

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

tert-Butyl N-[[5-(5-oxohexanamido)-pyridin-2-yl]amino]carbamate

 Luisa Ronga,^a Noel Pinaud,^b Charlotte Rimbault,^a Mathieu Marchivie^a and Jean Guillon^{a*}
^aUniversité Bordeaux Segalen, CNRS FRE 3396 -Pharmacochimie, F-33076 Bordeaux, France, and ^bISM-CNRS UMR 5255, Université de Bordeaux, F-33405 Talence cedex, France

Correspondence e-mail: jean.guillon@u-bordeaux2.fr

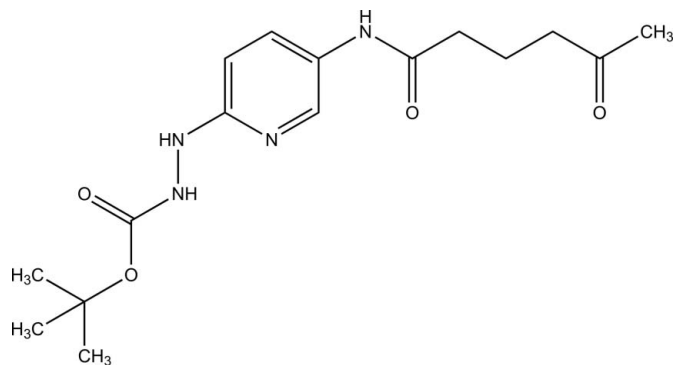
Received 25 July 2013; accepted 3 September 2013

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.053; wR factor = 0.147; data-to-parameter ratio = 14.9.

In the crystal structure of the title compound, $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_4$, molecules are linked by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the carbonyl groups of the carbamoyl and amido functional groups and the amino groups, and by $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds between the amino group and the pyridine ring, forming two-dimensional networks parallel to the ab plane.

Related literature

For the synthesis, properties and biological activity of 2-hydrazinopyridine derivatives, see: Ardisson *et al.* (2005); Jurisson & Lydon (1999); Abrams *et al.* (1994); Liu *et al.* (2011); Lu *et al.* (2011); Schwartz *et al.* (1990). For the crystal structures of related compounds, see: Banerjee *et al.* (2005); Rose *et al.* (1998); Zora *et al.* (2006). For synthesis, see: Cugola *et al.* (1995).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_4$
 $M_r = 336.39$

 Triclinic, $P\bar{1}$
 $a = 6.2598$ (4) Å

 $b = 9.2822$ (6) Å
 $c = 16.0437$ (12) Å
 $\alpha = 84.387$ (6)°
 $\beta = 88.957$ (6)°
 $\gamma = 79.358$ (6)°
 $V = 911.79$ (11) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 293$ K
 $0.84 \times 0.17 \times 0.06$ mm

Data collection

 Bruker-Nonius KappaCCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.928$, $T_{\max} = 0.994$

 20299 measured reflections
 3295 independent reflections
 2187 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.147$
 $S = 1.04$
 3295 reflections

 221 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O3}^{\text{i}}$	0.86	2.06	2.888 (2)	161
$\text{N3}-\text{H3}\cdots\text{N2}^{\text{ii}}$	0.86	2.21	2.957 (3)	145
$\text{N4}-\text{H4}\cdots\text{O2}^{\text{iii}}$	0.86	2.06	2.827 (3)	149

 Symmetry codes: (i) $-x + 1, -y + 2, -z + 2$; (ii) $-x, -y + 2, -z + 2$; (iii) $-x + 1, -y + 1, -z + 2$.

Data collection: COLLECT (Nonius, 1998); cell refinement: DIRAX/LSQ (Duisenberg, 1992); data reduction: EVALCCD (Duisenberg *et al.*, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: publCIF (Westrip, 2010).

This publication was supported by a grant from the Ligue Nationale contre le Cancer (Comité Aquitaine-Charentes, Bordeaux, France).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2115).

References

- Abrams, M. J., Bridger, G. J., Schwartz, D. A., Padmanabhan, S. & Ultee, M. E. (1994). World Patent WO 94/10149.
- Ardisson, V., Mathieu, J. P., Ghezzi, C. & Fagret, D. (2005). *Med. Nucl.* **29**, 168–178.
- Banerjee, S. R., Schaffer, P., Babich, J. W., Valliant, J. F. & Zubieta, J. (2005). *Dalton Trans.* pp. 3886–3897.
- Cugola, A., Di Fabio, R. & Pentasuglia, G. (1995). World Patent WO 95/10517.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Jurisson, S. S. & Lydon, J. D. (1999). *Chem. Rev.* **99**, 2205–2218.
- Liu, L., Zhang, M., Zhong, G. & Wang, X. (2011). *J. Radioanal. Nucl. Chem.* **287**, 847–852.
- Lu, J., Pang, Y., Xie, F., Guo, H.-J., Li, Y., Yang, Z. & Wang, X.-B. (2011). *Nucl. Med. Biol.* **38**, 557–565.
- Nonius (1998). COLLECT. Nonius BV, Delft, The Netherlands.
- Rose, D. J., Maresca, K. P., Nicholson, T., Davison, A., Jones, A. G., Babich, J., Fischman, A., Graham, W., DeBord, J. R. D. & Zubieta, J. (1998). *Inorg. Chem.* **37**, 2701–2716.

Schwartz, D. A., Abrams, M. J., Giandomenico, C. M. & Zubieta, J. A. (1990). Eur. Patent EP 384769.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zora, M., Turgut, G., Odabaşoğlu, M. & Büyükgüngör, O. (2006). *Acta Cryst.* **E62**, o2677–o2679.

supplementary materials

Acta Cryst. (2013). E69, o1531–o1532 [doi:10.1107/S1600536813024598]

***tert*-Butyl *N*-{[5-(5-oxohexanamido)pyridin-2-yl]amino}carbamate**

Luisa Ronga, Noel Pinaud, Charlotte Rimbault, Mathieu Marchivie and Jean Guillon

1. Comment

Radioisotopes conjugated to proteins provide a means for imaging and treatment of disease. The bifunctional 2-hydrazinopyridine derivatives are useful linker molecules for attaching metal ions such as ^{99m}Tc to macromolecules (Ardisson *et al.*, 2005; Jurisson & Lydon, 1999). Hence, this 2-hydrazinopyridinyl moiety has previously been used for labeling bioactive molecules (Abrams *et al.*, 1994; Banerjee *et al.* 2005; Rose *et al.*, 1998; Schwartz *et al.*, 1990). Thus, the use of Tc-labeled hydrazine derivatives continues to undergo further development (Liu *et al.*, 2011; Lu *et al.*, 2011). The wide spectrum of medicinal applications of this class of radiolabeled chelates prompted us to work in this domain and we report herein on the synthesis and crystal structure of the title compound, designed as a potential chelate for ^{99m}Tc .

The title compound, $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_4$, has the triclinic ($P\bar{1}$) symmetry. It crystallizes with one molecule in the asymmetric unit. In the crystal, the molecules are linked together by $\text{N—H}\cdots\text{O}$ hydrogen bonding between the carbonyl groups of the carbamoyl and amido functional groups and the amino groups and by $\text{N—H}\cdots\text{N}$ hydrogen bonding between amino and pyridine moiety leading to a two-dimensional network within the *ab* plane. The network cohesion in the 3rd direction is assured by Van der Waals interactions and H-bond like interactions between the carbonyl and the BOC group.

2. Experimental

To a stirred solution of 5-oxohexanoic acid (2.45 mmol) in 15 ml of tetrahydrofuran was added triethylamine (2.45 mmol). After 10 min of stirring at room temperature was added isobutyl chloroformate (2.45 mmol). The reaction mixture was stirred at room temperature for 5 h, then 2-(*t*-butoxycarbonyl hydrazine)-5-amino-pyridine (2.23 mmol) (Cugola *et al.*, 1995) was added and the reaction stirred for 12 h. The mixture was evaporated to dryness, and the residue was triturated in water. The solid precipitate was filtered off and washed with water then with ethanol, and purified by column chromatography using CHCl_3 /methanol (9/1, *v/v*) as eluent to give the title compound as white crystals ($R_f = 1/4$). Yield is 48%. The single-crystal of the title product was obtained by slow crystallization from a mixture DMSO/methanol (9/1, *v/v*). *M.p.* = 219°C. IR (KBr), ν/cm^{-1} : 3270, 3230, 3185, 3082, 2982, 1704, 1662, 1601, 1537, 1276, 1182. ^1H NMR (300 MHz, DMSO-d_6 , 298 K): δ = 1.41 (s, 9H, 3 CH_3), 1.75 (qt, 2H, $J = 6.10$, CH_2), 2.09 (s, 3H, CH_3), 2.26 (t, 2H, $J = 6.10$, CH_2), 2.48 (t, 2H, $J = 6.10$, CH_2), 6.49 (d, 1H, $J = 7.50$, H-3), 7.71 (dd, 1H, $J = 7.50$ and 1.55, H-4), 7.95 (s, 1H, NH), 8.20 (d, 1H, $J = 1.55$, H-6), 8.75 (s, 1H, NH), 9.70 (s, 1H, NH). Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_4$: C, 57.13; H, 7.19; N, 16.66 Found: C, 57.26; H, 7.25; N, 16.52.

3. Refinement

Crystallographic data were collected at 293 K on a Bruker nonius k-CCD diffractometer with monochromatic $\text{Mo—K}\alpha$ radiation ($\lambda = 0.71073$ Å). At 293 K, the full sphere data collection was performed using φ scans and ω scans. The unit cell determination and data reduction were performed using *DIRAX/LSQ* (Duisenberg, 1992) and *Collect* (Nonius, 1998) programs on the full set of data. The crystal structure was solved by direct methods and successive Fourier difference

syntheses with *SHELXS97* program (Sheldrick, 2008). The refinements of the crystal structure were performed on F2 by weighted anisotropic full-matrix least squares methods using the *SHELXL97* program (Sheldrick, 2008). Both pieces of software were used within OLEX2 package (Dolomanov *et al.*, 2009). All the non-H atoms were refined with anisotropic temperature parameters. The positions of the H atoms were deduced from coordinates of the non-H atoms and confirmed by Fourier synthesis and treated according to the riding model during refinement with isotropic displacement parameters, corresponding to the atom they are linked to. H atoms were included for structure factor calculations but not refined.

Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

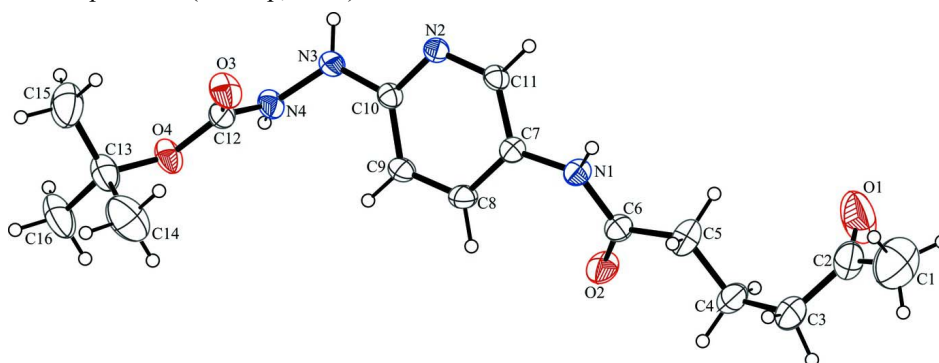


Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

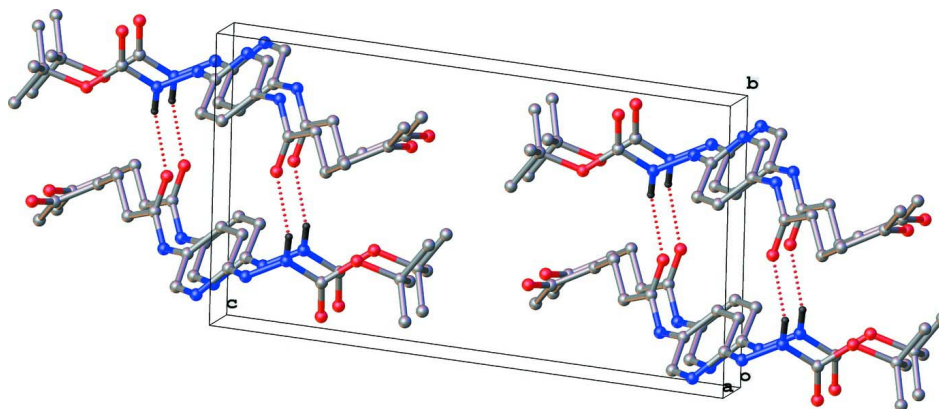


Figure 2

Crystal packing of the title compound viewed down the *a* axis. Only hydrogen atoms involved in hydrogen bonding (dashed lines) are shown.

tert-Butyl *N*-{[5-(5-oxohexanamido)pyridin-2-yl]amino}carbamate

Crystal data

$C_{16}H_{24}N_4O_4$
 $M_r = 336.39$

Triclinic, $P\bar{1}$
 $a = 6.2598(4) \text{ \AA}$

$b = 9.2822$ (6) Å
 $c = 16.0437$ (12) Å
 $\alpha = 84.387$ (6)°
 $\beta = 88.957$ (6)°
 $\gamma = 79.358$ (6)°
 $V = 911.79$ (11) Å³
 $Z = 2$
 $F(000) = 360$

$D_x = 1.225$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 8003 reflections
 $\theta = 3.2$ – 25.3 °
 $\mu = 0.09$ mm⁻¹
 $T = 293$ K
 Plate, colourless
 $0.84 \times 0.17 \times 0.06$ mm

Data collection

Bruker–Nonius KappaCCD
 diffractometer
 intensities from φ scan and ω scan
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.928$, $T_{\max} = 0.994$
 20299 measured reflections

3295 independent reflections
 2187 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 25.3$ °, $\theta_{\min} = 3.2$ °
 $h = -7 \rightarrow 7$
 $k = -11 \rightarrow 11$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.147$
 $S = 1.04$
 3295 reflections
 221 parameters
 0 restraints

Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.4578P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.29$ e Å⁻³
 $\Delta\rho_{\min} = -0.25$ e Å⁻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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N2	0.2722 (3)	0.91380 (18)	0.96382 (11)	0.0383 (4)
N1	0.8167 (3)	0.79747 (19)	0.88090 (12)	0.0420 (5)
H1	0.8436	0.8828	0.8633	0.050*
C8	0.6222 (4)	0.6875 (2)	0.99807 (14)	0.0452 (6)
H8	0.7405	0.6120	1.0105	0.054*
N3	0.0661 (3)	0.8185 (2)	1.06579 (12)	0.0480 (5)
H3	-0.0492	0.8704	1.0424	0.058*
O4	0.0851 (3)	0.71283 (17)	1.28015 (10)	0.0579 (5)
C10	0.2624 (3)	0.8083 (2)	1.02536 (13)	0.0376 (5)
C11	0.4549 (3)	0.9045 (2)	0.91869 (13)	0.0388 (5)
H11	0.4618	0.9774	0.8752	0.047*
O2	0.9342 (3)	0.55429 (18)	0.87934 (12)	0.0663 (5)
N4	0.0544 (3)	0.7449 (2)	1.14426 (12)	0.0476 (5)
H4	0.0149	0.6605	1.1495	0.057*

C7	0.6329 (3)	0.7943 (2)	0.93254 (13)	0.0369 (5)
O3	0.1590 (3)	0.92288 (18)	1.21135 (11)	0.0640 (5)
C6	0.9535 (4)	0.6804 (2)	0.85656 (14)	0.0439 (6)
C9	0.4362 (4)	0.6941 (2)	1.04441 (14)	0.0462 (6)
H9	0.4260	0.6226	1.0884	0.055*
C12	0.1045 (4)	0.8044 (2)	1.21198 (15)	0.0461 (6)
C5	1.1308 (4)	0.7170 (3)	0.79916 (18)	0.0620 (7)
H5A	1.0644	0.7759	0.7499	0.074*
H5B	1.2121	0.7776	0.8272	0.074*
C2	1.4473 (6)	0.7179 (4)	0.6461 (2)	0.0740 (8)
C13	0.1179 (5)	0.7546 (3)	1.36427 (16)	0.0663 (8)
C4	1.2840 (5)	0.5918 (4)	0.7717 (2)	0.0931 (12)
H4A	1.2109	0.5423	0.7334	0.112*
H4B	1.3307	0.5222	0.8199	0.112*
O1	1.2875 (5)	0.7200 (4)	0.60720 (16)	0.1353 (12)
C15	-0.0383 (7)	0.8914 (4)	1.3805 (2)	0.1030 (13)
H15A	0.0014	0.9742	1.3473	0.154*
H15B	-0.0341	0.9063	1.4388	0.154*
H15C	-0.1825	0.8815	1.3658	0.154*
C3	1.4820 (5)	0.6376 (5)	0.7287 (2)	0.1002 (13)
H3A	1.5420	0.6983	0.7646	0.120*
H3B	1.5906	0.5497	0.7237	0.120*
C1	1.6198 (8)	0.7953 (5)	0.6113 (3)	0.1350 (18)
H1A	1.6100	0.8071	0.5513	0.203*
H1B	1.7593	0.7387	0.6279	0.203*
H1C	1.6022	0.8903	0.6321	0.203*
C16	0.0675 (7)	0.6234 (4)	1.41952 (19)	0.0943 (11)
H16A	-0.0786	0.6116	1.4092	0.142*
H16B	0.0821	0.6391	1.4772	0.142*
H16C	0.1669	0.5363	1.4072	0.142*
C14	0.3522 (7)	0.7691 (5)	1.3740 (2)	0.1111 (13)
H14A	0.4454	0.6793	1.3617	0.167*
H14B	0.3770	0.7881	1.4304	0.167*
H14C	0.3832	0.8491	1.3359	0.167*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0429 (11)	0.0323 (10)	0.0384 (10)	-0.0052 (8)	0.0023 (8)	-0.0001 (8)
N1	0.0428 (11)	0.0303 (10)	0.0531 (12)	-0.0092 (8)	0.0086 (9)	-0.0018 (8)
C8	0.0449 (14)	0.0346 (12)	0.0516 (14)	0.0005 (10)	0.0001 (11)	0.0037 (10)
N3	0.0438 (12)	0.0504 (12)	0.0432 (11)	-0.0003 (9)	0.0058 (9)	0.0115 (9)
O4	0.0911 (13)	0.0425 (10)	0.0428 (10)	-0.0241 (9)	0.0090 (8)	0.0042 (7)
C10	0.0424 (13)	0.0334 (12)	0.0373 (12)	-0.0090 (9)	0.0000 (9)	-0.0020 (9)
C11	0.0465 (14)	0.0312 (12)	0.0383 (12)	-0.0090 (10)	0.0011 (10)	0.0016 (9)
O2	0.0826 (13)	0.0343 (10)	0.0792 (13)	-0.0052 (9)	0.0231 (10)	-0.0060 (9)
N4	0.0630 (13)	0.0354 (10)	0.0437 (11)	-0.0130 (9)	0.0095 (9)	0.0049 (9)
C7	0.0384 (12)	0.0313 (11)	0.0424 (12)	-0.0096 (9)	0.0017 (9)	-0.0046 (9)
O3	0.0948 (14)	0.0404 (10)	0.0608 (11)	-0.0279 (9)	0.0081 (10)	0.0031 (8)
C6	0.0468 (14)	0.0367 (13)	0.0488 (14)	-0.0076 (10)	0.0007 (10)	-0.0077 (10)

C9	0.0507 (14)	0.0358 (13)	0.0471 (13)	-0.0022 (10)	0.0045 (11)	0.0100 (10)
C12	0.0535 (15)	0.0349 (13)	0.0479 (14)	-0.0088 (11)	0.0110 (11)	0.0050 (11)
C5	0.0559 (16)	0.0620 (17)	0.0733 (18)	-0.0168 (13)	0.0195 (13)	-0.0244 (14)
C2	0.073 (2)	0.089 (2)	0.0620 (19)	-0.0139 (17)	0.0123 (17)	-0.0204 (17)
C13	0.096 (2)	0.0598 (18)	0.0455 (15)	-0.0248 (15)	0.0073 (14)	0.0013 (13)
C4	0.089 (2)	0.079 (2)	0.087 (2)	0.0318 (18)	0.0401 (19)	0.0168 (18)
O1	0.112 (2)	0.239 (4)	0.0606 (16)	-0.050 (2)	-0.0055 (15)	-0.0106 (19)
C15	0.154 (4)	0.075 (2)	0.080 (2)	-0.018 (2)	0.038 (2)	-0.0189 (18)
C3	0.063 (2)	0.147 (3)	0.071 (2)	0.027 (2)	0.0151 (16)	0.000 (2)
C1	0.126 (4)	0.117 (4)	0.169 (5)	-0.046 (3)	0.046 (3)	-0.009 (3)
C16	0.156 (3)	0.077 (2)	0.0518 (18)	-0.037 (2)	0.0132 (19)	0.0112 (16)
C14	0.122 (3)	0.133 (4)	0.086 (3)	-0.050 (3)	-0.025 (2)	0.011 (2)

Geometric parameters (Å, °)

N2—C10	1.330 (3)	C5—C4	1.462 (4)
N2—C11	1.336 (3)	C2—O1	1.185 (4)
N1—H1	0.8600	C2—C3	1.454 (4)
N1—C7	1.409 (3)	C2—C1	1.476 (5)
N1—C6	1.339 (3)	C13—C15	1.494 (4)
C8—H8	0.9300	C13—C16	1.513 (4)
C8—C7	1.382 (3)	C13—C14	1.510 (5)
C8—C9	1.365 (3)	C4—H4A	0.9700
N3—H3	0.8600	C4—H4B	0.9700
N3—C10	1.372 (3)	C4—C3	1.517 (4)
N3—N4	1.380 (2)	C15—H15A	0.9600
O4—C12	1.336 (3)	C15—H15B	0.9600
O4—C13	1.468 (3)	C15—H15C	0.9600
C10—C9	1.386 (3)	C3—H3A	0.9700
C11—H11	0.9300	C3—H3B	0.9700
C11—C7	1.372 (3)	C1—H1A	0.9600
O2—C6	1.219 (3)	C1—H1B	0.9600
N4—H4	0.8600	C1—H1C	0.9600
N4—C12	1.333 (3)	C16—H16A	0.9600
O3—C12	1.209 (3)	C16—H16B	0.9600
C6—C5	1.495 (3)	C16—H16C	0.9600
C9—H9	0.9300	C14—H14A	0.9600
C5—H5A	0.9700	C14—H14B	0.9600
C5—H5B	0.9700	C14—H14C	0.9600
C10—N2—C11	117.63 (18)	O4—C13—C16	101.9 (2)
C7—N1—H1	116.9	O4—C13—C14	109.3 (3)
C6—N1—H1	116.9	C15—C13—C16	110.7 (3)
C6—N1—C7	126.27 (18)	C15—C13—C14	112.9 (3)
C7—C8—H8	120.4	C14—C13—C16	110.8 (3)
C9—C8—H8	120.4	C5—C4—H4A	109.1
C9—C8—C7	119.3 (2)	C5—C4—H4B	109.1
C10—N3—H3	120.2	C5—C4—C3	112.4 (3)
C10—N3—N4	119.59 (18)	H4A—C4—H4B	107.8
N4—N3—H3	120.2	C3—C4—H4A	109.1

C12—O4—C13	121.02 (19)	C3—C4—H4B	109.1
N2—C10—N3	114.92 (18)	C13—C15—H15A	109.5
N2—C10—C9	122.0 (2)	C13—C15—H15B	109.5
N3—C10—C9	123.07 (19)	C13—C15—H15C	109.5
N2—C11—H11	117.9	H15A—C15—H15B	109.5
N2—C11—C7	124.12 (19)	H15A—C15—H15C	109.5
C7—C11—H11	117.9	H15B—C15—H15C	109.5
N3—N4—H4	120.0	C2—C3—C4	116.5 (3)
C12—N4—N3	120.07 (19)	C2—C3—H3A	108.2
C12—N4—H4	120.0	C2—C3—H3B	108.2
C8—C7—N1	123.77 (19)	C4—C3—H3A	108.2
C11—C7—N1	118.68 (19)	C4—C3—H3B	108.2
C11—C7—C8	117.5 (2)	H3A—C3—H3B	107.3
N1—C6—C5	114.7 (2)	C2—C1—H1A	109.5
O2—C6—N1	122.5 (2)	C2—C1—H1B	109.5
O2—C6—C5	122.8 (2)	C2—C1—H1C	109.5
C8—C9—C10	119.5 (2)	H1A—C1—H1B	109.5
C8—C9—H9	120.3	H1A—C1—H1C	109.5
C10—C9—H9	120.3	H1B—C1—H1C	109.5
N4—C12—O4	109.39 (19)	C13—C16—H16A	109.5
O3—C12—O4	125.6 (2)	C13—C16—H16B	109.5
O3—C12—N4	125.0 (2)	C13—C16—H16C	109.5
C6—C5—H5A	108.3	H16A—C16—H16B	109.5
C6—C5—H5B	108.3	H16A—C16—H16C	109.5
H5A—C5—H5B	107.4	H16B—C16—H16C	109.5
C4—C5—C6	116.1 (2)	C13—C14—H14A	109.5
C4—C5—H5A	108.3	C13—C14—H14B	109.5
C4—C5—H5B	108.3	C13—C14—H14C	109.5
O1—C2—C3	121.4 (3)	H14A—C14—H14B	109.5
O1—C2—C1	120.7 (4)	H14A—C14—H14C	109.5
C3—C2—C1	117.8 (4)	H14B—C14—H14C	109.5
O4—C13—C15	110.7 (3)		
N2—C10—C9—C8	-1.1 (3)	C7—N1—C6—C5	178.0 (2)
N2—C11—C7—N1	-179.53 (19)	C7—C8—C9—C10	-0.6 (4)
N2—C11—C7—C8	-0.9 (3)	C6—N1—C7—C8	34.9 (3)
N1—C6—C5—C4	179.6 (3)	C6—N1—C7—C11	-146.5 (2)
N3—C10—C9—C8	176.3 (2)	C6—C5—C4—C3	-168.4 (3)
N3—N4—C12—O4	-178.94 (18)	C9—C8—C7—N1	-179.9 (2)
N3—N4—C12—O3	1.0 (4)	C9—C8—C7—C11	1.5 (3)
C10—N2—C11—C7	-0.7 (3)	C12—O4—C13—C15	59.1 (3)
C10—N3—N4—C12	82.6 (3)	C12—O4—C13—C16	176.9 (2)
C11—N2—C10—N3	-175.89 (18)	C12—O4—C13—C14	-65.8 (3)
C11—N2—C10—C9	1.7 (3)	C5—C4—C3—C2	-70.8 (4)
O2—C6—C5—C4	-0.5 (4)	C13—O4—C12—N4	-176.3 (2)
N4—N3—C10—N2	-160.78 (19)	C13—O4—C12—O3	3.8 (4)
N4—N3—C10—C9	21.6 (3)	O1—C2—C3—C4	-15.7 (5)
C7—N1—C6—O2	-1.8 (4)	C1—C2—C3—C4	165.3 (3)

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O3 ⁱ	0.86	2.06	2.888 (2)	161
N3—H3 \cdots N2 ⁱⁱ	0.86	2.21	2.957 (3)	145
N4—H4 \cdots O2 ⁱⁱⁱ	0.86	2.06	2.827 (3)	149

Symmetry codes: (i) $-x+1, -y+2, -z+2$; (ii) $-x, -y+2, -z+2$; (iii) $-x+1, -y+1, -z+2$.