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Crystal structure of 4-(prop-2-ynyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl

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The title compound, $C_{12}H_{20}NO_2$, was synthesized from 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (hydroxy-TEMPO) and propargyl bromide. The six-membered ring adopts a flattened chair conformation and carries a propynyloxy substituent in an equatorial orientation at the 4-position. The N—O bond length of the piperidin-1-oxyl unit is 1.289 (3) Å. In the crystal, C—H$\cdots$O hydrogen bonds combine with unusual C—H$\cdots\pi$ interactions involving the alkyne unit as acceptor to generate a three-dimensional network.
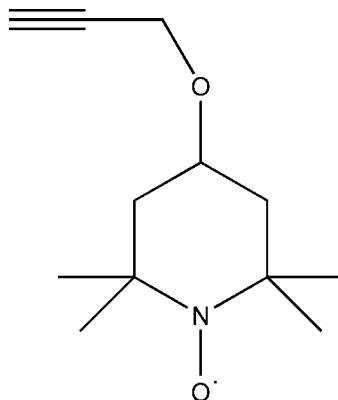
1. Chemical context

TEMPO, 2,2,6,6-tetramethylpiperidin-1-oxyl, and its derivatives have attracted significant interest in recent years as functional organic radicals with considerable chemical stability (Soegiarto et al., 2011). They are known to exhibit both ferromagnetism and antiferromagnetism at low temperatures (Togashi et al., 1996; Ishida et al., 1995), and the effect of intermolecular contacts on their magnetic properties has been examined (Iwasaki et al., 1999a,b). TEMPO and its derivatives have been utilized in applications as diverse as catalysis in organic synthesis (Zhao et al., 2005), pulsed electron–electron double-resonance (PELDOR) spectroscopy (Bode et al., 2007), and use as qubits (quantum bits) in quantum computing (Nakazawa et al., 2012).

Our interest in TEMPO derivatives is as reversible redox-active subunits in polymer-gel actuators (Goswami et al., 2013). In particular, the alkyne group present in the title compound, (1), allows us to utilize the versatile CuAAC 'click' cycloaddition with organic azides (Hein & Fokin, 2010; Lewis et al., 2013) as a means to attach the TEMPO unit to the gel skeleton.
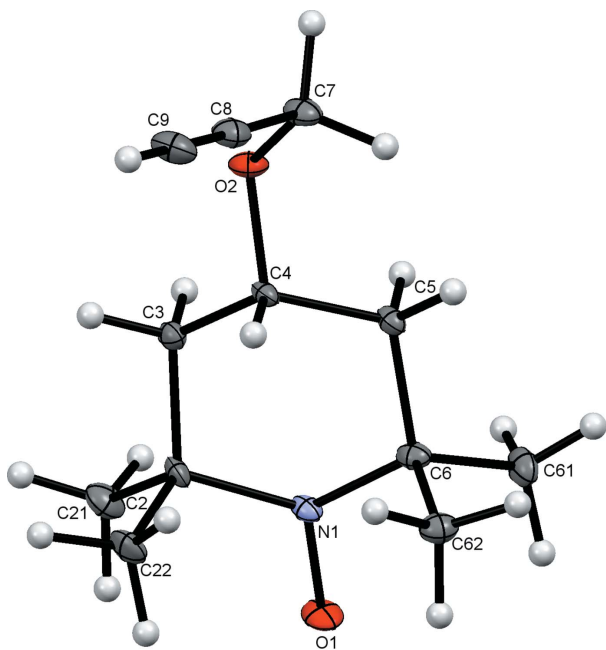
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Cg is the mid-point of the C8–C9 bond.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9$\cdots$O1[i]	0.95	2.28	3.205 (4)	163
C7—H7B$\cdots$O2[ii]	0.99	2.52	3.298 (4)	135
C61—H61A$\cdots$O1[iii]	0.98	2.56	3.481 (4)	157
C5—H5B$\cdots$Cg[iv]	0.99	2.93	3.885 (4)	156

Symmetry codes: (i) $x, y+1, z$; (ii) $x+\frac{1}{2}, -y+\frac{5}{2}, -z+1$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x-1, y+\frac{5}{2}, -z+\frac{3}{2}$.

Figure 1
The structure of (1), showing the atom numbering and with displacement ellipsoids drawn at the 50% probability level.

2. Structural commentary

The structure of (1) and its atom numbering are shown in Fig. 1. The molecule comprises a standard TEMPO unit with a propynyloxy substituent at the 4-position. The N1/C2–C6 ring adopts a flattened chair conformation with the C4 atom 0.706 (4) Å from the best fit plane through the remaining four C atoms, while N1 lies only 0.384 (4) Å from the plane in the opposite direction. The propynyl C7–C9 unit points away from this plane in the same direction as C4, with C7—C8—C9 = 178.6 (3)°. The N—O bond is 1.289 (3) Å long, which compares favorably with the average value of 1.285 (18) Å for other TEMPO structures (Macrae *et al.*, 2008).

3. Supramolecular features

In the crystal structure of (1), C9—H9$\cdots$O1 hydrogen bonds link molecules into $C(9)$ chains along *b* (Table 1). Additional C61—H61A$\cdots$O1 contacts form $R_3^2(16)$ rings, resulting in double chains of molecules along *b* (Fig. 2). In an almost
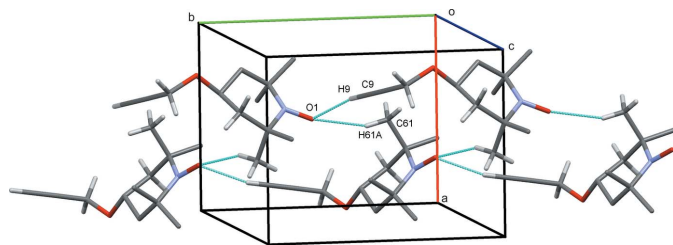
orthogonal direction, C7—H7B$\cdots$O2 hydrogen bonds form $C(3)$ chains along *a*. An interesting feature of these latter contacts is the support provided by C5—H5B$\cdots$Cg interactions (Cg is the mid-point of the C8—C9 bond) involving the alkyne unit (Fig. 3). Such contacts are often overlooked, but they have been reported previously for both terminal and non-terminal alkyne systems (Banerjee *et al.*, 2006; Thakur *et al.*, 2010; McAdam *et al.*, 2012). Overall, these contacts generate a three-dimensional network with molecules stacked in interconnected columns along the *b* axis (Fig. 4).

4. Database survey

The Cambridge Structural Database (CSD; Version 5.35, November 2013 with 2 updates; Allen, 2002) reveals a total of 175 structures of TEMPO and its derivatives. However, structures of alkoxy-TEMPO derivatives are rare with only a single example, albeit in two separate papers in which Polovyanenko *et al.* (2008) and Soegiarto *et al.* (2011) report the structure of 4-(methoxy)-TEMPO, 4-(methoxy)-2,2,6,6-tetramethylpiperidin-1-oxyl. The first paper examines the TEMPO derivative as an inclusion complex of *p*-hexanoyl calix[4]arene

Figure 2
Double chains formed from molecules of (1) along *b*. In this and subsequent Figures, C—H$\cdots$O hydrogen bonds are drawn as dashed lines and H atoms bound to atoms not involved in hydrogen bonding are not shown.
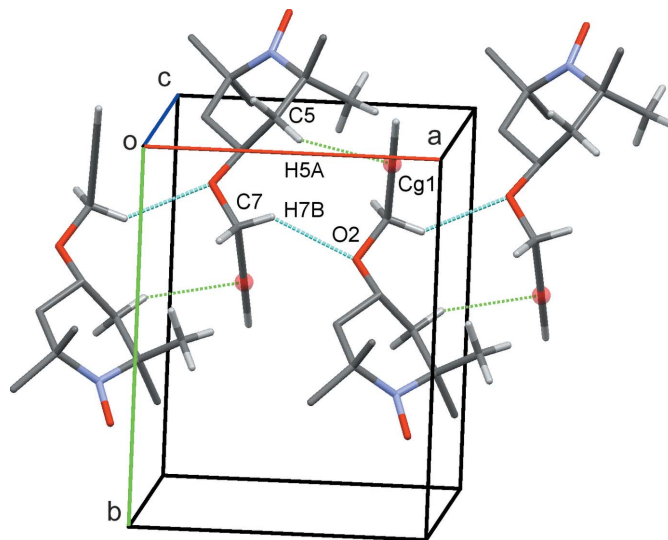

Figure 3
Zigzag chains formed along *a* from C—H$\cdots$O and C—H$\cdots\pi$ (green dotted lines) contacts. The mid-point of the C8≡C9 triple bond is shown as a red sphere.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{20}NO_2$
M_r	210.29
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	7.94506 (13), 10.17919 (16), 14.8052 (3)
V (Å^3)	1197.36 (4)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.63
Crystal size (mm)	$0.18 \times 0.15 \times 0.08$
Data collection	
Diffractometer	Agilent SuperNova (Dual, Cu at zero, Atlas)
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.522, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6622, 2307, 2203
R_{int}	0.046
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.123, 1.15
No. of reflections	2307
No. of parameters	140
No. of restraints	90
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.22, −0.28
Absolute structure	Flack x determined using 858 quotients [$(I^+)-(I^-)$]/[$(I^+)+(I^-)$] (Parsons & Flack, 2004)
Absolute structure parameter	0.0 (3)

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SIR2011* (Burla *et al.*, 2012), *SHELXL2013* (Sheldrick, 2008), *TITAN2000* (Hunter & Simpson, 1999), *Mercury* (Macrae *et al.*, 2008), *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip 2010).
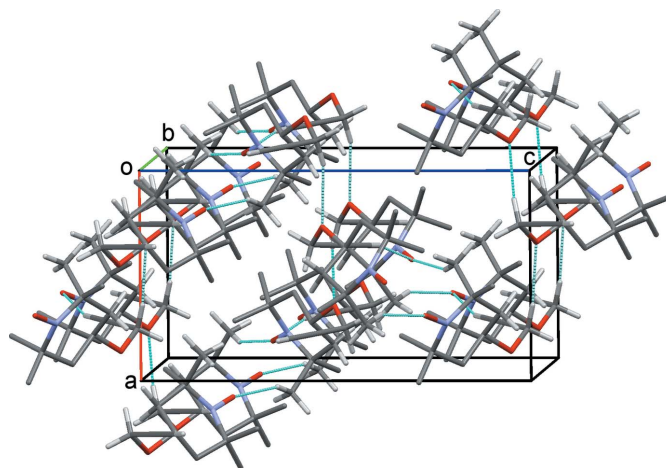

Figure 4
The overall packing for (1), viewed along the *b* axis.

centrosymmetric structure, the absolute structure could not be reliably determined. Friedel opposites were not, however, merged. All H atoms were refined using a riding model, with C—H = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene H atoms, C—H = 1.00 Å and U_{iso}(H) = 1.2U_{eq}(C) for methine H atoms, C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms, and C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for the terminal alkyne H atom. Anisotropic refinement of the non-H atoms was constrained using the ISOR command in *SHELXL* to prevent atoms becoming non-positive definite. 10 reflections with $F_o \gg F_c$ were omitted from the final refinement cycles.

(C$_6$OH), and investigates the magnetism and orientation dependent motion of the encapsulated radical. In the second, the molecule is included in the cavities of two porous frameworks derived from guanidinium cations and two organodisulfonate anions; the magnetic behaviour of the radical guest is investigated. Aryloyloxy-TEMPO derivatives are more abundant with 19 entries in the CSD (see, for example, Pang *et al.*, 2013; Nakazawa *et al.*, 2012; Akutsu *et al.*, 2005). Again, the focus is very much on the magnetic properties of the materials.

5. Synthesis and crystallization

Synthesis and characterization (IR and mass spectroscopy) are as previously described (Gheorghe *et al.*, 2006; Kulis *et al.*, 2009). Colourless blocks were obtained from diethyl ether solution at room temperature. Analysis calculated for C$_{12}$H$_{20}$NO$_2$: C 68.54, H 9.59, N 6.66%; found: C 68.57, H 9.66, N 6.68%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. With no heavy atom in the non-

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supporting information

Crystal structure of 4-(prop-2-ynyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SIR2011* (Burla *et al.*, 2012); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008) and *TITAN2000* (Hunter & Simpson, 1999); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip 2010).

4-(Prop-2-ynyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl

Crystal data

$C_{12}H_{20}NO_2$	$D_x = 1.167$ Mg m^{-3}
$M_r = 210.29$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 4862 reflections
$a = 7.94506$ (13) Å	$\theta = 5.3$–74.2°
$b = 10.17919$ (16) Å	$\mu = 0.63$ mm^{-1}
$c = 14.8052$ (3) Å	$T = 100$ K
$V = 1197.36$ (4) Å^3	Block, colourless
$Z = 4$	$0.18 \times 0.15 \times 0.08$ mm
$F(000) = 460$	

Data collection

Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer	$T_{min} = 0.522$, $T_{max} = 1.000$
	6622 measured reflections
Radiation source: SuperNova (Cu) X-ray Source	2307 independent reflections
	2203 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.046$
Detector resolution: 5.1725 pixels mm^{-1}	$\theta_{max} = 74.3°$, $\theta_{min} = 5.3°$
ω scans	$h = -9 \rightarrow 9$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)	$k = -12 \rightarrow 12$
	$l = -18 \rightarrow 13$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.029P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.15$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
2307 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}
140 parameters	Absolute structure: Flack x determined using 858 quotients [(I^+)-(I^-)]/[(I^+)+(I^-)] (Parsons & Flack, 2004)
90 restraints	
Hydrogen site location: inferred from neighbouring sites	Absolute structure parameter: 0.0 (3)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.3936 (3)	0.73046 (19)	0.71556 (15)	0.0174 (5)
N1	0.3444 (3)	0.8315 (2)	0.67027 (16)	0.0107 (5)
C2	0.2036 (4)	0.9093 (3)	0.71116 (19)	0.0116 (6)
C21	0.2698 (4)	0.9827 (3)	0.7945 (2)	0.0169 (6)
H21A	0.3310	0.9214	0.8335	0.025*
H21B	0.1750	1.0205	0.8280	0.025*
H21C	0.3457	1.0533	0.7753	0.025*
C22	0.0670 (4)	0.8118 (3)	0.7398 (2)	0.0179 (7)
H22A	0.0301	0.7611	0.6872	0.027*
H22B	−0.0289	0.8599	0.7651	0.027*
H22C	0.1125	0.7520	0.7856	0.027*
C3	0.1325 (3)	1.0046 (3)	0.6408 (2)	0.0119 (6)
H3A	0.0654	0.9543	0.5964	0.014*
H3B	0.0558	1.0671	0.6714	0.014*
C4	0.2663 (4)	1.0812 (3)	0.59126 (19)	0.0099 (6)
H4	0.3331	1.1364	0.6341	0.012*
C5	0.3796 (4)	0.9843 (3)	0.54137 (19)	0.0112 (6)
H5A	0.4664	1.0342	0.5078	0.013*
H5B	0.3110	0.9357	0.4966	0.013*
C6	0.4674 (4)	0.8850 (3)	0.6036 (2)	0.0114 (6)
C61	0.6167 (4)	0.9461 (3)	0.6539 (2)	0.0152 (6)
H61A	0.5803	1.0270	0.6840	0.023*
H61B	0.7065	0.9665	0.6108	0.023*
H61C	0.6587	0.8839	0.6991	0.023*
C62	0.5300 (4)	0.7698 (3)	0.5464 (2)	0.0168 (6)
H62A	0.5934	0.7087	0.5846	0.025*
H62B	0.6031	0.8028	0.4982	0.025*
H62C	0.4335	0.7240	0.5197	0.025*
O2	0.1772 (3)	1.16202 (19)	0.52724 (14)	0.0140 (5)
C7	0.2733 (4)	1.2682 (3)	0.4916 (2)	0.0149 (6)
H7A	0.2201	1.2992	0.4350	0.018*
H7B	0.3877	1.2362	0.4765	0.018*
C8	0.2872 (4)	1.3793 (3)	0.5551 (2)	0.0160 (6)
C9	0.2975 (4)	1.4705 (3)	0.6048 (2)	0.0198 (7)
H9	0.3058	1.5435	0.6445	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0281 (11)	0.0083 (9)	0.0159 (11)	0.0025 (9)	0.0015 (10)	0.0060 (8)
N1	0.0172 (11)	0.0066 (10)	0.0085 (10)	0.0001 (9)	0.0007 (10)	0.0011 (8)
C2	0.0163 (13)	0.0110 (12)	0.0075 (12)	−0.0005 (11)	0.0037 (12)	0.0002 (10)
C21	0.0245 (15)	0.0169 (14)	0.0092 (14)	−0.0002 (12)	−0.0002 (13)	−0.0026 (11)
C22	0.0208 (15)	0.0190 (15)	0.0140 (15)	−0.0056 (12)	0.0028 (13)	0.0044 (12)
C3	0.0145 (12)	0.0110 (12)	0.0101 (13)	0.0020 (10)	0.0011 (11)	−0.0008 (10)
C4	0.0148 (13)	0.0087 (12)	0.0061 (12)	0.0005 (10)	0.0000 (11)	0.0012 (9)
C5	0.0160 (12)	0.0092 (12)	0.0084 (13)	−0.0001 (10)	0.0009 (11)	0.0009 (10)
C6	0.0161 (12)	0.0090 (12)	0.0090 (13)	0.0008 (10)	−0.0008 (11)	0.0015 (10)
C61	0.0165 (13)	0.0132 (13)	0.0160 (15)	−0.0004 (11)	−0.0003 (13)	0.0025 (11)
C62	0.0229 (14)	0.0122 (13)	0.0153 (16)	0.0036 (11)	0.0048 (13)	−0.0019 (11)
O2	0.0178 (10)	0.0102 (9)	0.0140 (10)	0.0000 (8)	−0.0032 (9)	0.0041 (7)
C7	0.0209 (14)	0.0105 (12)	0.0133 (14)	0.0004 (11)	−0.0017 (12)	0.0040 (10)
C8	0.0178 (13)	0.0139 (13)	0.0161 (14)	−0.0007 (11)	−0.0008 (12)	0.0057 (11)
C9	0.0275 (15)	0.0155 (15)	0.0164 (15)	−0.0025 (12)	−0.0026 (14)	0.0022 (12)

Geometric parameters (Å, º)

O1—N1	1.289 (3)	C5—C6	1.535 (4)
N1—C6	1.492 (4)	C5—H5A	0.9900
N1—C2	1.498 (4)	C5—H5B	0.9900
C2—C3	1.531 (4)	C6—C62	1.530 (4)
C2—C22	1.531 (4)	C6—C61	1.532 (4)
C2—C21	1.536 (4)	C61—H61A	0.9800
C21—H21A	0.9800	C61—H61B	0.9800
C21—H21B	0.9800	C61—H61C	0.9800
C21—H21C	0.9800	C62—H62A	0.9800
C22—H22A	0.9800	C62—H62B	0.9800
C22—H22B	0.9800	C62—H62C	0.9800
C22—H22C	0.9800	O2—C7	1.424 (3)
C3—C4	1.509 (4)	C7—C8	1.475 (4)
C3—H3A	0.9900	C7—H7A	0.9900
C3—H3B	0.9900	C7—H7B	0.9900
C4—O2	1.441 (3)	C8—C9	1.187 (5)
C4—C5	1.526 (4)	C9—H9	0.9500
C4—H4	1.0000		
O1—N1—C6	115.9 (2)	C4—C5—C6	113.8 (2)
O1—N1—C2	116.0 (2)	C4—C5—H5A	108.8
C6—N1—C2	124.3 (2)	C6—C5—H5A	108.8
N1—C2—C3	109.6 (2)	C4—C5—H5B	108.8
N1—C2—C22	107.3 (2)	C6—C5—H5B	108.8
C3—C2—C22	109.7 (2)	H5A—C5—H5B	107.7
N1—C2—C21	109.1 (2)	N1—C6—C62	107.4 (2)
C3—C2—C21	111.4 (2)	N1—C6—C61	109.5 (2)

C22—C2—C21	109.6 (2)	C62—C6—C61	109.2 (2)
C2—C21—H21A	109.5	N1—C6—C5	109.9 (2)
C2—C21—H21B	109.5	C62—C6—C5	108.7 (2)
H21A—C21—H21B	109.5	C61—C6—C5	112.1 (2)
C2—C21—H21C	109.5	C6—C61—H61A	109.5
H21A—C21—H21C	109.5	C6—C61—H61B	109.5
H21B—C21—H21C	109.5	H61A—C61—H61B	109.5
C2—C22—H22A	109.5	C6—C61—H61C	109.5
C2—C22—H22B	109.5	H61A—C61—H61C	109.5
H22A—C22—H22B	109.5	H61B—C61—H61C	109.5
C2—C22—H22C	109.5	C6—C62—H62A	109.5
H22A—C22—H22C	109.5	C6—C62—H62B	109.5
H22B—C22—H22C	109.5	H62A—C62—H62B	109.5
C4—C3—C2	113.5 (2)	C6—C62—H62C	109.5
C4—C3—H3A	108.9	H62A—C62—H62C	109.5
C2—C3—H3A	108.9	H62B—C62—H62C	109.5
C4—C3—H3B	108.9	C7—O2—C4	114.4 (2)
C2—C3—H3B	108.9	O2—C7—C8	112.7 (2)
H3A—C3—H3B	107.7	O2—C7—H7A	109.1
O2—C4—C3	105.6 (2)	C8—C7—H7A	109.1
O2—C4—C5	109.9 (2)	O2—C7—H7B	109.1
C3—C4—C5	108.5 (2)	C8—C7—H7B	109.1
O2—C4—H4	110.9	H7A—C7—H7B	107.8
C3—C4—H4	110.9	C9—C8—C7	178.6 (3)
C5—C4—H4	110.9	C8—C9—H9	180.0
O1—N1—C2—C3	−166.8 (2)	O1—N1—C6—C62	49.9 (3)
C6—N1—C2—C3	36.2 (4)	C2—N1—C6—C62	−153.1 (3)
O1—N1—C2—C22	−47.7 (3)	O1—N1—C6—C61	−68.6 (3)
C6—N1—C2—C22	155.3 (3)	C2—N1—C6—C61	88.4 (3)
O1—N1—C2—C21	71.0 (3)	O1—N1—C6—C5	167.9 (2)
C6—N1—C2—C21	−86.0 (3)	C2—N1—C6—C5	−35.1 (4)
N1—C2—C3—C4	−47.6 (3)	C4—C5—C6—N1	45.1 (3)
C22—C2—C3—C4	−165.2 (2)	C4—C5—C6—C62	162.3 (2)
C21—C2—C3—C4	73.2 (3)	C4—C5—C6—C61	−76.9 (3)
C2—C3—C4—O2	178.6 (2)	C3—C4—O2—C7	163.0 (2)
C2—C3—C4—C5	60.8 (3)	C5—C4—O2—C7	−80.2 (3)
O2—C4—C5—C6	−174.6 (2)	C4—O2—C7—C8	−77.8 (3)
C3—C4—C5—C6	−59.5 (3)		

Hydrogen-bond geometry (Å, º)

Cg is the mid-point of the C8–C9 bond.

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O1[i]	0.95	2.28	3.205 (4)	163
C7—H7B···O2[ii]	0.99	2.52	3.298 (4)	135

C61—H61A···O1^{iii}	0.98	2.56	3.481 (4)	157
C5—H5B···Cg^{iv}	0.99	2.93	3.885 (4)	156

Symmetry codes: (i) x, y+1, z; (ii) x+1/2, −y+5/2, −z+1; (iii) −x+1, y+1/2, −z+3/2; (iv) −x−1, y+5/2, −z+3/2.