Acta Cryst E STRUCTURE REPORTS

ISSN 1600-5368

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

**Shailesh K. Goswami, Lyall R. Hanton, C. John McAdam, Stephen C. Moratti and Jim Simpson***

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. *Correspondence e-mail: jsimpson@alkali.otago.ac.nz

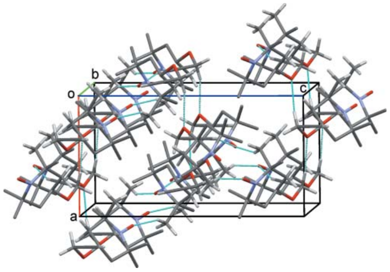
Received 4 August 2014
Accepted 5 August 2014

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

**Keywords**: crystal structure; TEMPO derivative; C—H⋯alkyne contact

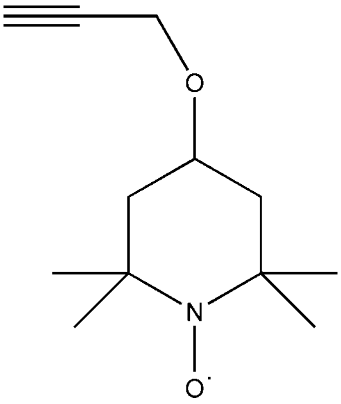
**CCDC reference**: 1017949
**Supporting information**: this article has supporting information at journals.iucr.org/e

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⋯O hydrogen bonds combine with unusual C—H⋯$\pi$ 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.*, 1999*a*,*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.

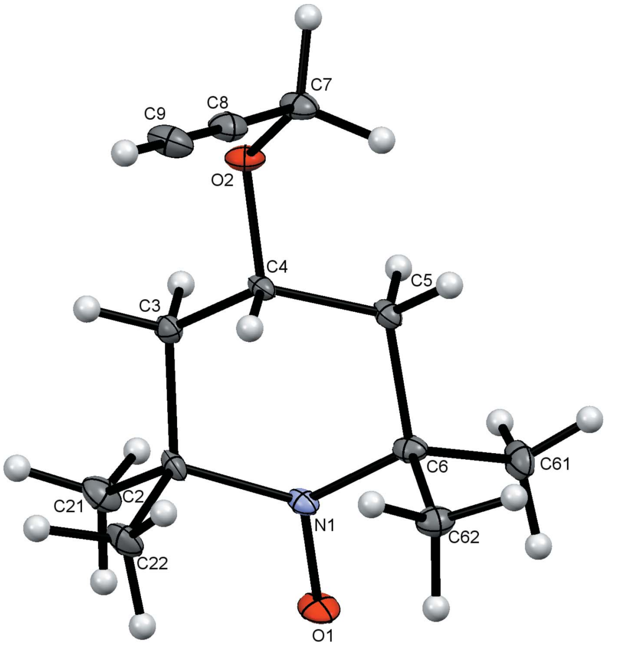


**Figure 1**
The structure of (1), showing the atom numbering and with displacement ellipsoids drawn at the 50% probability level.

## 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⋯O1 hydrogen bonds link molecules into *C*(9) chains along *b* (Table 1). Additional C61—H61*A*⋯O1 contacts form $R_3^2(16)$ rings, resulting in double chains of molecules along *b* (Fig. 2). In an almost orthogonal direction, C7—H7*B*⋯O2 hydrogen bonds form *C*(3) chains along *a*. An interesting feature of these latter contacts is the support provided by C5—H5*B*⋯*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).

**Table 1**
Hydrogen-bond geometry (Å, °).

*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—H7*B*⋯O2$^{ii}$ | 0.99 | 2.52 | 3.298 (4) | 135 |
| C61—H61*A*⋯O1$^{iii}$ | 0.98 | 2.56 | 3.481 (4) | 157 |
| C5—H5*B*⋯*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) $-x-1, y+\frac{5}{2}, -z+\frac{3}{2}$.

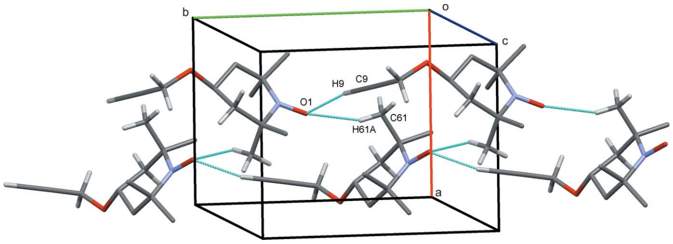


**Figure 2**
Double chains formed from molecules of (1) along *b*. In this and subsequent Figures, C—H⋯O hydrogen bonds are drawn as dashed lines and H atoms bound to atoms not involved in hydrogen bonding are not shown.

## 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

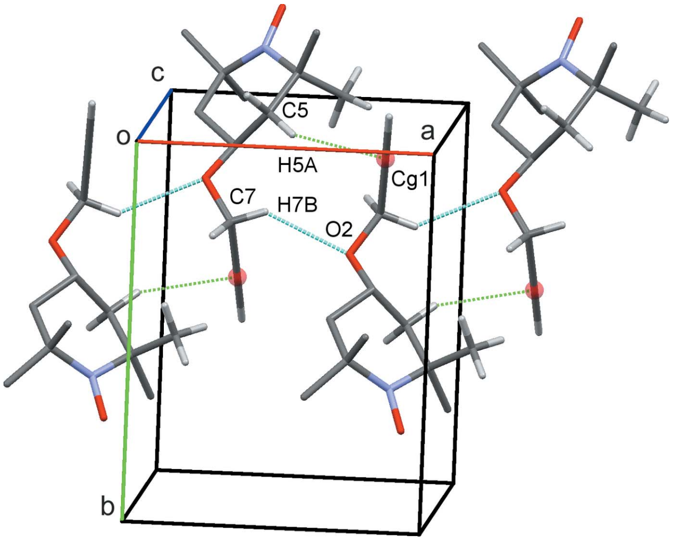


**Figure 3**
Zigzag chains formed along *a* from C—H⋯O and C—H⋯π (green dotted lines) contacts. The mid-point of the C8≡C9 triple bond is shown as a red sphere.

**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 $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.63 |
| Crystal size (mm) | 0.18 × 0.15 × 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).

($C_6OH$), 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-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. Anisiotropic refinement of the non-H atoms was constrained using the ISOR command in *SHELXL* to prevent atoms becoming non-positive definite. 10 reflections with $F_o >> F_c$ were omitted from the final refinement cycles.

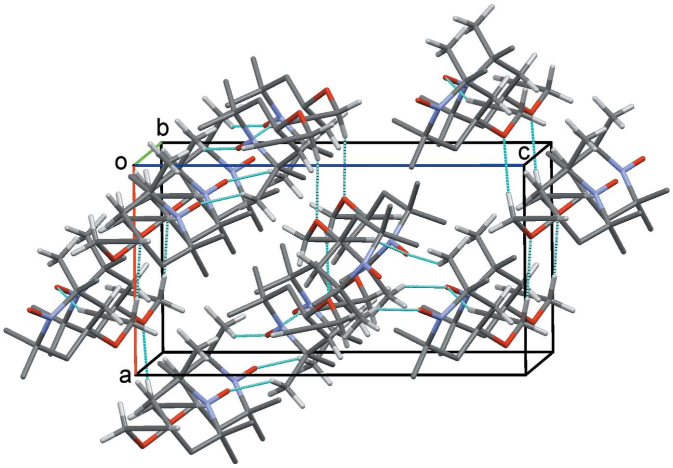


**Figure 4**
The overall packing for (1), viewed along the *b* axis.

## Acknowledgements

We thank the University of Otago for the purchase of the diffractometer.

## References

Agilent (2013). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.

Akutsu, H., Masaki, K., Mori, K., Yamada, J. & Nakatsuji, S. (2005). *Polyhedron*, **24**, 2126–2132.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Banerjee, R., Mondal, R., Howard, J. A. K. & Desiraju, G. R. (2006). *Cryst. Growth Des.* **6**, 999–1009.

Bode, B. E., Margraf, D., Plackmeyer, J., Dumer, G., Prisner, T. F. & Schiemann, O. (2007). *J. Am. Chem. Soc.* **129**, 6736–6745.

Camalli, M., Carrozzini, B., Cascarano, G. L. & Giacovazzo, C. (2012). *J. Appl. Cryst.* **45**, 351–356.

Gheorghe, A., Matsuno, A. & Reiser, O. (2006). *Adv. Synth. Catal.* **348**, 1016−1020.

Goswami, S. K., McAdam, C. J., Lee, A. M. M., Hanton, L. R. & Moratti, S. C. (2013). *J. Mater. Chem. A*, **1**, 3415–3420.

Hein, J. E. & Fokin, V. V. (2010). *Chem. Soc. Rev.* **39**, 1302−1315.

Hunter, K. A. & Simpson, J. (1999). *TITAN2000*. University of Otago, New Zealand.

Ishida, T., Tomioka, K., Nogami, T., Yoshikawa, H., Yasui, M., Iwasaki, F., Takeda, N. & Ishikawa, M. (1995). *Chem. Phys. Lett.* **247**, 7–12.

Iwasaki, F., Yoshikawa, J. H., Yamamoto, H., Kan-nari, E., Takada, K., Yasui, M., Ishida, T. & Nogami, T. (1999*a*). *Acta Cryst.* B**55**, 231–245.

Iwasaki, F., Yoshikawa, J. H., Yamamoto, H., Takada, K., Kan-nari, E., Yasui, M., Ishida, T. & Nogami, T. (1999*b*). *Acta Cryst.* B**55**, 1057–1067.

Kulis, J., Bell, C. A., Micallef, A. S., Jia, Z. & Monteiro, M. J. (2009). *Macromolecules*, **42**, 8218–8227.

Lewis, J. E. M., McAdam, C. J., Gardiner, M. G. & Crowley, J. D. (2013). *Chem. Commun.* **49**, 3398–3400.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

McAdam, C. J., Cameron, S. A., Hanton, L. R., Manning, A. R., Moratti, S. C. & Simpson, J. (2012). *CrystEngComm*, **14**, 4369–4383.

Nakazawa, S., Nishida, S., Ise, T., Yoshino, T., Mori, N., Rahimi, R. D., Sato, K., Morita, Y., Toyota, K., Shiomi, D., Kitagawa, M., Hara, H., Carl, P., Hofer, P. & Takui, T. (2012). *Angew. Chem. Int. Ed.* **51**, 9860–9864.

Pang, X., Wang, H., Zhao, X. R. & Wei Jin, W. J. (2013). *Dalton Trans.*, **42**, 8788–8795.

Parsons, S. & Flack, H. (2004). *Acta Cryst.* A**60**, s61.

Polovyanenko, D. N., Bagryanskaya, E. G., Schnegg, A., Mobius, K., Coleman, A. W., Ananchenko, G. S., Udachin, K. A. & Ripmeester, J. A. (2008). *Phys. Chem. Chem. Phys.* **10**, 5299–5307.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Soegiarto, A. C., Yan, W., Kent, A. D. & Ward, M. D. (2011). *J. Mater. Chem.* **21**, 2204–2219.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Thakur, A., Adarsh, N. A., Chakraborty, A., Devi, M. & Ghosh, S. (2010). *J. Organomet. Chem.* **695**, 1059–1064.

Togashi, K., Imachi, R., Tomioka, K., Tsuboi, H., Ishida, T., Nogami, T., Takeda, N. & Ishikawa, M. (1996). *Bull. Chem. Soc. Jpn*, **69**, 2821–2830.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zhao, M. M., Li, J., Mano, E., Song, Z. J. & Tschaen, D. M. (2005). *Org. Synth.* **81**, 195–203.

# supporting information

*Acta Cryst.* (2014). E**70**, 130-133 [doi:10.1107/S1600536814017991]

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

**Shailesh K. Goswami, Lyall R. Hanton, C. John McAdam, Stephen C. Moratti and Jim Simpson**

### 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*

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

*Data collection*

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

*Refinement*

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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—H7*B*···O2$^{ii}$ | 0.99 | 2.52 | 3.298 (4) | 135 |

| | | | | |
|---|---|---|---|---|
| C61—H61*A*···O1$^{\text{iii}}$ | 0.98 | 2.56 | 3.481 (4) | 157 |
| C5—H5*B*···*Cg*$^{\text{iv}}$ | 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.