2,3,3-tetramethylbutane.[16]

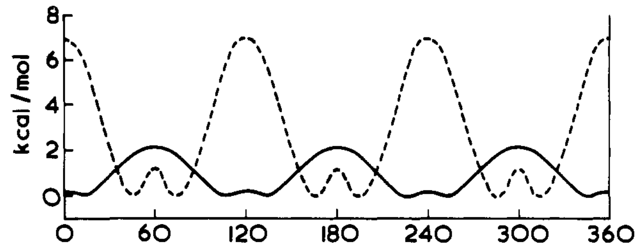

Figure 5. Potential energy diagram (kcal mol^{-1}) for rotation about the CH_2-*tert*-butyl bond in **7** (solid line) and for rotation about the central bond in 2,2,3,3-tetramethylbutane (broken line).

The barrier to rotation about the CH_2–R or O–R β-bond was calculated for **5–12** with results as shown in Figure 6. Staggered compounds **6** and **8–12** have barriers which are low in comparison with simple conventionally staggered compounds, for the methyl group rotational barrier is 3.2 kcal/mol in propane[17] and the *tert*-butyl group rotational barrier is 4.9 kcal/mol in 2,2-dimethylbutane.[18] The eclipsed conformation of these compounds is thus unusually close to the staggered ground state in energy, reflecting in reduced measure the same steric interactions which lead to **5** and **7** having eclipsed ground states.

All the barriers calculated about the β-bond are too low for observation by dynamic NMR measurements, and the NMR signals for the β-substituent are indeed single lines at all accessible temperatures for **8** and for the parents of **5** and **6** without the 4-benzoyloxy group. There is in these three molecules and other analogues an NMR-visible exchange process which involves a complex combination of ring inversion, nitrogen inversion, and rotation about the α-bond.[19] This has no bearing on the eclipsed β-bond and will be discussed elsewhere.

The particular stability of the eclipsed conformation in the series **5–12** whether as the ground state or the transition state is related to features which increase the interactions of the β-substituent with the ring methyl groups. These last encumber the space that a staggered β *tert*-butyl group would occupy but leave room for a staggered β methyl group, so the former group is the more likely to be eclipsed. The encumbrance is greater when nitrogen or oxygen atoms are involved with shorter bonds than in the carbon analogues, so eclipsing is most likely in the alkoxy-TMP series. Finally eclipsing is inherently more likely when a carbon–oxygen β-bond is involved, since the barrier to rotation in methanol[20] (1.07 kcal/mol) is lower than that in ethane[21] (2.88 kcal/mol). Several pairwise comparisons of results in Figure 6 bear out these points.

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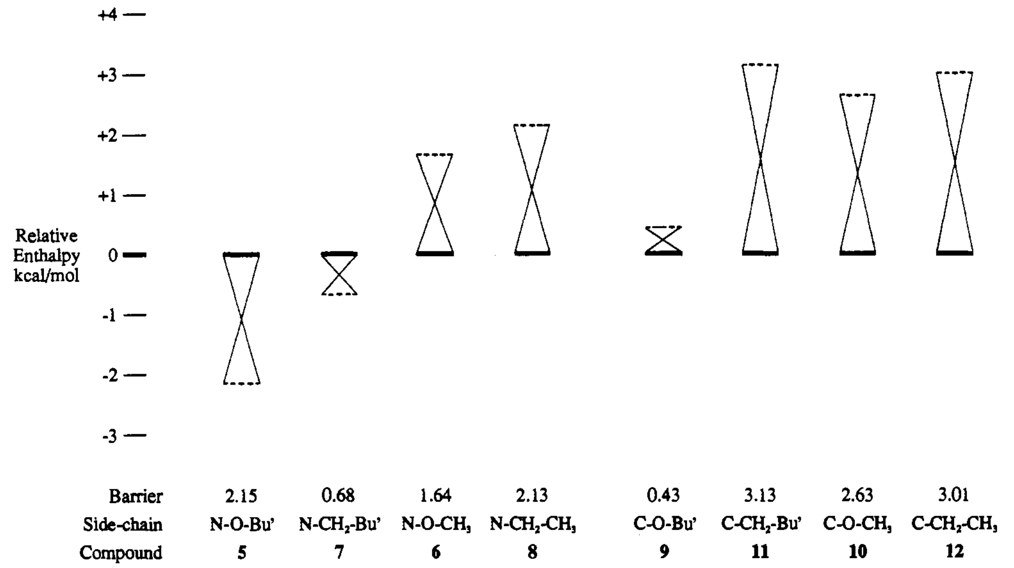


Figure 6. Calculated barriers (kcal/mol) to rotation about the β X–R bond in compounds **5**–**12** shown in terms of the relative energy of the staggered conformation, (solid line, arbitrarily 0 kcal/mol) and the eclipsed conformation (broken line).

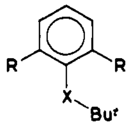
Table III. Preferred Ring–X and X–R Bond Conformations of –XR Axial Conformations of Derivatives of TMP and TMC

		energy relative to equatorial	conformation of α bond (mean torsion angle, deg)	conformation of β bond (mean torsion angle, deg)
5	TMP-O-*t*-Bu	2.40	eclipsed (2)	eclipsed (1)
6	TMP-O-Me	2.45	eclipsed (2)	staggered (60)
7	TMP-CH$_2$-*t*-Bu	1.96	eclipsed (8)	staggered (48)
	TMP-CH$_2$-*t*-Bu	1.99	eclipsed (2)	eclipsed (23)
8	TMP-CH$_2$-Me	6.42	eclipsed (7)	staggered (54)
9	TMC-O-*t*-Bu	0.67	eclipsed (1)	staggered (59)
10	TMC-O-Me	0.66	eclipsed (2)	staggered (60)
11	TMC-CH$_2$-*t*-Bu	2.36	eclipsed (5)	staggered (59)
12	TMC-CH$_2$-Me	3.44	eclipsed (16)	staggered (60)

It is worth comparing calculations of equatorial conformations of TMP or TMC compounds **5**–**12** and those of their isomers with an *axial*-X–R substituent. The four flanking methyl groups make the steric environment of the –X–R group quite similar in the two series, viz. *gauche* to either methyl or methylene groups. Previous experimental evidence suggests[22] that the equatorial conformation is the more stable nonetheless, and our calculations bear this out as shown in Table III. The preference for eclipsed conformations for the exocyclic α-bond persists in all the axial conformations, but the tendency for β-bond eclipsing is reduced, for it is preferred only in the *tert*-butoxy-TMP compound **5**, although neopentyl-TMP (**7**) is almost as stable in the eclipsed as in the staggered conformation.

Molecular mechanics calculations suggest further examples of as yet unknown compounds with three equivalent eclipsed conformational minima. In **13**, a benzene analogue of **5** or **7**, the methyl–R interactions shown in the staggered conformation **14** are smaller in an eclipsed conformation **15**. MM3 calculations of the preferred conformation of **16** and **17** show however that the X-*tert*-butyl bond is staggered, presumably because the ortho substituents can distort. Analogues **18** and **19** have less flexibility and the calculations suggest that there are minima at both the staggered and eclipsed conformations along the X–R bond. The preferred conformation of **18** is eclipsed along the O-*tert*-butyl bond, this being more stable than the staggered conformation by 2.79 kcal/mol. In agreement with the trend of results in the TMP series, staggered conformations of **19**–**21** are slightly more stable than the eclipsed.

The majority of β-bonds calculated in this work have a potential maximum near the staggered conformation if there is a minimum near the eclipsed conformation, or vice versa. Compounds **18** and **19** and the axial conformation of **7** are different in that there are minima at both the staggered and the eclipsed conformations and six equivalent rotational maxima during 360° of rotation.



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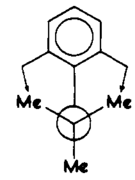

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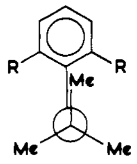

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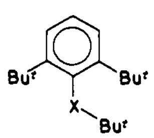
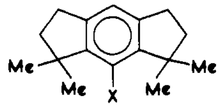


16 X = –O–

17 X = –CH$_2$–



18 X = –O–Bu^t

19 X = –CH$_2$–Bu^t

20 X = –O–Me

21 X = –CH$_2$–Me

Experimental Procedures

General Procedures. Melting points are uncorrected. Microanalyses were carried out at the Chemical Analysis Centre, University of Kent, Canterbury, U.K. Flash chromatography was carried out using Merck 9385 silica gel. ^{1}H NMR spectra were recorded at 90 MHz (JEOL FX90Q instrument) in deuterochloroform, with tetramethylsilane as internal reference.

4-Benzoyloxy-1-*tert*-butoxy-2,2,6,6-tetramethylpiperidine (13). A solution of 4-benzoyloxy-TEMPO (3.4 g, 12.3 mmol) and *tert*-butyl iodide (3.58 g, 19.4 mmol) in dry chlorobenzene (7.5 mL) was cooled to 5 °C under nitrogen and treated with Bu$_3$SnH (2.65 g, 9.14 mmol) at a rate to keep the temperature below 10 °C. An excess of Bu$_3$SnH was required because of free iodine in the *tert*-butyl iodide. The mixture was then

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stirred at room temperature until completely decolorized and the chlorobenzene was removed under reduced pressure. The residue was stirred with hexanes and the precipitated 1-hydroxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine was filtered. The identity of this material was confirmed by acetylation (Ac_2O-pyridine) to give 1-acetoxy-4-benzoyloxy-2,2,6,6-tetramethylpiperidine as plates (1.45 g, 4.4 mmol, 36%) from hexanes, mp 111–112 °C (lit.[23] mp 111–112 °C).

The filtrate after separation of 1-hydroxy-4-benzoyloxy-TMP was evaporated and the residue was purified by flash chromatography (hexanes, then 1:9 ethyl acetate/hexanes), followed by crystallization from methanol to afford **5** (1.45 g, 4.35 mmol, 35%) as rods, mp 75–76 °C (lit.[14] mp 80–82.5 °C): ^{1}H NMR δ 1.21 and 1.24 (12 H, 2 × s, gem-$(CH_3)_2$), 1.30 (9 H, s, *t*-Bu), 1.70 (2 H, dd collapsed to t, J = 11.8 Hz, H-3,5$_{ax}$), 1.99 (2 H, dd, J = 11.8, 3.0 Hz, H-3,5$_{eq}$), 5.25 (1 H, tt, J = 11.8, 3.0 Hz, H-4), 7.36–8.08 (5 H, m, Ph). Anal. Calcd for $C_{20}H_{31}NO_3$: C, 72.04; H, 9.37; N, 4.20. Found: C, 72.12; H, 9.69; N, 4.21.

4-Benzoyloxy-1-methoxy-2,2,6,6-tetramethylpiperidine (14). A solution of 4-benzoyloxy-TEMPO (1.0 g, 3.62 mmol) and methyl iodide (0.81 g, 5.7 mmol) in dry chlorobenzene (2.25 mL) was cooled to 5 °C under nitrogen and treated dropwise with Bu_3SnH (0.52 g, 1.78 mmol) at a rate to keep the temperature below 10 °C. The mixture was kept at 10–15 °C for 15 min by intermittent cooling and then allowed to warm to room temperature. The solution became colorless over 1 h and the chlorobenzene was evaporated under reduced pressure. Without removing the 4-benzoyloxy-1-hydroxy-TMP, the total residue was subjected to flash chromatography (hexanes, then 1:9 ethyl acetate/hexanes) followed by crystallization from methanol to afford **6** (0.25 g, 0.86 mmol, 24%) as plates, mp 68–69 °C (lit.[15] mp 67–68 °C); ^{1}H NMR δ 1.23 (12 H, s, gem-$(CH_3)_2$), 1.69 (2 H, dd collapsed to t, J = 11.6 Hz, H-3,5$_{ax}$), 1.97 (2 H, dd, J = 11.7, 4.4 Hz, H-3,5$_{eq}$), 3.62 (3 H, s, OCH_3), 5.25 (1 H, tt, J = 11.6, 4.4 Hz, H-4), 7.38–8.07 (5 H, m, Ph). Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 70.01; H, 8.86; N, 4.80.

Crystallography. Both structures were solved by direct methods and refined using alternating cycles of difference Fourier synthesis and full-matrix least-squares refinement. In both structures the non-hydrogen atoms were defined anisotropically. In **5** the hydrogens were placed in idealized positions (C–H = 0.96 Å) and assigned a common isotropic thermal parameter (v = 0.08 Å^2). In **6**, hydrogens were treated similarly with the exception of those of the *O*-methyl group which were located directly from a difference Fourier map, although the coordinates were not subsequently refined.

Σ thresholds were chosen to optimize the data/parameter ratios. Although the structure of **5** is intrinsically less accurate, individual bond lengths and angles in the two crystallographically independent molecules are completely consistent.

Crystal data for 4-benzoyloxy-1-*tert*-butoxy-2,2,6,6-tetramethylpiperidine: $C_{20}H_{31}NO_3$, triclinic, $P\bar{1}$, a = 12.385(5) Å, b = 12.861(6) Å, c = 14.107(5) Å, α = 94.04(3)°, β = 94.52(3)°, γ = 115.29(3)°, V = 2012 Å^3, Z = 4, D_{calc} = 1.10 g·cm^{-3}, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ = 0.68 cm^{-1}, Nicolet R3mV diffractometer, 5362 reflections ($5° \leq 2\theta \leq 45°$) on a colorless crystal 0.7 × 0.3 × 0.2 mm, 5089 independent, 3165 [$I \geq 1.5\sigma(I)$] used, 433 parameters, R = 0.0769, R_w = 0.0684.

Crystal data for 4-benzoyloxy-1-methoxy-2,2,6,6-tetramethylpiperidine: $C_{17}H_{25}NO_3$, monoclinic, $P2_1/a$, a = 8.017(3) Å, b = 11.239(5) Å, c = 18.621(7) Å, β = 96.24(3)°, V = 1668 Å^3, Z = 4, D_{calc} = 1.16 g·cm^{-3}, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ = 0.74 cm^{-1}, Nicolet R3mV diffractometer, 4079 reflections ($5° \leq 2\theta \leq 55°$) on a colorless crystal 0.8 × 0.1 mm, 3637 independent, 1793 [$I \geq 3\sigma(I)$] used, 190 parameters, R = 0.0578, R_w = 0.0649. All computations used the SHELXTL PLUS program package (G. M. Sheldrick, University of Göettingen, Germany 1986) on a Microvax II computer.

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Supplementary Material Available: Tables of fractional coordinates, anisotropic thermal parameters, complete lists of bond lengths and interbond angles for X-ray analyses of **5** and **6**, and description of data collection and structural refinement (13 pages); listing of structure factors (32 pages). Ordering information is given on any current masthead page.

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